# Physico-Chemical Property Determinations of Chlorinated *n*-Alkanes ($C_{10}$ to $C_{12}$). Parameters for Estimation of the Environmental Fate of Chlorinated *n*-Paraffins

By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

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July 1996

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# PHYSICO-CHEMICAL PROPERTY DETERMINATIONS OF CHLORINATED n-ALKANES ($C_{10}$ to $C_{12}$). PARAMETERS FOR ESTIMATION OF THE ENVIRONMENTAL FATE OF CHLORINATED n-PARAFFINS

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KEN G. DROUILLARD

A Thesis/Practicum submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

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## Abstract

Chlorinated *n*-paraffins (CPs) are a class of organochlorine compounds utilized in a wide variety of consumer products and industrial processes. Despite their wide spread use, little information is available on important physico-chemical properties necessary for estimating environmental fate and risk assessment of CPs. In this research, individual chlorinated alkane isomers of polychlorinated decanes, undecanes and dodecanes were utilized to assess physico-chemical properties for CPs. Subcooled-liquid vapor pressures ($P_{(sub)}$) were determined using the GLC-relative retention correlation technique. $P_{(sub)}$ ranged from $1.4 \times 10^{-4}$ to 0.51 Pa at 25°C among the compounds studied. Clear trends were observed for decreases in $P_{(sub)}$ with increasing carbon chain length and degree of chlorination. Henry's Law Constants (H) were determined using gas sparging techniques. Hs were observed to range from 0.68 to 19.18 $Pa \cdot m^3 \cdot mol^{-1}$ for tetra- and pentachloro-congeners and from 499.4 to 648.1 $Pa \cdot m^3 \cdot mol^{-1}$ for dichloro-congeners. No trends between Hs and carbon chain length were evident, although decreases in Hs with increasing degree of chlorination were observed.

Subcooled-liquid water solubilities ($S_{w(sub)}$) were determined using the generator column technique and calculated by the ratio of $P_{(sub)}/H$. Chlorinated alkanes were not availabe in pure form and were added to the generator column as a mixture. The effect of adding solutes as a mixture caused a depression in the apparent solubilities. The magnitude of the solubility depression was modelled using dichlorodecane as a reference compound to correct the apparent solubilites to their true solubilities. Corrected solubilities for selected chlorinated alkane congeners ranged from 22.4 to 995 $\mu g \cdot L^{-1}$ and were well correlated to solubilities independently calculated from the ratio of $P_{(sub)}/H$. Increases in solubility with increasing degree of chlorination were observed, in contrast to that reported for chlorinated aromatic compounds.

Organic carbon/water partition coefficients ($K_{OC}$) and sorption/desorption kinetics were determined for a $^{14}$C-polychlorododecane mixture. Batch experiments were performed yielding log $K_{OC}$s which ranged from 4.58 to 5.95 among 7 solids concentrations and three sediment types. Sorption/desorption kinetics were determined using gas sparging techniques on pre-equilibrated chemical/sediment/water solutions. Sorption kinetics, indicated pseudo steady state within 12 h followed by slower uptake over a period of 40 d. Desorption rates, over 4 solids concentrations, had half lives ranging from 15 to 47 days and were dependent on the solids concentration employed. Results indicate that the solids concentration effect on $K_{OC}$ may be an artifact of insufficient equillibration periods in the sorptive uptake phase.

## Acknowledgments

I would like to thank both my supervisor and co-supervisor Dr. Ken J. Friesen and Dr. Derek C.G. Muir for giving me the opportunity to perform this research and their many contributions to this project. Both Ken and Derek taught a series of excellent courses in environmental chemistry, and through many informative discussions, helped form the basis for many of the ideas, techniques and directions taken in this work. I would also like to acknowledge my committee members, Dr. G.R.B. Webster and Dr. J.B. Westmore who, in addition to reviewing the thesis, provided a great deal of direction in the project through their many contributions to discussions and ideas at the CP group meetings.

I thank Tim Hiebert who worked on the solubility studies as part of his undergraduate research project and as a summer student. I also thank Phuong Tran who also worked on the solubility and $K_{OC}$ studies as part of her summer employment and undergraduate research project. Both Phuong and Tim were highly efficient and dedicated students and, without their efforts, many aspects of the project could not have been completed.

I am particularly grateful for the many contributions from Aaron Fisk who helped me greatly over the last few years through several intellectual conversations, his support in joint research efforts and his help in unraveling so many administrative tie ups. My personal friendship with him and his family, Melissa and Zoe, have also added a special character to this project. Special thanks are also given to Debbie Armstrong for her friendship and intellectual contributions. Finally, I'd like to thank my parents, who have encouraged my curiosity and given me the will to seek the answers to so many questions.

This project was financially supported by the Natural Sciences and Engineering Research Council of Canada, through a strategic research grant and scholarship funds.

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## 1.1. Literature Review of Chlorinated Paraffins

Chlorinated paraffins (CPs) represent a widely utilized class of industrial organochlorine compounds which are produced and consumed in high quantities, yet have received little attention with respect to their characterization for important environmental parameters. CPs are generally classified as chlorinated *n*-alkanes with carbon chain lengths ranging from $C_{10}$ to $C_{30}$ and chlorine contents of 30 to 70% by weight. CPs are produced and utilized as complex formulations of mixtures consisting of chlorinated alkanes having large numbers of structural isomers, congener groups (chlorinated alkanes of the same carbon chain length but varying degrees of chlorination) and compounds varying in carbon chain length. Recent risk assessments and reviews on chlorinated paraffins have expressed concern regarding the potential toxicity and environmental concentrations of these compounds (Environment Canada 1993a; Mukherjee 1990; U.S. EPA 1992; Willis et al. 1992). Despite their wide spread use, specific conclusions regarding exposure and effects of CPs often cannot be made because of data gaps associated with physical properties, a lack of standardized analytical techniques and the availability of purified compounds for conducting valid studies on toxicity, bioaccumulation, biodegradation and abiotic degradation processes.

CPs have been broadly classified into three categories of carbon chain length and degrees of chlorination based on common technical formulations of commercial mixtures. These categories include short ($C_{10}$-$C_{13}$), intermediate ($C_{14}$-$C_{17}$) and long ($>C_{17}$) carbon chain lengths which are subcategorized into 40 to 50%, 50 to 60% and 60 to 70% chlorine content by weight (U.S. EPA 1992; Environment Canada 1993a). There are over 200 types of commercially produced CP mixtures (Serrone et al. 1987; Mukherjee 1990) which have a wide array of chemical compositions designed to provide desirable product properties of volatility, viscosity and density. As such, the composition of compounds in a given commercial mixture may not necessarily be restricted to a single category as described above (P. Ostrowski, Occidental Chemicals Corp., Niagara Falls; personal communication).

CPs have been in production since 1930 and world production estimates are 300 kt/y (Environment Canada 1993a). Total consumption in the U.S.A. and Canada are 44 to 45 and 3.5 to 5 kt/y, respectively (Environment Canada 1993a). Mukherjee (1990) estimated that 50% of the world CP production consists of intermediate carbon chain lengths with chlorine percentages in the range of 45 to 52%. CPs are generally used where the demand for chemical stability is high (Svanberg and Lindén 1979; Mukherjee 1990). Common applications include high pressure lubricants, plasticizers, flame retardants and additives in adhesives, paints, rubber and sealants (Environment Canada 1993a; Mukherjee 1990). In the U.S. and Canada, the two greatest sources of consumption of CPs involve their use as high pressure lubricants and metal cutting oils and as additives in plastics (Environment Canada 1993a; Mukherjee 1990).

High pressure metal cutting fluids and lubricants represent 50% of total consumption of CPs in the U.S. and 20% in Canada. CP formulations of lubricants generally consist of short or intermediate carbon chain length compounds of 50 to 60% Cl (Mukherjee 1990). The release of HCl during degradation of CPs under high pressure and thermal conditions during the cutting process produces metal chlorides which improves lubricating properties and extends tool life (Mukherjee 1990). Cutting oil applications are considered to be the greatest potential source of release of CPs to the environment. Cutting oils are often emulsified with surfactants to form water soluble products, greatly enhancing their potential release and introduction to the aqueous environment. Mukherjee (1990) estimated that 4% of CPs on cutting oils are lost to emulsions, 25% remain stuck to metal chips and 71% are partially degraded during the cutting process. Reiger and Ballschmiter (1995) found that CPs in sewage sludge materials from cities in Germany reflect the presence of metal working industries. Areas receiving wastes from metal working plants had CP concentrations in sewage sludges which were greater then residential areas by factors of 2.5 to 15 fold.

CPs as additives to plastics represent 20% of U.S. consumption and 65% of total Canadian consumption (Environment Canada 1993a; Mukherjee 1990). In such applications, CPs are used as secondary plasticizers, as cheaper alternatives to primary plasticizers, and also as additives to yield flame retardant characteristics (Environment Canada 1993a). Plasticizer formulations consist of intermediate carbon chain lengths and degree of chlorination in the 40 to 50% range, whereas CPs used to impart flame retardant characteristics contain high chlorine contents in the 60 to 70% range (Environment Canada 1993a; Willis et al. 1992). Dumping of products such as PVC, leather and textiles may result in the slow release of CPs by leaching out of the product matrix. Kells and Solomon (1995) indicated that leaching of hydrophobic compounds from plastic matrices could occur to varying extents and was dependent on the nature of the plastic matrix. Low density plastic matrices allowed greater leaching releases of imbedded pesticides than high density matrices which exhibited only surface leaching. The extent of release of CPs from plastics, although thought to be low (Campbell and McConnell 1980), remains largely unknown. This is particularly true for landfill sites which may contain a variety of cosolvents and surfactants in leachates which would result in enhanced CP losses (Munz and Roberts 1986; Suresh et al. 1990; Boyd and Sun 1990; West and Harwell 1992). Campbell and McConnell (1980) reported a vapor pressure for an intermediate carbon chain length CP of 52% Cl content in PVC at $4.0 \times 10^{-7}$ Pa, indicating a small but finite release of CPs is possible from plastics by volatilization.

A summary of published physical properties for chlorinated paraffins is outlined in Table 1.1. CPs are considered persistent under most environmental conditions. Photolysis, hydrolysis and oxidation are considered negligible at ambient temperatures (Willis et al. 1992; Environment Canada 1993a; Mukherjee 1990). CPs do not undergo direct photolysis, but may degrade when exposed to light in the presence of oxidizing radicals. Theoretical half lives of CPs in the atmosphere are estimated at 0.5 to 1.8 days (Atkinson 1986). CPs degrade at elevated temperatures above 200°C, and are completely destroyed at 300 to 400°C (Environment Canada 1993a; Svanberg and Lindén 1979).

There is some evidence for biodegradation of CPs, with decreases in biodegradation occurring with increasing carbon chain length and chlorine contents. Half-lives of 25 d were reported for short chain CPs (50% Cl) when acclimated cultures were exposed to 20 and 50 mg/L mixtures (Madeley and Birtly 1980). Madeley and Gillings (1983) found evidence of degradation of short and intermediate chain CPs equilibrated in water over a period of 173 d. Disparity between total activity of a radiolabelled $C_{15}$ CP of 51% Cl content and a radiolabelled $C_{11}$ CP of 59% chlorination and parent compound analysis, by TLC, indicated degradative losses by factors of 3 to 5 fold. The authors attributed the discrepancies to microbial biodegradation.

Few experimental data are available for environmentally important physical properties of chlorinated paraffins, particularly for pure compounds. Vapor pressures, estimated from QSAR models, for various CP congeners have been reported to range from $6 \times 10^{-15}$ to 0.066 Pa, although few experimental measurements have verified such estimates. Log $K_{OW}$ (octanol/water partition coefficients), measured by TLC-$K_{OW}$ correlation techniques and estimated for various CPs using the fragment constant methods of Lyman (1990), were reported in the range of 5.06 to 12.7 (Renberg et al. 1980; Environment Canada 1983b). Sijm and Sinnige (in press) recently reported log $K_{OW}$ values for short chain CPs measured by more standardized slow stirring techniques. In this study, log $K_{OW}$s were reported in the range of 5.85 to 7.14 among homologous compounds separated from the mixture by gas chromatography. Results indicated

**Table 1.1** Published Physical Properties of Chlorinated Paraffins

| Property | Chain Length | %Cl | Method | Value | Unit | Reference |
|---|---|---|---|---|---|---|
| Vapor Pressure | $C_{10}$-$C_{13}$ | 49-71 | Est. | $2.8 \times 10^{-7}$- 0.066 | Pa | Env.Can.1993 b |
| | $C_{14}$-$C_{17}$ | 37-71 | Est. | $1.7 \times 10^{-8}$ - $2.5 \times 10^{-4}$ | Pa | Env.Can.1993 b |
| | $C_{18}$-$C_{26}$ | 34-54 | Est. | $6.3 \times 10^{-15}$-$7.9 \times 10^{-7}$ | Pa | Env.Can.1993 b |
| | $C_{14}$-$C_{17}$ | 52 | NA | $1.3 \times 10^{-4}$ | Pa | Campbell and McConnell 1980 |
| | $C_{23}$ | 42-54 | NA | $2.7 \times 10^{-3}$ | Pa | Willis et al. 1992 |
| Water Solubility | $C_{10}$-$C_{13}$ | 49-71 | Est. | $4.9 \times 10^{-4}$ - 1.26 | $mg \cdot L^{-1}$ | Env.Can.1993 b |
| | $C_{14}$-$C_{17}$ | 37-71 | Est. | $2.9 \times 10^{-5}$ - 0.014 | $mg \cdot L^{-1}$ | Env.Can.1993 b |
| | $C_{18}$-$C_{26}$ | 34-54 | Est. | $1.6 \times 10^{-9}$ - $8.6 \times 10^{-5}$ | $mg \cdot L^{-1}$ | Env.Can.1993 b |
| | C11 | 59% | Batch | 0.150 | $mg \cdot L^{-1}$ | Madeley and Gillings 1983 |
| | C15 | 43% | Batch | 0.005 | $mg \cdot L^{-1}$ | |
| | C25 | 51% | Batch | <0.005 | $mg \cdot L^{-1}$ | " |
| | C25 | 70% | Batch | <0.005 | $mg \cdot L^{-1}$ | " |
| | C16 | 42% | NA | 0.010 | $mg \cdot L^{-1}$ | Campbell and McConnell 1980 |
| HLC | $C_{10}$-$C_{13}$ | 49-71 | Est. | 0.34 - 14.67 | $Pa \cdot m^{3} \cdot mol^{-1}$ | Env.Can.1993 b |
| | $C_{14}$-$C_{17}$ | 37-71 | Est | 0.01 - 51.28 | $Pa \cdot m^{3} \cdot mol^{-1}$ | Env.Can.1993 b |
| | $C_{18}$-$C_{26}$ | 34-54 | Est | 0.003 - 54.82 | $Pa \cdot m^{3} \cdot mol^{-1}$ | Env.Can.1993 b |
| | $C_{14}$-$C_{17}$ | 52 | Est | 10.9 | $Pa \cdot m^{3} \cdot mol^{-1}$ | Willis et al. 1992 |
| log $K_{OW}$ | $C_{10}$-$C_{13}$ | 49-71 | Est | 5.06 - 8.12 | | Env.Can.1993 b |
| | $C_{14}$-$C_{17}$ | 37-71 | Est | 6.83 - 8.96 | | Env.Can.1993 b |
| | $C_{18}$-$C_{26}$ | 34-54 | Est | 8.70 - 12.68 | | Env.Can.1993 b |
| | C10 | 43% | Slow Stir | 5.85 | | Sijm and Sinnige (In Press) |
| | C10 | 50% | | 5.93 | | |
| | C10 | 56% | " | 6.04-6.20 | | " |
| | C11 | 48% | " | 5.93 | | " |
| | C11 | 54% | " | 6.20-6.40 | | " |
| | C11 | 58% | " | 6.40 | | " |
| | C12 | 56% | " | 6.40-6.77 | | " |
| | C12 | 60- | " | 7.00 | | " |
| | C13 | 63% | " | 6.61 | | " |
| | C13 | 49% | " | 6.77-7.00 | | " |
| | C13 | 54% | " | 7.14 | | " |
| Photolysis | $C_{10}$-$C_{13}$ | NA | Est | 1.2 - 1.8 $^{\dagger}$ | d | Atkinson 1986 |
| | $C_{14}$-$C_{17}$ | NA | Est | 0.85 - 1.1$^{\dagger}$ | d | " |
| | $C_{18}$-$C_{30}$ | NA | Est | 0.5 - 0.8$^{\dagger}$ | d | " |
| | | | Direct | Negligible | | Willis et al. 1992 |
| Hydrolysis | | | | Negligible | | Willis et al. 1992 |
| Oxidation | | | | Negligible | | Willis et al. 1992 |
| Biodegradation | $C_{10}$-$C_{13}$ | 58% | BOD | Not degraded 28 d | | Env.Can.1993 b |
| | $C_{10}$-$C_{20}$ | 42% | $^{14}CO_2$ | 11% - 8 weeks$^{\ddagger}$ | | Madeley and Birtley 1980 |
| | $C_{10}$-$C_{13}$ | 50% | | 100% - 25 d$^{\ddagger}$ | | |
| | $C_{20}$-$C_{30}$ | 42% | | 80% - 28 d$^{\ddagger}$ | | " |
| | $C_{24}$ | 70% | | 40% - 28 d$^{\ddagger}$ | | Willis et al. 1992 |

Note: $^{\dagger}$Photolysis based on estimated half life in atmosphere in presence of hydroxy radicals
$^{\ddagger}$Refers to % of compound degraded and duration of study
Est. refers to estimated value using quantitative structure activity relationship models

increases in compound hydrophobicities with increasing carbon chain length and increasing degree of chlorination.

Water solubility ($S_w$) measurements were available from only two studies. Campbell and McConnell (1980) reported a solubility for $C_{16}$ CP containing 52% Cl of 10 $\mu g \cdot L^{-1}$ at temperatures of 16 to 20°C. Madeley and Gillings (1983) measured solubilities, as quantified by parent compound analysis, for 59% chlorinated undecane, 51% chlorinated pentadecane, 43% chlorinated pentacosane and 70% chlorinated pentacosane at 150, 5, <5 and <5 $\mu g \cdot L^{-1}$, respectively, at room temperature. The authors of the latter study, however, observed significant disparity between water concentrations measured by radioactivity and parent compound analysis indicating chemical degradation had occurred during the experimental duration. Estimated solubilities (based on $K_{ow}$ correlations) of CPs were reported to range from $1.6 \times 10^{-6}$ to 1260 $\mu g \cdot L^{-1}$ for compounds among the three carbon chain length categories (Environment Canada 1993a).

There are relatively few reports of environmental levels of chlorinated paraffins. Quantitation has been based on technical products as references, since pure reference compounds are not available. However, the inability to resolve individual isomers in technical mixtures makes selection of appropriate representative standard mixtures among the wide variety of commercially available products difficult. In addition, changes in the character of CP mixtures in environmental samples due to differential partitioning, selective degradation over time and the presence of co-eluting non-CP contaminants remain problems in the quantification and interpretation of levels of CPs among environmental samples (Jansson et al. 1993; Reiger and Ballschmiter 1995; Metcalfe-Smith et al. 1995). The few attempts at quantifying CPs have been restricted to the reporting of levels based on the sum of compounds over broad ranges of carbon chain lengths and degree of chlorination. Interpretation of such levels, with respect to the toxicology database and assessment of risk, is difficult because the sum of concentrations of a number of compounds does not necessarily reflect exposure to individual compounds with varying physico-chemical properties and possible independent mechanisms of toxicity.

Environmental concentrations of chlorinated paraffins reported in the literature are summarized in Table 1.2. Levels of short and intermediate chain length CPs were reported to range from non detectable (ND < 50 ng) to 4 $\mu g \cdot L^{-1}$ in remote freshwater and marine waters from the UK, and up to 6 $\mu g \cdot L^{-1}$ in waters closer to industrial sources (Campbell and McConnell 1980). CPs were not detectable (ND < 1 $\mu g \cdot L^{-1}$) in water samples from the St. Lawrence River, but effluent concentrations of intermediate carbon chain length CPs were reported at 12.7 $ug \cdot L^{-1}$ (Metcalfe-Smith et al. 1995). Sediment concentrations of CPs in remote and industrial areas are reported to range from non-detection (ND < 50 ng) to 14 $mg \cdot kg^{-1}$ on a dry weight basis (Campbell and McConnell 1980; Murray et al. 1988; Reiger and Ballschmiter 1995). A recent study of CPs in sediments from the Detroit River, using a more selective high resolution mass

**Table 1.2** Environmental Concentrations of Chlorinated Paraffins

| Compound | Media | Location | Level | Reference |
|---|---|---|---|---|
| $C_{10}$-$C_{20}$ 45-52%Cl | Freshwater Remote | UK | <0.05 - 1.0 ug·L$^{-1}$ | Campbell & McConnell 1980 |
| $C_{20}$-$C_{30}$45-52% Cl | Freshwater Remote | UK | <0.05 - 0.5 | " |
| $C_{10}$-$C_{20}$45-52% Cl | Freshwater Ind. | UK | 2.0 - 6.0 | " |
| $C_{20}$-$C_{30}$45-52% Cl | Freshwater Ind. | UK | <0.05 - 0.5 | " |
| $C_{10}$-$C_{20}$ | Freshwater Remote | UK | 0.12 - 1.45 | Willis et al. 1992 |
| $C_{20}$-$C_{30}$ | Freshwater Ind. | UK | 0.52-3.75 | " |
| $C_{10}$-$C_{13}$ 60% Cl | Freshwater | Germany | 0.032-0.080 | Reiger & Ballschmiter 1995 |
| $C_{14-17}$, 52% Cl | Industrial Effluent | Canada | 12.7 | Metcalfe-Smith et al. 1995 |
| $C_{10}$-$C_{13}$ 60% Cl | Industrial Effluent | Germany | 0.115 | Reiger & Ballschmiter 1995 |
| $C_{10}$-$C_{20}$45-52% Cl | Marine Water | UK | <0.05 - 4.0 | Campbell & McConnell 1980 |
| $C_{20}$-$C_{30}$45-52% Cl | Marine Water | UK | <0.05 - 2.0 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Sediments Remote | UK | ND-1.0 mg·kg$^{-1}$[‡] | Campbell & McConnell 1980 |
| $C_{20}$-$C_{30}$ 45-52%Cl | Sediments Remote | UK | ND - 0.6 | " |
| $C_{10}$-$C_{13}$ 60-70%Cl | Sediment Industrial | Canada | 0.342-1.07 | Fisk et al. 1996 |
| $C_{10}$-$C_{20}$ 45-52%Cl | Sediment Industrial | UK | ND - 14.0 | Campbell & McConnell 1980 |
| $C_{10}$-$C_{20}$ 45-52%Cl | Sediment Industrial | UK | ND - 3.2 | " |
| $C_{10}$-$C_{20}$ | Sediment Industrial | US | 0.0068 -0.014 | Murray et al. 1988 |
| $>C_{20}$ | Sediment Industrial | US | 0.0098 - 0.021 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Sewage sludge | UK | ND- 10 | Campbell & McConnell 1980 |
| $C_{10}$-$C_{13}$ 60% Cl | Sewer films/sludge | Germany | 0.5 - 65 | Reiger & Ballschmiter 1995 |
| $C_{10}$-$C_{13}$ 60-70%Cl | Fish | Canada | 0.01-3.2mg·kg$^{-1}$[§] | Fisk et al. 1996 |
| $C_{10}$-$C_{13}$ 60-70%Cl | Mussels | Canada | 0.11-1.83 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Fish Tissue | UK | ND - 0.2 | Campbell & McConnell 1980 |
| $C_{10}$-$C_{20}$ 45-52%Cl | Mussels | UK | 0.1-12.0 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Seal Liver and | UK | 0.04-0.1 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Blubber | UK | ND-2.0 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Seabird Eggs | UK | ND-1.5 | " |
| $C_{10}$-$C_{20}$ 45-52%Cl | Human Tissue | UK | ND - 0.3 | " |
| $C_{20}$-$C_{30}$ 45-52%Cl | Human Food | UK | ND - 0.2 | " |
| $C_{20}$-$C_{30}$ 45-52%Cl | Fish Tissue | UK | ND - 0.1 | " |
| $C_{20}$-$C_{30}$ 45-52%Cl | Mussels | UK | ND - <0.05 | " |
| $C_{20}$-$C_{30}$ 45-52%Cl | Seal Liver/Blubber | UK | ND - 0.1 | " |
| CP | Seabird Eggs | Sweden | 2.9[†] | Jansson et al. 1993 |
| CP | Rabbit | Sweden | 4.4[†] | " |
| CP | Moose | Sweden | 0.14[†] | " |
| CP | Reindeer | Sweden | 1.0[†] | " |
| CP | Whitefish | Sweden | 0.57[†] | " |
| CP | Arctic char | Sweden | 1.4 - 1.6[†] | " |
| CP | Herring | Sweden | 0.13 - 0.28[†] | " |
| CP | Seal | Sweden | 0.53[†] | " |

Note: Industrial/Ind. = Sampling Site Near Industrial Areas
Remote = Sampling Sites remote from industrial areas
[‡] Concentration expressed on a dry weight basis
[§] Concentration expressed on a wet weight basis
[†] Concentration expressed on a lipid normalized basis (mg·kg$^{-1}$ lipid)
ND = non detection. Detection limits for Campbell and MacConnell (1980) studies reported at 50 ng extracted

spectrometry technique (GC-ECNI/HRMS), indicate North American levels of short chain CPs ranging from 0.34 to 1.07 $mg{\cdot}kg^{-1}$, similar to levels reported in industrial areas of the U.K (Fisk et al.1996). Fisk et al. (1996) identified CPs as major organochlorine contaminants in Detroit River mussel and fish samples with levels of CPs exceeding ∑PCBs, ∑DDT and ∑chlorinated benzenes. Jansson et al. (1993) also recognized CPs as major contaminants in wildlife species from Sweden, particularly among terrestrial mammals of rabbit and moose. CP concentrations (CP mixture character not identified) among 11 wildlife species including fish, birds, and terrestrial and aquatic mammals ranged from 0.13 to 4.40 $mg{\cdot}kg^{-1}$ on a lipid weight basis.

Results from these limited studies indicate that CPs are entering the environment and may exhibit significant mobility as indicated by their presence in wildlife samples remote from industrial sources. Developing a database on key physical properties such as water solubilities, Henry's law constants and various partition coefficients is, therefore, a necessary step in further modeling the environmental fate and distribution of chlorinated paraffins. To date, the available physical property data on CPs is limited to technical mixtures with little or no data on individual isomers. The complexity of technical mixtures, which may consist of hundreds of molecular species and larger numbers of positional isomers, has precluded the determination of physical properties of single compounds, a necessary pre-requisite for many thermodynamic based environmental fate models in use today.

Of particular interest are the short chain chlorinated paraffins (carbon chain lengths $C_{10}$ to $C_{13}$) which have the greatest potential for environmental release (Environment Canada 1993a), appear to exhibit the highest toxicity (Serrone et al. 1986; Mukherjee 1990; Willis et al. 1992) and have the greatest environmental mobility. In this research, synthesized polychlorinated decanes, undecanes and dodecanes (Tomy et al. 1993, 1994, 1995) containing resolvable tetra-, penta- and hexachloro- congeners were utilized as chlorinated alkanes to estimate selected physical properties of chlorinated paraffins. In addition, a $^{14}C$-polychlorinated dodecane mixture (Bergman et al. 1981) was studied in order to validate the use of surrogate compounds in estimating the behavior of chlorinated paraffin mixtures. The physical property determinations included vapor pressures, water solubilities, Henry's law constants, and $K_{OC}$s (organic-carbon water partition coefficients) for individual short chain CP isomers and the $^{14}C$-polychlorinated dodecane mixture. These data were combined with studies on purified 1,10-dichlorodecane and 1,12-dichlorododecane, available from Aldrich Chemical Company, in order to derive relationships between degree of chlorination and physical properties for chlorinated alkanes having carbon chain lengths greater than $C_{10}$.

## 1.2. Synthesis of Chlorinated Paraffins (Commercial Mixtures of Chlorinated Alkanes)

CPs are produced commercially by free-radical substitution in which chlorine gas is bubbled through a petroleum fraction at elevated temperature (50 to 100°C). In some cases the reaction is also carried out under elevated pressure or in the presence of UV light. The reaction involves the formation of free radicals (Zlatkis et al. 1973) with the eventual substitution of H atoms by Cl atoms as outlined by Mukherjee:

$$\mathrm{Cl_2} \xrightarrow[\text{or light}]{\text{heat}} \mathrm{2Cl\cdot} \qquad \text{Chain Initiation}$$

$$\mathrm{Cl\cdot + RH} \longrightarrow \mathrm{R\cdot + HCl} \qquad \text{Chain Propagation}$$
$$\mathrm{R\cdot + Cl_2} \longrightarrow \mathrm{RCl + Cl\cdot}$$

The reaction is moderated by the presence of trace amounts of oxygen, iodine, aromatic sulfides and nitric oxide which react with radicals to form less reactive radicals (Mukherjee 1990; Zlatkis et al. 1973). The chlorination reaction produces a large number of congeners and positional isomers, but shows some selectivity at lower temperatures. Substitutions occur most readily on secondary carbons followed by primary carbons and are mainly nonvicinal at lower degrees of chlorination (Campbell and McConnell 1980; Zlatkis et al. 1973). In addition, steric constraints limit a maximum of one Cl atom per carbon atom, to yield a maximum degree of chlorination of approximately 70% (i.e., 70% of the molecular weight of the compound is composed of chlorine; Mukherjee 1990; Willis et al. 1992).

The properties of the chlorinated product are regulated by the choice of hydrocarbon feedstock utilized, duration of reaction, temperature, pressure and gas flow rates employed (Willis et al. 1992; Mukherjee 1990). Feedstocks generally consist of alkane fractions which are 98% linear, since the presence of branched chain hydrocarbons reduces the stability of the chlorinated products (Environment Canada 1993a; Mukherjee 1990). Feedstocks include pure alkanes and petroleum fractions which will vary depending on the petroleum oil source (Willis et al. 1992; Environment Canada 1993a). In addition, another class of industrial compounds known as chlorinated olefins are produced, employing similar reaction conditions but utilizing olefinic fractions as starting materials (P. Ostrowski 1996, Occidental Chemical Corp., Niagara Falls; personal communication). The reaction mechanism for chlorination of olefins include chlorine addition across the double bonds in addition to random free radical substitution when the reaction is performed at elevated temperatures or pressures. Chlorinated olefins differ from CPs in that chlorination at adjacent carbons will occur more readily in formulations containing lower degrees of chlorination, and Cl addition at primary carbons can be more readily obtained provided that the double bond in the starting material is at the 1,2 position (i.e. terminal double bond which results in vicinal chlorines in the product).

## 1.3. Synthesis of Chlorinated Alkanes Utilized for Physical-Chemical Property Determinations

Free radical substitution produces large numbers of congeners and isomers which cannot easily be resolved by high resolution gas chromatography. The inability to isolate individual isomers makes characterization and physical property determination difficult, and in some cases impossible given the available experimental techniques. As a result, chlorinated alkane compounds were synthesized and supplied to our laboratory by an alternative approach by G. Tomy (Tomy et al. 1993; 1994; 1995). The synthesis involved bubbling chlorine gas through pure starting materials of 1,9-decadiene, 1,10-undecadiene or 1,11-dodecadiene at 0°C in the absence of light. Such reaction conditions favour chlorine addition, which occurs across the double bonds, and leads to products containing vicinal Cls at the terminal ends for the above starting olefinc materials.

The major product for each reaction included 1,2,9,10-tetrachlorodecane, 1,2,10,11-tetrachloroundecane and 1,2,11,12-tetrachlorododecane, respectively. In addition, free radical substitution produced smaller quantities of multiple isomers of penta-, hexa-, hepta- and octachloro- congeners. Note for the penta-, hexa-, hepta and octachloro-congeners, at least four of the chlorines have known substitution patterns residing on the adjacent primary and secondary carbons at the terminal ends of the molecule. The position of the Cl atoms added by free radical substitution are random and unknown and will be denoted for example as 1,2,x,9,10 pentachlorodecane or 1,2,x,x,11,12 hexachlorododecane, where x refers to a Cl added to the molecule by free radical substitution. Tomy et al. (1994; 1995) interpreted GC/EI-MS and GC/ECNI-MS spectra of the products to verify the identification of the components within each mixture.

Along with the three synthesized chlorinated alkane products, 1,9-dichlorodecane and 1,12-dichlorododecane were purchased from Aldrich Chemical Co.. For brevity, the following acronyms will be defined for the two dichlorinated alkanes and the chlorinated alkanes synthesized by the above reaction. Di-, tetra-, penta- or hexachloro- congeners are to be denoted as $D_2$, $T_4$, $P_5$ and $H_6$, respectively. Hepta- and octachlorinated compounds represented a negligible mass of total product and were not measured in physical property determination experiments. The carbon chain length of the molecule will be denoted as $C_X$, where $_X$ refers to the number of carbons. Table 1.3 lists the compounds which are present in each of the mixtures and their respective acronyms.

**Table 1.3** Chlorinated Alkanes Utilized in Physical Property Determinations

| Chemical | Formula | Acronym | MW |
|---|---|---|---|
| 1,10-dichlorodecane (pure) | $C_{10}H_{20}Cl_2$ | $D_2C_{10}$ | 211.12 |
| 1,2,9,10-tetrachlorodecane | $C_{10}H_{18}Cl_4$ | $T_4C_{10}$ | 280.07 |
| 1,2,x,9,10-pentachlorodecane | $C_{10}H_{17}Cl_5$ | $P_5C_{10}$ | 314.51 |
| 1,2,x,x,9,10-hexachlrodecane | $C_{10}H_{16}Cl_6$ | $H_6C_{10}$ | 348.95 |
| 1,2,10,11-tetrachloroundecane | $C_{11}H_{20}Cl_4$ | $T_4C_{11}$ | 294.09 |
| 1,2,x,10,11-pentachloroundecane | $C_{11}H_{19}Cl_5$ | $P_5C_{11}$ | 328.54 |
| 1,2,x,x,10,11-hexachloroundecane | $C_{11}H_{18}Cl_6$ | $H_6C_{11}$ | 362.98 |
| 1,12-dichlorododecane (pure) | $C_{12}H_{24}Cl_2$ | $D_2C_{12}$ | 239.23 |
| 1,2,11,12-tetrachlorododecane | $C_{12}H_{22}Cl_4$ | $T_4C_{12}$ | 308.12 |
| 1,2,x,11,12-pentachlorododecane | $C_{12}H_{21}Cl_5$ | $P_5C_{12}$ | 342.56 |
| 1,2,x,x,11,12-hexachlorododecane | $C_{12}H_{20}Cl_6$ | $H_6C_{12}$ | 377.01 |

Note: x in chemical name indicates unknown chlorine position, in which chlorine was added by free radical substitution.

It should be noted that the chlorinated alkanes synthesized by the chlorine addition method may differ from chlorinated alkanes found in commercial CP mixtures. All of the synthesized products utilized in this study contain chlorines substituted at both primary carbons and at the adjacent secondary carbons. Such substitution patterns are less likely to occur under free radical substitution reactions, particularly for compounds containing a lower degree of chlorination. However, synthesizing the compounds in this manner yields information regarding the exact substitution pattern (for at least 4 chlorines in a given compound). In addition, chlorine substitution patterns for each congener series within a carbon chain length, and among different carbon chain lengths remained consistent allowing for better interpretation of physical property results on a quantitative structure activity relationship basis.

Chlorinated alkanes in industrial mixtures are defined according to the hydrocarbon feedstock employed during the chlorination process (e.g., chlorinated paraffins *vs* chlorinated olefins). Both types of feedstocks result in the formation of chlorinated alkane compounds, although chlorine substitution patterns may differ among the products formed. Exact characterization of components in technical CP grades cannot be performed because of the complexity of the mixtures which exhibit broad and weak peaks when utilizing IR or NMR techniques (Hollies et al. 1979). Confirmation of the presence of the chlorinated alkanes synthesized for this study in commercial formulations of chlorinated paraffin or chlorinated olefin mixtures cannot at present be made. However, since the compounds utilized in this study reflect some of the first documented physical properties on pure chlorinated alkane isomers of carbon chain lengths of $C_{10}$ and greater, it is proposed that the compounds utilized in this study can be defined as surrogate compounds for assessing the environmental fate and behavior of components of technical grade short chain CP and chlorinated olefin mixtures.

## 1.4. Methods

### 1.4.1. Chemicals

1,10-Dichlorodecane and 1,12-dichlorododecane were purchased from Aldrich Chemical Co., Milwaukee, WI, with reported purities of 99 and 98%, respectively. Analysis of the two chemicals by GC/EI-MS in full scan mode indicated no secondary peaks. Polychlorinated decanes, undecanes and dodecanes were synthesized and supplied by G. Tomy, Department of Chemistry, University of Manitoba. The characterization and purity of these compounds is reported in Section 1.5. A 1-chloro[1-$^{14}$C]polychlorinated dodecane mixture was supplied by Å. Bergman, University of Stockholm (Bergman et al. 1981). The purity of this mixture and its characterization is summarized in Section 1.6. The specific activity of the mixture was reported by Bergman et al. to be 42.7 μCi/mg.

Lindane (γ-HCH), which was utilized as an internal standard for all samples in subsequent physical property determination experiments, purchased from Supelco Canada, Mississauga, ON, had a reported purity of 99%. Several calibration compounds, used in vapor pressure determinations, including p,p'-DDT, aldrin, heptachlor and mirex were from Supelco Canada, Mississauga, ON. All chemicals had reported purities of 99%. No secondary peaks were observed when chemicals were analyzed by GC-ECD analysis. Vapor pressure calibration compounds also included a mixture containing 12 PCB congeners (IUPAC numbers: 4, 5, 27, 48, 74, 95, 110, 132, 187, 156, 198 and 205) which were prepared from purchased standards and supplied by D.C.G. Muir from the Freshwater Institute, Fisheries and Oceans, Winnipeg, MB. The PCBs were dissolved in isooctane, with each congener having a concentration of 0.2 $ng \cdot \mu L^{-1}$.

All solvents utilized in physical property determination experiments were of GC, HPLC and spectrophotometry grade. Acetone, hexane, methanol and isooctane (2,2,4-trimethylpentane) were purchased from Anachemia, Winnipeg, MB. HPLC grade water, utilized in solubility, HLC and $K_{OC}$ studies, was purchased from Anachemia, Winnipeg, MB. The scintillation cocktail, utilized for analysis of the 1-chloro[1-$^{14}$C]polychlorinated dodecane mixture, was ScintiVerse® II purchased from Fisher Scientific, Edmonton, AB. Anhydrous sodium sulfate, purchased from Anachemia, Winnipeg, MB, was washed with several rinsings of hexane prior to use. Tenax resin (35/60 mesh), utilized as a solid phase for trapping volatilized chlorinated alkanes in HLC experiments, was purchased from Chromatographic Specialties, Brockville, ON. Solid phase extraction cartridges ($C_{18}$, 200 mg; SepPak® Plus), used to extract water in solubility experiments and in reverse-phase separation experiments for $K_{OC}$ determinations, were purchased from Millipore-Waters Chromatography, Milford, MA.

### 1.4.2. Instrumentation

The chlorinated alkanes were analyzed by high resolution gas chromatography (GC/ECNI-MS) using a Hewlett Packard 5890 GC coupled with a HP5989B MS in negative chemical ionization mode. The column was a 30 m x 0.25 μm x 0.25 μm HP-5 (5% phenyl). Selected standards and samples were also quantified with either a HP 5890 GC coupled with a HP 5970 EI-MSD (mass selective detector) using a 60 m x 0.25 mm x 0.10 μm column (Supelco SPB-5) or a HP 5890 GC equipped with a $^{63}$Ni-electron capture detector (ECD) and 30 m x 0.25 mm x 0.10 μm column (Supelco SPB-5). In the latter system, analysis was performed by manual injection of 1 to 2 μL of sample on a splitless injection port held at 200°C. Nitrogen was used as the makeup and helium as the carrier gas. For the two MS systems, 1 to 2 μL of sample was injected, via a HP7673 autosampler, into a splitless injection port held at 200°C. Helium carrier flow rates, for all three instruments, were adjusted to 60 mL/min. A typical temperature program was as follows: initial temperature held at 90°C (2 min), 10°C/min to 180°C, 5°C/min to 250°C (30 min). Analysis was performed in a block manner where every third sample analyzed consisted of a standard. Solvent and extracted HPLC-water blanks were analyzed periodically to check for chlorinated alkane contamination.

## 1.5. Characterization of Chlorinated Alkanes

Although radical substitution reactions in each synthesized mixture produced multiple isomers, the number of isomers generated was sufficiently small that at least some isomers could be separated and individually quantified by high resolution gas chromatography.

Figures 1.1, 1.2 and 1.3 represent sample GC/ECD chromatograms of the polychlorinated decanes, undecanes and dodecanes. A major peak in each chromatogram, denoted by the $Cl_2$, was identified as a dichloro-olefin in which Cl addition occurred across only one of the double bonds of the starting materials. The molecular ions for the 1,2-dichlorodecene (208), 1,2-dichloroundecene (222) and 1,2-dichlorododecene (236) were identified by Tomy et al. (1994, 1995) using GC-EI-MS. The relative abundance of the dichloro-olefin varied from batch to batch and was likely dependent on the duration of the chlorination step and small variations in reaction conditions during synthesis.

The second peak in each chromatogram, denoted by $Cl_4$, represents the favored tetrachlorinated product in which chlorine addition occurred across both double bonds. Penta-, hexa-, hepta- and octachlorinated congeners follow in elution sequence. Mass spectra (EI-MS), as identified by G. Tomy, were nearly identical among the 4 peaks of pentachlorodecanes (denoted as Cl5a, b, c and d), 5 peaks of pentachloroundecanes (denoted as Cl5a, b, c, d and e) and 5 peaks of pentachlorododecanes. Similarly, nearly identical mass spectra were observed among the hexachlorinated isomer groups and heptachlorinated isomer groups for each product.

Although molecular ions were not apparently produced using EI-MS for the tetra-, penta- or hexachlorinated isomers, prominent [M-$HCl^+$], [M-$Cl^+$] and [M-$2HCl^+$] ions were identified for each grouping (Tomy et al. 1994, 1995). Other investigators have also

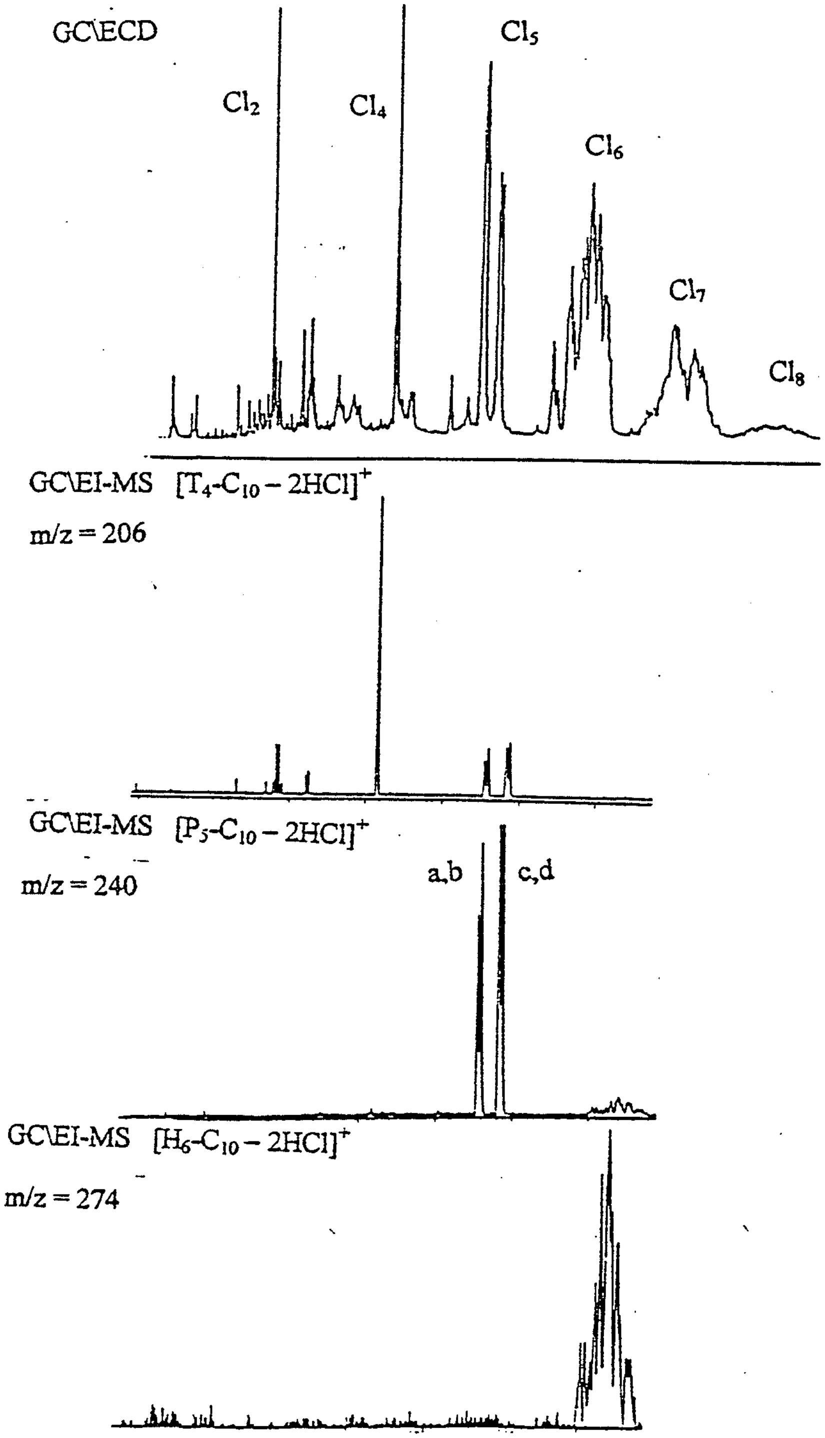

Figure 1.1 GC/ECD and GC/EI-MS characterization of polychlorinated decanes. First chromatogram analyzed by GC/ECD using a 30 m x 0.25 mm x 0.10 µm SPB-5 column. Second, third and fourth chromatograms analyzed by GC/EI-MS using a 60 m x 0.25 mm x 0.10 µm SPB-5 column under selective ion monitoring mode (SIM). The major ion and its corrosponding m/z value analyzed using SIM are identifed at the top of each chromatogram for those employing EI-MS detection.

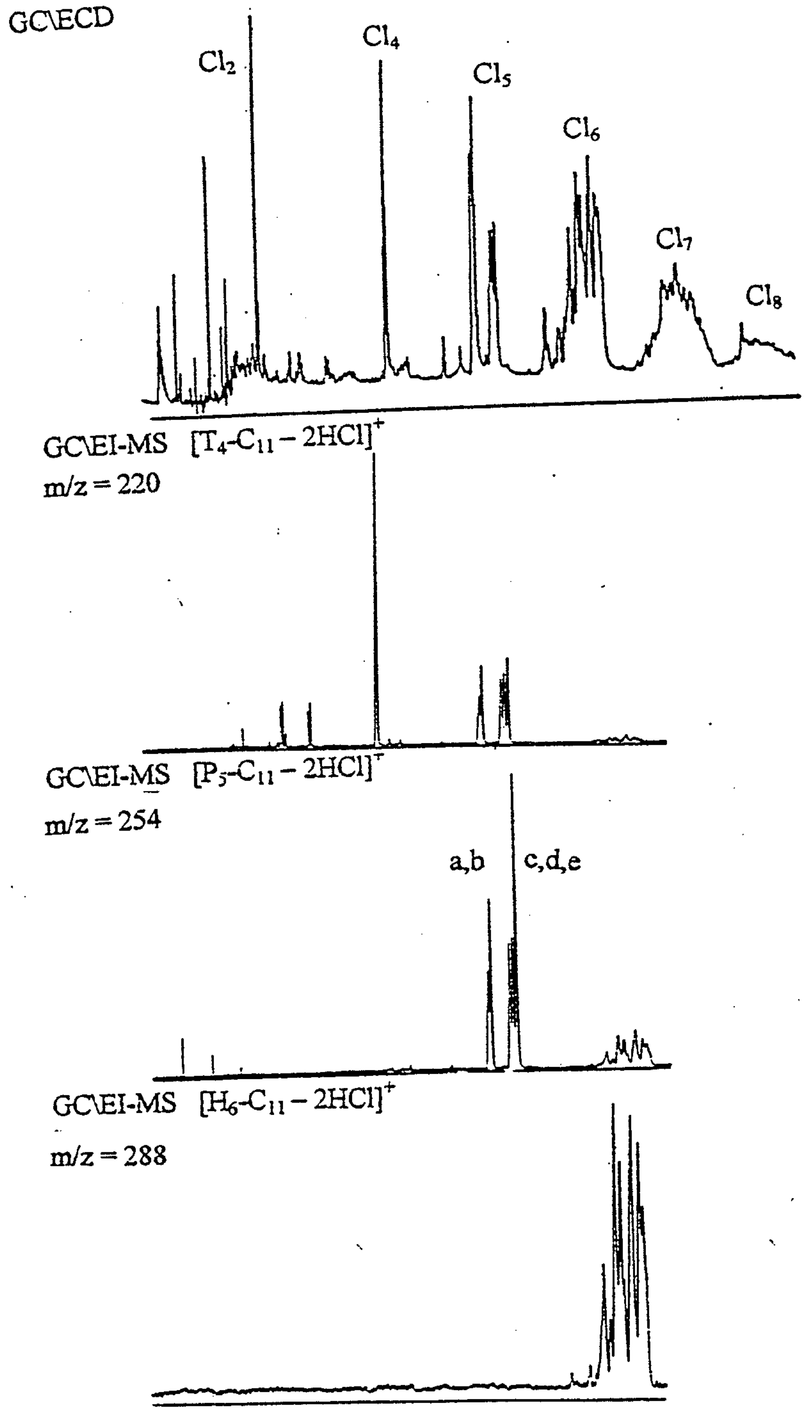

Figure 1.2 GC/ECD and GC/EI-MS characterization of polychlorinated undecanes. First chromatogram analyzed by GC/ECD using a 30 m x 0.25 mm x 0.10 µm SPB-5 column. Second, third and fourth chromatograms analyzed by GC/EI-MS using a 60 m x 0.25 mm x 0.10 µm SPB-5 column under selective ion monitoring mode (SIM). The major ion and its corrosponding m/z value analyzed using SIM are identifed at the top of each chromatogram for those employing EI-MS detection.

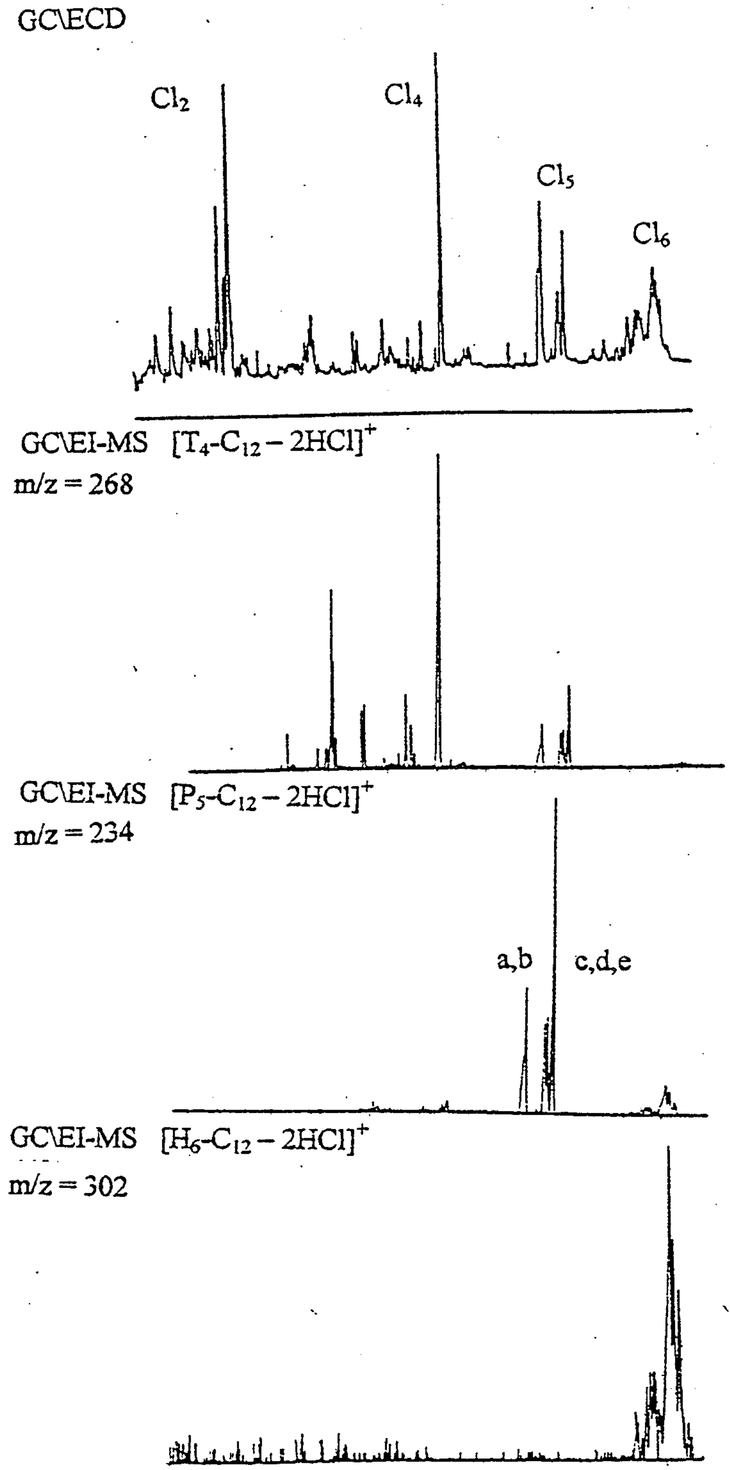

Figure 1.3 GC/ECD and GC/EI-MS characterization of polychlorinated dodecanes. First chromatogram analyzed by GC/ECD using a 30 m x 0.25 mm x 0.10 µm SPB-5 column. Second, third and fourth chromatograms analyzed by GC/EI-MS using a 60 m x 0.25 mm x 0.10 µm SPB-5 column under selective ion monitoring mode (SIM). The major ion and its corrosponding m/z value analyzed using SIM are identifed at the top of each chromatogram for those employing EI-MS detection.

indicated a lack of molecular ions in EI-MS spectra of chlorinated paraffin mixtures, with abundant ions formed by losses of HCl and HCl+Cl (Metcalfe-Smith et al. 1995; Gjøs et al. 1982; Zitko 1980). In addition to the GC/ECD traces, Figures 1.1, 1.2 and 1.3 also contain GC/EI-MS traces under selective ion monitoring (SIM) mode, in which the $[M-2HCl]^+$, the most prominant ion for each compound, was monitored over an entire chromatographic run for each of the tetra-, penta- and hexachlorinated congeners.

The second chromatogram in each figure corresponds to the selected ion trace in which only the $[T_4C_x–2HCl]^+$ ion was monitored ($T_4C_{10}$ m/z = 206, $T_4C_{11}$ m/z = 220, $T_4C_{12}$ m/z = 234). The tetrachlorinated congener was isolated from the other components in the mixture for all compounds, with only small amounts of pentachloro- and hexachlorinated congeners being detected. The detection of small quantities of penta- and hexachloro-congeners in these traces are likely due to the formation of fragment ions corresponding to ions of $[P5C_x–2Cl–HCl]^+$ and $[H_6C_x–4Cl]^+$, respectively. Likewise, selective ion monitoring for $[P_5C_x–2HCl]^+$ and $[H_6C_x–2HCl]^+$, corresponding to the third and fourth chromatograms of Figures 1.1 to 1.3, successfully identified the pentachloro- and hexachlorinated groupings within each mixture. As with tetrachlorinated congeners, some hexachloro- compounds were detected during the $[P_5C_x–2HCl]^+$ selective ion scan as a result of $[H_6C_x–2Cl–HCl]^+$. For all three mixtures, the fourth chromatogram contains only the hexachlorinated grouping, indicating no overlap in chromatographic behaviour of different congeners within each mixture.

Long GC programs (3 h) were employed using GC/ECD to further separate and detect the hexachlorinated isomers from each of the mixtures. A total of 24 peaks were observed in the $H_6C_{10}$ grouping, and 15 $H_6C_{11}$ (Figure A.1 of Appendix) and $H_6C_{12}$ (Figure A.2 of Appendix) peaks were noted in each of the products. The hepta- and octachlorinated congeners could not be resolved sufficiently to determine the number of isomers present, but this group represented a very small component of the total mixture.

### 1.5.1. Quantification of Chlorinated Alkanes

Quantification of individual compounds in each of the synthesized chlorinated alkane products was obtained using both an internal standard, and an external standard method. In the internal standard method, standards of two chlorinated aliphatics (lindane and $D_2C_{10}$ dissolved in isooctane) were prepared by gravimetrically. The internal standards were then added at 10 $ng \cdot \mu L^{-1}$ to each of the diluted synthesized chlorinated alkane mixtures, and the mixture was analyzed using a non-selective detector, GC/EI-MS under full scan (m/z range of 50 to 500) conditions. The ratio of peak area of each compound in the synthesized chlorinated alkane mixtures to the internal standard peak areas were used to estimate concentrations under the assumption that the ionization efficiency of the chlorinated alkane congeners were similar to that of lindane and $D_2C_{10}$. Comparison of the MS response to $D_2C_{10}$ and lindane yielded response factors which were similar within a factor of 1.25 ± 0.04 (n=13) when both compounds were added at the same concentration. This agreement in the detector response between the two compounds supports the assumption that the EI-MS was behaving as a non-selective detector.

In the external standard method, a small quantity (<1 mg) of purified 1,2,9,10-tetrachlorodecane was supplied by A. Fisk. The $T_4C_{10}$ compound was isolated by a GC preparative technique (A. Fisk, University of Manitoba, MB, personal communication). The isolated material was transferred to a pre-weighed 0.3 mL reaction vial using successive washings of hexane and the solvent was allowed to evaporate to constant mass in a dessicator over a period of 7 days. The mass of isolated product was determined using a micro balance and subsequently diluted with isooctane to produce a series of standards used for quantifying the $T_4C_{10}$ component in the polychlorinated decane mixture.

Both the internal standard and external standard quantitation methods yielded comparable estimates of concentrations for the $T_4C_{10}$, and for the $P_5C_{10}$ and $H_6C_{10}$ components, when the assumptions of non-selective detection by EI-MS were made. The agreement between the two methods was within a factor of 1.46±0.02 (n=13). Greater confidence was placed in the internal standard method of quantifying the $T_4C_{10}$, since the purified tetrachlorodecane used to develop standards contained trace impurities and was subject to greater relative error as a result of weighing a small mass (<1 mg). Concentrations of all other chlorinated alkane congeners were quantified using the internal standard method in a similar manner to that described for $T_4C_{10}$.

Both quantification methods accounted for only 21 to 45% of the total product which was gravimetrically added to each standard. The remaining mass was assumed to be unreacted starting material of 1,9-decadiene, 1,10-undecadiene or 1,11-dodecadiene, which eluted out with the solvent front under the chromatographic conditions employed. Other major impurities in the mixtures included the dichloro-alkenes, quantified by EI-MS, which consisted of 4.1 to 13.5% of the total product mass.

The percent composition of individual components in the polychlorinated decane, undecane and dodecane mixtures are summarized in Table 1.4. Standards were prepared by weighing a quantity of synthesized product into a 100 mL volumetric flask, and diluting to volume with isooctane. Individual congener concentrations were calculated using Table 1.4.

Standard calibration curves were found to be linear (coefficient of determination > 0.93) when analyzed by GC/ECD, GC/EI-MS and GC/ECNI-MS over concentration ranges of 1.3 to 70.6 ng injected. Detection limits were lowest using GC/ECD, particularly for the most highly chlorinated congeners, and were found to be similar among compounds of the three carbon chain lengths for a given number of chlorines. Detection limits, based on the minimum quantifiable peak area, for tetra-, penta- and hexachlorinated congeners ranged from 0.4 to 0.8, 0.2 and 0.03 to 0.05 ng injected, respectively. The observed detection limits for chlorinated alkanes using GC/ECD were considerably higher than those observed for chlorinated aromatics of a similar degree of chlorination. Other investigators have also indicated a lower sensitivity of GC/ECD to chlorinated paraffins (Svanberg and

**Table 1.4** Percent Composition of Synthesized Chlorinated Alkanes in Polychlorinated Decane, Undecane and Dodecane Mixtures

| Compound | Polychlorinated Decane | Polychlorinated Undecane | Polychlorinated Dodecane |
|---|---|---|---|
| diene[†] | 54.8 | 65.0 | 78.9 |
| $Cl_2$ (Olefin) | 8.4 | 4.1 | 13.5 |
| $Cl_4$ | 13.3 | 11.0 | 5.2 |
| $Cl_5$ | 15.0 | 12.9 | 2.4 |
| $Cl_6$ | 8.5 | 7.0 | <1 |

Note: Yield based on percent wt. basis of total synthesized product
[†] Amount of diene starting material calculated by forcing a mass balance, i.e. as 100% - (olefin + $Cl_4$ + $Cl_5$ + $Cl_6$)
chlorined alkene and chlorinated alkane congeners quantified by EI/MS using the internal standard method

Lindén 1979; Metcalfe-Smith et al. 1995). Metcalfe-Smith et al. (1995) reported a detection limit for chlorinated paraffin mixtures in water analyzed by GC/ECNI-MS of 1 $\mu g \cdot L^{-1}$, corresponding to a mass injected of approximately 1 ng, similar to that reported here.

## 1.6. Characterization of Chlorinated Dodecanes Synthesized by Free Radical Substitution

A 1-chloro-1-$^{14}$C-polychlorinated dodecane mixture synthesized by free radical substitution was provided by Å. Bergman, Stockholm University (Bergman et al. 1981). The polychlorinated dodecane mixture was utilized for determination of physical properties in order to validate the assumption that the chlorinated alkanes synthesized by chlorine addition are appropriate surrogates for physical property determinations of chlorinated paraffins which are synthesized by free radical substitution.

The mixture contained a chlorine substituted at a primary carbon yielding a 1-chloro-polychloro-1-$^{14}$C-dodecane mixture with an activity of 42.7 $\mu Ci \cdot mg^{-1}$. The average chlorine content was 55.9% as determined by elemental analysis after cleanup on a silica gel column and subsequent washings with an aqueous solution (Bergman 1981). The average chlorine content of 55.9% corresponds to an average molecular formula of $C_{12}H_{20.1}Cl_{5.9}$. The total ion chromatogram presented in Figure 1.4 of the $^{14}$C-polychlorinated dodecane standard obtained using GC\ECNI-MS shows four broad bands having an elution time in the range of 25 to 35 minutes. Each of the broad bands appear to contain numerous unresolvable compounds.

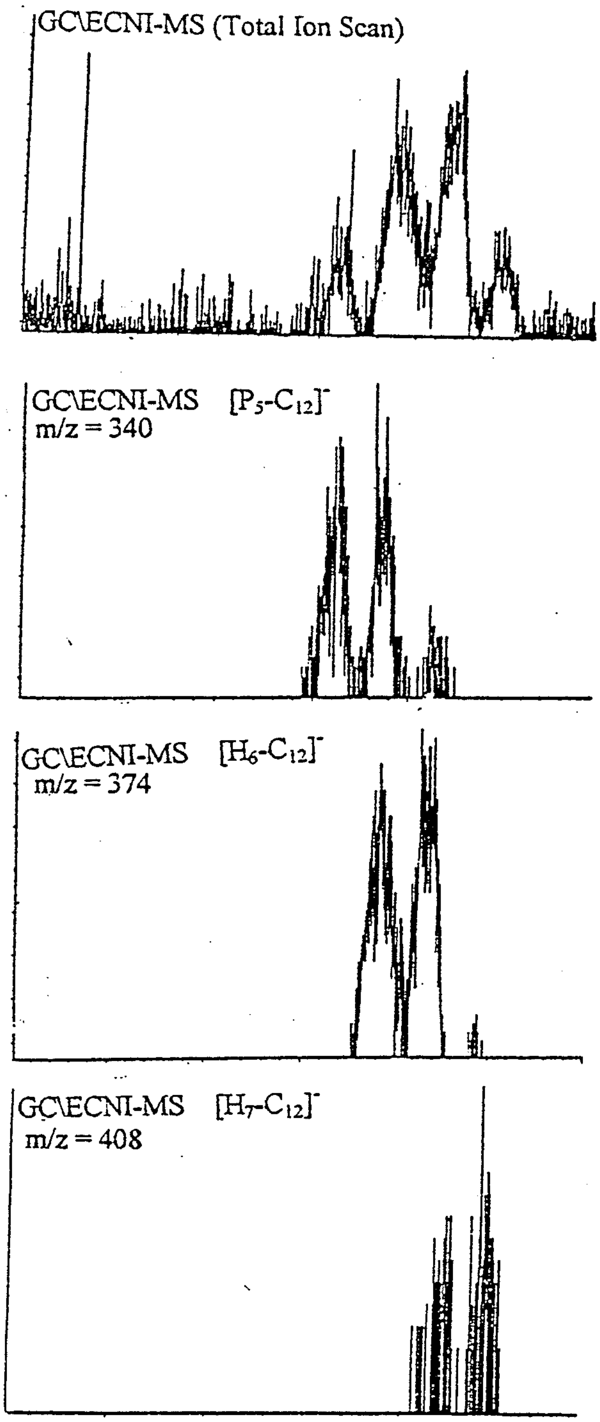

Figure. 1.4 GC/ECNI characterization of $^{14}$C-polychlorinated dodecane mixture. All chromatograms analyzed using a 30 m x 0.25 µm x 0.25 µm HP-5 column under identical chromatographic conditions. First chromatogram represents a total ion scan (m/z 100 to 550) using negative chemical ionization. Second third and fourth chromatograms analyzed under selective ion monitoring mode (SIM). The major ion and its corrosponding m/z value analyzed using SIM are identified at the top of each chromatogram.

The detection limits of full scan GC/EI-MS were not sufficient to allow characterization of the $^{14}$C-polychlorinated dodecane standard. Mass spectra based on ECNI-MS were available, but difficult to interpret due to overlap of congeners within the broad chromatographic bands. Selective ion monitoring for molecular ions of $[T_4C_{12}]^-$, $[P_5C_{12}]^-$, $[P_6C_{12}]^-$, $[H_7C_{12}]^-$ and $[O_8C_{12}]^-$ was performed. Molecular ions were chosen, since negative ionization produces less fragmentation relative to EI-MS. The selective ion chromatograms are summarized in Figure 1.4 (second, third and fourth chromatograms). No $[T_4C_{12}]^-$ or $[O_8C_{12}]^-$ molecular ions were observed in the $^{14}$C-polychlorinated dodecane mixture, however, abundant , $[P_5C_{12}]^-$, $[P_6C_{12}]^-$ and $[H_7C_{12}]^-$ ions corresponding to portions of the broad bands were noted. The $[P_5C_{12}]^-$ ions appeared to be mainly associated with the first and second bands and a small portion of the third band, the $P_6$-$C_{12}^-$ appeared to be a dominant component of the second and third bands, and a smaller amount of $[H_7C_{12}]^-$ ions were associated mainly with the fourth band. Results from the GC/ECNI-MS characterizations are consistent with the elemental analysis performed by Bergman et al. (1981), indicating an average molecular formula for the mixture approximately corresponding to a hexachlorododecane.

All subsequent quantification of the $^{14}$C-polychlorinated dodecane standard in physical property determination experiments, with the exception of the vapor pressure determinations, were performed by scintillation counting techniques. This method quantifies total activity in the sample and, therefore, reflects the sum of congeners in the sample. Extracted samples were placed in 20 mL scintillation vials to which was added 10 mL of scintillation cocktail. Samples were analyzed on a Beckman LS7500 liquid scintillation counter with automatic quench compensation based on the H-number method. Solvent blanks were performed periodically during sample work up and utilized to correct sample counts. The detection limit, operationally defined as 2 times the background instrument counts, for the $^{14}C$-polychlorinated dodecane mixture was 0.7 ng.

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# 2. Vapor Pressures of Chlorinated Alkanes

## 2.1. Introduction

Vapor pressure (P) is a fundamental physical property which describes the equilibrium distribution of a chemical between its pure condensed state and the gaseous state at a specified temperature. Vapor pressure is important in environmental fate modeling and is required for the estimation of evaporation rates during chemical spills and used as the reference state for fugacity corrections between phase changes in thermodynamic models. The volatility of a compound also partially governs the distribution of a compound between air and particulate phases and air-water partitioning as described by octanol-air partition coefficients and Henry's law constant (Chapter 3; Schwarzenbach et al. 1993; Grain 1990; Bidleman 1984).

## 2.2. Definition of Vapor Pressure

Under ambient gas pressures near 1 atm, molecular interactions in the vapor phase are assumed to be ideal, and therefore the vapor pressure essentially reflects the nature of the intermolecular interactions of the condensed phase (Grain 1990; Schwarzenbach et al. 1993; Atkins 1982). For neutral hydrophobic compounds, these interactions mainly consist of van der Waals or dispersion forces and dipole-dipole interactions. The vapor pressure is defined as the partial pressure contributed by a solute at a specified temperature in which the condensed phase and gas coexist in equilibrium.

The temperature dependence of vapor pressure for liquids as described by the Clausius Clapeyron Equation (Grain 1990; Atkins 1982) is:

$$\frac{\partial \ln P}{\partial T} = \frac{\Delta H_v}{\Delta Z \cdot RT^2} \tag{2}$$

where: $\Delta H_v$ is the heat of vaporization ($kJ \cdot mol^{-1}$)
R is the gas constant ($8.314\ J \cdot mol^{-1} \cdot K^{-1}$)
T is the temperature (K)
$\Delta Z$ is the compressibility factor set to 1 under all conditions for an ideal gas

Under the general assumption of constant heat of vaporization and $\Delta Z = 1$, integration of the Clausius Clapeyron equation yields:

$$\ln P = -\frac{\Delta H_v}{R \cdot T} + c \text{ (for liquids)} \tag{3}$$

$$\ln P = -\frac{\Delta H_s}{R \cdot T} + c \text{ (for solids)} \tag{4}$$

where: $\Delta H_s$ is the heat of sublimation for a solid ($kJ \cdot mol^{-1}$)

The assumption of constant $\Delta H_v$ is generally met over short temperature ranges which do not involve a phase change. At temperatures well below the boiling point, $\Delta H_v$ remains essentially constant, becomes strongly temperature dependent at temperatures approaching the boiling point ($T_b$), and becomes 0 above the critical temperature ($T_c$) (Schwarzenbach et al. 1993; Atkins 1982). For solids, $\Delta H_s$ corresponds to the heat of sublimation and is equivalent to $\Delta H_{melting} + \Delta H_v$ such that $\Delta H_s > \Delta H_v$ (Atkins 1982). The heat of fusion ($\Delta H_{melting}$) represents the enthalpy required to overcome intermolecular interactions in the crystal lattice, allowing individual molecules freedom of orientation such as observed in the liquid state. For solids, extrapolation of Equation 3 below the melting point ($T_m$) will yield vapor pressures corresponding to the subcooled-liquid state ($P_{(sub)}$), a hypothetical liquid cooled below its melting point without crystallization (Schwarzenbach et al. 1993).

The utility of the $P_{(sub)}$ *vs* the solid vapor pressure for describing the environmental fate of a compound is dependent on the means of introduction of a solute into the environment. When a compound, which is ordinarily a solid at environmental temperatures is in solution under dilute conditions, then $P_{(sub)}$ is preferred over the solid P. For solutes introduced into the environment in the pure condensed solid phase, the solid P is the appropriate thermodynamic parameter describing volatilization.

With the exception of the parent *n*-alkanes and $D_2C_{10}$, the remaining chlorinated alkanes utilized in this study are all solids at ambient temperatures when present in their purified form. However, when present as mixtures both the synthesized products utilized in this study and many commercial mixtures of short chain CPs remain liquids at ambient temperatures and, therefore, behave according to the subcooled parameter. Also, once released into the environment, weathering and differential partitioning of individual components of the mixture will alter the characteristics or the mixture and eventually result in individual compounds which behave under ideal infinitely dilute conditions. In such cases, the $P_{(sub)}$ would be the appropriate parameter for modeling volatility of chlorinated alkanes in the environment.

## 2.3. Experimental Determination

### 2.3.1. Direct Measurement Techniques

$P_{solid}$ for semi- and low volatility compounds ($P < 100$ Pa) have been directly measured using gas saturation and effusion techniques. Such methods generally yield results which vary by factors of the order of 2 to 5 (Bidleman 1984; Schwarzenbach et al. 1993; Suntio et al. 1988). The effusion method is based on the loss of solute through a small orifice into a vacuum and the rate of solute lost is measured gravimetrically over time or P measured directly by torsion at the orifice created by the pressure of the exiting solute (Spencer and Cliath 1970; Bidleman 1984).

The gas saturation technique has found more recent success relative to the gas effusion technique for deriving P of low volatile compounds. The gas saturation method is similar to the generator column technique (Chapter 4), such that an inert gas stream, usually at ambient temperatures, is passed through a packed column of solute sorbed to a support base at flow rates which allow vapor saturation of the exit gas. The solute in the vapor state is subsequently trapped on an activated sorbent and gas concentrations are calculated using the ideal gas law (Westcott et al. 1981; Spencer and Cliath 1970; Sonnefeld and Zoller 1983). Reported error for this technique is 9%, with increased error for measurements of P less than $10^{-6}$ Pa (Sonnefeld and Zoller 1983). Interlaboratory precision of the technique has been reported to be 45% (Bidleman 1984). The gas saturation technique has been recommended as a standard technique for measurement of P for low volatile compounds (U.S. EPA 1981). Both gas saturation and effusion techniques are sensitive to the assumption of equilibration, require large amounts of pure solute (> 20 mg) and are affected by the presence of impurities or sorptive material which change the fugacity coefficient of the condensed solute (Sonnefeld and Zoller 1983; Westcott et al. 1981; Spencer and Cliath 1970).

### 2.3.2. Gas Liquid Chromatography Correlation Technique

The vapor pressure - gas liquid chromatography (P-GLC) correlation technique is based on a correlation between the retention time of a solute ($t_{R1}$) relative to the retention time of a reference compound ($t_{R2}$) and vapor pressure at elevated temperatures, with subsequent extrapolation of the vapor pressure to ambient temperatures (Hamilton 1980; Bidleman 1984). The retention time of a solute is dependent on the temperature, physical characteristics of the GC capillary column, volatility of the solute and activity of the solute in the stationary phase (Bidleman 1984; Hinckley et al. 1990; Spieksma et al. 1994). Since the solute is dissolved within the stationary phase, and the mass of stationary phase greatly exceeds the mass of solute injected, the P calculated by this technique corresponds to the subcooled-liquid vapor pressure and not the solid vapor pressure (Bidleman 1984; Schwarzenbach et al. 1993).

In order to characterize the activity of the compound in the stationary phase, a reference compound of known vapor pressure at both the GC operating temperatures and ambient temperatures with similar structure/partitioning characteristics as the solute is required.

For a solute which has reached equilibrium between the gas/stationary phase, the activity, P and retention times are related as follows:

$$\frac{t_{R1}}{t_{R2}} = \frac{P_2}{P_1} \cdot \frac{\gamma_2}{\gamma_1} \qquad (5)$$

where: $t_{R1}/t_{R2}$ is the retention time of solute ($t_{R1}$) relative to the standard ($t_{R2}$)
$\gamma$ is the activity coefficent of the chemical in the stationary phase
(Hinckley et al. 1990)

Assuming $\gamma_1 = \gamma_2$, the vapor pressure of the solute at the GC operating temperature can be directly related to the P of the reference compound and the solute's relative retention time ($t_{R1}/t_{R2}$). By determining the relative retention of the solute over a series of temperatures, additional information can be gained on the temperature dependence of vaporization, allowing extrapolation of the calculated P for the solute to environmentally relevant temperatures. The necessary equations for this approach have been derived by Hamilton (1980) such that:

$$\ln P_{1(sub)25oC} = \frac{\Delta H_{v1}}{\Delta H_{v2}} \ln P_{2(sub)25oC} + C \qquad (6)$$

and

$$\ln \frac{t_{R1}}{t_{R2}} = \left(1 - \frac{\Delta H_{v1}}{\Delta H_{v2}}\right) \ln P_{2(sub)temp} - C \qquad (7)$$

where: $\Delta H_{v1,2}$ is the heat of vaporization for unknown and reference compound, respectively
$P_{(sub)25oC}$ is the subcooled-liquid vapor pressured extrapolated to 25°C
$P_{(sub)temp}$ is the subcooled-liquid vapor pressure at the GC operating temperature
C is a constant

A plot of ln ($t_{R1}/t_{R2}$) *vs* ln $P_{2(sub)temp}$ (Equation 7) over the different GC operating temperatures yields a linear relationship with slope ($1-\Delta H_{v1}/\Delta H_{v2}$) and intercept -C. The ratio of the heat of vaporization for solute and reference compound and constant determined from Equation 7 are then utilized in Equation 6 to calculate the vapor pressure of the solute at an extrapolated temperature (usually 25°C) for which vapor pressure data of the reference compound are available.

In this latter set of equations, it is assumed that $\Delta H_{v1}$ and $\Delta H_{v2}$ are constant over the temperature range of extrapolation. As previously mentioned $\Delta H_v$ has been shown to be temperature dependent over large temperature ranges which encompass phase changes. In the GLC technique, phase changes between solid and liquid over the temperature extrapolation should not affect results since the solute already exists in the subcooled state within the stationary phase. However, if the temperature range of GC operating conditions approaches or exceeds the boiling point of solute or reference compound, then the assumption of constant $\Delta H_v$ will not be valid and Equation 6 may yield erroneous results. When $\Delta H_{v2}$ for the reference compound is known, $\Delta H_{v1}$ can be calculated from the slope of the plot of ln ($t_{R1}/t_{R2}$) *vs* ln $P_2$. The $\Delta H_{v1}$ and extrapolated vapor pressure at the environmentally relevant temperature can then be used to solve for C of Equation 3, allowing calculation of P for any given temperature.

Bidleman (1984) and Hinckley et al. (1990) observed that the P determined by the GLC technique ($P_{GLC}$) for several PAH and organochlorine compounds correlated well with the subcooled-liquid P ($R^2$ = 0.97-0.98) calculated from direct measurement methods, however, the slope of the correlation equation was less than 1 (0.85 to 0.95). The authors attributed this discrepancy to differences in the activity coefficient of the solute relative to the activity coefficient of the reference compound in the stationary phase, i.e. $\gamma_1 \neq \gamma_2$. It was, therefore, suggested that a regression between $P_{GLC}$ for a number of standard compounds *vs* their measured $P_{(sub)}$ determined from direct-measurement techniques could be used to account for differences in activities among compounds within the stationary phase. This technique essentially averages the activity differences among the standard compounds and attributes this average activity difference to the unknown. Since the standard compounds are correcting for activity differences between unknown and reference compound, the standard compounds should be structurally similar or at least exhibit similar mechanisms of retention as the unknown within the chromatographic system. Generally, non-polar stationary phases are employed in the P-GLC correlation technique, since these phases exhibit lower functional group selectivity and retention is based primarily on solute hydrophobicity and volatility.

P-GLC techniques have been utilized to determine $P_{(sub)}$ for a wide variety of low and semi-volatile chemical classes including PAHs, organochlorine pesticides, PCBs, chlorinated dioxins, chlorinated dibenzofurans, chlorobenzenes, chlorophenols, organophosphates, toxaphenes and phthalates (Bidleman 1984; Eitzer and Hites 1988; Spieksma et al. 1994; Hinckley et al. 1990). The GLC technique has several attractive features in that it is suitable for compounds of low volatility, can be performed on mixtures of solutes, requires low quantities of analyte, yields information on the heat of vaporization ($\Delta H_v$) and is fast and precise relative to other direct P determination methods. Since the chlorinated alkanes, utilized in this study, exhibit low vapor pressures and are not available in pure form, the GLC-correlation technique was selected as the most applicable method for determining $P_{(sub)}$.

## 2.4. Methods

The P-GLC correlation technique was employed to determine the subcooled-liquid P of the synthesized polychlorinated decanes, undecanes and dodecanes, the purchased $D_2C_{10}$ and $D_2C_{12}$ and components of the $^{14}C$-labeled polychlorinated dodecane mixture. A 10 m HP-5 column (0.5 mm i.d. x 0.25 μm) was utilized to obtain retention data under isothermal GC conditions. DDT was chosen as a reference compound, since it is easily detected using the ECD detector, has GC retention times similar to several of the more highly chlorinated compounds of study, and has reported vapor pressure data both at environmentally relevant temperatures and at the GC operating temperatures in the range of 125 to 150°C (Eitzer and Hites 1988).

In order to correct for activity differences between the chlorinated alkanes and reference compounds within the stationary phase, 16 additional compounds including chlorinated aliphatic pesticides and PCB congeners were used in the calibration of the $P_{GLC}$ in relation to their reported $P_{(sub)}$. The calibration compounds included aldrin, lindane, heptachlor, mirex and 12 PCB congeners (IUPAC numbers 4, 5, 27, 48, 74, 95, 110, 132, 187, 156, 198 and 205) which had retention times which bracketed the retention of the chlorinated alkanes of study.

Depending on the detector response, from 0.4 to 40 ng of solute was injected onto the column through a splitless injection port maintained at 200°C. The polychlorinated alkane mixtures, pesticides and PCBs were detected using an ECD detector. For detection of the $D_2C_{10}$ and $D_2C_{12}$, the detector end of the column was switched to an FID detector located adjacent to the ECD on the GC oven. Additional lindane injections were made during the characterizations of the dichlorinated alkane compounds in order to ensure similar chromatographic conditions relative to experiments performed with ECD detection.

Solutes were injected as mixtures with the exception of the $D_2C_{10}$ and $D_2C_{12}$. The calibration compounds were divided into two mixtures which included the four pesticides and DDT reference compound as one mixture and the PCBs as a second mixture. Lindane was added to each mixture including the chlorinated alkanes prior to GC characterization in order to confirm identical chromatographic conditions between the unknown injections and the reference compound injections.

The retention times for each solute were determined under isothermal conditions at 130, 135, 140, 145 and 150°C. A plot of ln $t_{R1}/t_{R(DDT)}$ *vs* $P_{DDT(sub)temp}$ over the various GC operating temperatures for each solute was made in order to calculate $(1-\Delta H_{v1}/\Delta H_{v(DDT)})$ and C corresponding to Equation 7. Equation 6 was then employed to determine the

GLC-derived $P_{GLC}$ of the solute at 25°C. The linear regression between the $P_{GLC}$ of the calibration compounds and their respective $P_{(sub)}$, derived from the literature, was then used to correct the P data of the chlorinated alkanes for any activity differences between solute and reference compound in the stationary phase.

A heat of vaporization for DDT ($\Delta H_{v(DDT)}$) of 88.84 kJ/mol (calculated from data of Hinckley et al. 1990) was used to calculate the $\Delta H_v$ for each compound of study by employing Equation 6. The $\Delta H_v$, in addition to the corrected vapor pressure at 25°C was used to complete the integrated Clausius Clapeyron equation (Equation 3) allowing calculation of temperature dependence of the $P_{(sub)}$ for each compound.

## 2.5. Results

Although sample loadings onto the column spanned 2 orders of magnitude (0.4 to 40 ng injected), the high capacity of the 0.53 mm megabore column yielded gaussian peaks for each individual solute of study. The larger column diameter and small column length resulted in limited resolution of chlorinated alkane isomers relative to the 30 m x 0.1 μm x 0.25μm DB-5 column previously employed in chlorinated alkane quantification (Chapter 1). As a result, the four $P_5C_{10}$ isomers and five isomers of $P_5C_{11}$ and $P_5C_{12}$ could only be separated into two groups denoted as $P_5C_{10}$(a+b) and $P_5C_{10}$(c+d), $P_5C_{11}$(a+b), $P_5C_{11}$(c+d+e), $P_5C_{12}$(a+b) and $P_5C_{12}$(c+d+e). Similarly, there was a great deal of co-elution of the numerous $H_6$ isomers present in each synthesized product. Co-eluting peaks were treated as having the same vapor pressures. For the hexachloro-isomers, two to four broad peaks within the grouping (each containing a number of isomers) were often recognized by the integrator. Each of these peaks was assigned a vapor pressure value to obtain a range of vapor pressures for these isomers.

Considerable peak broadening occurred for late eluting compounds. The extremely long retention times and large degree of band broadening for PCB congeners #156, #198 and #205 resulted in peaks to which were difficult to assign accurate retention times for peak maxima. Therefore, these compounds were excluded from the calibration plots. Similarly, the congeners associated with the fourth band from the $^{14}$C-polychlorinated dodecane mixture were not determined because of the extremely long retention on the GC column.

The retention times of DDT ranged from 52.11 to 158.00 min over the 5 temperatures and were intermediate in retention among the calibration compounds and chlorinated alkanes of study. The most volatile calibration compound (PCB #4) had retention times ranging from 2.52 to 5.29 min and were slightly longer than $D_2$-$C_{10}$ (the most volatile chlorinated alkane of study) which had retention times ranging from 1.71 to 3.75 min. Similarly the latest eluting quantifiable calibration compounds (mirex and PCB 187) had retention times ranging from 61.10 to 103.33 min over four temperatures which were less than the two latest eluting components ($H_6C_{11}$ and band 3 of the $^{14}$C-labeled polychlorinated dodecane mixture) which had retention times ranging from 92.18 to 162.29 min over the same three temperatures. With the exception of these two chlorinated alkanes, all other compounds of study had retention times which were closely bracketed by the calibration compounds.

Figure 2.1 summarizes the retention of the calibration compounds relative to DDT over the 5 temperatures. All plots exhibited a linear relationship between the natural logarithm of relative retention and ln $P_{(sub)Temp}$ of the reference compound indicating a constant heat of vaporization. Only four temperatures were used for the least volatile calibration compounds, PCB #132 and mirex, because of the extremely long retention times at the lowest operating temperature. Figure 2.2 summarizes the relative retention of polychlorinated decanes, undecanes and dodecanes over the various temperatures. All curves conform to the expected linear trend. Due to extremely long retention times and problems with increasing peak width for groups of isomers, retention data for the hexachlorododecanes and peaks of the $^{14}$C-polychlorinated dodecane mixture were only available for the three highest GC operating temperatures.

Figure 2.3 presents the regression plot between the P of the calibration compounds determined by the P-GLC method and their literature reported vapor pressures at 25°C. The figure also summarizes the extrapolated chlorinated alkane vapor pressures utilizing the regression equation. As described above, only two compounds are outside the range of volatilities encompassed by the calibration compounds. Table 2.1 summarizes the mean and SE of

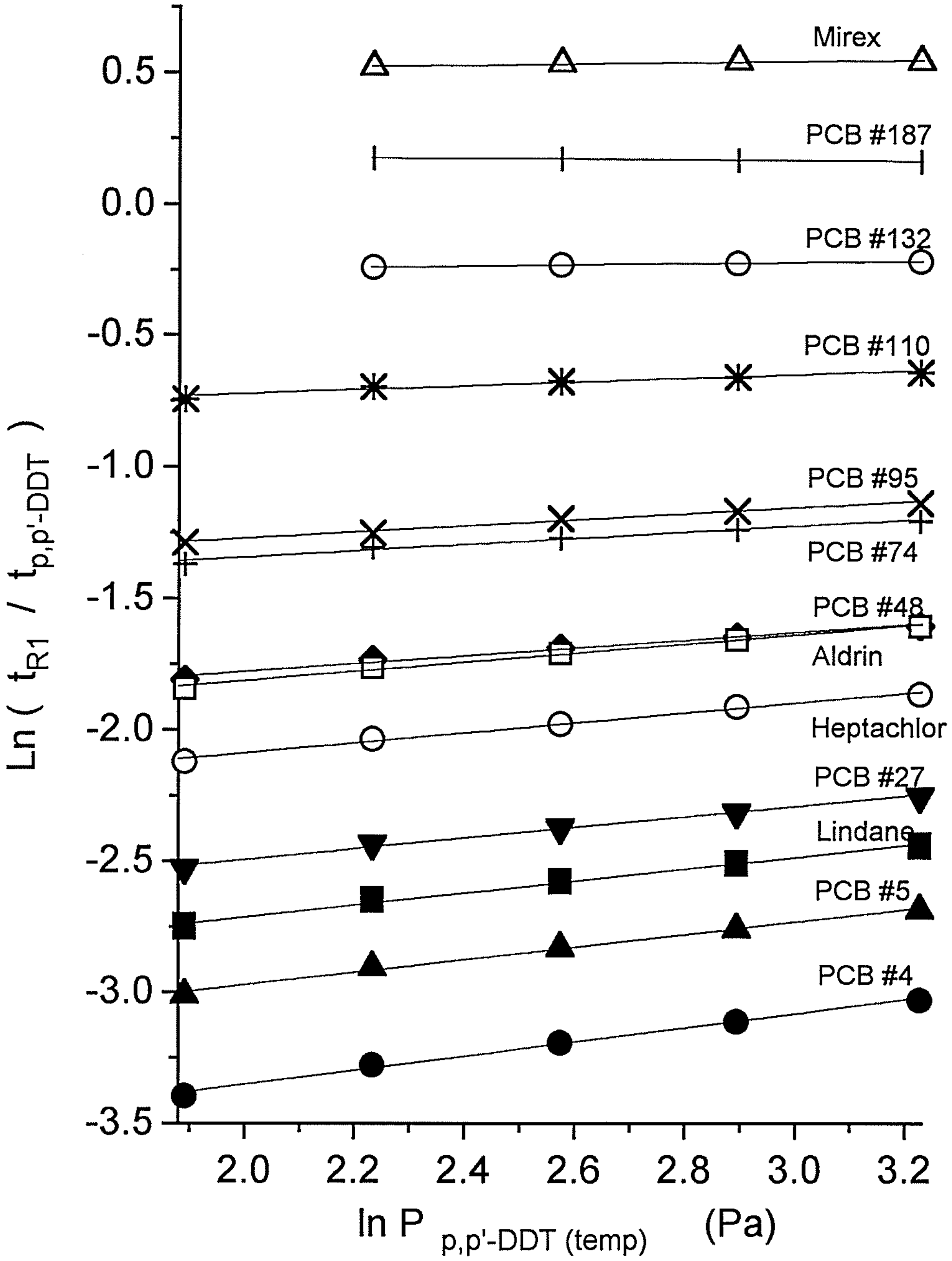
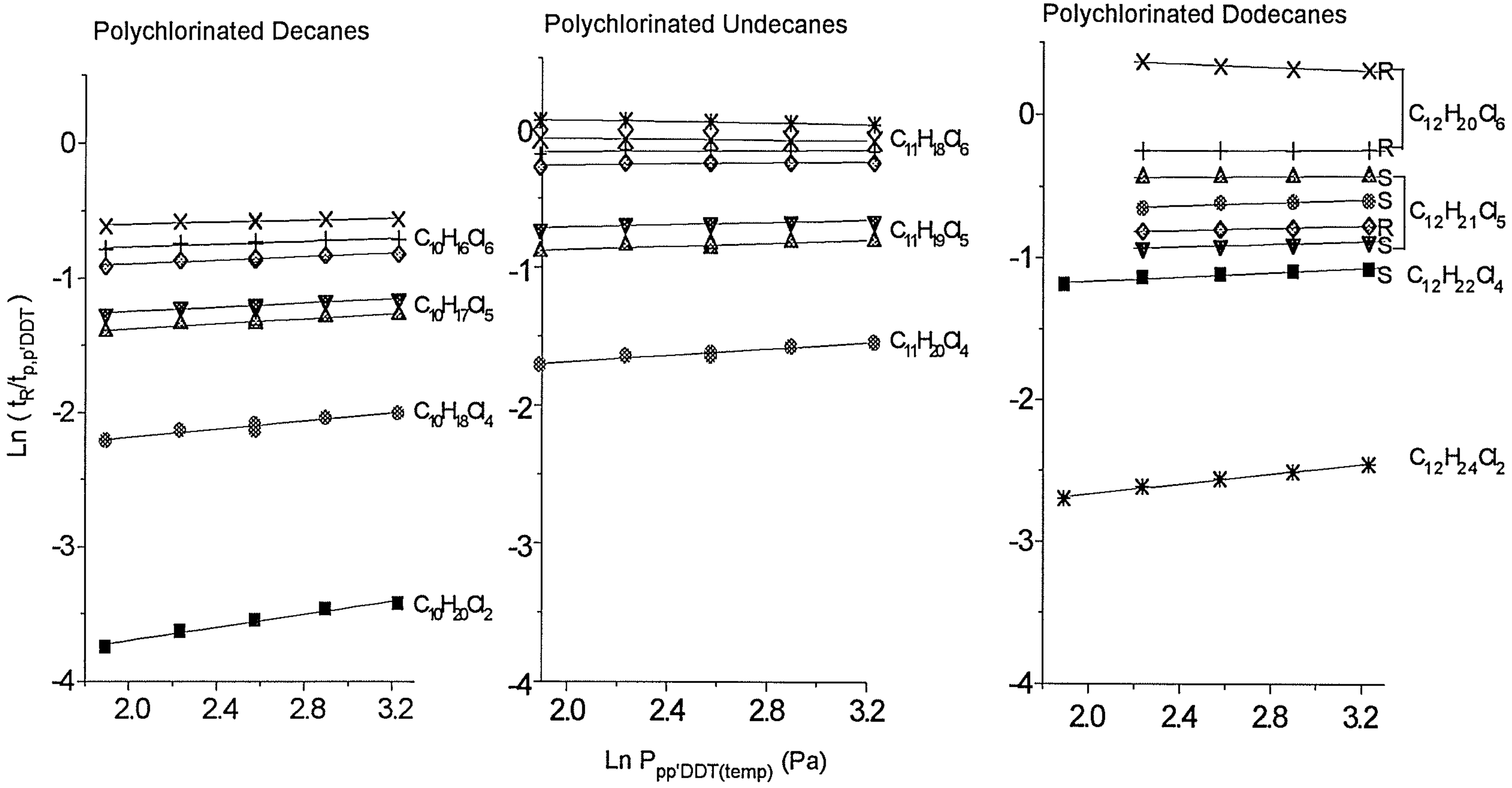


Figure 2.1 Relative retention of calibration compounds at GC operating temperatures ranging from 130 to 150°C $P_{p,p'\text{-DDT(temp)}}$ refers to the logarithm of vapor pressure of p,p'-DDT at the GC operating temperature



Note: R = Synthesized by Free Radical Substitution
S = Synthesized by Chlorine Addition

Figure 2.2 Relative retention of chlorinated alkanes over GC temperatures of 130 to 150°C
Ln $P_{p,p'\text{-}DDT(temp)}$ refers to the logarithm of vapor pressure of p,p'-DDT at the GC operating temperature

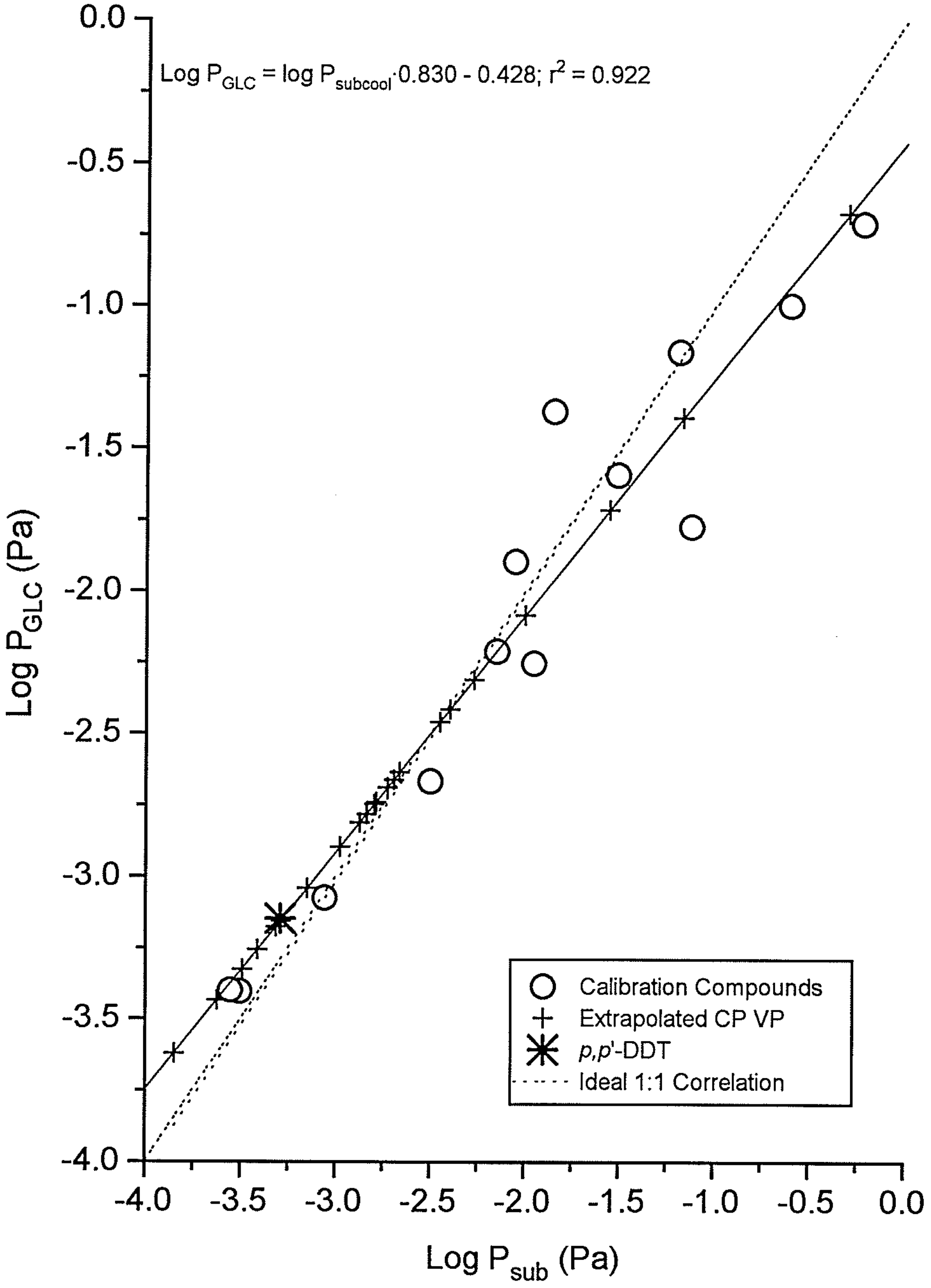


Figure 2.3. Correlation Between $P_{GLC}$ and $P_{sub}$ For Calibration Compounds at 25°C

**Table 2.1** Vapor Pressures of Chlorinated Alkanes at 25°C Estimated by the GLC Correlation Method.

| Chemical[*] | Formula | P (Pa) | SE[§] |
|---|---|---|---|
| n-decane[†] | $C_{10}H_{22}$ | 175 | NA |
| $D_2C_{10}$ | $C_{10}H_{20}Cl_2$ | 0.50 | 0.2 |
| $T_4C_{10}$ | $C_{10}H_{18}Cl_4$ | 0.028 | 0.02 |
| $P_5C_{10}$ (a+b) | $C_{10}H_{17}Cl_5$ | 0.0054 | 0.004 |
| $P_5C_{10}$ (c+d) | $C_{10}H_{17}Cl_5$ | 0.0040 | 0.003 |
| $H_6C_{10}$ | $C_{10}H_{16}Cl_6$ | 0.0022 | 0.001 |
| $H_6C_{10}$ | $C_{10}H_{16}Cl_6$ | 0.0016 | 0.001 |
| $H_6C_{10}$ | $C_{10}H_{16}Cl_6$ | 0.0011 | 0.0006 |
| n-undecane[†] | $C_{11}H_{24}$ | 52.2 | NA |
| $T_4C_{11}$ | $C_{11}H_{20}Cl_4$ | 0.010 | 0.008 |
| $P_5C_{11}$(a+b) | $C_{11}H_{19}Cl_5$ | 0.0020 | 0.001 |
| $P_5C_{11}$ (c+d+e) | $C_{11}H_{19}Cl_5$ | 0.0013 | 0.0008 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 0.00049 | 0.0002 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 0.00039 | 0.0002 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 0.00032 | 0.0001 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 0.00024 | 0.00009 |
| n-dodecane[†] | $C_{12}H_{26}$ | 15.7 | NA |
| $D_2C_{12}$ | $C_{12}H_{24}Cl_2$ | 0.068 | 0.04 |
| $T_4C_{12}$ | $C_{12}H_{22}Cl_4$ | 0.0035 | 0.002 |
| $P_5C_{12}$ (a+b) | $C_{12}H_{21}Cl_5$ | 0.0015 | 0.0009 |
| $P_5C_{12}$ (c+d+e) | $C_{12}H_{21}Cl_5$ | 0.00070 | 0.0004 |
| $^{14}$C-Polychlorinated dodecane (Band 1) | $C_{12}H_{21}Cl_5$ | 0.0019 | 0.001 |
| $^{14}$C-Polychlorinated dodecane (Band 1) | $C_{12}H_{21}Cl_5$ | 0.0016 | 0.001 |
| $^{14}$C-Polychlorinated dodecane (Band 2) | $C_{12}H_{20}Cl_6$[‡] | 0.00052 | 0.0002 |
| $^{14}$C-Polychlorinated dodecane (Band 3) | $C_{12}H_{20}Cl_6$ | 0.00014 | 0.00005 |

Note: [§] Standard Error based on SE of y estimate from linear regression of $P_{GLC}$ and $P_{(sub)}$ for calibration compounds

$^{14}$C-Polychlorinated dodecane mixture synthesized by free radical substitution[4]

[†] $P_{(sub)}$ taken from Mackay and Shiu (1981)

[‡] Also contains $C_{12}H_{21}Cl_5$ isomers (Chapter 1)

[*] See Table 1.3 for description of chemicals

vapor pressures for each compound of study. The standard errors were calculated based on the standard error of the y estimate derived from the linear regression between $P_{(sub)}$ and $P_{GLC}$ for the calibration compounds. The SEs ranged from 16.1 to 64.70% of the $P_{(sub)}$ estimates. The actual error may be higher depending on the accuracy of the literature reported $P_{(sub)}$. Hinckley et al. (1990) suggested that most literature values of Ps for compounds of low volatility vary by factors of 2 to 3.

Table 2.2 summarizes the $\Delta H_v$ and constants calculated for each of the chlorinated alkane compounds. The $\Delta H_V$ for the chlorinated alkanes range from 67.3 to 92.5 kJ/mol and are significantly different (2-way ANOVA; $p<0.0001$) among compounds differing in number of chlorines and number of carbons.

## 2.6. Discussion

The most volatile compound, $D_2C_{10}$, has a reported boiling point of 167-168°C (Aldrich Chemical Co. 1995), which is near the maximum temperature run of 150°C. It should be noted that extrapolation of vapor pressures to 25°C for this compound may be more prone to error due to the proximity of the GC operating temperature to the boiling point, which may violate the assumption of constant $\Delta H_v$. However, the linearity of the data over the five temperatures indicate a constant $\Delta H_v$ over the 130 to 150°C temperature range where the temperature dependence is expected to be strongest and, therefore, errors in the extrapolation are considered to be relatively low.

**Table 2.2** Enthalpy of Vaporization for Chlorinated Alkanes

| Compound | Formula | $\Delta H_{V(sub)}$ ($kJ \cdot mol^{-1}$) | $C^{\dagger}$ |
|---|---|---|---|
| $D_2C_{10}$ | $C_{10}H_{20}Cl_2$ | 67.3 | 11.55 |
| $T_4C_{10}$ | $C_{10}H_{18}Cl_4$ | 75.4 | 11.61 |
| $P_5C_{10}$ (a+b) | $C_{10}H_{17}Cl_5$ | 80.6 | 11.75 |
| $P_5C_{10}$ (c+d) | $C_{10}H_{17}Cl_5$ | 81.7 | 11.79 |
| $H_6C_{10}$ | $C_{10}H_{16}Cl_6$ | 83.1 | 11.75 |
| $H_6C_{10}$ | $C_{10}H_{16}Cl_6$ | 84.3 | 11.82 |
| $H_6C_{10}$ | $C_{10}H_{16}Cl_6$ | 85.9 | 11.91 |
| $T_4C_{11}$ | $C_{11}H_{20}Cl_4$ | 78.7 | 11.70 |
| $P_5C_{11}$(a+b) | $C_{11}H_{19}Cl_5$ | 83.5 | 11.79 |
| $P_5C_{11}$ (c+d+e) | $C_{11}H_{19}Cl_5$ | 85.2 | 11.88 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 88.7 | 12.03 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 89.6 | 12.08 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 90.2 | 12.11 |
| $H_6C_{11}$ | $C_{11}H_{18}Cl_6$ | 91.3 | 12.16 |
| $D_2C_{12}$ | $C_{12}H_{24}Cl_2$ | 73.1 | 11.62 |
| $T_4C_{12}$ | $C_{12}H_{22}Cl_4$ | 81.9 | 11.77 |
| $P_5C_{12}$ (a+b) | $C_{12}H_{21}Cl_5$ | 84.1 | 11.72 |
| $P_5C_{12}$ (c+d+e) | $C_{12}H_{21}Cl_5$ | 87.6 | 12.02 |
| $^{14}C$-Polychlorinated dodecane (band 1) | $C_{12}H_{21}Cl_5$ | 84.7 | 11.97 |
| $^{14}C$-Polychlorinated dodecane (band 1) | $C_{12}H_{21}Cl_5$ | 84.8 | 11.91 |
| $^{14}C$-Polychlorinated dodecane (band 2) | $C_{12}H_{20}Cl_6^{\ddagger}$ | 88.3 | 11.98 |
| $^{14}C$-Polychlorinated dodecane (band 3) | $C_{12}H_{20}Cl_6$ | 92.5 | 12.12 |

Note: $^{\dagger}$Constant from integrated Clausius-Clapeyron equation:

$$\log P = -\frac{\Delta H_{V(sub)}}{2.303 \cdot R \cdot T} + C$$

$^{\ddagger}$ Band 2 also contains $C_{12}H_{21}Cl_5$ isomers (Chapter 1)

There is a degree of scatter among some of the calibration compounds about the regression line which may be related to i) errors in the vapor pressures reported in the literature ii) errors in extrapolating solid vapor pressures to the subcooled-liquid state, or iii) activity differences between calibration compounds in the stationary phase which are not correlated to volatility (Bidleman 1984). Three calibration compounds show different chromatographic elution orders relative to their reported volatilities. Literature derived $P_{(sub)}$ are reported to increase in the order of aldrin < lindane < heptachlor (Hinckley et al. 1990) whereas the chromatographic retention times follow the trend lindane < heptachlor < aldrin. The same trends in retention among the three compounds were also observed by Hinckley et al. (1990) indicating that the mechanisms of column selectivity of the BP-1 stationary phase employed by Hinckley et al. and Bidleman (1984) are similar to the HP-5 stationary phase utilized in this study. Since the literature cited $P_{(sub)}$ for these three compounds were within a factor of 2.5, the discrepancy in elution order *vs* P may simply reflect error in the reported P determined from direct measurement techniques or error in extrapolating $P_{(sub)}$ from $P_{solid}$.

Data for the $P_{(sub)}$ of the individual PCB calibration compounds were taken from Murphy et al. (1987) who measured the equilibrium distribution of Arochlor mixtures between air and water in sealed containers at 20°C, and subsequently calculated $P_{(sub)}$ based on solubility and H determinations. Comparison of $P_{(sub)}$ for equivalent PCB congeners with those reported at 25°C as reviewed by Mackay et al. (1992) and measured by Bidleman (1984) revealed that the Murphy et al. values were generally underestimated by an average factor of 2.9 x the $P_{(sub)}$ measured by standard P determination techniques. This underestimate simply corresponds to temperature differences of $P_{(sub)}$ at 20 and 25°C, respectively. The heat of vaporization and constant required to extrapolate temperature dependence using Equation 3 were not available to estimate the $P_{(sub)}$ at 25°C for the calibration PCBs used in this study. Therefore, the correlation between $P_{(sub)}$ for 19 PCB congeners reported by both Murphy et al. (1987) and recommended by Mackay et al. (1992) and Bidleman (1984) was employed to estimate a correction factor for $P_{(sub)}$ at 25°C for the Murphy et al. data set. The correlation equation was:

$$P_{(sub)}\text{ (Murphy et al)} = 0.259 \cdot P_{(sub)}\text{(Mackay et al.)} + 0.00237;\ r^2 = 0.914$$

Utilizing the above equation to correct for temperature dependence of $P_{(sub)}$ for PCBs imparts an average $\Delta H_v$ and constant for all PCB congeners extrapolated. $P_{(sub)}$ for the remaining calibration compounds were obtained from Hinckley et al. (1991).

The slope of the regression between the logarithm of P determined by the P-GLC method and literature cited $P_{(sub)}$ of the calibration compound was less than 1 at 0.830. Bidleman (1984) observed slopes slightly closer to 1 (0.85 to 0.95) on Apolane 87 and BP-1 stationary phases using two *n*-alkane reference compounds. Similarly, Hinckley et al. (1990) observed slopes of the order of 0.84 to 0.91 using eicosane or p,p'-DDT as reference compounds on a BP-1 stationary phase. The underprediction of $P_{GLC}$ for more volatile compounds arises from the low volatility of the reference compound, and large difference in retention times among the reference and solute. Utilization of a second, more volatile reference compound for the most volatile compounds would have increased the slope and improved the correspondence of the regression line to the ideal 1:1 correlation. However, since only a few of the chlorinated alkane congeners exhibited relatively high volatilities, which were adequately bracketed by calibration compounds, the regression technique is considered a suitable method of $P_{(sub)}$ estimation for these compounds.

Much of the error associated with the P-GLC correlation technique is associated with choosing an appropriate independently measured $P_{(sub)}$ for the reference and calibration compounds. The coefficient of variation (CV) of retention times for lindane, a compound added in both pesticide mixtures and chlorinated alkane mixtures, was low and averaged 0.60% (n=19) over the 5 temperatures. Assuming little error in the $P_{GLC}$ determination, a standard error of the log $P_{(sub)}$ for a given log $P_{GLC}$ can be calculated for the individual chlorinated alkanes based on the 95% confidence interval of the regression performed on the calibration compounds. The residual variability in the regression allows the calculation of a standard error of the y estimate as summarized in Table 2.1 (Sokal and Rohlf 1969).

There was a close correspondence between $P_{(sub)}$ measured for the individual congeners of the synthesized polychlorinated dodecanes and the equivalent isomer groups from the $^{14}$C-polychlorinated dodecane mixture. The $P_5C_{12}$ isomers with $P_{(sub)}$s of $0.7 \times 10^{-3}$ to $1.5 \times 10^{-3}$ Pa were within factors of 1.1 to 2.6 of the $P_{(sub)}$ determined for the pentachlorododecane isomers present in the first band of the $^{14}$C-polychlorododecane mixture. Similarly, pentachlorododecane congeners associated with band 2, which contains a mixture of penta- and hexachlorododecane isomers (Chapter 1), of the $^{14}$C-polychlorododecane mixture had a $P_{(sub)}$ within a factor of 1.4 of the the $P_5C_{12}$ (c+d+e) isomers. The similarity in P determined for corresponding isomers of the two mixtures indicates that the chlorinated alkanes synthesized by chlorine addition are adequate surrogates for describing $P_{(sub)}$ of chlorinated alkanes synthesized by free radical substitution.

The log transformed $P_{(sub)}$ data were subjected to 2-way ANOVA in order to interpret effects of chlorine content and carbon chain length. The dichloro-compounds had to be removed from the data set, since data were not available for a dichloroundecane congener. Table A.1 of the Appendix lists the ANOVA results which indicate significant differences ($p<0.001$) among $P_{(sub)}$ for compounds which differ either by chlorine content or carbon chain length. The interaction term was not significant, indicating the Ps of compounds of different carbon chain length were responding in a similar manner to addition of chlorine atoms to the molecule. The above trends are readily observed in Figure 2.4 which plots the $P_{(sub)}$ *vs* chlorine content and carbon chain length, respectively. Vapor pressures tend to fall in exponential fashion with each additional carbon or each additional chlorine. Multiple regression analysis yielded the empirical model:

$$\log P_{(sub)} = -0.353\cdot(\#\ \text{Carbons}) - 0.645\ (\#\ \text{Chlorines}) + 4.462;\ r^2 = 0.947$$

The model predicted vapor pressures for the various chlorinated alkanes well, with predicted $P_{(sub)}$ having an average error of 1.44 relative to measured values. The maximum error was observed for hexachlorododecane from the $^{14}$C-polychlorinated dodecane (band

2) which had a predicted $P_{(sub)}$ which was 2.3 times greater than the measured value. Predicted $P_{(sub)}$s for $H_6C_{10}$ and $H_6C_{11}$ congeners were also observed to be in error by 1.9 and 2.1 times relative to observed values. All other predictions were within a factor of 1.8 of the measured values. The additional error associated with estimated P for hexachlorinated congeners may reflect the long retention times and increased band broadening of these compounds relative to more volatile congeners.

The empirical model predicts a 2.3 fold decrease in $P_{(sub)}$ for each additional carbon in a molecule containing the same number of chlorines and a 4.4 fold decrease in $P_{(sub)}$ for each additional Cl added to a carbon chain length. The decrease in log $P_{(sub)}$ with increasing carbon chain length is considerably lower than that reported for *n*-alkanes over carbon chain lengths ranging from $C_5$ to $C_{26}$. The slope of the log $P_{(sub)}$ with increasing carbon chain length of *n*-alkanes was 0.772 relative to the slope of 0.353 observed in this study (analysis of data of Mackay and Shiu 1981).

Several investigators have observed decreases in $P_{(sub)}$ with increasing degree of chlorination for diverse chemical classes including chlorinated methanes, ethanes, propanes, benzenes, toluenes, styrenes, naphthalenes, biphenyls, dioxins and furans

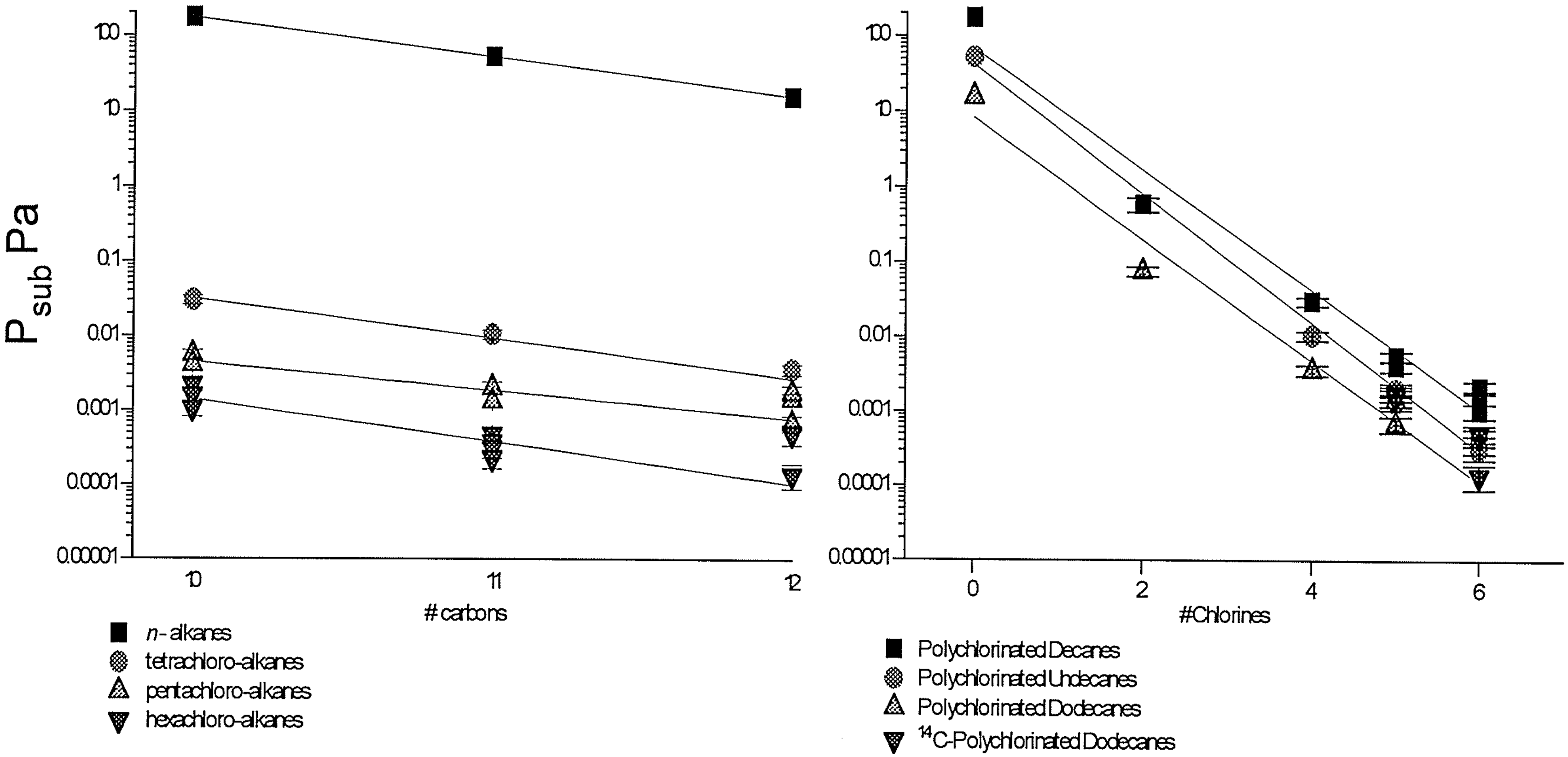


Figure 2.4. Effects of Carbon Chain Length and Number of Chlorines on $P_{sub}$ of Chlorinated Alkanes at 25°C

(Mackay and Shiu 1981; Spieksma et al. 1994; Weast 1981; Bopp 1983; Bidleman 1984; Mackay et al. 1992). Linear regressions between the log $P_{(sub)}$ *vs* number of chlorines for each chemical class were performed for the data cited in the above studies. Results from these correlations were similar to the negative slope of 0.645 observed for the chlorinated alkanes of this work. Regression slopes for log $P_{(sub)}$ of polychlorinated alkanes ($C_1$, $C_2$, $C_3$) *vs* increasing # Cl ranged from 0.483 to 1.03 (data of Mackay and Shiu 1981; Mackay et al. 1993). Similarly, the regression slopes observed for chlorinated benzenes and PCBs ranged from 0.583 to 0.776 (data of Mackay and Shiu 1981; Spieksma et al. 1994; Bopp 1983; Bidleman 1984; Hinckley et al. 1990; Murphy et al. 1987; Mackay et al. 1992; Rordorf 1985).

The heat of vaporization calculated for lindane, aldrin, heptachlor and mirex at 68.6, 73.3, 72.0 and 86.4 kJ/mol were of similar magnitude but slightly lower than reported by Hinckley at 70.5, 75.1, 76.5 and 90.3 kJ/mol, respectively. $\Delta H_v$ for the chlorinated alkanes were found to increase with both increasing carbon chain length and increasing degree of chlorination. Rordorf (1985) also noted linear relationships between enthalpy of vaporization and the chlorine number for 10 chlorinated dibenzo-*p*-dioxins. As with $P_{(sub)}$, there was no significant interaction between carbon chain length and degree of chlorination for the compounds studied. Based on these $\Delta H_V$ values, $P_{(sub)}$ are expected to change by factors ranging from 7 to 15 fold over the temperature range of 5 to 25°C for the chlorinated alkanes of study.

## 2.7. Conclusions

Subcooled-liquid vapor pressures were measured for the polychlorinated alkanes using the P-GLC correlation technique. $P_{(sub)}$ of the polychlorinated decanes, undecanes and dodecanes ranged from $1.4 \times 10^{-4}$ to 0.51 Pa at 25°C. Ps for individual compounds of the synthesized polychlorinated dodecanes were well correlated to Ps measured for equivalent isomers from the $^{14}$C-polychlorinated dodecane mixture, indicating that the chlorinated alkanes synthesized by chlorine addition may be considered good surrogates for determination of physical properties for chlorinated alkanes synthesized by free radical substitution. Clear trends were observed for decreasing $P_{(sub)}$ with increasing carbon chain length and increasing degree of chlorination, allowing the development of a general empirical model for estimating $P_{(sub)}$ of chlorinated alkanes based on the number of carbons and number of chlorines in the molecule.

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# 3. Henry's Law Constant of Chlorinated Alkanes

## 3.1. Introduction

The Henry's law constant (H) describes the equilibrium partitioning of a solute between vapor and pure water phases. Hs are required in order to predict mass transfer between air and water and for the calculation of fugacity capacities (Z) of solutes in water, sediment, water-saturated soils and biota (Suntio et al. 1988; Mackay and Shiu 1981; Mackay and Paterson 1981; Mackay et al. 1979). The deviation between field associated solute concentrations in air and water from the equilibrium H also gives an indication of the direction and magnitude of flux. In addition, when the H is used in conjunction with kinetic models such as the Two-Film model (Liss and Slater 1974; Southworth 1979; Thomas 1990) or fugacity models (Level I, II, III, QWASI) (Mackay et al. 1983; 1985) the rate of volatilization or dissolution of a compound can be predicted for a number of diverse processes including transfer between air and freshwater lakes/rivers, rain, fog and dew (Suntio et al. 1988; Glotfelty et al. 1987; Ligocki et al. 1985; Matter-Müller et al. 1981; Eisenreich et al. 1981).

Modeling volatilization rates for a chemical, as described by the Two-Film model, generally requires a knowledge of the H, molecular diffusion coefficients in air and water and characteristics of the air and water interface such as boundary layer dimensions (Liss and Slater 1974; Thomas 1990; Suntio et al. 1988). The magnitude of the H is often used to generalize the behavior and resistance to mass transfer of a compound in the environment. Suntio et al. (1988) and Eisenreich et al. (1981) summarized a series of rules for describing partitioning behavior of compounds between air and water based on H. Chemicals having H ≥ 100 $Pa{\cdot}m^3{\cdot}mol^{-1}$ tend to rapidly volatilize to the vapor state and exhibit the greatest resistance to diffusion in the liquid boundary layers. When H is of the order of 25 to 100 $Pa{\cdot}m^3{\cdot}mol^{-1}$, volatilization rates are intermediate, with resistance to diffusion occurring in both air and water boundary layers. An H below 1 $Pa{\cdot}m^3{\cdot}mol^{-1}$ suggests that a compound will exhibit very slow volatilization rates with the chief resistance to diffusion occurring in the air boundary layer. Suntio et al. (1988) suggested that volatilization becomes a non-significant environmental process when Hs are < 1 $Pa{\cdot}m^3{\cdot}mol^{-1}$, except under limited conditions where a small volume of water is equilibrated with a large volume of air.

## 3.2. Definition of Henry's Law Constant

The H is dependent on both $P_{(sub)}$ (solute:solute intermolecular interactions in the condensed phase) and solute:solvent intermolecular interactions in the aqueous medium. The H can be expressed in terms of fugacity which is defined as the 'escaping tendency' of a chemical from a phase and is directly related to the chemical potential (Atkins 1982). The fugacities of the solute, present in the subcooled-liquid state, in the vapor and aqueous phases are defined as:

$$f_g = x_v \cdot \gamma_v \cdot P_T = P_i \cdot \gamma_v \qquad (1)$$

$$f_w = \gamma_w \cdot x_w \cdot P_{(sub)} = \gamma_w \cdot C_w \cdot V_w \cdot P_{(sub)} \qquad (2)$$

where: $f_g$ = fugacity of solute in vapor phase (Pa)
$P_T$ = total pressure (~ 101325 Pa)
$P_i$ = partial pressure of solute in vapour phase (Pa)

$P_{(sub)}$ = vapor pressure of pure liquid solute, or subcooled extrapolated vapor pressure of solid solute.
$x_v$, $x_w$ = mole fraction of solute in vapor/aqueous phase
$\gamma_v$ = fugacity coefficient of solute in the vapor phase (~ 1)
$f_w$ = fugacity of solute in aqueous phase (Pa)
$\gamma_w$ = activity coefficient of solute in aqueous phase
$C_w$ = concentration of solute in aqueous phase ($mol{\cdot}L^{-1}$)
$V_w$ = molar volume of water saturated with solute ($L{\cdot}mol^{-1}$)

(Suntio et al. 1988; Atkins 1982)

It should be noted that the vapor pressure and water solubilities are assumed to be in the subcooled-liquid state for non-associating compounds which are solids at ambient temperatures. This implies that the solute concentrations in both aqueous and vapor phases are sufficiently dilute such that solute-solute interactions are negligible. Equation 1 assumes that the partial pressure of the solute is sufficiently small such that $\gamma_v \approx 1$, a condition generally achieved except for compounds which associate or during conditions of high gas densities (Atkins 1982; Mackay and Shiu 1981). Burkhard et al. (1985) suggested that the above assumption breaks down only after pressures exceeding 5 to 10 atm, a condition unlikely to be met under most environmental situations.

H is defined as:

$$H = \frac{P_i}{C_w} \qquad (Pa{\cdot}m^3{\cdot}mol^{-1}) \qquad (3)$$

When the solute is present in the aqueous phase under dilute conditions, then $\gamma_v = 1$. Combining equations 1, 2 and 3 and assuming equilibrium yields the expression:

$$H = P_{(sub)} \cdot \gamma_w \cdot V_w \qquad (4)$$

When the aqueous solubility of a compound is low, the subcooled-liquid solubility ($S_{w(sub)}$), in concentration units of $mol{\cdot}m^{-3}$, can be defined as (See Chapter 4 for detailed definition):

$$S_{w(sub)} = \frac{x_{w(sat)}}{V_w} = \frac{1}{\gamma_w \cdot V_w} \quad (5)$$

where: $x_{w(sat)}$ = the mole fraction of chemical in water at saturation

H may then be approximated by:

$$H = \frac{P_{(sub)}}{S_w} \quad (6)$$

Alternatively, H is sometimes more conveniently expressed in dimensionless form as:

$$K_{aw} = \frac{H}{R \cdot T} \quad (7)$$

where: $K_{aw}$ = dimensionless Henry's law constant
$R$ = gas constant ($\mathrm{Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}}$)
$T$ = temperature (K)

Based on Equations 4 and 7, H is essentially independent of solute concentration under ideal dilute conditions (Atkins 1982) for which the molar volume of the mixture does not differ from that of pure water ($V_w$), and $\gamma_w = \gamma_{w\ (\mathrm{pure})}$ (i.e., water does not significantly dissolve into the pure condensed organic phase). It has been suggested that solute:solute interactions can be neglected when the solute or sum of cosolute concentrations in the aqueous phase is less than 3 to 5 mole % (~ 1.5 $\mathrm{mol \cdot L^{-1}}$; Schwarzenbach et al. 1993; Suntio et al. 1988). Such conditions are generally valid for most relatively hydrophobic contaminants present in dilute concentrations in the environment. The H as defined in Equation 3 can, therefore, be calculated from either the ratio of vapor pressure to solubility (when both parameters are expressed in either the solid or subcooled-liquid state) or measured by experimental means.

## 3.3. Experimental Determination of H

Hs have been determined by direct measurement of equilibrated vapor/aqueous solutions and by techniques which determine the kinetics of solute stripping from vapor or aqueous phases. Direct H measurement techniques include bulk equilibration methods, wetted-wall columns and fog chambers. Indirect methods for determining Hs have been determined using gas sparging/dynamic equilibration techniques (Murphy et al. 1987; Fendinger and Glotfelty 1988; Mackay et al. 1979).

### 3.3.1. Bulk Equilibration Techniques

Bulk equilibration methods involve batch type systems in which the solute is introduced, at varying concentrations, in the vapor headspace or in aqueous solution and allowed to equilibrate. After a given equilibration period, solute concentrations are quantified in headspace and aqueous solutions to derive the H. This technique is applicable for compounds with high H values ($H > 25 - 100\ \mathrm{Pa{\cdot}m^3{\cdot}mol^{-1}}$; Mackay and Shiu 1981; Fendinger and Glotfelty 1990). However, because of experimental limitations in the volume of headspace or aqueous solution which can be sampled, analytical difficulties in quantifying solute concentrations for compounds exhibiting low solubilities or low vapor pressures limit the applicability of the technique for a number of compounds of environmental relevance (Ten Hulsher et al. 1992; Burkhard et al. 1985; Mackay et al. 1979; Fendinger and Glotfelty 1988; Nielsen et al. 1994). Increasing the size of water/headspace volumes also results in technical complications for quantitatively extracting large headspace volumes and necessitates an increase in equilibration period.

This technique is also particularly sensitive to errors during the determination of absolute solute concentrations in both solution and vapor and is, therefore, undesirable when analytical uncertainties associated with determination of low solute concentrations become large.

### 3.3.2. Wetted-Wall Column

The wetted-wall column technique is a direct H measurement technique developed by Fendinger and Glotfelty (1988) and further utilized by Fendinger and Glotfelty (1990) and Brunner et al. (1990). In this method the solute is introduced in either the vapor phase or aqueous phase via a generator column. The solute is then equilibrated between a thin film of water which flows down the inside of a vertical glass column (10-57 cm length; 2.2 cm i.d.) with a concurrent flow of air. The small film of water (~0.1 mm thick) permits a more rapid approach to equilibration relative to batch experiments. The degree of equilibration can be controlled by modifying the column height and vapor flow rate which control the vapor/air contact time.

The advantages of this technique are that larger volumes of vapor and water can be utilized, permitting analytical detection of solutes present at low concentrations in either phase. Fendinger and Glotfelty (1990) found reasonable agreement between Hs of 4 PAHs determined by the wetted-wall column technique compared to experimental values measured from gas sparging procedures. Both techniques yielded Hs within 33 to 57% of each other for individual compounds, and the authors ascribed much of the differences to the analytical methods employed. The major disadvantages of this technique are that it requires a relatively complex non-commercially available apparatus and, like the bulk equilibration method, is sensitive to the accurate determination of chemical concentrations in both the air and vapor phases. In addition, relatively few compounds have been calibrated with this technique, and therefore assumptions of equilibration must be rigorously tested for each new compound of study.

### 3.3.3. Gas Sparging/Dynamic Equilibration Methods

The gas sparging approach has been the most popular method of experimentally determining Hs for sparingly soluble and low vapor pressure compounds. The technique has been calibrated for a wide variety of chemical classes including aliphatic pesticides, PAHs, chlorinated benzenes and PCBs. The sparging apparatus involves bubbling an inert gas through a column containing an aqueous solution of the chemical and following the rate of solute stripping from the aqueous phase. As an individual bubble rises through the water column, it initially has a low fugacity relative to water, and it is this fugacity gradient which provides the mechanism of flux of solute from water to air. The rate of solute volatilization into the bubble is dependent on the surface area of the bubble, diffusive path length of the air and water boundary layers surrounding the bubble, the magnitude of mass transfer coefficients describing solute molecular diffusion and the magnitude of the H (Mackay et al. 1979; Sproule et al. 1991). Several papers provide rigorous theoretical descriptions of bubble-water partitioning as it relates to the Two-Film model of volatilization (Sproule et al. 1991; Mackay et al. 1979; Matter-Müller et al. 1981).

The major assumption when using the gas sparging apparatus for determination of Hs is that the air bubble and water achieve equilibrium prior to exiting the sparger outlet. Failure to achieve equilibrium between the bubble and water will result in an underestimate of the true H value. As with the wetted-wall column, the degree of equilibration can be controlled by adjustment of the water column height and gas flow rates (Nielsen et al. 1994). In addition, utilization of a glass frit at the vapor inlet, ensures the production of small bubbles, which exhibit high surface area:volume ratios, allowing for more rapid equilibration. Several studies have investigated the effect of column height on Hs in gas sparging experiments for a variety of compounds. Generally, chemicals of greater H require longer columns to attain equilibration (Matter-Müller et al. 1981).

Since H determination is dependent on the rate of solute stripping, only relative concentrations of chemical in water or air need be measured. Therefore, the sparging method is less sensitive to initial adsorptive losses of solute than the wetted-wall column or bulk equilibration studies. Adsorptive losses of solute can be minimized by employing a conditioning purge period prior to data collection, provided that the solute isn't significantly stripped from the water during the conditioning period.

Provided the assumptions of equilibration and constant solution volume are met, the H is calculated according to:

$$H = k_v \cdot \frac{VRT}{F} \qquad (8)$$

where:
$V$ = volume of water sparged (L)
$F$ = gas flow rate ($L \cdot h^{-1}$)
$R$ = gas constant
$T$ = temperature (K)
$k_v$ = first order volatilization rate constant of chemical from solution ($h^{-1}$).

The volatilization rate constant ($k_v$) is calculated by assuming first order kinetics and fitting the fraction of solute remaining in solution with time to the model:

$$\ln \frac{C_w}{C_{w(o)}} = -kv \cdot t \qquad (9)$$

In practice, however, chemical concentrations are more conveniently measured in the exiting purge gas since sampling the purging solution violates the assumption of constant aqueous volume. As described by Dunnivant et al. (1988), the $k_v$ can be estimated by either linear regression fit to:

$$\ln\left(m_{w(o)} - m_{air}\right) = -kv \cdot t \qquad (10)$$

or non-linear regression fit to the equation:

$$m_{air} = m_{w(o)} \cdot (1 - e^{-k_v t}) \qquad (11)$$

where: $m_{air}$ is the cumulative mass of chemical purged to air (ng)
$m_{w(o)}$ is the initial mass of chemical added to the sparger at time zero (ng)
t is the time ($h^{-1}$)

Equation 11 has the added advantage in that both $k_v$ and $m_{w(o)}$ can be calculated iteratively using non-linear regression and, therefore, does not require determination of initial water concentrations. This is particularly important if solute adsorption onto sparger glassware significantly changes the initial solute concentration in the water prior to purging. The disadvantage of Equation 11 is that it requires the solute to be completely, or nearly completely, stripped from the purge solution during the course of the experiment. As a result, compounds having very low Hs will require substantial experimental sparging periods. Equation 10 requires accurate determination of initial solute concentrations in the purge solution, but does not require that the solute be completely stripped from solution and may be preferential for use when compounds which have relatively high analytical detection limits and low Hs are characterized.

In this study, the gas sparging technique was employed to determine Hs for individual congeners of the chlorinated alkanes and for the $^{14}C$-labeled polychlorododecane mixture. The sparging technique was chosen because of its sensitivity for compounds of low solubility and vapor pressure and because the technique has been previously calibrated for a wide range of compounds of varying chemical classes and compound hydrophobicities.

## 3.4. Methods

The chemicals utilized for determination of Hs by the gas sparging technique included individual congeners from the synthesized polychlorinated decanes, undecanes and dodecanes and the $^{14}C$-polychlorinated dodecane mixture. The analytical methods for quantification and characterization of these compounds are described in detail in Chapter 1. Two sparging columns were utilized which consisted of a 60 cm x 2.5 cm i.d. column having a total capacity of 600mL and a 78 cm x 4.5 cm i.d. column having a total capacity of 1400 mL. Each column was equipped with a fritted disk at the sparger inlet to ensure the formation of small gas bubbles and a sparging head modified to minimize carry over of water ejected from the bursting of the bubbles at the air-water interface (Figure 3.1). A magnetic stir bar was placed at the bottom of the sparger to ensure constant mixing of the purge solution. Stirring resulted in a circular pattern of rise for gas bubbles throughout the water column, ensuring turbulent flow conditions in the solution during the sparging period.

Industrial grade nitrogen, purchased from Canadian Liquid Air, Winnipeg, MB, was passed through a 5 cm x 3 mm i.d. Tenax trap and prewetted by passing it through 300 mL HPLC grade water prior to entering the sparger. The sparging column was filled with 500 mL (column 1) or 1000 mL (column 2) of water containing the polychlorinated decane, undecane, dodecane or $^{14}$C-polychlorododecane mixtures (described in Chapter 1) at 8% to 100% water saturation for the mixture. Saturated aqueous solutions of chlorinated alkanes were prepared by utilizing the generator column technique (May et al. 1978a) with subsequent dilution with HPLC grade water. A detailed description of the generator column method is provided in Chapter 4. Sparging flow rates were controlled by a two stage regulator and needle valve combination and set to 300 or 400 mL/min over

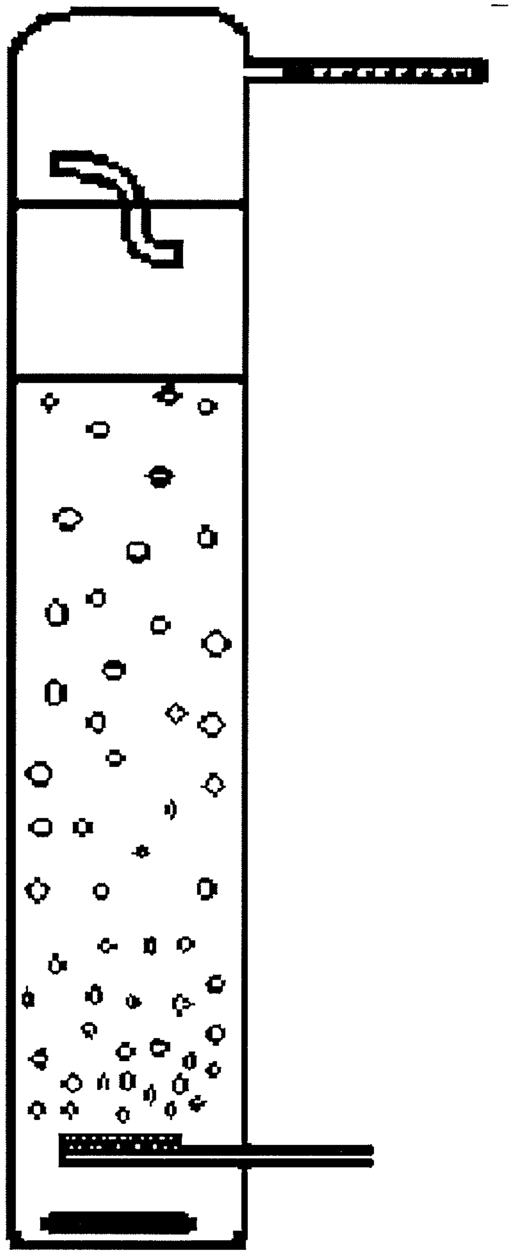

Figure 3.1 Gas Sparger Apparatus Used for Determining H. Column rise height 56 cm when sparger contains 1 L water. Tenax resin trap located at sparger outlet, and teflon coated magnetic stir bar located at bottom.

the various experimental trials. Gas flow rates were measured at regular intervals at the trap outlet with a bubble flow meter. The sparger apparatus was maintained at room temperature, without further control. Temperatures were recorded at each sampling time.

The gas exiting from the sparger outlet was extracted by bubbling it through hexane (300ml hexane in a column 20 cm by 4 cm i.d) or by passing it through a solid phase Tenax resin trap (5 cm x 3 mm i.d., ~ 1 g Tenax) as described for a number of other studies (Sproule et al. 1991; Ten Hulsher et al. 1992; Fendinger and Glotfelty 1988; Yin and Hassett 1986). Total sparging periods ranged from 18 h to 7 days among the various trials. The traps were exchanged over time periods of 20 minutes to 2 hours during the commencement of gas sparging and at longer time intervals during prolonged sparging. Maximum sparging time per trap was 24 h.

Breakthrough of chlorinated alkanes from the tenax traps was tested by spiking traps with $^{14}$C-polychlorinated dodecanes and sparging over a period of 24 h to obtain recovery efficiencies. Both the solvent and tenax traps were pre-spiked with lindane (57 ng) prior to gas sparging for use as an internal standard. The hexane from the solvent trap was transferred to a 250 mL round bottom flask with three washings of 20 mL hexane, roto-evaporated to approximately 1 mL, quantitatively transferred to a 15 mL tapered centrifuge tube along with 100 μL isooctane and brought down to a volume of 100 μL under nitrogen stream. The tenax trap was extracted by elution with 10 mL pesticide grade hexane (at flow rate of 1 mL/min) into a 15 mL centrifuge tube and prepared in a manner similar to the method described above.

Concentrations of chemical in both the water initially added to the sparger and in the final sparged solutions were determined by solid phase extraction for selected sparging runs. This allowed the solute depletion rate constant to be determined by Equation 10 and also provided a mass balance analysis to verify the trap efficiency and estimate the degree of solute adsorption to the sparging apparatus. The solid phase extraction involved passing 100 to 300 mL of water through an activated $C_{18}$ cartridge (Waters Enviro-plus Sep-Pak®) containing 200 mg of stationary phase under vacuum at flow rates ranging from 3 to 7 $mL \cdot min^{-1}$ (Landrum et al. 1984). The $C_{18}$ cartridges were activated by passing 5 mL hexane, 5mL acetone, 5 mL methanol and 5 mL HPLC grade water through the column. The solute was recovered from the $C_{18}$ cartridge by eluting with 14 mL hexane (at $< 1$ $mL \cdot min^{-1}$) and dried by passing the eluent over a 2 cm column of sodium sulfate. The extracts were collected into a 15 mL centrifuge tube, spiked with 1 ng lindane as an internal standard and prepared as described previously for tenax and solvent traps.

The first order volatilization rate constant ($k_v$) was calculated according to Equations 10 or 11 depending on the degree of curvature in the plots of cumulative mass purged *vs* time. When depletion was evident, Equation 11 was utilized by fitting the curve to the non-linear regression using SYSTAT statistical software allowing iterative calculation of both $k_v$ and $m_{w(o)}$ parameters. In cases where depletion of a compound did not occur over the experimental duration, Equation 10 was employed using measured initial water concentrations or cumulative mass purged in air + mass of chemical remaining in sparged water and fit by linear regression. Analysis of Variance (ANOVA) statistical tests on log transformed data were performed using SYSTAT statistical software in order to interpret differences in Hs determined for the different compounds of study.

### 3.5. Results

The sparging trials were performed under ambient temperatures. Temperatures ranged from 18 to 24.5°C (average 23.2 ± 0.3°C) over ten polychlorinated decane purge experiments, 18.5 to 27°C (average 24.0 ± 0.3°C) over five polychlorinated undecane experiments and from 18 to 23.5°C (average 21.2 ± 0.1°C) for three $^{14}$C-polychlorinated dodecane trials. There were no correlations (ANOVA, slope = 0, $p > 0.1$) between average temperature for a given run and calculated H among individual chemicals, and no significant differences between average temperatures of polychlorodecane, undecane and dodecane experiments (ANOVA, $p > 0.4$). Therefore the temperature variability among individual trials reflects random error and will not affect comparisons of H among the different compounds.

Breakthrough of tenax traps was tested by spiking tenax with 10 μL of $^{14}$C-polychlorinated dodecane standards and sparging the trap with nitrogen gas at 382 mL/min for a period of 24 hours (the longest sparging duration for any given trap). Recovery efficiencies ranged from 86.6 to 90.7% (n=3). The solvent traps for collection of solute in the purge gas were less efficient than the solid phase tenax traps because of losses of hexane by evaporation over extended sparging periods. The solvent traps were discontinued in favor of the Tenax traps after the first two trials of the polychlorinated decane sparging experiments and in all other H characterizations. Recovery efficiencies of the internal standard in hexane traps ranged from 43 to 105%. Concentration data for samples collected from both tenax and solvent traps were corrected to lindane internal standard recovery efficiencies to account for losses due to trap breakthrough and losses during sample workup procedures. No differences between Hs determined using solvent traps or Tenax traps were observed for the polychlorinated decane trials.

Among the ten polychlorinated decane sparging trials, two gas flow rates (300 mL/min *vs* 400 mL/min) and two sparging columns of 1 L (56 cm column length) and 0.5 L (53 cm column length) capacities were employed. Two-way ANOVA indicated no significant differences ($p>0.1$) between Hs derived using the fast or slow flow rates or different sparging columns. These results are similar to that of Murray and Andren (1991) who found slight but non-significant differences in Hs for PCBs when flow rates ranging from 48 ml/min to 470 mL/min were utilized during the purging of 10 PCB congeners.

To test for conditions of equilibration, the 1 L sparger column was utilized with 3 different water volumes to alter the bubble:water contact time. Saturated $^{14}$C-polychlorododecane water was added to the sparger to produce bubble rise heights of 40, 50 and 60 cm. Five purge samples (20 min at 300 mL/min) were collected for each column height. The low H for this compound and short purge duration (100 min total) resulted in negligible changes in water concentrations over the purge duration. Total activity collected on the tenax traps ranged from 0.27 to 0.57% of total water activity and therefore each sample was used to calculate an independent H based on the ratio of $C_{air}/C_{w}$. Figure 3.2 summarizes the calculated Hs derived from the 40, 50 and 60 cm column height trials, in addition to the 56 cm column height employed in the three kinetically derived (total sparging durations from 36 to 106 h) H trials. There were no significant differences (ANOVA; Tukey's HSD; $p>0.1$) between calculated Hs derived from the various column heights tested.

A mass balance analysis was performed on two polychlorinated decane trials and one polychlorinated undecane trial by comparing measured initial water concentrations determined as the mass of chemical remaining in sparged water plus cumulative mass sparged to air. The results of two mass balance studies are summarized in Tables A.2 and A.3 of the Appendix. Total recovery of tetra and pentachloro congeners (calculated as: [cumulative mass sparged to air + mass of chemical remaining in sparged water] / initial mass of chemical in water) were variable among the 6 compounds and ranged from 55.4 to 128.3%, averaging 97.9 ± 8.9 % (mean ± SE; n =8).

The variable recoveries are attributed to either underestimates in $C_{w(o)}$ or sparged water concentrations due to the high flow rates of water through the $C_{18}$ cartridge during water extractions or due to sorptive losses of chemical onto glassware within the sparging apparatus. The ratio of the iteratively calculated $m_{w(o)}$ parameter from the non-linear regression fit of the

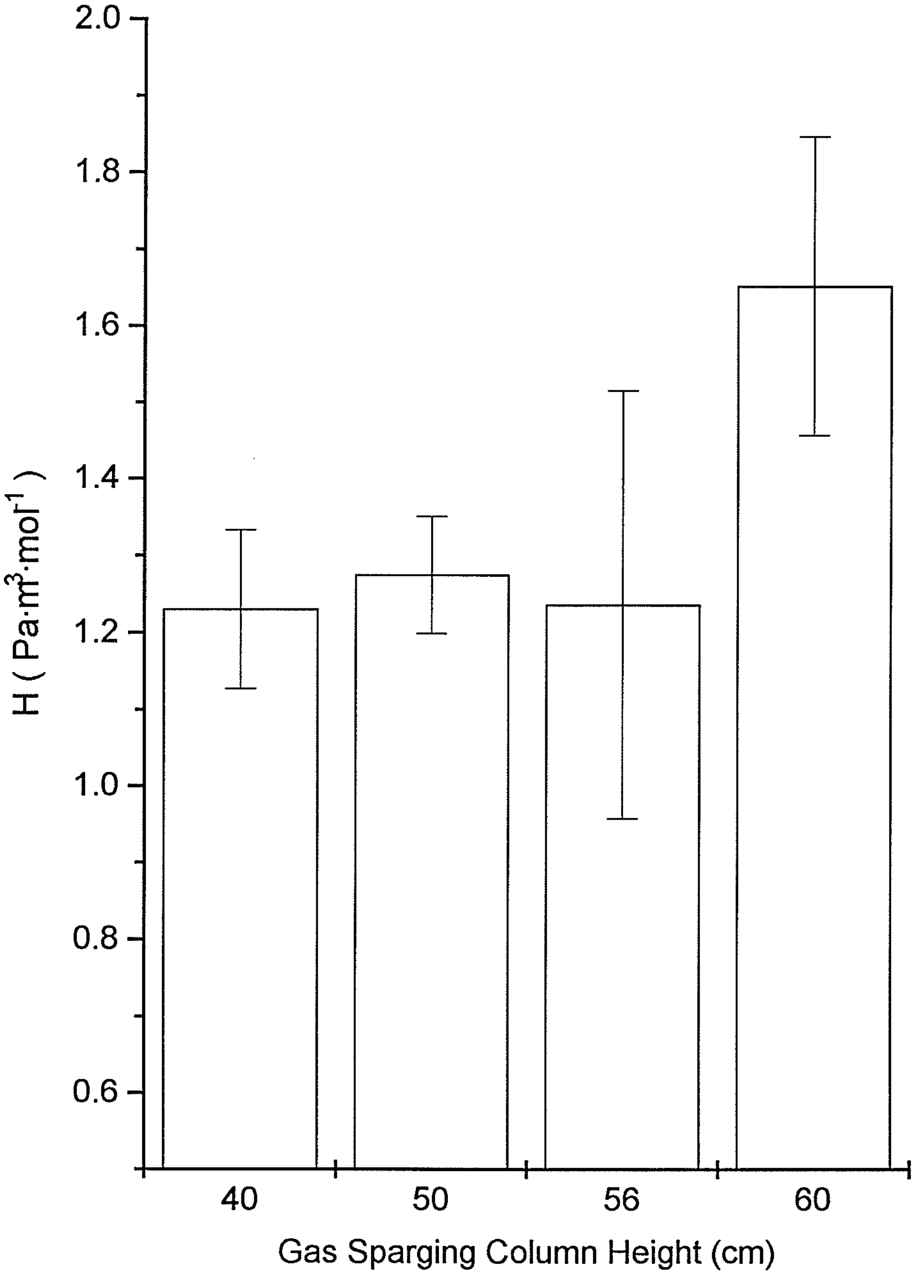

Figure 3.2 Effect of column height on H for $^{14}$C-polychlorinated dodecanes. Errors bars refer to standard errors.

data to Equation 11 *vs* the experimentally determined initial mass of chemical in the water also gives an indication of the mass balance. The recoveries of the $m_{w(o)}$ parameter ranged from 76.1 to 135.1%, averaging 106.4 ± 10.0% of the experimentally determined initial chemical mass in water for 6 chemicals in two experimental trials. For some experimental trials, the total sparging period was not of sufficient duration to permit significant depletion of chemical from water in order to fit the data to Equation 11. In these cases, Equation 10 was employed. It should be noted that Equation 10 is particularly sensitive to determination of initial water concentrations. As described in the mass balance analysis, estimates of initial water concentrations can vary depending on whether they were determined as measured initial mass of chemical in water, $m_{w(o)}$, cumulative mass purged to air + mass of chemical remaining in sparged water, or iteratively determined by non-linear regression fit to Equation 11. Initial water concentrations, determined by all three of the above procedures from the mass balance trials, were utilized to determine the sensitivity of calculated Hs to estimates of initial $m_{w(o)}$ in Equation 10.

The maximum deviation in calculated Hs, for a given chemical and trial, ranged from 1.9 to 3.7 fold depending on the method in which $m_{w(0)}$ was measured. Generally, Hs determined using the cumulative mass sparged to air + mass of chemical remaining in sparged water as an estimate of $m_{w(o)}$ yielded values more closely associated with Hs determined by the non-linear regression fit to Equation 11. In addition, the above approach can more correctly account for sorptive losses onto sparging glassware. Therefore, those trials which employ a linear fit to

Equation 10 utilized the cumulative mass sparged + mass of chemical remaining in sparged water as an estimate of $m_{w(o)}$ to determine the H value.

Figure 3.3 summarizes representative sparging rates for individual congeners of the three polychlorinated alkane mixtures. The first plot summarizes the gas sparging rates of $T_4C_{10}$ and $P_5C_{10}$ (a+b) and $P_5C_{10}$ (c+d isomers) congeners. Experimental flow rates, water volumes, temperatures and calculated Hs for individual trials are summarized in Table A.4 of the Appendix. Sparging durations among the various trials ranged from 18 to 113 h. The mean H, SE and coefficient of variation (CV) for each of the compounds of study are summarized in Table 3.1. Individual Hs for $T_4C_{10}$ calculated from eight separate trials were highly variable and ranged from 7.5 to 43.9 $Pa{\cdot}m^3{\cdot}mol^{-1}$. The $P_5C_{10}$ isomers a+b and c+d were not chromatographically resolved in all experimental determinations and quantification of cumulative mass sparged reflects the sum of the two co-eluting peaks. Since calculation of H is based on the initial slope of the cumulative mass sparged *vs* time curve, however, the Hs reported for $P_5C_{10}$ a+b and c+d reflect an average H for the two isomers. In one trial, where rigorous chromatographic conditions were utilized to partially resolve the $P_5C_{10}$ isomers a+b, there was no difference in H determined for the two compounds. Sparging data for ten and nine experiments yielded $P_5C_{10}$ a+b and c+d Hs ranging from 1.3 to 8.4 and from 1.0 to 7.4 $Pa{\cdot}m^3{\cdot}mol^{-1}$, respectively.

The average H for $T_4C_{10}$ was significantly greater (ANOVA; Tukey's HSD; $p<0.05$) than the Hs determined for the $P_5C_{10}$ isomers, but there was no differences between the Hs for the two

**Table 3.1** Summary of Hs for Polychlorinated Alkanes at 24°C

| Compound | H $\mathrm{Pa \cdot m^{3} \cdot mol^{-1}}$ | SE | n | CV (%) |
|---|---|---|---|---|
| *n*-decane[‡] | $7.0 \times 10^{5}$ | | | |
| $D_2C_{10}$[†] | 499.4 | | | |
| $T_4C_{10}$ | $17.67^{a}$ | 4.6 | 8 | 75.4 |
| $P_5C_{10}$ (a+b) | $4.92^{bc}$ | 0.71 | 9 | 45.6 |
| $P_5C_{10}$ (c+d) | $2.62^{bd}$ | 0.64 | 8 | 73.4 |
| *n*-undecane[‡] | $1.9 \times 10^{6}$ | | | |
| $T_4C_{11}$ | $6.32^{c}$ | 1.79 | 5 | 63.2 |
| $P_5C_{11}$ (a+b) | $1.46^{de}$ | 0.33 | 5 | 50.0 |
| $P_5C_{11}$ (c+d+e) | $0.68^{e}$ | 0.2 | 5 | 66.4 |
| *n*-dodecane[‡] | $7.5 \times 10^{5}$ | | | |
| $D_2C_{12}$[†] | 648.1 | | | |
| $^{14}C$-polychlorododecane mixture | $1.37^{d}$ | 0.07 | 17[*] | 21.2 |

Note: [‡]Hs taken from Mackay and Shiu (1981) estimated as ratio of $P_{(sub)}/S_{w(sub)}$
[†]H calculated as ratio $P/S_w$ for $D_2C_{10}$, and $P_{(sub)}/S_{w(sub)}$ for $D_2C_{12}$
Numbers with different superscript indicate significant differences at $p<0.05$ (Tukey's HSD)
[*]H trials include 3 kinetically derived values, and 14 single time point studies using three sparging column lengths

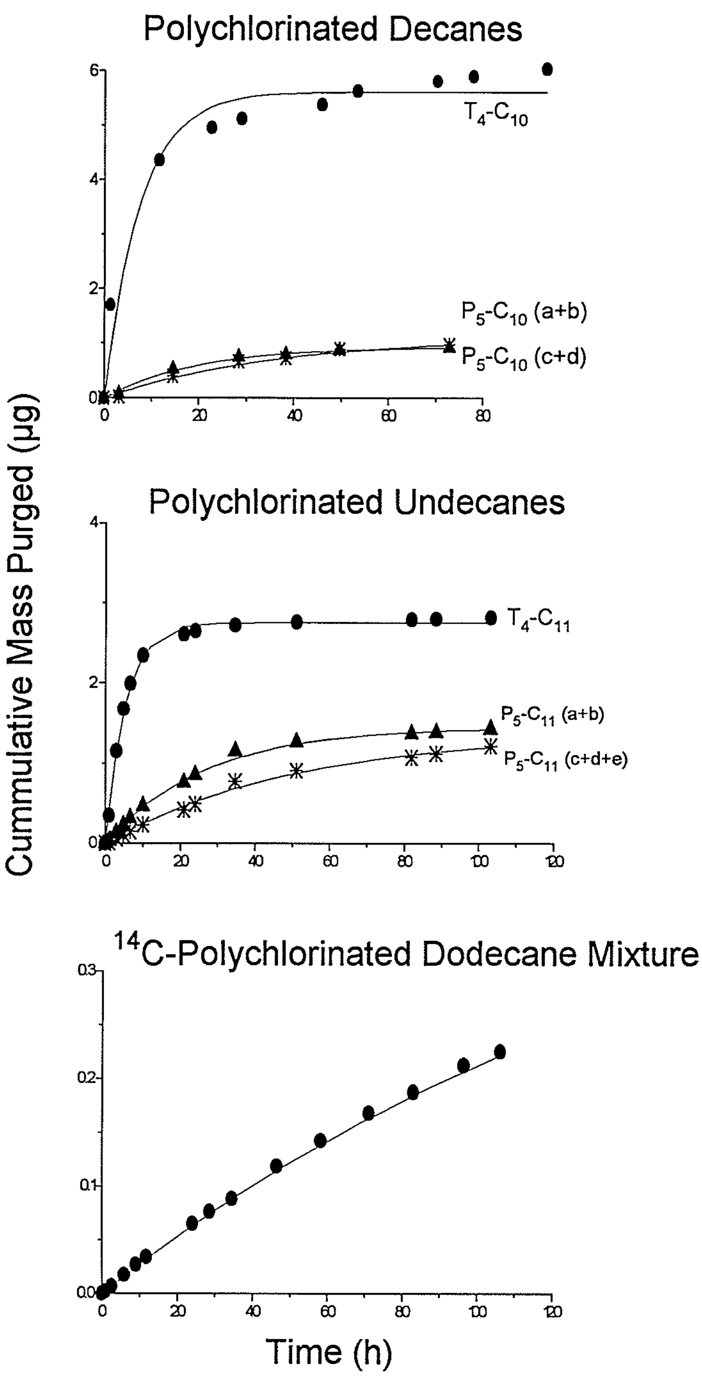

Figure 3.3 Gas sparging rates of polychlorinated alkanes.

$P_5C_{10}$ isomers. A $H_6C_{10}$ H could not be calculated from the various sparging trials. Slow air-water depuration rates, complex chromatography and co-elution of the isomers with tenax resin contaminants prevented H characterization of these compounds.

Representative gas sparging rates of polychlorinated undecanes are presented in the second plot of Figure 3.3. Individual Hs for $T_4C_{11}$ calculated from five separate trials ranged from 3.5 to 13.3 $Pa \cdot m^3 \cdot mol^{-1}$. As with the polychlorinated decanes, $P_5C_{11}$ isomers were averaged over two groups of the a+b isomers and c+d+e isomers. Calculated Hs from five experiments ranged from 0.69 to 2.6 $Pa \cdot m^3 \cdot mol^{-1}$ for the a+b isomers, and from 0.19 to 1.37 $Pa \cdot m^3 \cdot mol^{-1}$ for the c+d+e isomers. Hs for the $H_6C_{11}$ were not determined for similar reasons as indicated for the hexachlorodecanes. As with the polychlorinated decanes, Hs for the $T_4C_{11}$ congener were found to be significantly different from the $P_5C_{11}$ congeners (ANOVA; Tukeys HSD; $p<0.05$), but no significant differences between the two groups of pentachloro- congeners occurred.

One trial was performed on the synthesized polychlorinated dodecane. The mixture was, however, found to have a low solubility, requiring the extraction of at least 1 L of saturated water in order to detect and quantify individual compounds. As a result, a sufficient mass of chemical could not be added to the sparger column to measure cumulative mass sparged to air with time. The limits of detection of the sparging technique for the chlorinated alkanes relative to other chlorinated compounds such as PCBs were much higher and result from a combination of the small capacity of the sparger column (1.4L) employed and relatively low sensitivity of the ECD detector to these compounds.

Hs were determined for the $^{14}$C-polychlorinated dodecanes, however, quantification was based on total activity sparged with time rather than for individual components of the mixture. Since the activity was associated with a number of congeners in the mixture, the Hs obtained refer to a weighted average H for all compounds present in the mixture. Representative sparging rates for the $^{14}$C-polychlorinated dodecane mixture are summarized in the third plot of Figure 3.3. Individual Hs derived from the three kinetic experiments ranged from 0.84 to 1.78 $Pa{\cdot}m^3{\cdot}mol^{-1}$ with a mean value of $1.24 \pm 0.28$ $Pa{\cdot}m^3{\cdot}mol^{-1}$. The kinetically derived Hs compared favorably with the single time point Hs derived from the column height experiments and therefore all data were subsequently utilized to estimate the mean H presented in Table 3.1.

Since $D_2C_{10}$ and $D_2C_{12}$ were substantially more volatile than the tetrachloro- congeners and available in pure form, the ratio of P to solubility was utilized to estimate the H for these compounds. Solubilities were determined using the generator column method at 25°C as outlined in Chapter 4. Ps were determined by the P-GLC correlation technique as described in Chapter 2. Table 3.1 summarizes the Hs calculated for the two congeners in addition to literature cited Hs for the parent *n*-alkanes.

### 3.6. Discussion

The maximum temperature variation during the various experiments differed by 9°C. A sensitivity analysis was performed to determine if temperature variability could have explained some of the experimental error in the H determinations for the chlorinated alkanes of study.

Heat of vaporization ($\Delta H_v$) and heat of solubilization ($\Delta H_s$) values determined in Chapter 1 (Table 2.2) and Chapter 4 (Figure 4.4) for the polychlorinated decanes were used to determine the temperature dependence of H for the $T_4C_{10}$ and $P_5C_{10}$ congeners. This was performed by calculating the changes in P and solubility over the maximum temperature range of the experiment (18 to 27°C) using the integrated Clausius Clapeyron equation and predicting H at each temperature using Equation 6. Maximum calculated changes in H for the three compounds over the 9°C temperature change were from 63.4 to 73.1%. For example, the predicted H for $T_4C_{10}$ was 12.9 $Pa{\cdot}m^3{\cdot}mol^{-1}$ at 18°C and 19.3 $Pa{\cdot}m^3{\cdot}mol^{-1}$ at 27°C. Similarly, predicted Hs for the $P_5C_{10}$ (a+b) and $P_5C_{10}$ (c+d) congeners were 3.4 and 2.1 $Pa{\cdot}m^3{\cdot}mol^{-1}$ at 18°C and 5.4 and 2.8 $Pa{\cdot}m^3{\cdot}mol^{-1}$ at 27°C, respectively. From the above calculations, it appears that the Hs for the chlorinated alkanes exhibits a relatively weak temperature dependence, and as a consequence, temperature differences during the various experiments could not account for most of the variability in experimental results.

Although no significant differences in Hs were found among the sparging trials which utilized different column heights (Figure 3.2), there appears to be a higher observed H for 60 cm column height experiment. This may suggest that the kinetically derived Hs are slightly underestimated as a result of either non-equilibrium between bubble and water at the sparger outlet or by losses of compound to glassware sorption in the sparger column headspace. The maximum deviation in Hs derived from the column height experiments was within a factor of 25%, well within the variability observed among the sparging experiments. It should also be noted that the 60 cm column height trial was performed with very little headspace (<15 cm) between the air-water interface and Tenax trap, and may be biased as a result of carry over of water into the vapor trap during bubble bursting (Friesen et al. 1993).

The bubble:water contact time required for equilibration will increase with the magnitude of H, and therefore the degree of underestimation of H may have been more pronounced for the tetrachloro-decane and undecane compounds if non-equilibrium conditions were responsible for the H depression effect. If, however, glassware sorption were responsible for the H depression, then the underestimate would have been expected to be related to compound hydrophobicity and not the magnitude of H. In this case, the most hydrophobic compounds, the polychlorinated dodecanes, would be expected to exhibit the greatest underestimate. Several investigators have observed that column heights ranging from 8 to 40 cm were sufficient to allow equilibration between bubble and water for PCBs, mirex, lindane, chlorinated benzenes and PAHs (Dunnivant et al. 1988; Ten Hulsher et al. 1992; Yin and Hassett 1986; Kucklick et al. 1991; Mackay et al. 1979; Southworth 1979). The compounds characterized in these latter studies had Hs on the order of 0.3 to 192 $Pa{\cdot}m^3{\cdot}mol^{-1}$ and encompassed the range of Hs derived in this study (0.68 to 17.67 $Pa{\cdot}m^3{\cdot}mol^{-1}$). For highly volatile compounds such as toluene, with an H on the order of 673 $Pa{\cdot}m^3{\cdot}mol^{-1}$, the estimated column height required for equilibration was 80 cm (Matter-Müller et al. 1981; Mackay et al. 1979). Considering the low magnitude of the Hs determined for the chlorinated alkanes and long column heights employed (53 to 56 cm) relative to other studies, equilibrium conditions between the bubble and water were most likely established. The trends observed among H determinations for different column heights were, therefore, likely related to either increased glassware sorption, due to the creation of a larger headspace volume when shorter column heights were employed, or to increased water carry over to the vapor trap at the greatest column height, or a combination of both processes.

The coefficient of variation (CV) of H outlined in Table 3.1 was quite high for the $T_4C_{10}$ congener at 75.4%, and were similar for the other chlorinated alkanes ranging from 45.6 to 73.4%. These values are comparable to the CVs of 9 to 61% reported for Hs of PAHs and pesticides and from 7.6 to 73.3% for PCBs determined using the wetted-wall column technique (Fendinger and Glotfelty 1988; Brunner et al. 1990). The authors of these studies attributed error to analytical uncertainty during sample extraction and preparation and sample degradation for labile compounds. The CVs observed in this study were, however, higher than reported by Dunnivant et al (1988) who observed CVs (calculated from reported mean and SD) in the range of 1.9 to 12.5% for PCBs using the gas sparging technique and three replicate trials. The CV of 21.2% for the combined Hs and 39.3% for the kinetically derived Hs obtained for the $^{14}$C-polychlorinated dodecane mixture was similar to the variability reported for $^{14}$C-labeled mirex (CV = 15 to 29%) by Yin and Hassett (1986). Therefore, it seems that much of the additional variability of the unlabeled compounds can be attributed to analytical errors during sample preparation. In addition, trials which utilized Equation 10 to calculate the first-order volatilization rate constant ($k_v$) would contain the additional error associated with estimating initial water concentrations. As described previously, calculated Hs may vary by a factor of up to 3.7 depending on how initial water concentrations were determined and which model was utilized to estimate $k_v$.

The dichlorodecane and dichlorododecane Hs were estimated using the ratio $P_{(sub)}$ to water solubility ($S_{w(sub)}$). A number of studies have found good agreement between experimentally derived Hs and those derived from $P/S_w$ calculations when the variance in P and $S_w$ measurements are taken into account (Mackay and Shiu 1981; Suntio et al. 1988; Southworth 1979). The correlation between measured and calculated Hs for 120 compounds was 0.997 with a mean standard deviation of 0.05 (Meylan and Howard 1991). Similarly Schwarzenbach et al. (1993) suggested that deviations between experimental and predicated H values could be less than 10% provided accurate P and $S_w$ data are available. Utilization of the gas sparging techniques for these compounds would have been problematic due to the large magnitude of Hs (499.4 to 648.1 $Pa \cdot m^3 \cdot mol^{-1}$) for the two compounds, which would require substantially increased sparging column heights to ensure equilibration.

The $D_2C_{12}$ was solid at room temperature, having a melting point of 27 to 28°C (Aldrich 1995). The solubility was converted to the subcooled-solubility using the equations outlined by Mackay and Shiu (1981):

$$S_{w(sub)} = S_{w(solid)} \cdot \frac{f_{liquid}}{f_{solid}} \qquad (13)$$

and

$$\ln\frac{f_{liquid}}{f_{solid}} = \frac{R}{-\Delta S_{fus}\left(\frac{T_M}{T} - 1\right)} \qquad (14)$$

where: $S_{w(solid)}$ is the solid aqueous solubility of the solute
$f_{liquid}/f_{solid}$ is the fugacity correction ratio describing the change in state from solid to subcooled-liquid state
$\Delta S_{fus}$ is the entropy of fusion ($J \cdot mol^{-1} \cdot K^{-1}$)
$T_M$ is the melting point of the solute (K)

The entropy of fusion ($\Delta S_{fus}$) was assumed to equal 56 $J \cdot mol^{-1} \cdot K^{-1}$, a value commonly applied to rigid organic molecules (Mackay and Shiu 1981). This assumption may not be valid for chlorinated alkanes which would exhibit considerable molecular flexibility relative to aromatic compounds. Since the melting point differed from the experimental temperature by only 3°C, the correction for solid to subcooled-liquid state had little impact on the calculated H. The solubility of the solid solute and the subcooled liquid for $D_2C_{12}$ differed only by 8%.

The H derived for the $^{14}C$-polychlorinated dodecane must be interpreted with some caution relative to the Hs determined for the individual synthesized chlorinated alkane congeners. Detection for this mixture was based on total activity, and therefore the measured H reflects an integration of the sum of vapor pressures divided by the sum of solubilities for all components within the mixture. As a result, lower and higher chlorinated isomers would skew the measured H towards greater or lower values than the average hexachloro-congener on account of different volatilization rates associated with each isomer. However, since this mixture exhibits an almost normal distribution of congeners varying in degree of chlorination, it is expected that the total activity should yield an H of similar order as the average congener (hexachlorododecane) present in the mixture. The observed H for this mixture was found to be within the range of Hs described for the $P_5C_{10}$ and $P_5C_{11}$ compounds.

One estimated H for tetrachlorodecane was reported, based on the ratio of solubility (estimated from a $K_{ow}$) and vapor pressure, at 14.7 $Pa \cdot m^3 \cdot mol^{-1}$, a value which is very similar to the experimental value determined in this study (Environment Canada 1993). The Hs for the tetra, penta and hexachloro compounds are generally within the range of Hs cited for PCB congeners of the same chlorine number. Tetra, penta and hexachlorobiphenyls have Hs ranging from 1.7 to 87.1, 5.4 to 151.4, and 3.0 to 86.6 $Pa \cdot m^3 \cdot mol^{-1}$, respectively (Dunnivant and Elzerman 1988; Murray and Andren 1991; Mackay et al. 1992; Brunner et al. 1990; Murphy et al. 1987).

The *n*-alkanes, monochlorinated alkanes ($C_1$ to $C_5$) and dichloro-alkanes ($C_1$ to $C_4$) exhibit a trend of increasing H with increasing carbon number (Mackay and Shiu 1981; Nirmalakhandan and Speece 1988). The trend arises from greater decreases in solubility relative to vapor pressure for a $CH_2$ group addition to a given molecule. Although this trend is observed for the calculated Hs of dichlorodecane and dichlorododecane, the effect is less clear for the measured Hs of the polychlorinated decanes and undecanes. The $T_4C_{10}$ had a significantly (Tukey's HSD; $p<0.05$) higher H than the $T_4C_{11}$ even though both compounds had similar chlorine substitution patterns. The $P_5C_{10}$s also appeared to have higher Hs then the $P_5C_{11}$s, although not statistically significant for all congeners studied. Unfortunately, Hs for the $T_4C_{12}$ and $P_5C_{12}$ could not be determined using the above experimental methods and insufficient data are available to interpret clear trends for Hs with carbon chain length.

Mackay and Shiu (1981) suggested that addition of halogen atoms to aromatic hydrocarbons causes a nearly equal reduction in both the vapor pressure and solubility with no resultant trend in H (Mackay and Shiu 1981). Similarly Burkhard et al. (1985) and Dunnivant et al. (1988) found no trends between Hs and molecular weights for PCBs, although chlorine substitution patterns appeared to be correlated with H within a given molecular weight class. Analysis of literature reported Hs for the complete congener set of the polychlorinated ethanes, ranging from parent alkane to hexachloroethane, reveals a weak decreasing trend of log H with number of chlorines up to the tetrachloro-congener, although considerable scatter is observed among isomers of the same degree of chlorination (Figure 3.4). Similar correlations were observed between degree of chlorination among the *n*-propane, monochloro and dichloropropane Hs. For both the polychlorinated methanes and ethanes, the fully chlorinated hydrocarbon deviated from the above trend, exhibiting an increased H over that of the chlorinated hydrocarbon containing 1 less chlorine.

The polychlorinated decanes, undecanes and dodecanes also exhibited a decreasing trend in Hs with increasing degree of chlorination similar to that observed for the chlorinated alkanes of lower carbon chain lengths (Figure 3.5). The decrease in observed Hs with increasing chlorination was found to be greater than the corresponding drop in vapor pressures for the same compounds. $P_{(sub)}$ decreases between the parent *n*-alkane and dichloro-alkane ranged

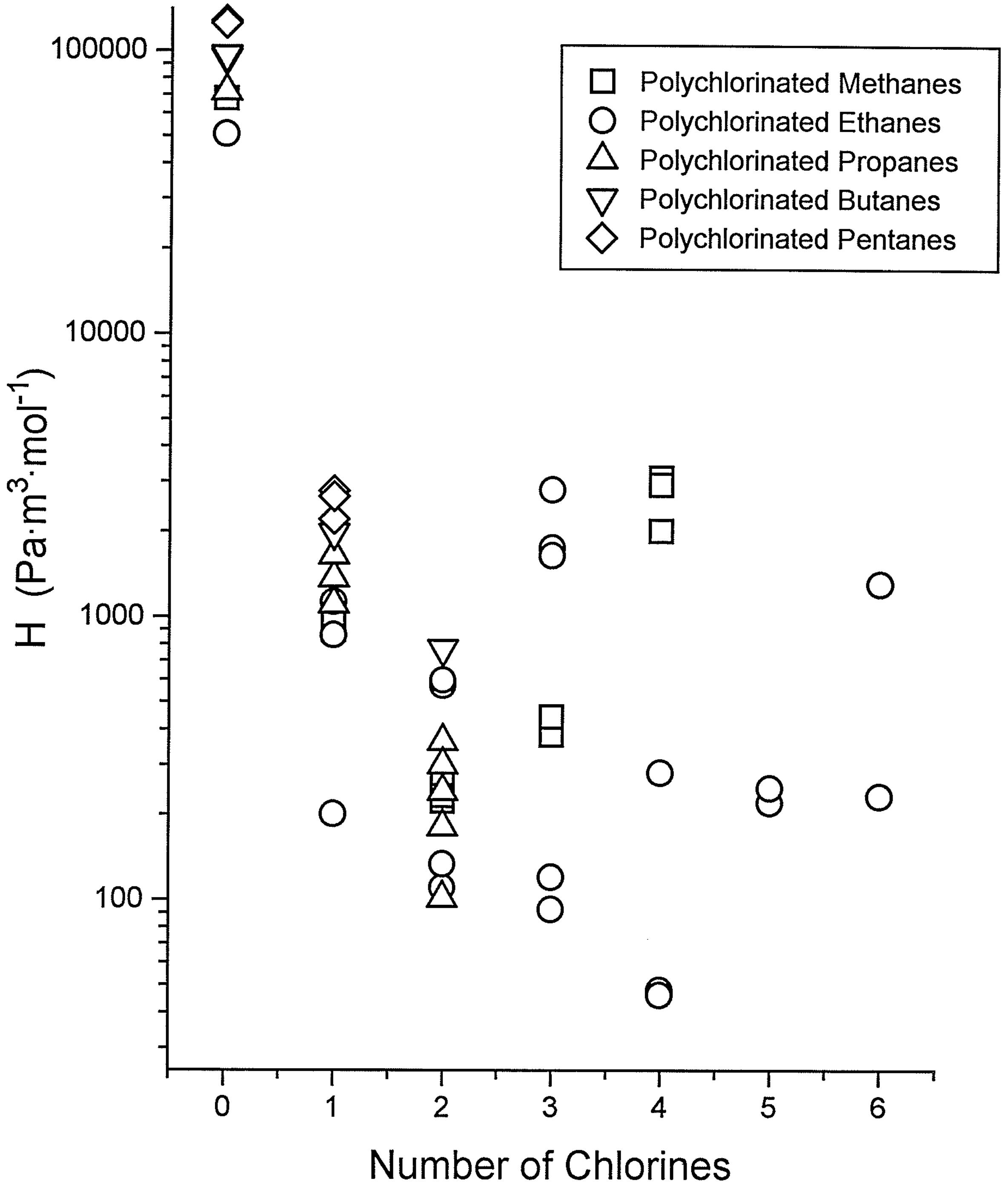

Figure 3.4. H *vs* chlorine number reported for chlorinated alkanes (C < 10). Data derived from Gossett 1987; Mackay and Shiu 1981; Nirmalakhandan and Speece 1988; Mackay et al. 1993

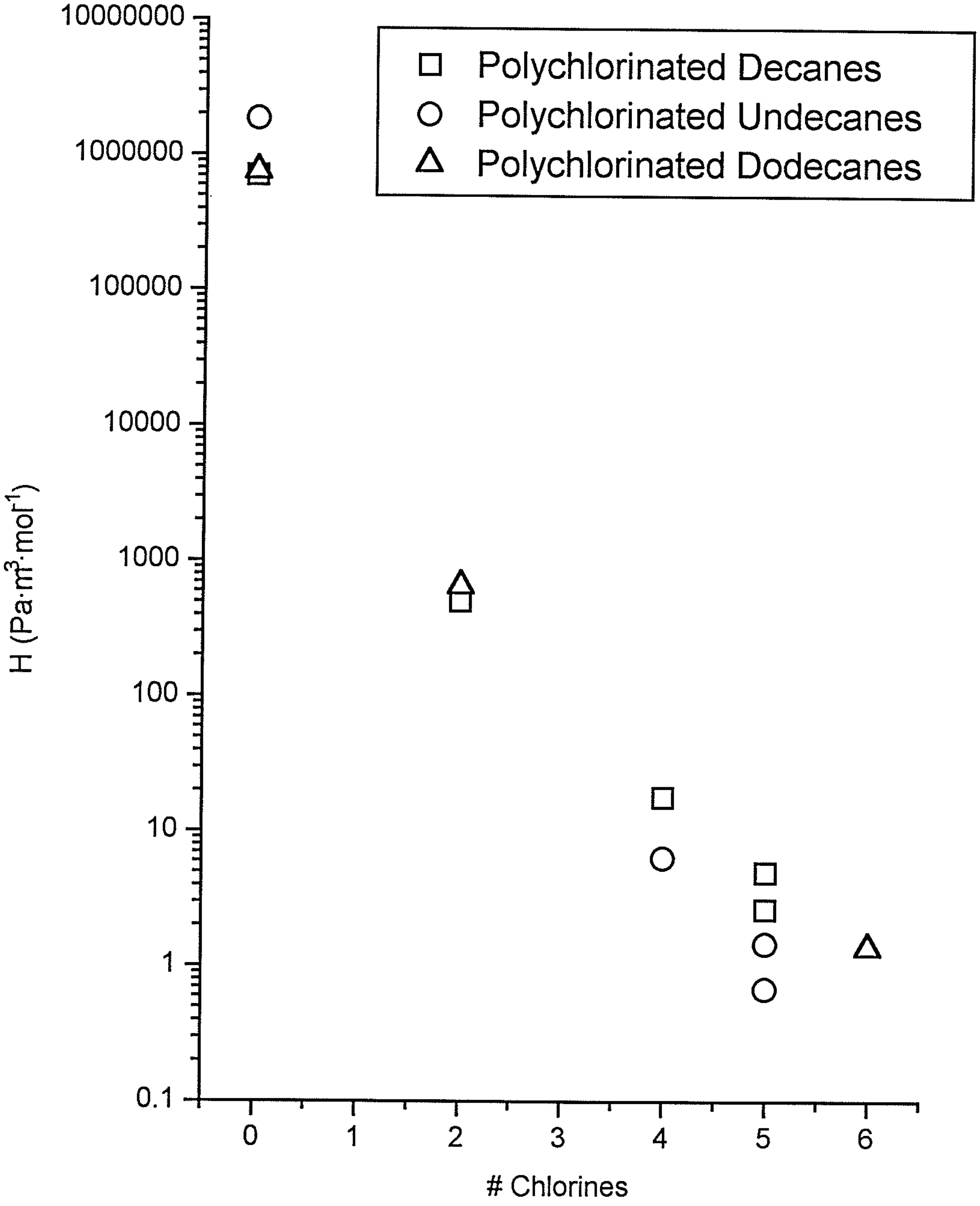

Figure 3.5. HLC *vs* chlorine number for chlorinated alkanes of study (C > 10) at 23°C.

from 200 to 300 fold, whereas Hs decreased by factors from 1200 to 1400. The drops in $P_{(sub)}$ for $D_2C_{10}$ to $T_4C_{10}$ and for tetrachloro- congeners to pentachloro- congeners were 18 and 5.0 to 7.7 fold, were closer to the corresponding drops in Hs of 26 and 4.1 to 9.4 fold, respectively. These results indicate that the mechanisms governing changes in $P_{(sub)}$ and $S_{w(sub)}$ with increasing chlorination are different for the two physical properties.

## 3.7. Conclusions

Henry's law constants (H) were experimentally determined for tetra- and pentachlorodecanes, tetra- and pentachloroundecanes and hexachlorododecane congeners using the gas sparging technique. The magnitude of mean Hs for these compounds ranged from 0.7 to 17.7 $Pa{\cdot}m^3{\cdot}mol^{-1}$ indicating volatilities in the range of negligible to low volatility according to the classification outlined by Suntio et al. (1988) and Eisenreich et al. (1981). The higher Hs observed for the tetrachloro-alkane congeners are within the range of Hs reported for PCBs of similar degree of chlorination. As a result, these compounds may exhibit significant environmental transport via volatilization. In addition, Hs for 1,10-dichlorodecane and 1,12-dichlorododecane were calculated based on the ratio of experimentally measured $P_{(sub)}$ to $S_{w(sub)}$. Hs for these lower chlorinated compounds were much higher at 499.4 and 648.1 $Pa{\cdot}m^3{\cdot}mol^{-1}$, respectively, and are considered to be highly volatile compounds which are expected to predominantly partition to the air. No clear trends were evident between Hs for the chlorinated alkanes and carbon chain length, although a trend of decreasing Hs with increasing degree of chlorination was observed.

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# 4. Water Solubility of Chlorinated Alkanes

## 4.1. Introduction

The aqueous solubility is a fundamental physical property directly related to the environmental mobility of a compound (Shiu et al. 1990). The solubility reflects the degree of non-ideality between a solute and water, and as such, is related to a large extent to a chemical's hydrophobicity (Opperhuizen et al. 1988). The inverse relationship between solubility and hydrophobicity has been demonstrated by numerous correlations between solubility and octanol/water partition coefficients, sediment/water partition coefficients and bioconcentration factors (Lyman et al. 1990; Shiu et al. 1990; Kenaga and Goring 1980). Compounds which exhibit relatively high solubilities, tend to become quickly dispersed in the environment via the hydrological cycle, are associated with sediment and biological phases to lower extents and often have higher degradation rates relative to sparingly soluble compounds (Lyman et al. 1990). In addition to prediction of environmental fate processes, knowledge of solubilities is also often required during remediation and bioremediation of contaminated sites.

## 4.2. Qualitative Description of the Solubilization Process

For molecular solvents, which exhibit relatively weak intermolecular interactions of dispersion and dipole forces, dissolution of a solute is essentially substitutional. The solute takes the place of a solvent molecule when intermolecular interactions between solute and solvent and solvent and solvent are similar (Grunwald 1986; Atkins 1982).

When the mixture is nearly ideal, the driving process of dissolution is the entropy gain associated with solute dispersal with little or no change in enthalpy (Atkins 1982).

The hydrogen-bonded structure of pure water classifies it as a network solvent and as a consequence, the mechanisms of solubilization of solutes in water are different from molecular solvents (Grunwald 1986; Opperhuizen et al. 1988). When non-ionic solutes, incapable of forming hydrogen bonds, are in contact with water, dissolution essentially requires that the water rearrange its network strands to create a cavity for the solute (Grunwald 1986). This endoergic process of cavity formation may be partially offset by enthalpy changes related to solute-solvent intermolecular interactions often characterized as solute polarizability (Taft et al. 1985; Kamlet et al. 1987; Grunwald 1986; Nirmalakhandan and Speece 1988). The dissolution of a non-ionic hydrophobic compound under dilute conditions is often described as a three step process:

i) Loss of solute-solute interactions in the pure condensed phase
ii) Creation of a suitable cavity in the network solvent
iii) Placement of a solute molecule into the cavity with formation of solute-solvent interactions

(Opperhuizen et al. 1988; Kamlet et al. 1987; Grunwald 1986)

This model assumes that each solute molecule is randomly distributed in a non-associated state within the solvent under dilute conditions such that the activity coefficient of the solvent remains close to 1. The latter assumption tends to be valid when the solubility, expressed on a mole fraction basis, is less than 0.005 to 0.01 (Mackay and Shiu 1981; Munz and Roberts 1986).

The step (i) of the solubilization process is directly related to the vapor pressure and enthalpy of vaporization, which characterizes the intermolecular forces between solute molecules in the condensed state. The magnitude of this term is dependent on the physical state of the solute and becomes increasingly important for high melting point solids. When dealing with solubilities corrected to the subcooled-liquid state, however, this term is generally less important than the non-ideality associated with solute-solvent interactions in the water phase (Grunwald 1986). Thus, trends in the subcooled-liquid solubilities among different compounds are related to the non-ideality of the chemical-water binary mixtures which is a measure of the hydrophobicity of the solute as, opposed to solid solubilities which reflect a combination of non-ideality effects and enthalpy of melting (Yalkowsky and Mishra 1990).

Many studies have reported strong correlations between solubility and various descriptors of solute molecular size (molecular weight, carbon chain length, total surface area, molecular volume) indicating the importance of the endoergic cavity formation term in the solubilization process of non-polar hydrophobic solutes (Hermann 1972; Kamlet et al. 1987; Taft et al. 1985; Shiu et al. 1990; Mackay et al. 1980; Suntio et al. 1988). The chief energetic constraint of the cavity formation term is thought to be due to decreases in entropy of the system from the ordering of solvent molecules surrounding the solute (Schwarzenbach et al. 1993). Although there is a positive entropy of mixing associated with the dispersal of solute into the solvent, the dipoles of water molecules immediately surrounding a non-polar solute become orientated relative to the next surrounding water layer yielding a fixed cavity of 'ice like' patches (Hermann 1972; Grunwald 1986; Alger 1994). The magnitude of entropy loss is directly related to cavity size and molecular surface area. However, adequate correlations between a given molecular size descriptor and solubility tend to be confined to homologous series of compounds or specific chemical classes. This constraint occurs because most molecular size indices cannot take into account differences in the ability of solutes to minimize the cavity volume required to accommodate the solute through molecular folding (Kan and Tomson 1996).

The exoergic polarizability term for molecules with permanent and induced dipoles represents the summation of all attractive forces which surround a molecule and is also correlated to molecular size and the number of polar functional groups (Rubino and Yalkowsky 1987a). Polarizability terms for various compounds have been correlated to molecular connectivity indices and dielectric constants, and estimated using the Hildebrand solubility parameter, group contribution methods and octanol-water partition coefficients (Nirmalakhandan and Speece 1988; Kier and Hall 1986; Rubino and Yalkowsky 1987a; Chen et al. 1993). Strong interactions between solute and water molecules will partially offset entropy losses due to cavity formation with subsequent increases in the observed solubility. For many hydrophobic, non-polar compounds, however, the polarizability term appears to be of second order importance in determining solubility relative to the energetics associated with cavity formation in the water network (Kamlet et al 1987).

### 4.2.1. Thermodynamic Description of Solubilization

The equilibrium solubility is reached when the chemical potential of a solute in its pure condensed phase is equal to the chemical potential of the solute in the saturated aqueous solution. Chemical potentials of the compound in the pure condensed phase and water phase are denoted by:

$$\mu_{org} = \mu^o + RT \ln \gamma_{org} \cdot x_{org} \qquad (1)$$

$$\mu_w = \mu^o + RT \ln \gamma_w \cdot x_w \qquad (2)$$

where: $\mu_{org}$, $\mu_w$ are the chemical potentials of the solute in the organic and water phases
$\mu^o$ is the chemical potential of the solute in the reference state (corresponding to the subcooled-liquid state)
$\gamma_{org}$, $\gamma_w$ are the activity coefficients of chemical in organic and water phase
$x_{org}$, $x_w$ are the mole fractions of chemical in organic and water phases

(Atkins 1982; Tewari et al. 1982)

The approach to equilibrium is expressed as the free energy of solution such that:

$$\Delta G_s = \mu_w - \mu_{org} = RT \ln \gamma_w \cdot x_w - RT \ln \gamma_{org} \cdot x_{org} - RT \ln \frac{f_{solid}}{f_{sub}} \qquad (3)$$

where: $\Delta G_s$ is the free energy of solubilization
$f_{solid}/f_{(sub)}$ is the fugacity correction used to correct for the energy required to overcome intermolecular interactions of the crystal lattice for solids

The fugacity correction is related to the melting point and this term becomes increasingly important when describing solubility for high melting solids. For liquids, the term $f_{solid}/f_{sub}$ equals 1 (Shiu et al. 1990). At equilibrium, $\Delta G_s = 0$ and the mole fraction of the compound in the water ($x_w$) defines the fundamental unit of solubility for the compound at a given temperature. For sparingly soluble compounds which exhibit a low solubility of water in the organic phase, the assumption: $\gamma_{org} \cdot x_{org} = 1$ is usually made reducing equation 3 to:

$$\Delta G_s = RT \ln \gamma_w + RT \ln x_w - RT \ln \frac{f_{solid}}{f_{sub}} \qquad (4)$$

Each of the terms in the free energy description of solubilization can be related to the model described previously. The fugacity correction term accounts for a portion of step (i) in that it corrects for enthalpy of melting associated with the intermolecular interactions of the solid organic solute. The term $RT \cdot \ln x_w$ refers to the ideal mixing term, whereas the term $RT \cdot \ln \gamma_w$ incorporates all of the differences betweeen the observed thermodynamic function of mixing and the function of mixing for an ideal mixture. This latter term is often described as the excess free energy of mixing and incorporates the excess enthalpies ($\Delta H_{excess}$) and entropies ($\Delta S_{excess}$) associated with cavity formation and polarizability described previously.

Since there is no direct method of observing chemical potential, Equations 3 and 4 are usually expressed in terms of activity or fugacity (Schwarzenbach et al. 1993; Atkins 1992; Shiu et al. 1990; Mackay and Shiu 1981;Lane and Loehr 1992).

$$a_i = x_i \cdot \gamma_i = f_i / f_{sub} \qquad (5)$$

Combining Equations 3 and 5 yields:

$$f_w = f_{org} = x_w \cdot \gamma_w \cdot f_{sub} = x_{org} \cdot \gamma_{org} \cdot f_{solid} \qquad (6)$$

and

$$x_w = \frac{x_{org} \cdot \gamma_{org}}{\gamma_w} \cdot \frac{f_{solid}}{f_{sub}} \qquad (7)$$

Employing the same assumptions of negligible solubility of water in the organic phase, then $x_{org} \approx 1$ and $\gamma_{org} \approx 1$ and Equation 7 reduces to:

$$x_w = \frac{1}{\gamma_w} \cdot \frac{f_{solid}}{f_{sub}} \qquad (8)$$

### 4.3. Solubility of Mixtures

The above models may not adequately describe the dissolution behavior of individual compounds which are introduced to water as a mixture in the organic phase (Banerjee 1984). Many chemicals entering the environment via disposal/spill sites and leachates may do so in combination with multiple solvents, co-solutes and surfactants which greatly influence their mobility relative to chemical introductions to water from the pure organic state (Suresh et al. 1990; Li et al. 1992; Boyd and Sun 1990). The mixture effect on the apparent solubility of individual components arises from the change in water network character with the introducion of multiple solutes. This change is related to the composition and concentration of compounds present in the organic mixture (Li et al. 1992; Eganhouse and Calder 1976; Suresh et al. 1990). The effect of the mixture on the apparent solubility may result in enhanced solubilization, solubility depression or little effect at all depending on the character of the mixture and concentrations of individual components partitioned into the water phase.

### 4.3.1. Cosolvent/Surfactant Effects

Increases in apparent solubility have been defined as the cosolvent effect (Yalkowsky et al. 1976; Rubino and Yalkowsky 1987a,b). The cosolvent effect occurs when compounds which are ionized, or capable of forming H-bonds, are present at sufficient concentrations in the water to modify or disrupt the water network structure creating a more favourable environment for dissolution of hydrophobic solutes (Rubino and Yalkowsky 1987a; Hermann 1972; Li et al. 1992). For aprotic cosolvents which are randomly distributed in the water phase, the combination of hydration of the cosolvent and water-cosolvent interaction via H-bonding leads to a maximum in the disruption of the water network structure at a specific cosolvent concentration. The disruption in water structure decreases the enthalpy of cavity formation to favour solubilization of hydrophobic solutes. The ability of a cosolvent to disturb the water network is also directly related to its H-bonding ability and inversely related to its molecular size relative to water. For amphiprotic cosolvents which exhibit surfactant qualities, the above mechanisms apply at low cosolvent concentrations. At concentrations exceeding the critical micelle concentration (CMC), self-association of cosolvent into micelles (3-4 nm diameter) within the water provides a non-polar partitioning medium for hydrophobic co-solutes present in the organic phase (West and Harwell 1992; Dickhut et al. 1991). This latter effect is analogous to dispersed oil droplets in solution. CMCs for highly active surfactants generally range between 2 to 20 x $10^{-5}$ mole fraction (West and Harwell 1992).

The effect of the cosolvent on the activity coefficient of a solute in water increases with a its hydrophobicity. Less soluble components in the mixture will exhibit a more pronounced increase in apparent solubility (Munz and Roberts 1986). However, as the cosolvent concentration approaches infinite dilution, perturbations to the water network become insignificant and little or no effect on apparent solubilty of hydrophobic solutes may be realized (Banerjee and Yalkowsky 1986; Munz and Roberts 1986). Many studies have been unable to quantify a significant cosolvent effect on the observed solubility at cosolvent concentrations below approximately 10% w/w (Banerjee and Yalkowsky 1986; Munz and Roberts 1986).

### 4.3.2. Cosolute Effects

A depression in apparent solubility relative to the true solubility will be referred to from here on as the cosolute effect. A cosolute refers to a hydrophobic, non-polar compound in the mixture which lacks the ability to significantly disrupt the water network and, as a consequence, generally exhibits a relatively low true solubility. The mechanism of the co-solute effect is a competitive one, such that the water network will accommodate only a limited number of cavities for solutes exhibiting weak solute-water interactions. The magnitude of the cosolute effect is bounded by: $0 < S_w' < S_w$, where $S_w'$ and $S_w$ refer to the apparent solubility of a compound introduced as a mixture and the true solubility of a compound introduced to water in pure form, respectively. The lower boundary is approached when the cavity formation capacity of the water network becomes limited (i.e. large numbers of low soluble cosolutes, or cosolutes of relatively high solubility are present) and the upper boundary is approached when the sum of cosolutes present do not significantly alter the cavity formation capacity of water (Tewari et al. 1982).

A number of studies have derived expressions relating the cosolute effect to the mole fraction of a solute in the organic mixture by treating the mixture as a linear combination of component solvents (Tewari et al. 1982; Banerjee 1984). The thermodynamic parameters for individual compounds from Equations 1 and 2 are replaced with mixture functions as follows:

$$\mu_{org} = \mu^{o} + RT\ln \gamma_{org(mix)i} \cdot x_{org(mix)i} \qquad (9)$$

$$\mu_{w} = \mu^{o} + RT\ln \gamma_{w(mix)i} \cdot x_{w(mix)i} \qquad (10)$$

where: (mix) denotes the mole fraction or activity coefficient in water and organic phases of the i'th component introduced to the water in a mixture.

Assuming the organic mixture is a liquid (Banerjee 1984) and ignoring the solid to subcooled-liquid correction term, the equilibrium saturation of component I in the mixture is given by:

$$x_{w(mix)i} = \frac{x_{org(mix)i} \cdot \gamma_{org(mix)}}{\gamma_{w(mix)i}} i \qquad (11)$$

Combining Equations 7 and 11 for liquid or subcooled-liquid solutes yields:

$$x_{w(mix)i} = \frac{\gamma_{w(i)}}{\gamma_{w(mix)i}} \cdot \frac{\gamma_{org(mix)i}}{\gamma_{(org)i}} \frac{x_{org(mix)i}}{x_{(org)i}} \cdot x_{w(i)} \qquad (12)$$

The solubility depression effect can be subsequently calculated by rearrangement of equation 12:

$$\frac{x_{w(mix)i}}{x_{w(i)}} = \frac{S_w'}{S_w} = \frac{\gamma_{w(i)}}{\gamma_{w(mix)i}} \cdot \frac{\gamma_{org(mix)i}}{\gamma_{(org)i}} \cdot \frac{x_{org(mix)i}}{x_{(org)i}} \tag{13}$$

In order to simplify Equations 12 and 13, several assumptions may be made based on the character of individual components within the organic mixture. If water is sparingly soluble in the pure organic phase of component i, then the assumption: $\gamma_{(org)i} \approx 1$ and $x_{(org)i} \approx 1$ may be made allowing:

$$\frac{S_w'}{S_w} = \frac{\gamma_{w(i)} \cdot \gamma_{org(mix)i} \cdot x_{org(mix)i}}{\gamma_{w(mix)i}} \tag{14}$$

Similarly if no solute:solute or cosolute:solute interactions occur in the aqueous phase (infinite dilution conditions are maintained) then: $\gamma_{w(i)} \approx \gamma_{w(mix)i}$ and:

$$\frac{S_w'}{S_w} = \gamma_{org(mix)i} \cdot x_{org(mix)i} \tag{15}$$

Finally, if the cosolute components in the organic mixture form an ideal solution then $\gamma_{org(mix)i} \approx 1$ and one obtains the most basic equation:

$$\frac{S_w'}{S_w} = x_{org(mix)i} \tag{16}$$

The applicability of Equations 13 to 16 is dependent on the number of cosolutes present in the organic mixture, the solubility of each cosolute in the mixture and the interactions between individual cosolutes in both the aqueous and organic phases. For simple mixtures of sparingly soluble compounds, Equations 15 and 16 have been described as adequate for predicting cosolute effects (Banerjee 1984; Tewari et al. 1982).

## 4.4. Experimental Determination of Solubilities

The major difficulties in experimentally determining water solubilities are attributed to the generation of equilibrated solute-water solutions, separation of organic and aqueous phases and quantititative extraction of solute from the aqueous phase. These difficulties tend to increase with solute hydrophobicity. The major methods employed for determining solubilities include batch type shake flask methods for more water soluble components, and the generator column technique for sparingly soluble analytes.

### 4.4.1. Shake Flask Method

Prior to 1978, the shake flask method was the traditional method employed for determining solubilities of relatively soluble compounds (McAuliffe 1963; Franks 1966; Sutton and Calder 1974; Mackay and Shiu 1977). The shake flask method generally involves the introduction of an excess of solute to water under temperature controlled conditions. The solution is mechanically stirred for 24 h, allowed to settle 24-48 h, filtered and extracted (Mackay and Shiu 1977; May et al. 1978 b). Although this method tends to be precise for compounds of high solubility ($S_w > 10^{-5}$ M; Mackay and Shiu 1977) it suffers from a number of problems when solubilities of sparingly soluble components are determined.

Incomplete equilibration between solute and water for high melting point compounds has been described for batch type systems. Jepsen et al. (1995) observed that from 10 to 20 days were required to allow dissolution of 85% of solid hexachlorobenzene added at less than the solubility of the compound. Other artifacts include the formation of colloidal dispersions and suspended microcrystals of solute in the water which tend to bias results towards overestimates of solubility (May et al. 1978 a,b; Wasik et al. 1983). The degree of colloidal, micellar or particulate dispersions is related to the method of solute introduction to water, settling time and filter pore size (May et al. 1978 a). In addition, adsorptive losses of dissolved hydrophobic solutes to glassware and onto filter surfaces, losses of volatile compounds from solution and degradation of analyte over long equilibration periods bias results towards underestimates (May et al. 1978 a,b; Wasik et al. 1983; Madeley and Gillings 1983b). Further improvements to the technique involve slow stirring to minimize colloidal dispersions, centrifuging as opposed to filtering and pre-rinsing glassware with equilibrated solutions to minimize adsorptive losses (Wasik et al. 1983).

Mackay and Shiu (1977) reported a precision for the shake flask technique of the order of 5-10% for compounds exhibiting solubilities greater than $10^{-5}$ M. Kishi and Hashimoto (1989) reported the results of an interlaboratory ring test on solubility determinations of anthracene and fluoranthene using a modified shake flask method. In this method, excess solute was first sorbed to glass beads, the beads were shaken with water at 50°C for 5 min, and the temperature brought down to 20°C. The solution was then allowed to equilibrate for 48 h and filtered through glass fibre filters prior to solution extraction. Solubility results from 17 labs for anthracene and fluoranthene ranged from 6.0 - 8.4 x $10^{-8}$ M (CV

51%) and from 9.8 to 13.3 x $10^{-7}$ M (CV 20%), respectively, and bracketed experimental determinations using the generator column method.

### 4.4.2. Generator Column Method

May et al. (1978a) developed the generator column technique to circumvent some of the problems associated with the shake flask method. As a result of the enhanced sensitivity of the method and applicability to sparingly soluble compounds, the generator column has become the method of choice for determination of aqueous solubilities for sparingly soluble compounds (Mackay and Shiu 1981; Kishi and Hashimoto 1989). The generator column is produced by coating the glass beads with solute (60-80 mesh) with subsequent evaporation of excess solvent. The glass beads are packed into a glass column or empty HPLC column containing 2 to 5 μm frits at the end and eluted with pure water at flow rates ranging from 0.2 to 5 ml/min (May et al. 1978 a,b; Wasik et al. 1983; Dickhut et al. 1986). After a conditioning period, which serves to saturate internal surfaces of the apparatus with the solute, the saturated solution exiting the column is extracted with a solid phase extraction column.

The generator column technique addresses several of the problems associated with the shake flask method. The combination of slow, even flow rates and 2 to 5 μm frits at the end of the column minimize the formation of colloidal dispersions in the exiting saturated solution. In addition, since the frits and internal tubing are preconditioned with the solute, adsorptive losses are minimized (May et al. 1978a). The large surface area of the coated stationary phase allows for rapid equilibration. May et al. (1978) found that PAH solubilities were independent of flow rates ranging from 0.1 to 5 mL/min indicating equilibration. Friesen et al. (1985) observed that flow rates greater then 2 mL/min might not allow equilibration for sparingly soluble chlorinated dibenzo-*p*-dioxin congeners, and that a lower flow rate of 1mL/min appeared to be adequate. A final confirmatory test of equilibration was performed by May et al. (1978a) who connected two identical generator columns in line sequentially. The first generator column was maintained at 24.3°C, while the second was maintained at temperatures ranging from 25.3 to 6.6°C. Solubilities measured from the eluent of the second column were found to yield identical results, for a given temperature, to determinations performed on a single column alone. At the lower temperatures, column B received solute in solution exceeding saturation levels for the experimental temperature and as a result excess solute was re-precipitated onto glass beads demonstrating equilibrium conditions.

The precision for solubilities of PAHs determined by the generator column technique was reported to be 3% (May et al. 1978 a,b). However, the precision may be lower when utilized for compounds of lower solubility. Errors ranging from 1.3 to 20% for solubility determinations on PCBs, polybrominated biphenyls, chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans were observed (Doucette and Andren 1988; Dickhut et al. 1986; Kishi and Hashimoto 1989). The least soluble compounds, octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran, with $S_w$ of the order of $10^{-12}$ and $10^{-13}$ M, had precisions of only 39 and 45%, respectively (Doucette and Andren 1988). Dickhut et al.

(1986) indicated that interlaboratory precision of solubility determinations for compounds having $S_w$ less than $10^{-9}$ M may only be within 25% to 1 order of magnitude because of difficulties associated with analytical quantitation of low concentrations.

### 4.4.3. Calculation of Solubility from $P_{(sub)}$ and H

As defined in Chapter 3, H is directly related to the subcooled-liquid P and aqueous solubility, provided the aqueous phase solute concentrations are sufficiently low at saturation to be considered infinitely dilute solutions. Several investigators have reported agreement between the above relationship (Mackay and Shiu 1981; Suntio et al. 1988; Southworth 1979; Meylan and Howard 1991). In addition, Meylan and Howard (1991) suggested that the relationship between $P_{(sub)}$, $S_{w(sub)}$ and H may hold for compounds with aqueous solubilites as high as 10 to 30% by weight. The subcooled-liquid solubilities may be converted to true solubilities for solids with knowledge of the melting point and entropy of melting ($\Delta S_{fusion}$) (Yalkowsky 1979, Shiu et al. 1990; Mackay and Shiu 1981). Although experimental precision of Hs tend to be lower than techniques for determining solubilities, there are several advantages in determining solubilities in this manner (Mackay et al. 1979; Nielsen et al. 1994). First, $S_{w(sub)}$ is directly related to the inverse of the activity coefficient, which correlates more appropriately with hydrophobicity than does the solubility of a solid, and as a consequence is better related to environmental fate of compounds present under dilute conditions (Opperhuizen et al. 1988). Second, experimental determination of $P_{(sub)}$ (using P-GLC correlation techniques) and Hs are independent of the number or concentration of co-solutes in the organic mixture, providing a cosolvent effect does not occur in the solution.

In this study, aqueous solubilities for individual congeners of polychlorinated decanes, undecanes and dodecanes were determined using the generator column technique. The chlorinated alkanes utilized in this study were not available in pure form and, as such, a method to correct the determined apparent solubilities to the true solubilities was developed based on Equations 14 through 16. These results are compared to estimates of aqeuous solubilities calculated from the ratio $P_{(sub)}/H$ derived from previous experiments (Chapters 2 and 3).

## 4.5. Methods

The generator column technique was utilized to saturate water with mixtures of the synthesized polychlorinated decanes, undecanes or dodecanes. Separate generator columns were prepared containing either pure $D_2C_{10}$ or pure $D_2C_{12}$ to determine the true solubilities for these two compounds. Approximately 20 mg of solute or polychlorinated alkane mixture was added to 7 g acid-washed, acetone rinsed glass beads (60/80 mesh) to yield a 0.3% by (w/w) coating as recommended by May et al. (1978 a,b). The glass beads and 20 mg of chemical were subsequently mixed with 50 mL acetone, rotated on a roto-evaporator for 1 h at normal pressure, and evaporated under reduced pressure to near dryness in order to ensure homogeneous sorption. The glass beads were allowed to dry overnight and packed into a 25 cm x 4 mm i.d. stainless steel HPLC column with a total capacity of 5.95 g glass beads. The generator column was placed into an HPLC column oven to maintain temperature (± 0.5°C), connected in line to a Waters M45 HPLC pump and eluted with filtered HPLC grade water. Water solubilities were determined at 25°C for all congeners of study. In addition, the temperature dependence of the polychlorinated decane mixture was determined over temperatures of 6, 10, 15, 20 and 25°C.

Prior to solubility determination or during a temperature change, the generator column was conditioned by eluting with 300 to 1000 mL HPLC grade water. Apparent solubility determinations at 20°C were performed at flow rates ranging from 0.1 to 0.5 mL/min to verify equilibration. Saturated water was extracted by placing a conditioned $C_{18}$ SepPak® (Waters, Enviro-Plus Cat # WAT020515) at the outlet of the generator column. The volume of water eluted from the generator column was measured gravimetrically. Each SepPak was pre-conditioned with 10mL acetone, 10 mL methanol and 10 mL water. SepPaks were extracted by eluting with 14 mL of hexane at flow rates of 1 to 5 mL/min. The eluent was dried over a 2 cm column of sodium sulfate and spiked with lindane to account for losses during subsequent sample work up procedures. Samples were roto-evaporated to less then 10 mL and quantitatively transferred to a 15 mL tapered centrifuge tube along with 100 μL of isooctane. The samples were further concentrated to 100 to 200 μL under nitrogen stream. Samples (1 to 2μL) were manually injected and quantified by GC-ECD analysis as described in Chapter 1.0.

The effect of loading a mixture onto the glass beads of the generator column on solubility determinations of individual compounds present in the mixture was studied by quantifying the co-solute effect of the polychlorinated decane mixture. A number of generator columns were created by adding $D_2C_{10}$ (available in pure form) to the polychlorinated decane mixture over varying mole fractions ranging from 0.00654 to 1 (pure compound). The apparent solubility behavior of the $D_2C_{10}$ was used to assess whether or not cosolvent effects (enhanced apparent solubility) or cosolute effects (solubility depression) were occurring as a result of the presence of the 1,9-decadiene, dichlorodecene, and $T_4C_{10}$, $P_5C_{10}$ and $H_6C_{10}$ congeners in the synthesized mixture.

## 4.6. Results

Solid phase extraction columns containing $C_{18}$ stationary phase have been successfully used with the generator column technique to extract saturated water in a number of studies (Friesen et al. 1990; May et al. 1978b; Dickhut et al. 1986; Li et al. 1992; Lane and Loehr 1992). SepPaks were spiked with 0.56 µg of polychlorinated decane mixture and eluted with 0, 500 and 1000 mL of clean HPLC grade water at flow rates of 1 mL/min. Recovery efficiencies ranged from 82 to 95% after extraction with 10 mL of hexane and drying over a $NaSO_4$ column. Blank extractions of HPLC grade water using SepPaks or liquid-liquid extraction yielded no detectable chlorinated alkane peaks. To verify equilibration, different water flow rates (0.1 - 0.5 mL/min) were utilized over two different temperatures. Data from different flow rates yielded equivalent results which were not significantly different ($p>0.9$; ANOVA; Figure A.3 of the Appendix).

Figures 4.1, 4.2, and 4.3, are representative chromatograms of the synthesized polychlorinated decane, undecane and dodocane in the synthesized organic mixture and extracted saturated water samples, respectively. There was little change in the distribution of congeners within the organic and water phases despite wide differences in degree of chlorination among individual compounds. Only 100 to 200 mL of water was required to quantify chlorinated alkane congeners from the polychlorinated decane and undecane mixtures; whereas the polychlorinated dodecane mixture required at least 1 L of water to extract sufficient solute for apparent solubility determinations. All four of the $P_5C_{10}$ congeners (a, b, c, d) were quantified for apparent solubilities, whereas only the last three peaks c, d, e were quantified for the $P_5C_{11}$. For the polychlorinated dodecane mixture, only the tetrachlorododecane could be characterized. Of the hexachlorinated isomer groupings for the polychlorinated decanes and undecanes, two partially resolved peaks (a and b; Figure 4.1 and 4.2) were chosen to represent a range of $C_{10}H_{16}Cl_6$ and $C_{11}H_{18}Cl_6$ solubilities.

To measure the precision of the generator column technique, at least 4 replicate samples were collected from each generator column. In addition, 2 generator columns were created for the polychlorinated decanes and 4 generator columns were prepared for the polychlorinated undecanes to measure column to column variability in the determined apparent solubilities at 25°C. The mean apparent solubility, standard error (SE) and coefficient of variation (CV) for each set is summarized in Table A.5 of the Appendix. Mean apparent solubilities for congeners of the polychlorinated decanes exhibited a high precision with CVs ranging from 6.3 to 20.8%.

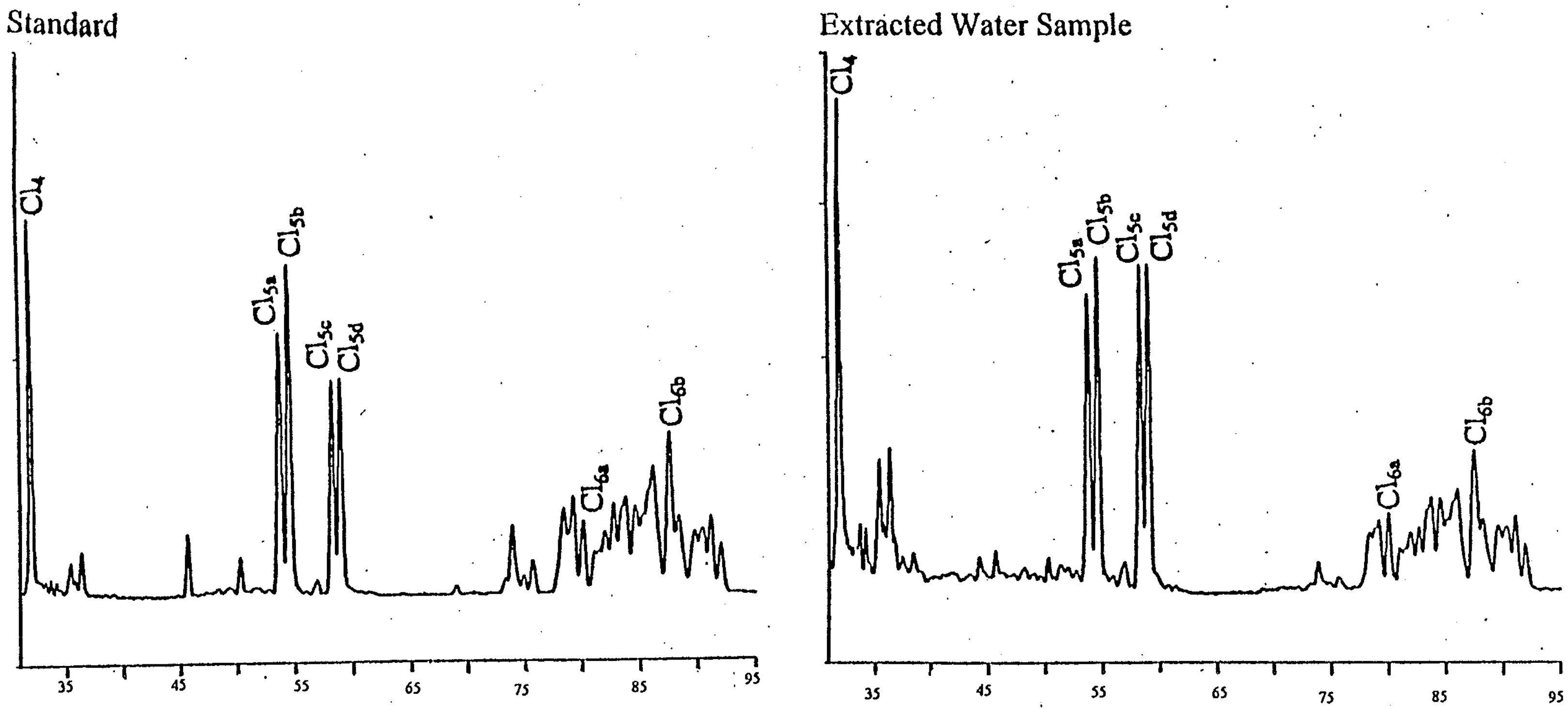

Figure 4.1 GC/ECD analysis of standard and extracted water samples saturated with polychlorinated decanes. Both chromatograms run under identical chromatographic conditions.

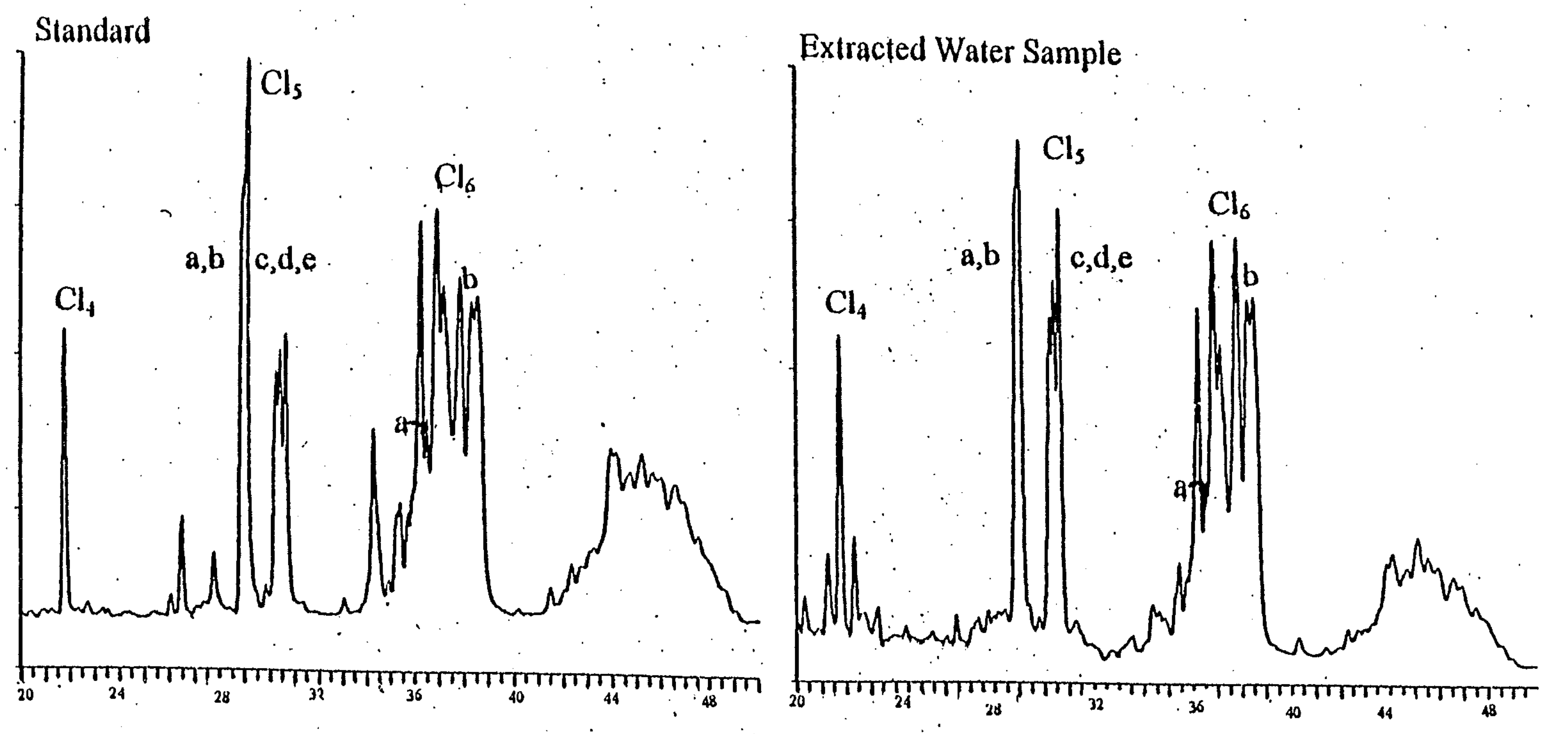

Figure 4.2 GC/ECD analysis of standard and extracted water samples saturated with polychlorinated undecanes. Both chromatograms run under identical chromatographic conditions.

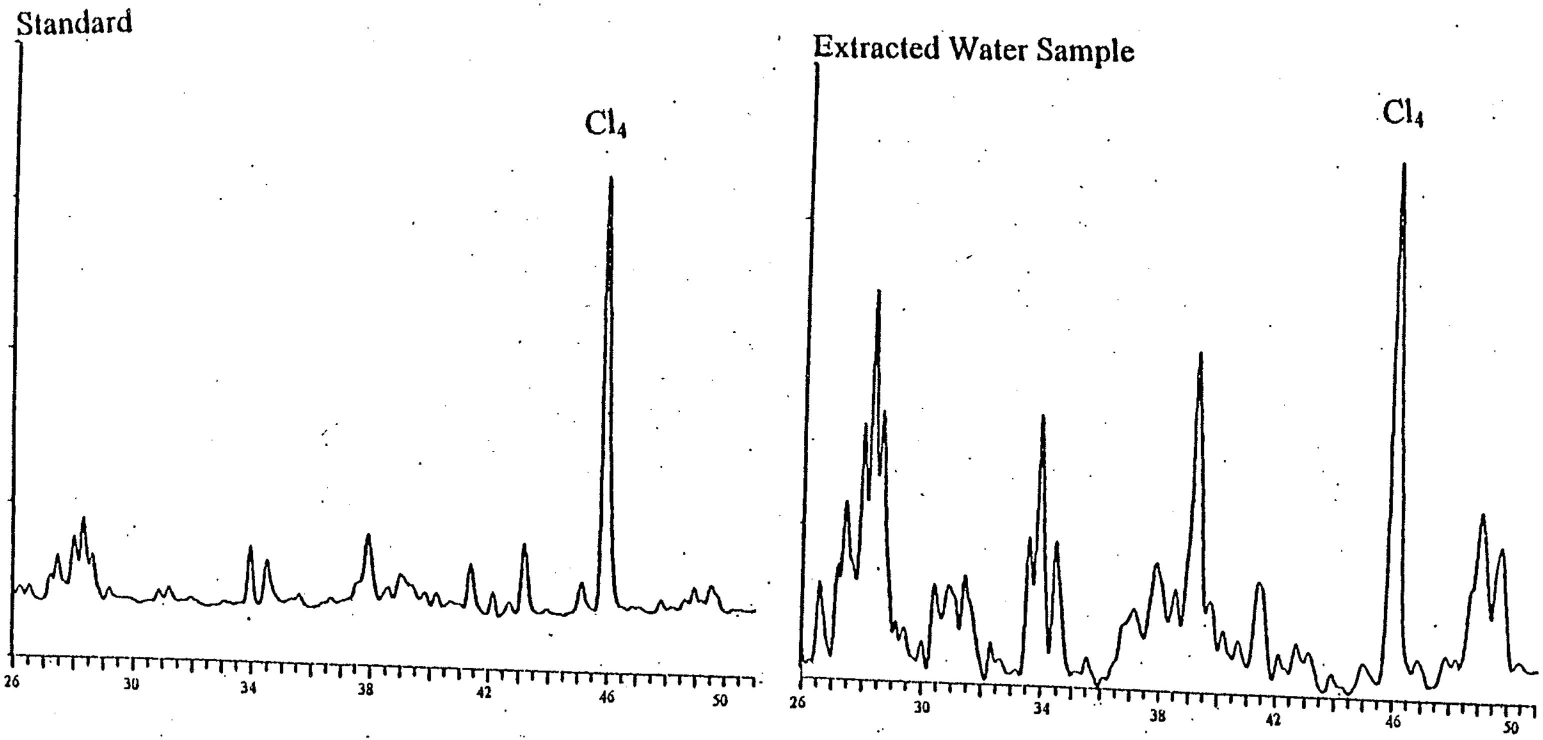

Figure 4.3 GC/ECD analysis of standard and extracted water samples saturated with polychlorinated dodecanes. Both chromatograms run under identical chromatographic conditions.

No significant differences (ANOVA $p>0.1$) in mean apparent solubilities of polychlorinated decane congeners derived from generator column #1 or generator column #2 were observed.

The precision in apparent solubilities among the four generator columns produced for the polychlorinated undecanes was lower exhibiting significant column to column variability in the mean apparent solubilities. Generally the CVs associated with the combined data (apparent solubilities derived from all generator column replicates), ranging from 24.4 to 45.2%, were considerably higher than CVs for a given generator column data set (10.4 to 24.6%). There were also highly significant differences (ANOVA; $p<0.01$) among mean apparent solubilities determined from the different generator columns. Generator column #2 yielded significantly lower apparent solubilities for all chemicals in the mixture, whereas generator column #4 tended to bias the results towards higher apparent solubilities for 5 of the 6 chemicals. An outlier test (Johnson and Leone 1964) could not reject any of the generator column specific data sets at the 95% confidence level and, therefore, all data were included in the calculation of mean apparent solubilities for these compounds.

Table 4.1 lists the solubility of the $D_2C_{10}$ and $D_2C_{12}$ (determined from pure compounds) and apparent solubilities of tetra-, penta- and hexachloro- congeners of the polychlorinated decane, undecane and dodecane congeners at 25°C. In addition, the literature reported solubility values of the non-chlorinated parent *n*-alkanes (Mackay and Shiu 1981) are included for comparison. Both the $D_2C_{10}$ and $D_2C_{12}$ had higher solubilities than observed for the parent *n*-alkanes, despite the large increases in molecular weight with addition of two chlorines to the molecule.

**Table 4.1** Apparent Solubilities of Chlorinated Alkanes at 25°C Determined by the Generator Column Technique

| Chemical | Apparent Solubility (ug·L$^{-1}$) | SE | CV (%) | n |
|---|---|---|---|---|
| n-decane | 24-52[†] | | | |
| $D_2C_{10}$ | 257.2[‡] | 15.3 | 17.8 | 9 |
| $T_4C_{10}$ | 140.9 | 4.1 | 10.0 | 8 |
| $P_5C_{10}$ (a) | 26.0 | 1.3 | 15.4 | 8 |
| $P_5C_{10}$ (b) | 28.6 | 1.2 | 15.4 | 8 |
| $P_5C_{10}$ (c) | 26.4 | 1.2 | 15.4 | 8 |
| $P_5C_{10}$ (d) | 25.9 | 1.2 | 15.4 | 8 |
| $H_6C_{10}$ (a) | 1.75 | 0.06 | 10.0 | 8 |
| $H_6C_{10}$ (b) | 4.52 | 0.23 | 14.1 | 8 |
| n-undecane | 44[†] | | | |
| $T_4C_{11}$ | 28.1 | 1.4 | 24.4 | 26 |
| $P_5C_{11}$ (c) | 13.3 | 1.2 | 45.2 | 26 |
| $P_5C_{11}$ (d) | 14.5 | 1.2 | 43.7 | 26 |
| $P_5C_{11}$ (e) | 20.9 | 1.3 | 31.9 | 26 |
| $H_6C_{11}$ (a) | 1.70 | 0.15 | 44.6 | 27 |
| $H_6C_{11}$ (b) | 7.90 | 0.68 | 44.6 | 27 |
| n-dodecane | 3.7-8.4[†] | | | |
| $D_2C_{12}$ | 22.4[‡] | 0.92 | 9.2 | 5 |
| $T_4C_{12}$ | 3.68 | 0.17 | 11.4 | 6 |

Note: [†] solubilities taken from Mackay and Shiu 1981
[‡] true solubility determined by using the pure compound as the organic phase.

The tetra-, penta- and hexachloro congeners generally exhibited decreasing trends in apparent solubility with increasing chlorination, however; the trends must be interpreted with caution since the measured solubilities are characteristic of the organic mixture rather than solubilities of the pure compound.

The van't Hoff plots (Figure 4.4) demonstrate the temperature dependence of apparent solubilities for tetra-, penta- and hexachlorodecane compounds. Enthalpies of solution ($\Delta H_s$) of 42.9, 43.9 and 56.4 $kJ \cdot mol^{-1}$ for tetra-, penta- and hexachlorodecane compounds were obtained from these plots. The two-way ANOVA indicate a non-significant interaction term for the compound x temperature ($p>0.05$), suggesting no significant differences in $\Delta H_s$s among the apparent solubilities of the individual congeners. The enthalpies of solution for the polychlorinated decanes were found to fall within ranges reported for chlorinated aromatic hydrocarbons (27.4 to 74.5 kJ/mole) as reviewed by Doucette and Andren (1988).

A separate study was performed to quantify error associated with determining solubilities from the synthesized mixture rather than using purified compounds for the polychlorinated decanes. The $D_2C_{10}$, which was available in pure form, was used as a reference compound to model the behavior of the polychlorinated decanes in the organic mixture. New organic mixtures were created by adding $D_2C_{10}$ to the polychlorinated decane mixture over varying concentrations. These organic mixtures were then used to create a series of generator columns for apparent solubility determinations of $D_2C_{10}$ and polychlorinated decane components at 25°C.

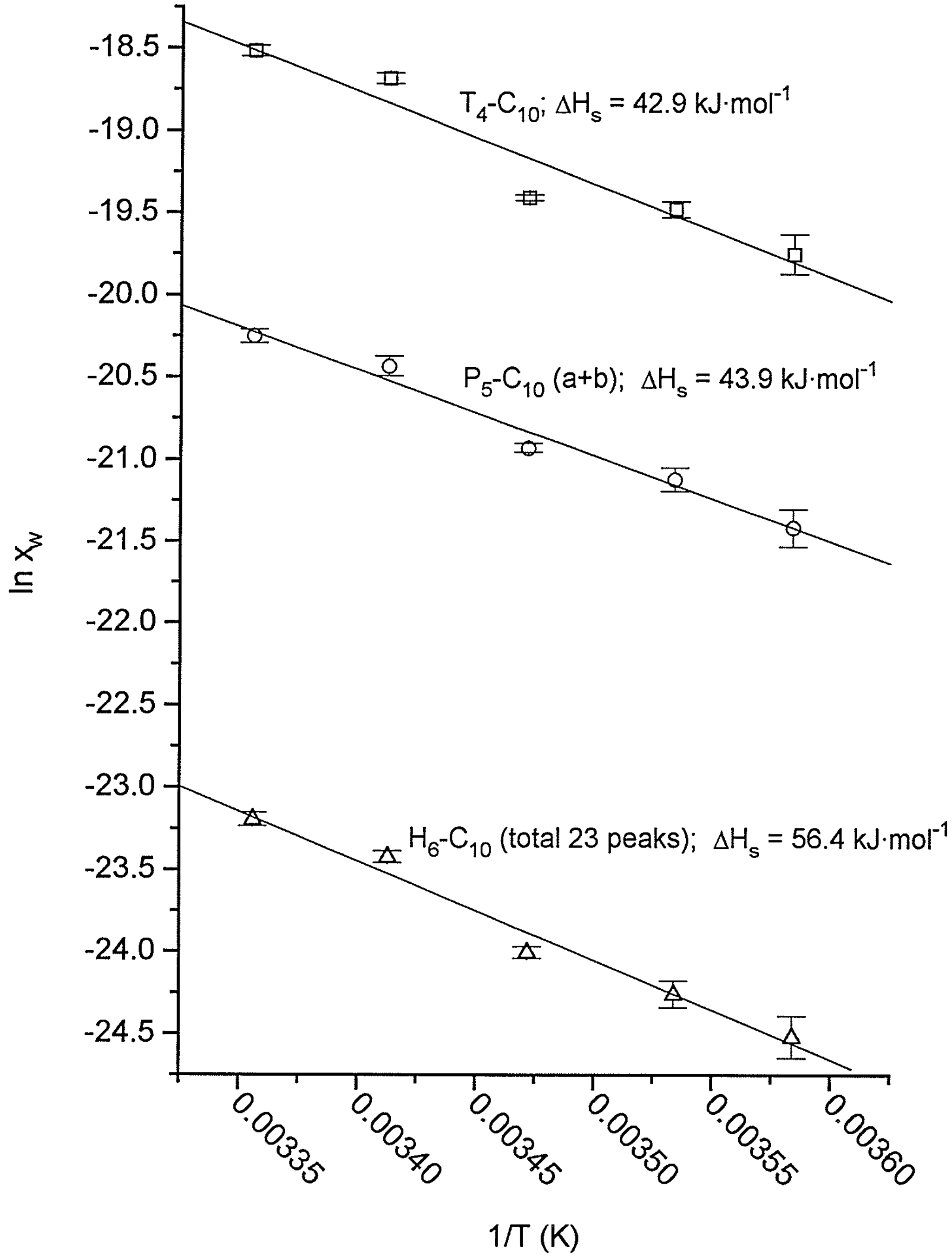

Figure 4.4 van't Hoff plots of polychlorinated decane solubilities over temperatures of 6 to 25°C

Mole fractions of individual congeners in the polychlorinated decane mixture were quantified using the data of Table 1.4 of Chapter 1. Much of the organic phase of the synthesized polychlorinated decane mixture was dominated by starting material (1,9-decadiene) and 1,2-dichlorodecene. Table 4.2 summarizes the mole fractions of individual compounds in the polychlorinated decane mixture and in the $D_2C_{10}$ + polychlorinated decane mixtures. The mole fractions of the $D_2C_{10}$ ranged from 0.0065 to 1 among the the 7 generator columns used to assess apparent solubility behavior of this compound relative to its true solubility. The range of $D_2C_{10}$ mole fractions bracketed the mole fractions observed for the $T_4C_{10}$ (0.065) and $P_5C_{10}$ congeners (0.013 - 0.015) in the synthesized mixture.

Figure 4.5 demonstrates the solubility behavior of the $D_2C_{10}$ added to the polychlorinated decane mixture over various mole fractions. It is clear that introduction of the solute to water as an organic mixture resulted in a co-solute effect on the apparent solubility of $D_2C_{10}$. Apparent solubilities of the reference compound were depressed by a factor of 46 relative to the true solubility at 0.0065 mole fraction. Apparent solubilities decreased in a linear manner with decreasing mole fraction as predicted from Equations 14, 15 and 16. The linear regression of apparent solubility *vs* mole fraction was highly significant (slope < 0; ANOVA; $p < 0.01$) yielding a correlation coefficient of 0.98. However, the linear regression tended to overpredict true solubilities for $D_2C_{10}$ for mixtures in which the chemical was present at very low mole fractions. This indicated some degree of non-ideality of the organic mixture arising from differences in intermolecular interactions between $D_2C_{10}$ and the dominant 1,9-decadiene or 1,2-dichlorodecene components of the mixture.

**Table 4.2** Mole Fractions of $D_2C_{10}$ and Polychlorinated Decane Components Used to Assess Apparent Solubility Behavior of the Reference Compound

| | Mole Fraction ($x_{org(mix)}$) x $10^{-2\dagger}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Trial 1,2 | Trial 5 | Trial 6 | Trial 7 | Trial 8 | Trial 9 | Trial 10 | Trial 3,4 |
| 1,9-decadiene$^{\ddagger}$ | 73.6 | 72.8 | 69.6 | 64.9 | 58.7 | 30.0 | 14.2 | 0 |
| 1,2-dichlorodecene | 12.2 | 12.1 | 11.6 | 10.8 | 9.75 | 4.98 | 2.37 | 0 |
| $T_4C_{10}$ | 6.51 | 6.44 | 6.16 | 5.74 | 5.20 | 2.65 | 1.26 | 0 |
| $P_5C_{10}$ a | 1.36 | 1.35 | 1.29 | 1.20 | 1.09 | 0.56 | 0.26 | 0 |
| $P_5C_{10}$ b | 1.50 | 1.48 | 1.42 | 1.32 | 1.20 | 0.61 | 0.29 | 0 |
| $P_5C_{10}$ c | 1.39 | 1.37 | 1.31 | 1.22 | 1.11 | 0.57 | 0.27 | 0 |
| $P_5C_{10}$ d | 1.36 | 1.35 | 1.29 | 1.20 | 1.09 | 0.56 | 0.26 | 0 |
| $H_6C_{10}$ (average) | 0.085 | 0.084 | 0.081 | 0.075 | 0.068 | 0.035 | 0.017 | 0 |
| $D_2C_{10}$ | 0 | 0.654 | 5.45 | 11.9 | 20.2 | 59.3 | 80.6 | 100 |

Note: $^{\dagger}$Mole Fraction of compound in organic mixture calculated from data of Table 1.4 and dilution with $D_2C_{10}$

$^{\ddagger}$Concentration of decadiene determined by forcing a mass balance, i.e. 100% - (chlorinated olefin + $Cl_4$ + $Cl_5$ + $Cl_6$)

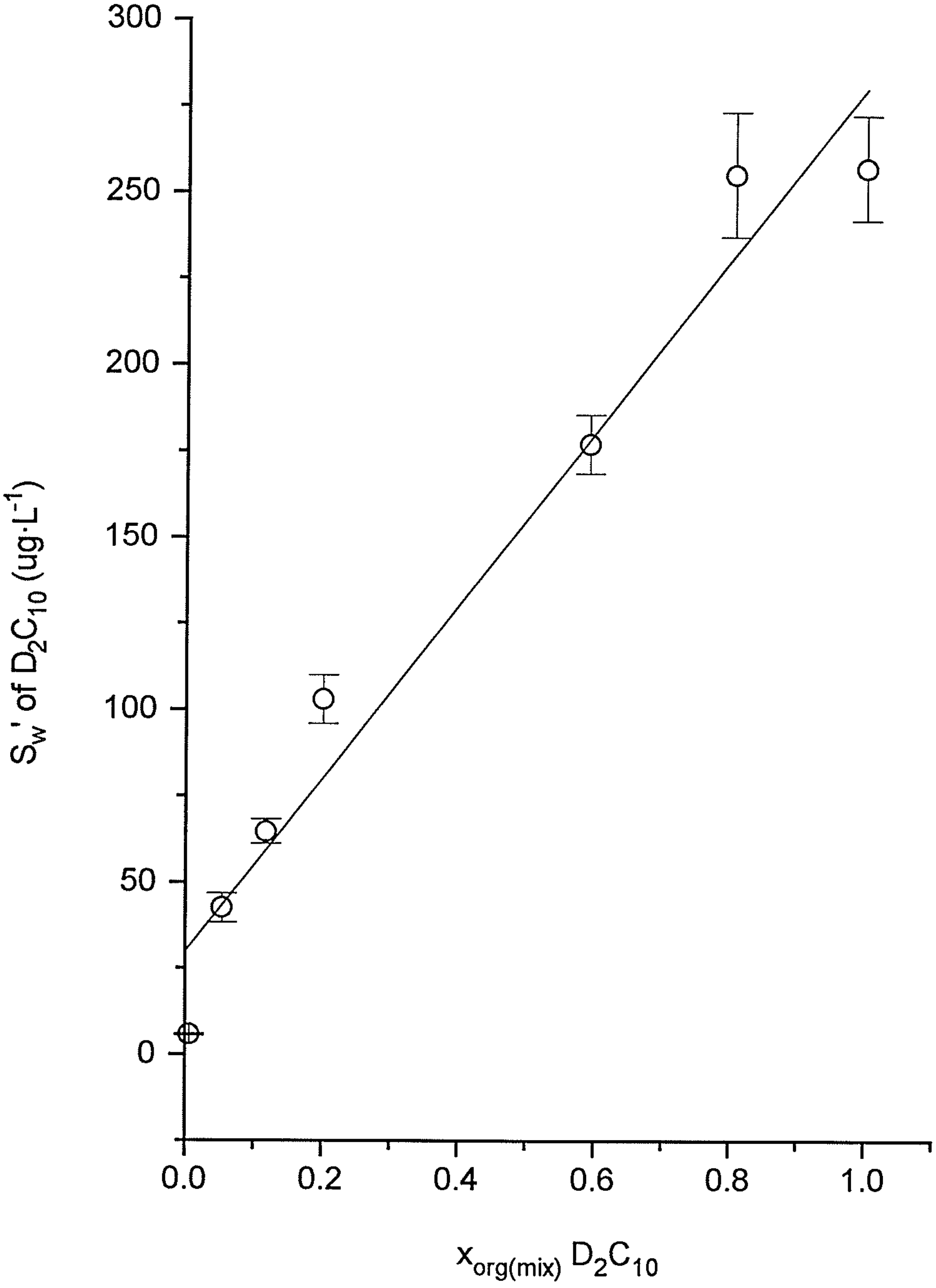

Figure 4.5. Apparent solubility behaviour of $D_2$-$C_{10}$ added to the polychlorinated decane mixture

Since the true solubility of $D_2C_{10}$ has been previously determined, the ratio of $S_w'/S_w$ and mole fraction were used to calculate the activity coeffcient of D2C10 in the organic phase for each generator column experiment using Equation 15. The results are summarized in Figure 4.6 which demonstrates a log-linear relationship between activity coefficient of the compound in the organic phase with mole fraction, yielding a correlation coefficient of 0.94. Activity coefficients for the reference compound can then be calculated for any mole fraction using the following empirical relationship:

$$\gamma_{org} = 10^{[0.450-0.492 \cdot x(org)]} \qquad (17)$$

Based on the above equation, an infinitely dilute activity coefficient, i.e where $x_{org}$ approaches 0, of 2.82 was calculated for $D_2C_{10}$ when present under dilute conditions in the polychlorinated decane mixture. Combining Equations 15 and 17 allows the correction of apparent solubility to true solubility for $D_2C_{10}$ when present at any mole fraction within the polychlorinated decane organic mixture, such that:

$$S_w = \frac{S'_w}{x_{org} \cdot 10^{[0.450-0.492 \cdot x(org)]}} \qquad (18)$$

Table 4.3 summarizes the observed and predicted apparent solubility of $D_2C_{10}$ in addition to the estimated true solubility of this congener from Equation 18. The predicted true solubility of $D_2C_{10}$ estimated from Equation 18 was found to be consistent, yielding a mean $S_w$ of 256 ± 17 $\mu g \cdot L^{-1}$ when combining all data from experiments varying in organic mixture compositions. This value is within the experimental error observed for the $S_w$ of $D_2C_{10}$ determined using the generator column technique with the pure compound at 257 ±15 $\mu g \cdot L^{-1}$.

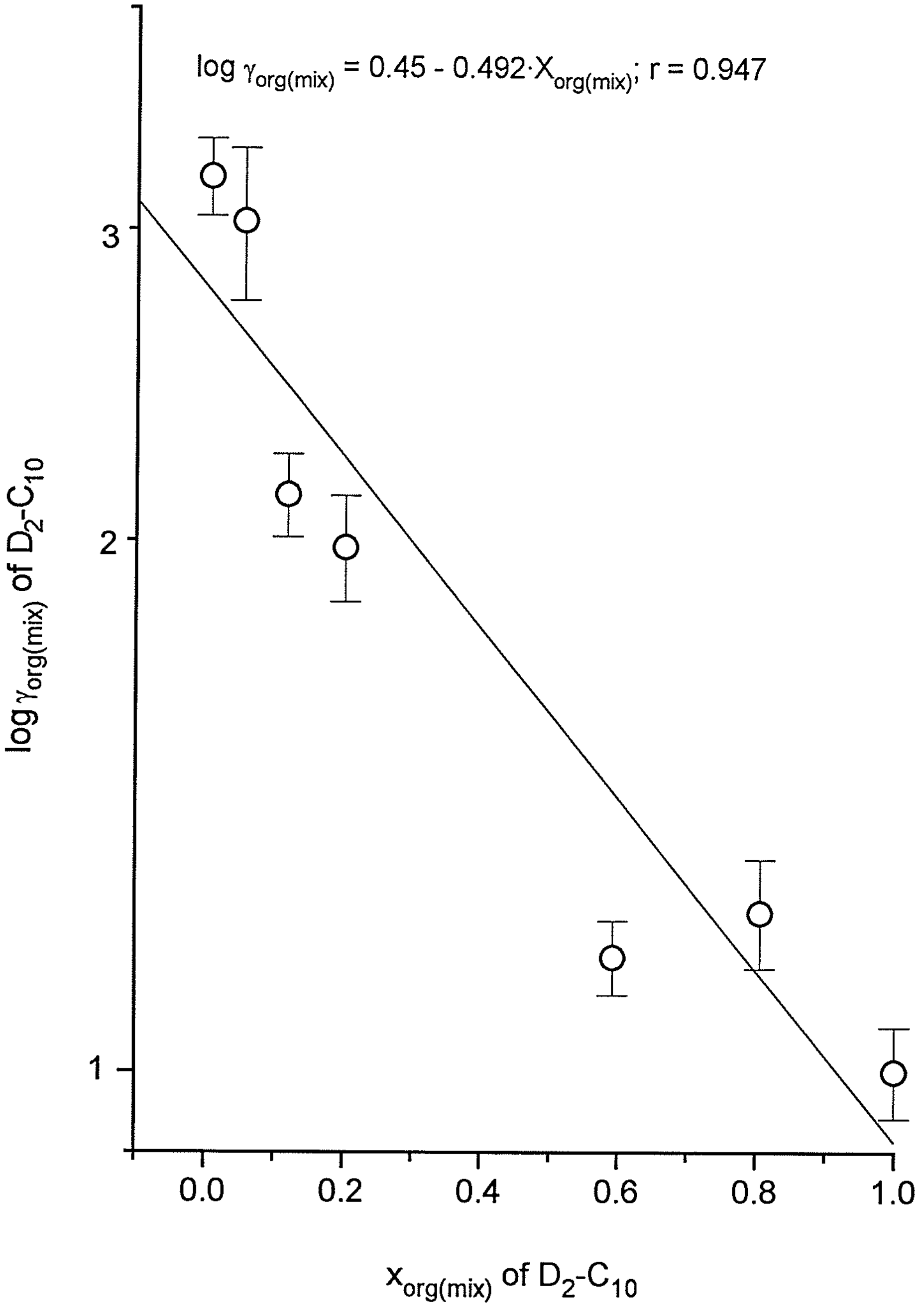

Figure 4.6. Relationship between $\gamma_{org(mix)}$ and $X_{org(mix)}$ for $D_2$-$C_{10}$ in the polychlorinated decane mixture.

**Table 4.3** Observed and Predicted $\gamma_{org(mix)}$, Apparent Solubilities and Predicted True Solubilities of $D_2C_{10}$ in the Polychlorinated Decane Mixtures

| $x_{org(mix)}$ of $D_2C_{10}$ | $S_w'$ Observed ($\mu g \cdot L^{-1}$) | SE | $S_w'$ Predicted[†] ($\mu g \cdot L^{-1}$) | $S_{w(pure)}$ Predicted[‡] ($\mu g \cdot L^{-1}$) | % Error[b] |
|---|---|---|---|---|---|
| 0.00 | | | | | |
| 0.0065 | 5.63 | 0.28 | 4.7 | 307 | 19.6 |
| 0.055 | 42.5 | 8.8 | 37.1 | 293 | 14.3 |
| 0.119 | 64.6 | 4.2 | 75.1 | 221 | 14.0 |
| 0.202 | 102.8 | 3.5 | 116.4 | 227 | 11.7 |
| 0.593 | 176.9 | 7.1 | 219.6 | 207 | 19.5 |
| 0.806 | 255.1 | 8.6 | 234.6 | 280 | 8.7 |
| 1.000 | 257.1 | 18 | 233.7 | | |
| | | | Average: | 256.0 | 14.6 |
| | | | SE: | 17 | |

Note: [†] Predicted apparent solubility using Equation 15; $\gamma_{org(mix)}$ predicted from Equation 17 and experimental values of $x_{org(mix)}$ and $S_{w(pure)}$
[‡] Predicted true solubility for each solution using Equation 18
[b] Error associated with observed and predicted apparent solubility

As previously mentioned, the $D_2C_{10}$ was chosen as a reference compound for modelling the apparent solubility of other polychlorinated decane congeners. It was assumed that the tetra- and pentachlorodecanes had activity coefficients in the polychlorinated decane mixture similar to that observed for the reference compound. Therefore, true solubilities for the tetra- and pentachlorodecanes were corrected using Equation 18. The predicted organic phase activity coefficients and corrected true solubilities for the $T_4C_{10}$ and $P_5C_{10}$ are presented in Table 4.4. True solubilities were not estimated for the $H_6C_{10}$, because the very low mole fractions of individual hexachloro-isomers present in the polychlorinated decane mixture were outside the range of mole fractions used to calibrate the reference compound (Table 4.2). The predicted true solubilities for the $T_4C_{10}$, and two estimates of $P_5C_{10}$ solubilities (average of a+b congeners and the average of c+d congeners) were well above the observed apparent solubilities. There was also no clear relationship between true solubility and number of chlorines as observed for the apparent solubilities.

## 4.7. Discussion

The precision of the generator column technique for estimating solubilities of chlorinated alkanes was slightly lower than reported for solubility determinations from other studies. Replicates of solubility from the same generator column were satisfactory with CVs ranging from 6.3 to 20.8%. May et al. (1978 a,b) estimated a precision of 3% for the generator column technique when determining solubilities of PAHs. However, their apparatus coupled the extractor column directly to a UV detector. After a specified elution volume, a switching

**Table 4.4** Corrected Solubilities of Tetra- and Pentachlorodecanes

| Cl4 | | | | Cl5 a+b | | | | Cl5 c+d | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_{org(mix)}$[†] | $\gamma_{org(mix)}$[‡] Predicted | $S'_w$ ($\mu g \cdot L^{-1}$) | $S_w$[§] Predicted ($\mu g \cdot L^{-1}$) | $x_{org(mix)}$[†] | $\gamma_{org(mix)}$[‡] Predicted | $S'_w$ ($\mu g \cdot L^{-1}$) | $S_w$[§] Predicted ($\mu g \cdot L^{-1}$) | $x_{org(mix)}$[†] | $\gamma_{org(mix)}$[‡] Predicted | $S'_w$ ($\mu g \cdot L^{-1}$) | $S_w$[§] Predicted ($\mu g \cdot L^{-1}$) |
| 6.51E-02 | 2.62 | 140.9 | 826 | 1.36E-02 | 2.78 | 26.0 | 686 | 1.39E-02 | 2.77 | 26.2 | 680 |
| 6.16E-02 | 2.63 | 139.1 | 859 | 1.29E-02 | 2.78 | 32.1 | 895 | 1.31E-02 | 2.78 | 49.7 | 1364 |
| 5.74E-02 | 2.64 | 123.0 | 811 | 1.20E-02 | 2.78 | 30.9 | 923 | 1.22E-02 | 2.78 | 45.9 | 1351 |
| 5.20E-02 | 2.66 | 70.6 | 511 | 1.09E-02 | 2.78 | 16.1 | 529 | 1.11E-02 | 2.78 | 26.2 | 850 |
| 2.65E-02 | 2.74 | 32.9 | 454 | 5.56E-03 | 2.80 | 7.0 | 448 | 5.65E-03 | 2.80 | 12.7 | 800 |
| 1.26E-02 | 2.78 | 19.2 | 547 | 2.64E-03 | 2.81 | 4.3 | 583 | 2.68E-03 | 2.81 | 7.0 | 922 |
| | | Average: | 668.0 | | | Average: | 677.5 | | | Average: | 994.5 |
| | | SE: | 74.7 | | | SE: | 79.9 | | | SE: | 119.2 |
| | | CV: | 22.1 | | | CV | 28.9 | | | CV | 29.4 |

Note: [†] Calculated from data of Table 1.4 (Chapter 1.0) and consideration of dilution by $D_2C_{10}$

[‡] Calculated from Equation 17 (assuming $\gamma_{org(mix)}$ of $D_2C_{10} = \gamma_{org(mix)}$ of chlorinated alkane congener

[§] Predicted true solubility for each solution using Equation 18 with similar assumptions as above valve allowed the extraction column to be eluted directly to the detector resulting in minimal sample handling, few adsorptive losses and quantitative detection of the extracted sample. In contrast, the chlorinated alkanes, which could not be detected by UV spectrophotometry, required substantially greater sample work up procedures prior to GC analysis. Unrecoverable solute losses to the SepPak matrix, volatile losses during nitrogen blow down and the injection of only 1% of extracted solute have led to a greater propagation of errors in the current work. Other studies have also reported CV's of the order of 20% for solubility determinations using the generator column technique when additional sample handling of the extraction column was required (Doucette and Andren 1988; Dickhut et al. 1986; Kishi and Hashimoto 1989).

The higher generator column to generator column variability (CVs from 24.4 to 45.2%) observed for the synthesized mixtures may indicate a lower precision of measuring apparent solubilities compared to the measurement of true solubilities using this technique. In this case, additional error associated with changing mixture characteristics in the organic phase, as the more soluble compounds become depleted during column elution, or during the sorption of components onto the glass beads may arise. The apparent solubility will directly reflect any changes in the mole fractions of individual components in the organic phase. Therefore, the higher apparent solubilities observed in Generator Column #2 in the polychlorinated undecane study may be attributed to enhanced losses of either the undecadiene or 1,2-dichloroundecene impurities from the organic phase during the preparation of this column.

Among the chemicals studied or otherwise present in the mixture, $D_2C_{10}$, the dichlorinated olefins and diene starting materials were all liquids at room temperature. The dichlorodecane has a reported melting point of 15.6°C (Aldrich 1995). Chlorinated paraffins tend to solidify with increased chlorination and increased carbon chain length (Environment Canada 1993). The 1,12-dichlorododecane a solid at room temperature with a melting point of 27 to 28°C. In addition, visual inspection of a small sample (<1 mg) of isolated $C_{10}H_{18}Cl_4$ (described in Chapter 1) indicates that this substance is solid at room temperature. It is therefore assumed that the tetra-, penta- and hexachloro congeners of the $C_{10}$ to $C_{12}$ carbon chain lengths all exist as solids in their purified states.

The observation of a co-solute effect indicates that the integrity of the organic mixture was maintained after sorption onto the glass beads of the generator column. Banerjee (1984) found that solids added together in water in shake flask type studies, exhibited individual solubilities independent of mixture effects. In contrast, solids added to the water by first dissolving into an organic liquid were appropriately modelled according to Equation 15 after correction of the solid solubilities to the subcooled-liquid state. Therefore, the apparent solubilities and subsequent corrected solubilities derived for the compounds of study correspond to solubilities for the subcooled-liquid state. The only exception is the dichlorododecane which was measured as a pure compound and added to the glass beads as a solid. However, because of the low melting point for this compound, the calculated subcooled solubility *vs* solid solubility are essentially identical within experimental error (calculated in Chapter 3).

Unfortunately, purified chlorinated alkane congeners are not available for determination of absolute solubilities. The polychlorinated decane mixture represents a simple mixture much less susceptible to cosolute effects compared to technical chlorinated paraffin mixtures which contain large numbers of isomers (of the order of 100's to 1000's of compounds). However, the individual isomers of the synthesized polychlorinated alkane mixtures characterized in this study reflect only a small percentage of the total mixture which is dominated by unreacted diene starting material and the dichloro-olefin. Based on the percent composition of each component, calculated $x_{org}$ for the polychlorinated decane congeners of study range from $8.5 \times 10^{-4}$ for $H_6C_{10}$ to 0.065 for $T_4C_{10}$ suggesting the potential for considerable error (1100 - 15 fold, respectively, based on equation 16) in the quantification of solubilities using this mixture. The range of mole fractions for $D_2C_{10}$ in the $D_2C_{10}$ + polychlorinated decane mixtures was chosen to bracket the $x_{org(mix)}$ observed for the $T_4C_{10}$ and $P_5C_{10}$ compounds.

The diene starting materials present as the dominant component in each of the synthesized alkane mixtures were expected to have a substantially higher solubility relative to the parent *n*-alkanes (McAuliffe 1966; Mackay and Shiu 1981). The reported solubility of lower carbon chain length 1,6-heptadiene was of the order of 44 mg/L (MacAuliffe 1966) and is expected to be lower for the higher carbon chain length ($C_{10}$, $C_{11}$ and $C_{12}$) dienes employed in this study. It is, therefore, unlikely that these compounds will contribute to a cosolvent effect in the water phase. Based on the trends observed for dichlorodecane and dichlorododecane solubilities relative to the parent alkanes, however, the dichloro-olefins may also exhibit enhanced solubilites over the starting materials. No solubility estimates were available for dichlorodecene, dichloroundecene or dichlorododecene present in the mixtures. Based on the observed depression in apparent solubilities of $D_2C_{10}$, it is apparent that a cosolute effect was occurring as opposed to any cosolvent interactions.

Banerjee (1984) determined apparent solubilities using shake flask type systems of liquid hydrophobic compounds mono-, di- and trichlorobenzenes and water. The results were compared to solubilities derived for pure compounds and the observed mixture effect modelled according to Equation 15. In all cases the mixture effect led to a depression in the apparent solubility. Several other observations of cosolute effects on apparent solubilities have been observed in the literature. Octanol was found to depress solubilities of chlorobenzene and PCBs in water (Resendes et al. 1992; Li et al. 1992; Miller et al. 1985). Eganhouse and Calder (1976) observed mutual solubility reductions when combinations of biphenyl and phenanthrene, biphenyl and 2-methyl naphthalene and 2-methylnaphthalene and phenanthrene were added together in the organic phase. Similarly, ethylbenzene and benzene were found to reduce the observed solubility of *n*-propyl benzene and PCBs (Tewari et al. 1982; Li et al. 1992).

Banerjee (1984) concluded that mixtures of hydrophobic compounds of similar structure can be assumed to have the properties: $\gamma_{w(pure)} \approx \gamma_{w(mix)}$ , $\gamma_{org(mix)} \approx \gamma_{org(pure)} \approx 1$ and that the solubility depression ($S_w'/S_w$) is linearly related and proportional to $x_{org(mix)}$ (Equation 16).

This was not observed in the apparent solubility behavior of the $D_2C_{10}$ which had an infinite dilute $\gamma_{org(mix)}$ of 2.82 in the organic mixture. The $\gamma_{org(mix)}$ quantifies the degree of non-ideality of intermolecular interactions between the solute and other components within the mixture. Therefore the maximum error in estimating the true solubility of $D_2C_{10}$ from the apparent solubility using Equation 16 as opposed to Equation 15 would be a factor of 3. Comparing the $\gamma_{org(mix)}$ of 2.82 to the $\gamma_{w(pure)}$ calculated at $4.6 \times 10^7$, it is also evident that the apparent solubility behavior is still directly related to the hydrophobicity of the solute when corrected for its mole fraction contribution. The validity of the assumption that $\gamma_{org(mix)}$ for $D_2C_{10} = \gamma_{org(mix)}$ for $T_4C_{10}$ and $P_5C_{10}$ cannot be directly tested due to the non-availability of pure tetra- or pentachlorodecane compounds. Based on the corrected solubility results, both the $T_4C_{10}$- and $P_5C_{10}$ compounds appear to exhibit a greater polarity than the $D_2C_{10}$ with corrected solubilities ranging from 2.6 to 3.8 times that of the reference compound. As a result of the high concentration of dichlorodecene in the organic mixture, the total polarity of the organic mix is expected to be higher than for the pure $D_2C_{10}$. The $\gamma_{org(mix)}$ may be slightly overestimated for the $T_4C_{10}$ and $P_5C_{10}$ compounds resulting in underestimates in corrected solubilities. As described above, the degree of this underestimate should not exceed a factor of 3.

## 4.8. Subcooled-Liquid Solubilities Calculated From P and H Data

The subcooled-liquid vapor pressures determined in Chapter 2 and Henry's law constants from Chapter 3 were utilized to estimate the solubilities of the chlorinated alkanes. As defined in Chapter 3, H can be directly related to vapor pressure and solubility (for sparingly soluble compounds) according to:

$$H = \gamma_{w(sub)} \cdot V_w \cdot P_{(sub)} = \frac{P_{(sub)}}{S_{w(sub)}} \quad (\mathrm{Pa \cdot m^3 \cdot mol^{-1}}) \quad (19)$$

Table 4.5 summarizes the calculated solubilities for the polychlorinated decane, undecane and dodecane congeners for which H data were available. In addition, the predicted $S_w$ from the apparent solubilities, determined by the generator column technique, for the polychlorinated decane congeners are included for comparision. The estimated solubilities based on the $P_{(sub)}/H$ calculation exhibited high CVs (26.8 to 118.8%) due to the variability associated with individual H measurements (Chapter 3) and sensitivity of the calculation technique to the magnitude of H. Both the $P_{(sub)}/H$ calculation and predicted $S_w$, from $S_w'$ data, yielded highly similar results for the $T_4C_{10}$ solubility, with mean solubility estimates for the two methods being within 6% of each other. Estimated true solubilities for the pentachlorodecanes were different between the two methods, but still yielded values within a factor of 1.5. This error margin is below the estimated maximum error of 2.82. As previously predicted, the error in solubility prediction from the $S_w'$ data led to an underestimate of the true pentachlorodecane solubilities, indicating that $\gamma_{org(mix)}$ for these two compounds was lower than predicted by Equation 17. It is also possible that errors in determining the mole fractions of the individual pentachlorodecane congeners in the organic mixture could have contributed to error in the corrected solubilities.

**Table 4.5** Solubilities of Chlorinated Alkanes Determined by Correction of Apparent Solubilities to True Solubilities and by Calculation from $P_{(sub)}/H$ Data

| Chemical | Solubility P/H (ug·$L^{-1}$) | SE | CV | n | Solubility Gen. Col. (ug·$L^{-1}$) | SE | CV | n |
|---|---|---|---|---|---|---|---|---|
| $D_2C_{10}$ | N.A. | | | | 257.1$^{\dagger}$ | 15.3 | 18.8 | 10 |
| $T_4C_{10}$ | 630 | 114 | 50.9 | 8 | 668 | 75 | 22.1 | 6 |
| $P_5C_{10}$ (a+b) | 449 | 100 | 66.5 | 10 | 678 | 80 | 28.9 | 6 |
| $P_5C_{10}$ (c+d) | 657 | 109 | 49.9 | 9 | 995 | 119 | 29.4 | 6 |
| $H_6C_{10}$ (a) | N.A. | | | | N.A. | | | |
| $T_4C_{11}$ | 575 | 93 | 40.3 | 5 | N.A. | | | |
| $P_5C_{11}$ (a+b) | 546 | 106 | 48.5 | 5 | N.A. | | | |
| $P_5C_{11}$ (c+d+e) | 962 | 300 | 78.0 | 5 | N.A. | | | |
| $H_6C_{11}$ (a) | N.A. | | | | N.A. | | | |
| $D_2C_{12}$ | N.A. | | | | 22.4$^{\dagger}$ | 0.9 | 9.2 | 5 |
| $^{14}$C-Polychlorinated Dodecane | 36.7 | 6.0 | 26.8 | 17 | N.A. | | | |

Note: $^{\dagger}$ Solubility determined using pure compound.

Table A.6 of the Appendix and Figure 4.7 summarize the statistical relationship between the solubilities of the tetra- and pentachlorodecanes generated from the two techniques. Two-way ANOVA indicates non-significant differences in solubilities between the $T_4C_{10}$ and $P_5C_{10}$ compounds of study. However, there were significant differences in the solubility estimates determined by the two techniques. Closer examination of the data using Tukey's HSD test, indicates that no significant differences in solubilities estimated for a given compound between the two techniques occurred. Only the $P_5C_{10}$ (a+b) congeners determined from the $P_{(sub)}/H$ calculation differed significantly from the $P_5C_{10}$ (c+d) solubility estimated using $S_w'$ data. Since there are fewer theoretical assumptions associated with the $P_{(sub)}/H$ method of determining solubilities than for the predicted values, greater confidence is placed in the values reported for this data set. As a result of the close correspondence in estimated solubilities for the two techniques, the aqueous solubilities presented in this study are of the correct order of magnitude and very likely approach the true solubility values.

True solubilities were not calculated from the apparent solubility data for the polychlorinated undecanes and dodecanes using the empirical relationships calibrated for $D_2C_{10}$ in the polychlorinated decane organic mixture. Utilization of Equation 18 for polychlorinated undecanes and dodecanes would have required the additional assumption that the activity coefficients of $D_2C_{10}$ in the polychlorinated undecane and dodecane mixtures remained similar to those found in polychlorinated decane mixture. Currently, there is evidence available to verify this latter assumption.

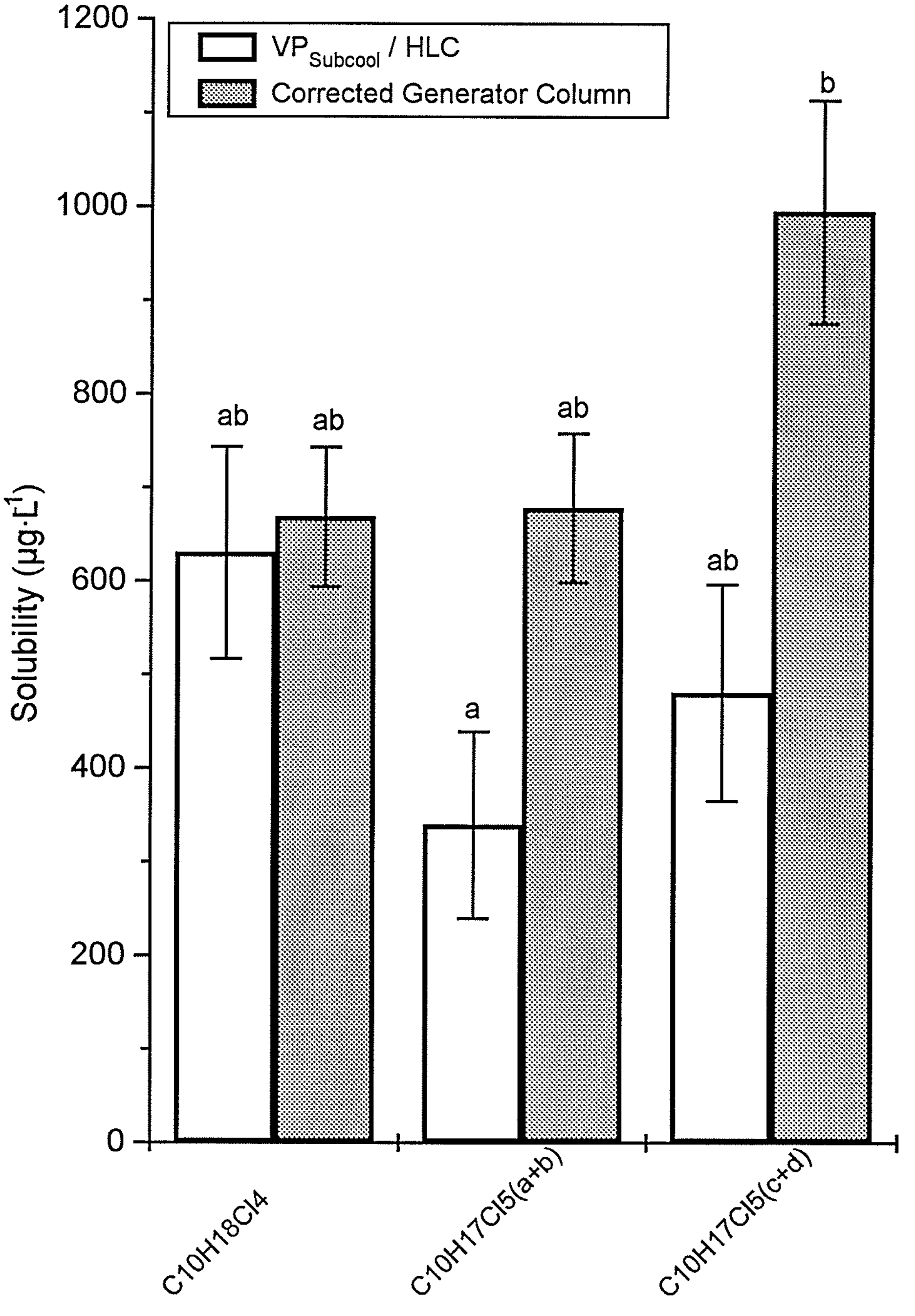

Figure 4.7. Solubilities of chlorinated alkanes determined from two independent techniques. Different letters above error bars indicate signifcant differences $p < 0.05$; Tukeys HSD)

There are few reported solubilities of chlorinated alkane compounds with carbon chain lengths > $C_{10}$ to compare with the results obtained in this study. Madeley and Gillings (1983 a,b) used a modified slow-stirring technique to determine solubilities of radiolabeled chlorinated undecane (59% Cl wt. ~ $C_{11}H_{18}Cl_6$), pentadecane (51% Cl wt. ~ $C_{15}H_{26}Cl_6$) and pentacosane (43% ~$C_{25}H_{(44\text{-}45)}Cl_{(8\text{-}7)}$ and 70 % Cl wt. $C_{25}H_{30}Cl_{22}$) after equilibrating chemical-water mixtures over a 6 month period. The solubilities determined by isolating the parent compound by TLC at 19°C were 120 to 150, 5, <5 and <5 $\mu g \cdot L^{-1}$ for the four compounds, respectively. However, the solubilities determined by Madeley and Gillings represent apparent solubilities since the synthetic method used to produce the $^{14}C$-compounds (free radical chlorine substitution) would have generated numerous isomers. Despite a purification step by a 1 m GLC preparative column and selective analysis by TLC, it is unlikely that the analytical techniques could have resolved individual isomers from the synthesized organic mixture. High resolution GC-ECD characterization of the $^{14}C$-hexachlorododecane (described in Chapter 1), revealed large numbers of isomers which could not be resolved using 30-60 m capillary columns (Chapter 1). Therefore, the solubilities reported by Madeley and Gillings (1983) are likely to have been influenced by cosolute effects as observed in this study and cannot be directly compared with the results obtained here. In addition, the authors noted degradation of the compound in experimental systems over time as indicated by discrepancies in water concentration determinations between parent compound analysis and concentrations based on total activity. One other solubility estimate for a tetrachlorodecane was reported at 1.26 mg/L based on a calculation from a $K_{OW}$ *vs.* $S_w$ correlation (Environment Canada 1993b). Considering the large range in reported $K_{OW}$s (log $K_{OW}$s ranging 5.06 - 8.12) for chlorinated paraffins, the estimated solubility is quite similar to that determined in this study.

### 4.9. Trends in Solubilities of Chlorinated Alkanes Relative to Other Chlorinated Hydrocarbons

The trends observed for solubilities of the chlorinated alkanes indicate clear increases in subcooled-liquid solubilities with increasing chlorination. It is notable that both the $D_2C_{10}$ and $D_2C_{12}$ solubilities, which were determined using the pure compound, were substantially greater (by factors of 5 to 6 on a mass basis) than the solubilities cited for the normal parent alkanes. Therefore the trend of increasing solubility with increasing degree of chlorination is not simply an artifact of the solubility correction procedure used for the higher chlorinated congeners. Figure 4.8 summarizes the increases in solubility with increasing degree of chlorination for the *n*-alkanes and polychlorinated decanes, undecanes and dodecanes. The parent *n*-alkane solubilities were obtained from McAuliffe (1966) and Sutton and Calder (1974). Mackay and Shiu (1981) cautioned the interpretation of these data since they were not derived using the preferred generator column method. The authors also suggested that errors in the *n*-alkane solubility determinations for the longer carbon chain lengths were biased towards overestimates due to potential colloidal dispersions in saturated solutions. The solubilities of the $T_4C_{10}$ and $P_5C_{10}$ are averages of data derived from both the prediction based on the apparent solubility data and $P_{(sub)}/H$ calculation techniques.

The increases in solubility with increasing degree of chlorination are evident for each carbon chain length. The effect of adding chlorines above the tetrachlorinated congener is less clear due to the variability in solubility data for the two sets of pentachloro-compounds of the $C_{10}$ and $C_{11}$ carbon chain lengths. This indicates that the chlorine substitution pattern greatly affects physical properties of chlorinated alkanes as has been observed for chlorinated aromatics (Burkhard et al. 1985). Chlorinated alkanes may be even more sensitive to the chlorine substitution patterns than 'rigid' chlorinated aromatics because of their greater pontential flexibility for molecular folding in polar solvents (Kan and Tomson 1996). Therefore, solubilities for chlorinated decanes may encompass a much wider range than reported for the congeners characterized here. The hexachlorododecane solubility, derived from the $P_{(sub)}/H$ data on the $^{14}C$-polychlorinated dodecane, is still above the solubilities observed for the dichlorododecane and parent *n*-alkane.

The trends observed for increasing solubility with increasing chlorination are in contrast to the trends observed for a number of other chemical classes. Several investigators have reported inverse correlations between solubility and molecular weight, molecular volume or total surface area for chlorinated aromatics and non-chlorinated aliphatics (Mackay and Shiu 1981; Mackay et al. 1980; Miller et al. 1984; Operhuizen et al. 1988; Burkhard et al. 1985; McAuliffe 1966; Hermann 1972). These correlations tend to be chemical class specific, however, and are limited to homologous groups of chemicals (Hermann 1972; McAuliffe 1966; Shiu et al. 1990).

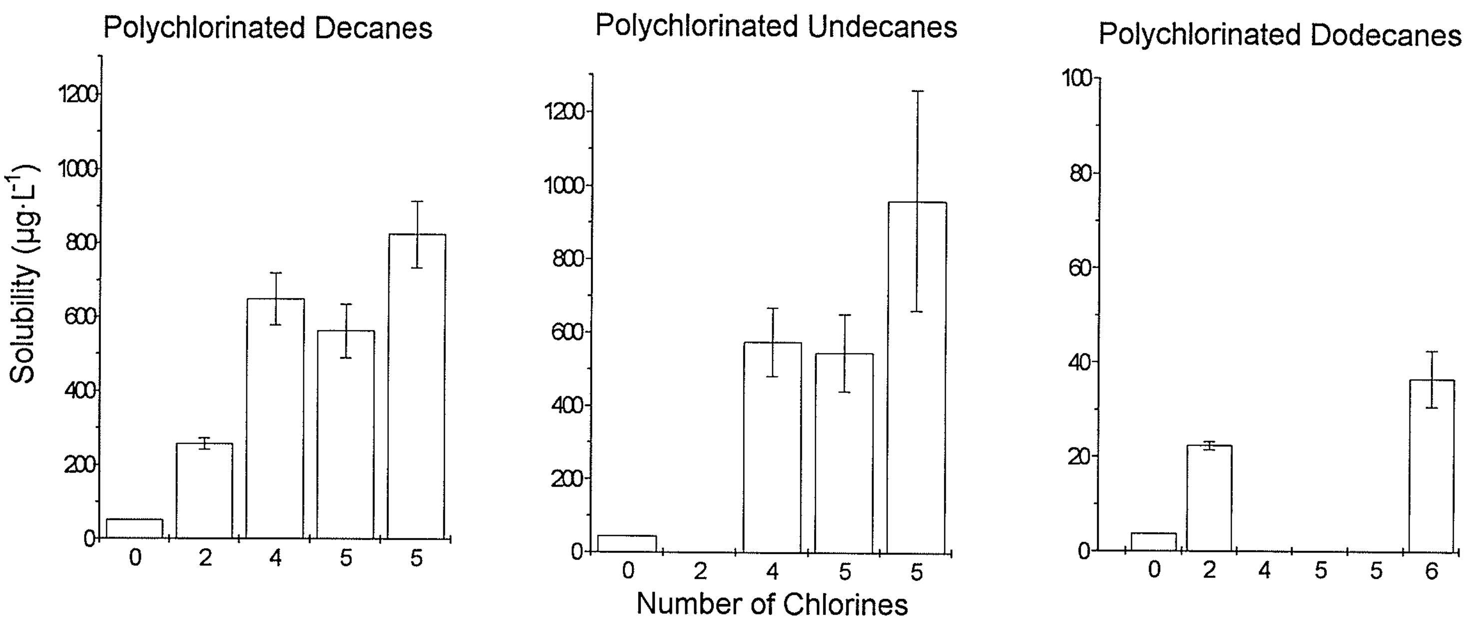

Figure 4.8. Relationship between solubility and chlorine content for chlorinated alkanes (C > 10). Solubilities based on true solubilities calculated from $P_{sub}/H$ data and corrected from $S_w'$ data. Parent alkane solubilities (0 chlorines) taken from McAuliffe 1966 and Sutton and Calder 1974.

For instance, branched alkanes tend to exhibit higher solubilities than *n*-alkanes of the same molecular weight, despite an increase in molar volume (Hermann 1972; Mackay and Shiu 1981). In addition, Kamlet et al. (1987) observed systematic differences between the trends in solubilities observed for aliphatic and aromatic solutes. Specifically, solubilities of aliphatic compounds tend to be more sensitive to increases in polarizability than aromatic compounds (Kamlet et al. 1987). This may be related to a greater flexibility in molecular folding of aliphatics in polar solvents relative to more 'rigid' aromatic compounds (Kan and Tomson 1996; Hermann 1972).

Complete data sets for the interpretation of the effects of degree of chlorination on alkane solubility are only availble for the $C_1$ and $C_2$ carbon chain lengths. Figure 4.9 summarizes the solubilities of chlorinated methanes and chlorinated ethanes obtained from the data of McAuliffe (1966), Mackay and Shiu (1981) and Mackay et al. (1993). Both data sets indicate increases in solubility with the addition of the first chlorine to the carbon backbone. The solubility continues to increase for the chloro-methanes up to a maximum of 2 chlorines and then decreases with the addition of further chlorines. In both cases, the solubility of the chlorinated compound does not approach that of the parent *n*-alkane until at least 4 chlorine atoms are added to the molecule. These trends were not observed for the chlorinated propanes, which exhibit decreases in solubility with the first, second and third chlorines added (Mackay and Shiu 1981).

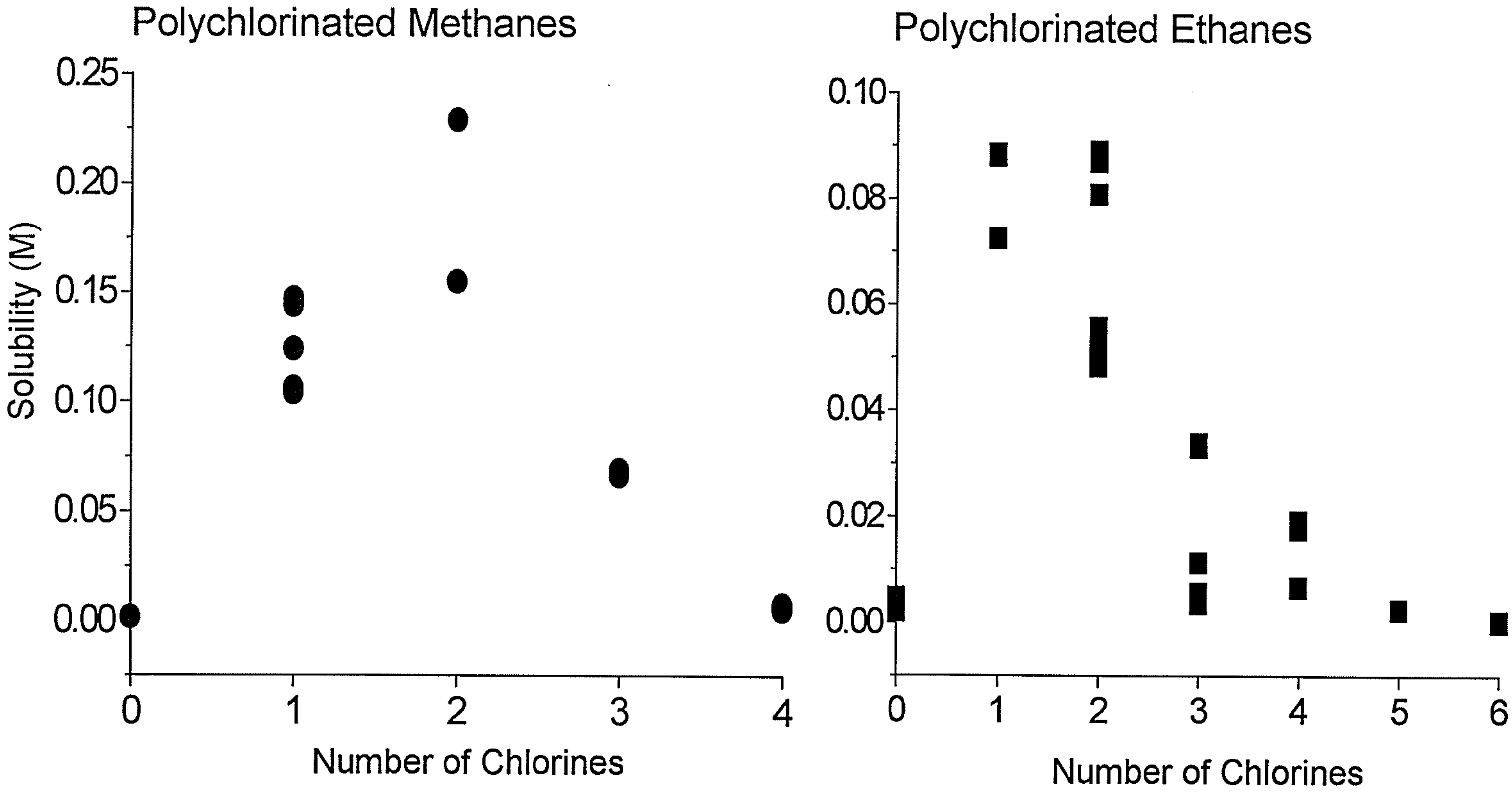

Figure 4.9. Relationship betweensolubility and chlorine content reported for polychlorinatedmethanes and ethanes. Data taken from McAuliffe 1966; Mackay and Shiu 1981 and Mackay et al. 1993

The continued increase in solubility with 4, 5 and possibly 6 chlorines added to the $C_{10}$, $C_{11}$ and $C_{12}$ carbon backbones indicates that there is an interaction between the effects of degree of chlorination and carbon chain length on solubility. The *n*-alkanes exhibit a time-averaged smooth distribution of electrons throughout their structure which contributes to the non-polar nature of these compounds (Schwarzenbach et al. 1993). Replacing a hydrogen on the *n*-alkane with an electronegative chlorine atom creates a permanent dipole and substantial increase in polarity. The increase in polarity will in turn affect solute:water interactions and ultimately govern the distribution of folded conformations of solute molecules in the water network. One might speculate, that, as the carbon chain length increases, the number of potential folding conformations of the molecule in the water network will increase and this might offset the effects of gains in molecular weight with increased chlorination.

The effects of carbon chain length on solubility are less apparent in this data set due to the lack of availability of dichloroundecane, and $T_4C_{12}$ and $P_5C_{12}$ solubility estimates. With the exception of the pentachloro- congeners, which exhibit the greatest variability, decreases in solubility for $D_2C_{10}$ *vs* $D_2C_{12}$ and for the $T_4C_{10}$ and $T_4C_{11}$ are apparent. The magnitude of solubility decreases from $D_2C_{10}$ to $D_2C_{12}$ (factor of 11.5) are similar to the observed decreases in solubility of *n*-decane to *n*-dodecane (factor of 14). Similarly, the 1.4 fold decrease in solubilities for $T_4C_{10}$ to $T_4C_{11}$ approached the 1.2 fold decrease found for solubility differences between *n*-decane and *n*-undecane.

## 4.10. Conclusions

Subcooled-liquid solubilities were determined for the chlorinated alkanes using a prediction method based on apparent solubility data, determined using the generator column technique, and calculated using the ratio of the $P_{(sub)}/H$, determined from previous experiments. The solubility prediction method involved determination of apparent solubilities of individual compounds added to the generator column as a mixture, and correction of the apparent solubility data to provide the true solubilities using the mole fraction and activity coefficient of the individual solute in the organic phase. Activity coefficients of solutes in the organic mixture were determined using a reference compound ($D_2C_{10}$) and monitoring its apparent solubility behavior relative to its true solubility when added to the synthesized chlorinated alkane mixture over varying concentrations. Results indicated that the chlorinated alkane mixture exhibited a cosolute effect on apparent solubilities of individual components. Corrected solubilities from the generator column technique agreed within a factor of 1.5 of the solubilities derived from $P_{(sub)}/H$ calculations. The solubilities of the chlorinated alkanes exhibited an increasing trend with increasing chlorination in contrast to that observed for chlorinated aromatic compounds. The solubilities continued to increase after 4 chlorines have been added to the carbon backbone, indicating that the solubilities of long chain chlorinated alkanes (carbon chain length > $C_{10}$) behave in a different manner from short chain chlorinated alkanes (carbon chain length < C3).

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# 5. Sorption of Chlorinated Alkanes to Organic Carbon

## 5.1. Introduction

The organic carbon/water partition coefficient ($K_{OC}$) describes the equilibrium distribution of a compound between water and organic carbon. $K_{OC}$ is derived by normalizing the distribution coefficient ($K_P$), which describes solute partitioning between water and a given sample of sediment, soil or dissolved/suspended organic matter, to the fraction of organic carbon ($f_{oc}$) in the solid organic phase. $K_{OC}$ has been correlated to the octanol/water partition coefficient ($K_{OW}$) and inversely correlated to the subcooled-liquid solubility for a number of non-ionic hydrophobic organic compounds (Karickhoff 1981; Chiou et al. 1986; Kenaga 1980). As a physico-chemical property, $K_{OC}$ is an important parameter necessary for the estimation of mobility and bioavailability of compounds in environmental fate models.

Although phases containing organic matter (OM) represent lower unit world volumes than air and water in many environments (Mackay and Paterson 1981), the high fugacity capacities of hydrophobic compounds in these phases make organic matter major sinks for the distribution of hydrophobic chemicals. Settling particles and sediments tend to reduce mobility of hydrophobic organic chemicals (HOC) by scavenging freely dissolved chemical from water, minimizing leaching during runoff events and reducing volatilization from soils and DOC enriched waters. The effect of dissolved organic carbon (DOC) may also act to enhance the environmental mobility of a compound by increasing the residence times of a compound in the water column relative to sediment burial, in addition to causing a net decrease in bioavailability of water column associated chemical (Caron 1989; Landrum et. al. 1992). As a result of the importance of organic carbon as a major sink for HOCs, the magnitude and approach to equilibrium of sorption and desorption processes must be understood to adequately estimate environmental behavior.

## 5.2. Definition of $K_{OC}$

Without reference to the kinetics of the sorption process, the equilibrium distribution coefficient for a compound exposed to a given sample of organic matter and pure water can be described by:

$$K_P = \frac{C_s}{C_w} \qquad (1)$$

where: $K_P$ is the distribution coefficient (L/kg)
$C_s$ is the concentration of solute associated with the solid phase (µg/kg)
$C_w$ is the concentration of solute in the aqueous phase (µg/L)

$K_P$ tends to be specific to the type of solid employed in the sorption study and varies significantly among different types of sediments, soils and various organic matter sources. Several past investigations have found that $K_P$ among different OM sources is linearly related to the fraction of organic carbon in the sample (Karickhoff 1981; Chiou et al. 1983; Kile et al. 1995). Normalization of $K_P$ to the fraction of organic carbon in the OM sample yields the $K_{OC}$:

$$K_{OC} = \frac{K_P}{f_{oc}} \qquad (2)$$

where: $f_{oc}$ is the fraction organic carbon in the organic matter (by wt.)

$K_{OC}$ has been found to be relatively constant for a given solute among a wide variety of organic matter sources and often differs by factors of less than 2 to 6 (Kishi et al. 1990; Kile et al. 1995; Karickhoff 1981; Gschwend and Wu 1985; DiToro et al. 1991). Although Equations 1 and 2 have found wide application in several environmental fate models, both equations entail several assumptions governing the mechanisms of sorption, homogeneity of the sorbant and rapid equilibration periods.

The Freundlich equation has more recently gained greater attention for describing the sorption process, since it is less constrained by mechanistic assumptions and more appropriate towards describing sorption on heterogeneous matrices (Weber et al. 1992). The Freundlich isotherm involves an empirical fit to sorption data derived from equilibrated batch systems in which the solute has been added to the aqueous phase over various concentration ranges. The data are fitted to the equation:

$$C_{OM} = K_F \cdot C_w^{\,n} \qquad (3)$$

where: $C_{OM}$ is the concentration of chemical associated with organic carbon ($\mu g \cdot kg\ OC^{-1}$)
$K_F$ is the Freundlich unit capacity factor (similar to $K_P$)
n is the Freundlich exponent

The Freundlich exponent (n) is a scaling factor which characterizes the degree of nonlinearity within the sorption isotherm. When n=1, Equation 3 becomes identical to Equation 1 and indicates a linear sorption isotherm over the concentration range employed in the experimental study. Over wide concentration ranges, however, n may exhibit values ranging from 0.4 to greater than 1 indicating either the influence of other mechanisms contributing to the sorption process (non partitioning mechanisms) or an interaction between the solute and sorbant or solute and water which changes the character of either the water network or sorbant phases (Williams et al. 1995; Karickhoff and Brown 1978; Weber et al. 1992). The consequence of non-linear isotherm behavior is that the mobility of the compound within the environment becomes dependent on the chemical concentration. Freundlich exponents > 1 have most often been interpreted as a result of changing sorbant character with excess loading of solute (Spurlock et al. 1995; Schwarzenbach et al. 1993). For example, surface coating of the solid phase with solute when present at high concentrations may decrease the polarity of the sorbant and increase the observed distribution coefficient for hydrophobic chemicals.

## 5.3. Mechanisms of Sorption

A large number of observations of sorption behavior of organic compounds have involved linear isotherms in organic carbon enriched sediments and soils (n=1) (O'Connor and Connolly 1980; Chiou et al. 1983; Karickhoff 1981) and nonlinear isotherms, particularly in subsurface soils, in which n<1 (Young and Weber 1995, Weber et al. 1992; McGinley et al. 1993; Ball and Roberts 1991). The frequent observations of both types of behavior have resulted in extended debate regarding the interpretation of mechanisms governing the sorption process. Sorption mechanisms may include adsorption or physical bonding of solutes to surface sites on the sorbant (van der Waals attractions, electrical attractions or complexation), absorption of sorbates into OM components (partitioning driven by hydrophobic exclusion of the chemical from water) or surface reactions (formation of covalent bonds) to OM components (Karickhoff and Brown 1978; Chen and Wu 1995). For non-ionic hydrophobic compounds, both partitioning mechanisms and surface adsorption phenomena have frequently been used to model the sorption process.

Chiou et al. (1983) and Young and Weber (1995) indicated that adsorption of nonionic hydrophobic organic compounds by mineral fractions of soils and sediments would be relatively unimportant under water saturated conditions due to the strong dipole interaction between mineral surfaces and water. In addition, under conditions of dilute solute concentrations, natural organic matter associated with solids is often present at higher concentrations, is generally much larger (and therefore exhibits greater dispersion interactions) and likely contains many more polar groups capable of direct interaction with the mineral surfaces than the chemical of interest. As a result, organic matter will generally out compete HOCs for direct adsorption and partitioning interactions with mineral surfaces (Chiou et al. 1983; Schwarzenbach et al. 1993). Therefore, the chief association of chemical with solids under water saturated conditions is likely associated with OM when organic matter is present at high enough concentrations. Schwarzenbach et al. (1993) suggested that OM dominates the sorption process when OM concentrations exceed 0.2 to 0.4% by weight of particles under conditions of water saturation. Most solids derived from aquatic systems generally contain from 0.1 to 10% OC (Autenrieth and DePinto 1991).

### 5.3.1. Partitioning Mechanisms

The relative consistency of $K_{OC}$ and its correlation to $K_{OW}$ and solubility (Karickhoff 1981; DiToro et al. 1991; Chiou et al. 1986; Kenaga 1980; Chin et al. 1988; Helmstetter and Alden 1994; Lyman et al. 1990) have led to the conclusion that a major mechanism of sorption involves partitioning of HOCs to the solid phase in much the same manner as dissolution of a solute in a solvent:water binary system (Chiou et al. 1983). When this type of mechanism predominates, the equilibrium $K_{OC}$ is predicted to exhibit linear isotherms independent of aqueous concentrations (n=1) and devoid of solute competitive effects. Fluorescence quenching studies strongly indicate that fluorophors associated with humic acids exist in a hydrophobic cage region consistent with the partitioning mechanism (Chen et al. 1994; Engerbretson et al. 1996). Many HOCs exhibit linear sorption isotherms in soils and sediments, provided that their aqueous concentrations are maintained below saturation. At concentrations approaching water saturation, isotherms will exhibit Freundlich exponents < 1 which may be interpreted as either:

i) a limitation in the number of binding sites (non-partition mechanism)
ii) change in activity coefficient of the chemical in the aqueous phase

Karickhoff (1981) indicated that if the equilibrium aqueous phase solute concentration is less than $10^{-5}$ molar or less than 50% of its solubility (which ever is less), then linear isotherms are generally observed for nonionic hydrophobic compounds. Others such as Chiou et al. (1983) and Kile et al. (1995) observed linear isotherms at aqueous solute concentrations up to 60 to 90% of their aqueous saturation. For carbon tetrachloride, linearity in the sorption isotherm was observed at aqueous concentrations up to 600 mg/L ($4x10^{-3}$ M; Kile et al. 1995).

Competition for sorption sites when several solutes have been added to the aqueous phase have been observed for some soil types, particularly subsurface soils, and not observed among others. Competitive effects on sorption for multiple solutes would occur if either the quantity of sorbed compounds approached the solids sorption capacity of the sorbant, or if interactions of the compounds in the fluid phase result in changes in the chemicals aqueous activity coefficient (McGinley et al. 1993; Chapter 4.0). Competitive effects due to the first case indicate site specific reaction sites on the solids (consistent with adsorption), whereas the latter reflects an apparent competitive effect. Most of the evidence for competitive sorption has, as a rule, been limited to polar or ionic compounds which associate with solids via reactions with specific functional groups in addition to the more generalized van der Waals attractions (McGinley et al. 1993). Less evidence exists for competitive sorption among non-ionic hydrophobic compounds. For example, Ozretich et al. (1995) added 37 PCB and PAH compounds to batch solutions near their individual solubilities, and found no competitive sorption effects, yielding $K_{DOC}$ (dissolved organic carbon/water partition coefficient) values which were comparable to those derived from other studies using single compounds. Other investigators reported similar non-competitive sorption effects when solutes were added as mixtures relative to single components added to the aqueous phase (Chiou et al. 1983; Carter and Suffet 1982; Eadie et al. 1990; Suresh et al. 1990).

Further evidence for the dominance of partitioning as a sorptive mechanism for non-polar, non-ionic hydrophobic compounds is drawn from several general and widespread observations (Karickhoff and Morris 1985; Beck et al. 1993; Brusseau and Rao 1989; Pignatello and Xing 1996; Piatt et al. 1996; Mackay and Powers 1987; Young and Weber 1995; Kopinke et al. 1995; Hu et al. 1995):

i) Positive Correlations between $K_P$ and $K_{OW}$
ii) Positive Correlations between $K_P$ and OM content
iii) Negative Correlation between $K_P$ and desorption rate
iv) Decrease in $K_P$ and desorption rates with addition of cosolvent to the aqueous phase
v) Decrease in desorption rates with increasing salinity (salting out effect)
vi) Enthalpy of sorption is small and negative and consistent with temperature dependence of $K_{OW}$ (strong solute-solid interaction would be expected to exhibit a large positive enthalpy)
vii) Isotherm non-linearity increases with increasing polarity of the solute

Despite the general success of $K_{OC}$ in the prediction of $K_P$s, significant differences in $K_{OC}$s among natural OM sources have been attributed to the chemical characteristics of different types of OM. Particularly, dissolved organic carbon/water partition coefficients have been found to be highly variable among different OM sources despite normalization to fraction of organic carbon (Kile et al. 1995; Weber et al. 1992; Eadie et al. 1990; Chiou et al. 1987; Kopinke et al. 1995; Landrum et al. 1984). Kile et al. (1995) also noted small but significant differences in $K_{OC}$s derived from bed sediments *vs* $K_{OC}$s characteristic of soils. In some cases, polarity differences as indicated by C:O, C:H, or C:N ratios have been observed to account for such differences in $K_{OC}$ (Chiou et al. 1987; Weber et al.

1992; Koelmans et al. 1995; Koelmans et al. 1993). Polarity differences are also consistent with the partition mechanism and may be accounted for by assessing the relative activity coefficients of the solute in both water and OM phases as has been attempted by incorporation of the Flory-Higgins theory to describe the sorption process (Chiou et al. 1983).

In addition, conformational changes of OM with solution pH and ionic strength also have been observed to affect $K_{OC}$ (Carter and Suffet 1982; Engebretson et al. 1996). Engerbretson et al. (1996) provided a series of mechanistic explanations to account for changes in the sorption of solutes to humic acids as a function of pH and ionic strength. Under high pH conditions, a greater degree of dissociation of carboxyl and phenolic hydroxyl functional groups leads to mutual repulsion of negatively charged sites causing the molecule to exhibit a stretched conformation. In addition to the polarity increase associated with ionized functional groups, the stretched conformation has a reduced ability to form hydrophobic micro-environments necessary for the absorption/partitioning processes. Similarly, the effect of ionic strength on aggregation of humic acid polymers was related to formation of hydrophobic regions and subsequent partitioning behavior.

### 5.3.2. Adsorption

Some models treat HOC association with OM as Langmuir in nature, and this will be generally true where chemical:OM interactions are not associated with intraparticle diffusion but rather due to sorptive processes involved with a finite number of surface active sites. Examples include ionizable compounds, compounds capable of forming H-bonds directly with mineral surfaces or to OM polar groups, pesticides containing reactive moieties capable of forming covalent bonds with sorbant functional groups, and van der Waals associations with surface active sites exhibiting low tortuosity and a high degree of crystallinity (e.g. diagenically altered OM exhibiting crystallinity; Weber and Huang 1996; Pignatello and Xing 1996). In such examples, true hysteresis effects (sorption/desorption non-singularity) are expected and rate limiting steps in the sorption process are attributed to different chemical reaction kinetics at sites of varying activation energies. The Langmuir isotherm is described by the equation:

$$C_{OM} = \frac{K_{Langmuir} \cdot a \cdot C_w}{1 + K_{Langmuir} \cdot C_w} \qquad (4)$$

where: $K_{Langmuir}$ refers to the affinity of the chemical to the surface
a reflects the maximum number of sorption sites

The major limitation of the Langmuir model is that its characteristic asymptotic shape between dissolved and sorbed chemical concentrations will only be followed when one type of surface active site predominates on the sorbant. Weber et al. (1992) have shown that when multiple surface active sites, consisting of different binding affinities, are available, the shape of the isotherm will approach that of the Freundlich isotherm described in Equation 3. Nonlinearity in the Freundlich equation ($n < 1$) at solute concentrations below aqueous saturation has been interpreted as evidence for adsorption phenomena. For example, the significantly greater uptake of organic compounds by dry and subsaturated soils and increased isotherm nonlinearity have been attributed to mineral adsorption in the absence of competing water (Rutherford and Chiou 1992). In addition, nonlinear isotherms are frequently observed for subsurface soil types of low organic carbon content (Young and Weber 1995, Weber et al. 1992; McGinley et al. 1993; Ball and Roberts 1991).

McGinley et al. (1993) have observed competitive sorption between two non-ionic HOCs in 2 of 4 sub-surface soils. The authors found that competitive sorption was limited to soils which exhibited the most non-linear Freundlich behavior (McGinley et al. 1993; Weber et al. 1992; Young and Weber 1995; Weber and Huang 1996). Further investigation indicated that the highly diagenically altered OM components (mainly shale) exhibited much of the non-linearity. It was speculated that the greater crystallinity of diagenically altered OM fractions, which exhibited lower polarity, increased aromaticity, and extremely slow effective diffusivities relative to other OM components, contributed to adsorption processes dominating the sorptive mechanism. Similar observations were found for sorption of HOCs to polymers which revealed nonlinear, competitive adsorption to glassy polymers, followed by a transition to linear isotherms when sorption experiments were performed on the same polymers above the polymer glass transition temperatures (Young and Weber 1995; Pignatello and Xing 1996). Soils containing less diagenically altered OM fractions were characterized as amorphous having greater effective diffusivities, linear isotherms and non-competitive effects consistent with the partitioning mechanisms. The above observations indicate that mechanisms other than partitioning may predominate the sorptive processes in certain sorbant systems and for such systems, models such as the distributed reactivity model which account for OM quantity, polarity and degree of crystallinity should be employed (Young and Weber 1995; Weber et al. 1992).

### 5.3.3. Solids Concentration Effect

A curious, but highly consistent observation of several sorption studies, including standard batch experiments and *in situ* field measurements, is the solids concentration effect (O'Connor and Connolly 1980; Horzempa and DiToro 1983; Voice et al. 1983; DiToro 1985; Karickhoff and Morris 1985; Servos and Muir 1989). Both adsorption and partitioning mechanisms predict that, in the absence of any particle-particle interaction over varying solids concentrations, the distribution coefficient should be independent of the concentration of sorbent. In contrast, the solids concentration effect is typically characterized by a decrease (two to three orders of magnitude) in the observed $K_P$ value with increasing solids concentration in a log-linear manner (O'Connor and Connolly 1980; DiToro 1985). The solids concentration effect has been observed for soils, sediments and clays all of which exhibit broad trends in the underlying mechanism of sorption (Horzempa and DiToro 1983). Despite the universality of the effect among sorbant types, the slope of $K_P$ *vs* solids concentration for the same compound often changes dramatically among different solid types indicating that the effect is a function of the sorbant and not the solute (O'Connor and Connolly 1980).

Various hypotheses have been devised to account for the solids concentration effect. Wu and Gschwend (1986) indicated that the effect was an artifact of the inability to analytically distinguish between freely dissolved chemical concentrations in the water, and colloidal or third phase associated chemical released during solids/water equilibration. The typical experimental batch system is considered to include three phases: water, suspended sediment and dissolved/colloidal organic material commonly referred to as third phase material. As greater solid concentrations are used in the batch systems a greater extent of third phase material is released into the water which may result in overestimation of freely dissolved water concentrations, if chemical associated with this material is not accounted for. The third phase is not readily separated from water by filtration or centrifugation (Wu and Gschwend 1986; Voice et al. 1983). In some cases, the solids concentration effect was reported to be removed by extensive washing of sediments prior to batch experiments to remove a large fraction of third phase material, utilization of three phase distribution models with dissolved organic carbon content measurements, and analytical methods such as extrapolation of cosolvent-partition coefficients (Wu and Gschwend 1986; Williams et al. 1995; Hegeman et al. 1995). Others, however, found that techniques such as reverse-phase separations, and gas sparging studies which also distinguish between freely dissolved and third phase associated solute, failed to completely eliminate the effect indicating that other processes may be involved (Yin and Hassett 1986; Servos and Muir 1989; Landrum et al. 1984).

Two other hypotheses have been put forward both of which interpret the solids concentration effect as a kinetic phenomena. The most elaborate of the two, first proposed by DiToro (1985) and expanded upon by Mackay and Powers (1988) involved the development of a theory which accounts for changes in desorption kinetics as a function of solids loading. As with multi-box models of sorption, the theory considers two sorption states consisting of labile (reversible) components and resistant components. DiToro hypothesized that additional particle induced desorption of labile sorbed components would occur with particle collisions, whose frequencies are dependent on the solids concentration. The basic premise of the model is that enhanced desorption rates would occur at higher solids concentrations, resulting in a net reduction in the magnitude of the equilibrium distribution coefficient. Although model results were found to fit sorption data sets well, the models employed several fitting parameters and no conclusive evidence for enhanced desorption at elevated particle concentrations were observed.

The second hypothesis suggests the opposite case, in which slower sorption/desorption kinetics are associated with larger solids loadings. In this case, the solids concentration effect is considered an experimental artifact resulting from insufficient sorptive equilibration times at higher solids loadings, resulting in the comparison of $K_P$ estimates which are at various degrees of non-equilibrium among the different solids loadings (Karickhoff and Morris 1985; Servos and Muir 1989; Tye et al. 1996). Karickhoff and Morris (1985) observed increases in solute desorption rates with both increasing chemical hydrophobicity and increased solids concentration. Such results are consistent with the solids concentration effect being more pronounced for highly hydrophobic compounds (O'Connor and Connolly 1980). Tye et al. (1996) and Jepsen et al. (1995) also provided evidence to suggest that the solids concentration was directly related to the size and density of aggregates formed in experimental batch systems. Therefore, additional kinetic rate-limiting steps towards sorptive equilibrium are expected at high solids concentrations due to the requirements of both intraggragate penetration of the chemical and interparticle diffusion.

### 5.3.4. Kinetics of Sorption and Desorption

Many environmental fate models in the past have employed a simplified one-compartment model to describe sorption and desorption kinetics.

$$\frac{\partial C_{OM}}{\partial t} = k_1 \cdot C_w - k_2 \cdot C_{OM} \qquad (5)$$

where: $k_1$ and $k_2$ refer to first-order rate constants for sorption and desorption, respectively ($h^{-1}$)
$C_w$ and $C_{OM}$ refer to the concentration of chemical in water and organic matter phases, respectively

Such models assume first-order rates of sorption and desorption, allowing calculation of an equilibrium distribution coefficient between sediment and water ($K_D$). Environmental fate models often further assume nearly instantaneous equilibrium for sorption in natural environments. Such assumptions were based on the rapid reaction rates for van der Waals interactions in solution of the order of $10^{-6}$ to $10^{-12}$ $s^{-1}$ (Pignatello and Xing 1996). Accumulating evidence from the literature, however, suggests that time to sorptive equilibration for HOCs are much longer than previously estimated (Karickhoff and Morris 1985; Tye et al. 1996).

Much of the sorption data utilizing standard batch experiments and small equilibration periods (1 to 3 days) have been called into question, since the true $K_D$ value may be underestimated by as much as an order of magnitude in these tests (Pignatello and Xing 1996). In addition, sorption/desorption processes fail to fit first-order rate models over long periods, consistently overestimating the amount of chemical desorbed. Observations such as sorption/desorption hysteresis (Corwin and Farmer 1984; DiToro and Horzempa 1982; DiToro 1985; Hu et al. 1995; Harmon and Roberts 1994) and increasing resistance to extraction, biodegradation or decreased bioavailability with increasing sediment-solute contact time (Landrum et al. 1992; Hatzinger and Alexander 1995; Spurlock et al. 1995; Young and Weber 1995; Karickhoff and Morris 1985) have further called into question the application of one-compartment sorption models.

As discussed previously, mechanistic descriptions of the sorption/desorption process have been discouraged by the heterogeneity of particles within soils and sediments. Particles are essentially viewed as aggregates consisting of large parent mineral grains, flocs of clay minerals and discontinuous distributions of adsorbed organic matter (Beck et al. 1993; Schwarzenbach et al. 1993; Pignatello and Xing 1996; Chen and Wu 1995; Phillips and Walling 1995). Such aggregates conceptually have different sub-regions varying in their capacities for binding the solute and varying in their accessibility to intra-aggregate pore waters (Schwarzenbach et al. 1993). For partitioning mechanisms, heterogeneities in effective diffusivities ($D_{eff}$) among different sub-regions within the particle/aggregate are thought to account for the multiple rates observed in long term sorption/desorption experiments. Effective diffusivities are related to the size of the compound, its hydrophobicity, the heterogeneity in composition of the sorbant matrix and the tortuosity and steric hindrance associated with the diffusion path (Wu and Gschwend 1986; Harmon and Roberts 1994; Pedit and Miller 1995).

Brusseau and Rao (1989) hypothesized a bicontinuum model for larger aggregates consisting of a mobile region infiltrated by pore water, where molecular diffusion was equivalent to that observed in bulk water, and an immobile region consisting of micro and dead-end pores, fractured mineral media and organic material characterized as having low $D_{eff}$ values. These less accessible sites not only increase the sorption/desorption equilibration periods but also act as a sink/source component when non-sorptive equilibration conditions prevail. The radial diffusion model developed by Wu and Gschwend (1986) indicates that sorption rates are directly related to particle size, a prediction verified by Tye et al. (1996) and Hatzinger and Alexander (1995). In addition, Tye et al. (1996) observed that lower equilibration periods (less by a factor of 16) were required when sediments were stripped of OC by acid digestion. Such observations further substantiate that the partitioning mechanism involves diffusion of solute within the OM matrix.

Sorption data from long term batch experiments typically exhibit a two, or multiple, stage approach to equilibrium (Karickhoff and Morris 1985; Brusseau and Rao 1989; Koelmans et al. 1993; Pignatello and Xing 1996) with roughly 50% sorption occurring on time scales of minutes to hours, and the remainder occurring over periods of days to months and even years (Brusseau and Rao 1989; Coates and Elzerman 1986; Karickhoff and Morris 1985). As a consequence, multiple compartment models have been developed to more accurately describe the sorption processes. Many studies have suggested that a two-compartment model consisting of an essentially instantaneously equilibrated labile compartment and a rate limited non-labile compartment is sufficient to account for observed desorption kinetics in gas sparging experiments (Karickhoff and Morris 1985; Autenrieth and DePinto 1991; Koelmans et al. 1993). Karickoff and Morris (1985) found that 2 or more non-labile compartments may be necessary to account for the extremely slow desorption of the last 5 to 10% of remaining sorbed chemical. Pignatello and Xing (1996) and Oliver (1985) suggested that there would be a continuum of desorption rates corresponding to increasingly resistant compartments within the aggregate.

Changes in desorption rates, and apparent non-equilibrium kinetics may be explained by bottlenecks in the diffusion process and failure to achieve sorptive equilibrium prior to initiating desorption (Karickhoff and Morris 1985; Harmon and Roberts 1994). OM within micropores and inaccessible positions within the aggregate will have slower $D_{eff}$ values and continue to exhibit intra-aggregate concentration gradients long after accessible sub-units of the particle have achieved steady state with mobile intra-aggregate pore water. Alternatively, when adsorption mechanisms predominate, multiple rates associated with sorption and desorption processes may be attributed to different chemical reaction kinetics to sites of varying activation energies. The mechanism of sorption, partitioning *vs* adsorption, for a particular sorbant can be assessed by determination of both the Freundlich behavior and the kinetics of sorption /desorption processes.

## 5.4. Experimental Determination

Traditional methods for studying sorption processes have involved batch type studies for high organic carbon content soils and sediments (OC > 1% weight) and flow through soil column studies for aquifer and low organic carbon containing organic materials. Both procedures have been found to yield similar results, provided that sufficient sorptive equilibration time is allowed (Harmon and Roberts 1994). In batch type studies, water-OM slurries are equilibrated with the chemical over a specified equilibration period and destructively sampled by measuring chemical concentrations in the water and OM phases. Soil column experiments involve introducing a chemical to a soil packed column, and following its chromatographic elution using water or water/cosolvent mixtures as the mobile phase. Much of the experimental work on sediment water partitioning, which generally involves high organic carbon contents, have utilized batch experiments.

Experimental designs for batch experiments involved determination of $K_P$ for a series of independent systems as described by Equation 1, addition of various quantities of chemical to different batch systems and utilization of the Fruendlich equation as described by Equation 3, or addition of different quantities of sediment among batch systems with utilization of Equation 3. The disadvantages of the latter approach are that the solids concentration effect remains undetected when the Freundlich equation is employed. Upon sampling, the batch systems are generally centrifuged to separate particulate and aqueous phases. Voice et al. (1983) and Gschwend and Wu (1985) indicated, however, that centrifugation and filtration were not sufficient to eliminate third phase material from aqueous phases and, as such, additional techniques are required to distinguish freely dissolved chemical concentrations in water *vs* chemical associated with non-settling colloids or dissolved organic matter. One method employed by Gschwend and Wu (1985) was to pre-wash the organic materials with water to eliminate much of the third phase material prior to commencement of the experiment.

### 5.4.1. Reverse-Phase Separation

The reverse-phase separation technique developed by Landrum et al. (1984) has been utilized in conjunction with batch studies to distinguish freely dissolved from DOM bound chemical (Servos and Muir 1989). At pH greater than 5, humic acids generally exist in a polarized form and are expected to quantitatively pass through a reverse-phase column (Landrum et al. 1984). Most studies have calibrated small commercial $C_{18}$ columns (SepPaks) containing approximately 200 mg of stationary phase packing. The aqueous phase isolated from the batch study is passed through the column at flow rates of approximately 12 mL/min resulting in sorptive losses of freely dissolved chemical to the stationary phase and elution of DOM bound chemical from the cartridge. A flow rate of 12mL/min is utilized, since this rate is found to minimize DOM-stationary phase interactions while ensuring adequate trapping efficiency of hydrophobic chemicals (Landrum et al. 1984; Kosian et al. 1995). The technique is limited to compounds which are sufficiently hydrophobic to maintain quantitative recovery of dissolved phase chemical at the relatively high flow rates employed.

Several studies have validated the assumption of near quantitative passage of DOC through the reverse phase cartridges. Morehead et al. (1986) found that 95% of DOC from four natural water samples eluted from the reverse phase columns when initially present at concentrations ranging from 3.4 to 35.4 mg/L. Other studies have also indicated that only 5 to 10% of DOC in water samples are retained by the $C_{18}$ columns when fresh water samples are employed (Ozretich et al. 1995; Servos and Muir 1989; Landrum et al. 1984). The technique, however, was found to be less satisfactory when salt water samples containing DOC are employed due to higher DOC retention by the stationary phase (Ozretich et al. 1995).

### 5.4.2. Gas Purging

In addition to traditional batch methods, several studies have employed gas sparging techniques in determining equilibrium $K_{OC}$ values using natural lake water DOC sources, and desorption rates from sediment:water slurries (Karickhoff and Morris 1985; Oliver 1985; Hassett and Milicic 1985; Yin and Hassett 1986; Kolemans et al. 1993; Wu and Gschwend 1986; Brusseau et al. 1990). The gas sparging methods are similar to those described in Chapter 3, except that water-DOC mixtures or dilute water-sediment slurries are added to the sparging apparatus. The gas sparging technique permits measurment of the fugacity of a chemical in the freely dissolved phase, and is ideally suited for discrimination between chemical concentrations in water and sorbant phases (Mackay et al. 1979). After equilibration of chemical and OM:water solutions, the net flux of compound released from solution in the sparger can be modeled according to:

$$C_{OM} \xrightarrow{k_2} C_{w(aq)} \xrightarrow{k_{(vol)}} C_{air} \qquad (6)$$

The model can also be extended to multi-box models by addition of resistant and labile sorption sites:

$$C_{OM(res)} \xrightarrow{k_{2(slow)}} C_{OM(labile)} \xrightarrow{k_{2(fast)}} C_{w(aq)} \xrightarrow{k_{(vol)}} C_{air} \quad (7)$$

where: $C_{OM}$, $C_{w(aq)}$ and $C_{air}$ refer to the concentration of chemical on the organic carbon, aqueous and purge gas phases
$k_2$ and $k_{vol}$ refer to the rates of desorption and volatilization, respectively
$k_{2(slow)}$ refers to desorption rates from resistant sorptive fractions
$k_{2(fast)}$ refers to desorption rates from labile sorptive fractions

Provided that the gas sparging duration is not sufficiently long to significantly alter the concentrations of chemical in the freely dissolved phase (i.e. to alter the position of equilibrium), the Henry's Law constant can then be utilized to determine the freely dissolved chemical concentrations for a given sample of purged air according to:

$$C_{w(aq)} = \frac{C_{air}}{K_{AW}} \qquad (8)$$

where: $K_{AW}$ is the dimensionless Henry's law constant

The concentration of chemical associated with organic matter can then be calculated by forcing the mass balance, such that:

$$C_{OC} = \frac{m_{OC}}{wt_{(OC)}} = \frac{m_{total} - m_w}{wt_{(OC)}} \qquad (9)$$

where: $C_{OC}$ is the concentration of chemical on OC (ng/kg)

$m_{OC}$ is the mass of chemical associated with OC (ng)
$wt_{(OC)}$ is mass of organic carbon in the sparger (kg)
$m_{total}$ is the total mass of chemical in the sparger (ng)
$m_w$ is the mass of chemical in the freely dissolved phase derived from Equation 8 and volume of water in the sparger.

Servos and Muir (1989) indicated a good correspondence between freely dissolved chemical concentration estimates for 1,3,6,8-TCDD in batch type studies utilizing reverse-phase separation techniques and gas sparging techniques.

When the solution is purged over long time periods, such that the chemical becomes depleted from the system, desorption kinetics may be determined, provided that the rates of desorption are significantly less than the rate of volatilization (Brusseau et al. 1990; Wu and Gschwend 1986). Under such conditions, the OM within the sparger can be modeled as an infinite depth/planar diffusion source for the chemical of interest (Karickhoff and Morris 1985). Brusseau et al. (1990) indicated that desorption rates may be determined from gas sparging techniques when $K_P$ values are within the range of 1 to $> 10^5$. Assuming first-order kinetics, the desorption rate can be estimated from model 6 according to:

$$\ln \frac{C_{OC(t)}}{C_{OC(o)}} = -k_2 \cdot t + A \qquad (10)$$

where:
$C_{OC(o)}$ is the initial sorbed concentration prior to purging
A is a constant
t is the time in hours

A plot of the natural logarithm of the total mass or concentration of chemical sorbed to organic carbon *vs* time will yield a straight line with a slope corresponding to the desorption rate ($k_2$). However, the sorbed concentration is not directly monitored with time, and must, therefore, be estimated by the mass balance Equations 8 and 9. The total mass of chemical in the sparger column can be calculated for a given time point by subtracting the cumulative mass of chemical purged to air from the initial mass of chemical added to the sparger.

$$m_{total(t)} = m_{total(o)} - m_{air(cummulative)} \tag{11}$$

The concentration of chemical freely dissolved in water is calculated for each time point in which an air sample was taken according to Equation 8. The mass of sorbed chemical is subsequently calculated by subtraction of the mass of solute in the freely dissolved state from the total mass of chemical in the sparger at given sampling time:

$$m_{sorbed(t)} = m_{total(t)} - C_{w(aq,t)} \cdot V \tag{12}$$

where: V is the volume of water in the sparger column

### 5.4.3. Other Techniques

In addition to the reverse-phase separation and gas sparging techniques outlined above, dialysis bag techniques and cosolvent partition coefficient determinations have been developed to distinguish between freely dissolved and third phase associated solute (Carter and Suffet 1982; Hegenab et al. 1995; Suresh et al. 1990). The dialysis technique uses a dialysis membrane of low molecular weight cutoff (<1000) to separate a solution of water containing DOM from a solution of pure water. The chemical, which is able to diffuse through the membrane, is added into one reservoir and allowed to equilibrate. Landrum et al. (1984) found that $K_{DOC}$ values obtained from the dialysis bag technique and reverse-phase separation method were well correlated and generally within a factor of 2 to 3. Similarly, Hassett and Milicic (1985) indicated that $K_{DOC}$ data derived from either gas sparging methods, reverse-phase techniques or dialysis techniques were within a factor of 2.5. Some of the problems associated with the dialysis bag method include long equilibration times, extensive sorptive losses of chemical to the dialysis membrane (particularly for highly hydrophobic compounds), and some leakage of OM through the membrane (Landrum et al. 1984; Carter and Suffett 1982).

The cosolvent partition coefficient method involves determination of $K_P$ in batch studies which contain various quantities of cosolvent in the water phase (Hegeman et al. 1995; Suresh et al. 1990). The presence of a cosolvent modifies the activity coefficient of the chemical in the aqueous phase, decreasing the magnitude of sorption. The relationship between the decrease in $K_P$ with increasing cosolvent concentration can be used to obtain the partition coefficient at zero cosolvent concentration by extrapolation. Although this technique also suffers from the difficulties involved with separation of third phase and determination of freely dissolved chemical, the influence of the third phase on sorption estimates becomes essentially negligible at high cosolvent concentrations. Hegeman et al. (1995) indicated good correspondence between $K_P$ values determined from the cosolvent partition method and standard batch studies which involved prewashing steps to remove third phase material. The major drawbacks for this method are the increased complexity in experiment design and number of replicate batch systems required to determine Freundlich isotherms and solids concentration effects since each replicate variable requires at least 5 batch systems of varying cosolvent concentrations.

All of the methods described above suffer from unrealistically high amounts of perturbation which present a large surface area of particles to the water relative to bed sediments which typically have low porewater exchange rates (Helmstetter and Alden 1994; Groilimund et al. 1995). The perturbation may also introduce artifacts associated with aggregate formation or particle size distributions which can affect the observed sorption/desorption rates. Therefore, verification of equilibrium conditions is essential in order to extrapolate experimental results to environmental conditions.

In this study, $K_{OC}$, $K_{DOC}$ and desorption kinetics were determined for the 1-$^{14}$C-polychlorinated dodecane mixture utilizing batch experiments in combination with reverse-phase separation techniques and gas sparging methods. Natural organic matter was obtained from sediments and filtered lake water samples from three lakes within the Experimental Lakes Area. In addition, the equilibration period required for the sorption process and the effect of solids concentration on the magnitude of $K_{OC}$, $K_{DOC}$ and the desorption rate was explored.

## 5.5. Methods

### 5.5.1. Batch Experiments

Batch studies were performed to determine steady-state $K_{OC}$ values for the $^{14}$C-polychlorinated dodecane mixture using three sources of natural sediment organic carbon. The batch systems consisted of a series of individual 50 mL glass centrifuge tubes containing distilled water, sediment and the polychlorinated dodecane mixture. The batch systems were topped up with distilled water to minimize headspace and sealed with teflon lined septa and screw cap for the duration of the equilibration period. Manual shaking of the centrifuge tubes was performed on a daily basis to minimize the time to equilibration.

Sediments were collected by a diver approximately 20 m offshore from three lakes within the Experimental Lakes Area (ELA) on July 7, 1995. ELA lakes 377, 239 and 222 were chosen based on reported variability in the range of suspended carbon and dissolved organic carbon concentrations found among the lakes (Servos and Muir 1989). Sediments were collected in 500 mL hexane rinsed glass jars, stored at low temperatures and processed within 48 h of collection. Upon returning to the laboratory, the sediments were passed through a 1 mm sieve to remove course materials and allowed to air dry over a period of 1 week. The sediments were subsequently stored in dried form in 500 mL glass jars.

The dried sediments were added to the batch systems followed by addition of 1 µg of $^{14}$C-polychlorinated dodecane (corresponding to 54% saturation of 50 mL water) spiked onto the sides of the centrifuge tube along with 20 μL of acetone carrier solvent. The centrifuge tubes were then topped up with distilled water, poisoned with 0.1% (by wt.) sodium azide and allowed to equilibrate. To test the validity of the spiking procedure and assess the Freundlich behavior of the solute, a separate study using Lake 222 sediments, with a solid concentration of 20 g/L, was performed in which varying quantities of polychlorinated dodecane were spiked into single batch systems at 0.1, 0.3, 0.4, 0.5, 0.8 and 1 μg quantities corresponding to a maximum solute addition of 56% water saturation. In addition, polychlorinated dodecane was introduced into the water in the freely dissolved state by saturating water with the chemical using the generator column technique and subsequently adding the generated water (at 20% saturation) to 3 centrifuge tubes containing Lake 222 sediments.

The assumption of equilibration of the batch systems was tested for sediments of Lakes 222 and 239 by employing 3 equilibration periods of 20, 33 and 39 days. Three replicate centrifuge tubes each containing 1 g of sediment (dry wt.) were sampled for each equilibration period for the two sediment types. The effect of particle concentration on the $K_{OC}$ value was examined for the three sediment types by employing 7 solids concentrations. Solids concentrations of 0.5, 2, 5, 10, 20, 50 or 75 g/L of sediment (dry wt.) were added to 1 centrifuge tube for each sediment type and allowed to equilibrate for 39 days for the Lake 222 and 239 sediments and 20 days for a separate study of Lake 222 and 377 sediments. The solids concentrations were chosen to reflect a range of environmental conditions associated with the sediment/water interface (2% solids loading; Oliver 1985) to bed sediments (~ 500 g/L; O'Connor and Connolly 1980).

Batch systems were centrifuged at 2000 rpm for 1 h at room temperature to separate suspended sediment and water phases, and the supernatant water was removed by pipette. Sediments were ground up with sodium sulfate and extracted by soxhlet extraction for 6 to 12 h using acetone:hexane (1:1) solvent. No differences in total mass of polychlorinated dodecane recovered between 6 and 12 h soxhlet durations were observed. The large amount of pigment extracted from the sediment interfered with quantification by scintillation counting, and, therefore, a cleanup step was performed using 1 g disposable florisil columns (Supelco Cat # 5-7057). The acetone was removed from the soxhlet extracts by roto-evaporating to near dryness, addition of 50 mL hexane and further roto-evaporation. This step was performed at least two times. The extracts were quantitatively added to a florisil column, previously conditioned with 5 mL hexane, 5 mL acetone and 5 mL hexane, and eluted with 300 mL of hexane. Further extraction of the florisil column with hexane and DCM yielded no additional polychlorinated dodecane. The eluant was then roto-evaporated to approximately 1 mL, quantitatively transferred to a scintillation vial along with 10 mL scintillation cocktail and counted using scintillation counting techniques.

For extraction of water, the reverse-phase separation technique (Landrum et al. 1984) was employed to distinguish among freely dissolved chemical concentrations and chemical associated with dissolved organic matter and non-settling colloid phases which were not separated by the centrifugation step. The water was passed through a $C_{18}$ reverse phase column (Waters Enviro-Plus SepPak cat # WAT020515; see Chapter 4) at high flow rates of 10 mL/min. The polychlorinated dodecane eluting from the reverse phase column was operationally defined as DOC associated chemical. The entire water sample was passed through the reverse phase column and the eluent water was collected in a 250 mL separatory funnel and extracted by liquid-liquid extraction with 40, 30 and 20 mL washings of hexane:DCM. The dissolved phase chemical was determined by recovering the chemical retained by the reverse phase column. The column was extracted with 10 mL of hexane, followed by two fractions of 10 mL hexane:DCM which was found to quantitatively extract all polychlorinated dodecane associated with the stationary phase.

In order to determine if sample degradation had occurred over the equilibration period, and to assess the effect of determining $K_{OC}$ on a mixture as opposed to a pure compound, the chromatographic behavior of sediment extracts and the standard was characterized by HPLC analysis. A 20 μL sample of sediment extracts from the 20 day batch experiments performed on Lake 377 and Lake 222 sediments and 20μL of standard was analyzed with a Beckman HPLC system consisting of a Model 334 pump and an injection port with a 20 μL sample loop and $C_{18}$ reverse phase column (Phenomenex Spherisorb 10 C18; 250 mm x 4.5 mm). The analysis was performed under isocratic conditions with methanol as the mobile phase, pumped at a flow rate of 0.2 mL/min. The column eluant was collected into scintillation vials at 30 s intervals for 14 min, and the activity quantified by scintillation counting techniques.

Samples for determination of the fraction of organic carbon in sediments and DOC concentrations in water were analyzed by the Freshwater Institute, Department of Fisheries in Oceans, Winnipeg, MB (Stainton et al. 1977). All concentrations of chemical associated with sediments were subsequently normalized to the fraction of organic carbon in sediment in the calculation of $K_{OC}$ values.

### 5.5.2. $K_{DOC}$ Determinations

Dissolved organic carbon/water partition coefficient ($K_{DOC}$) determinations were made using DOC obtained from filtered lake water and gas sparging techniques. A 4L water sample was taken from Lake 222 as the same location of sediment collection. The water was immediately filtered on site through a 1 µm glass fiber filter (Gelman # 61635) and stored in amber glass bottles for transport to the laboratory. At the laboratory, the water was further filtered through a 0.22 µm filter (Millipore # GVWP 04700) to remove any further particulates and poisoned with 0.1% (w/w) sodium azide to prevent microbial degradation of organic carbon. Samples of the filtered lake water were submitted for DOC analysis to the Freshwater Institute (Staintonet al. 1977).

Seven hundred and fifty mL of the filtered lake water was mixed with 750 mL of HPLC grade water saturated with the 14C-polychlorinated dodecane mixture using the generator column technique. The stock solution was allowed to equilibrate in a sealed 4 L amber bottle for 20 days. After equilibration of the stock solution, 100, 200, 300 and 500 mL aliquots of the stock solution were further diluted to 1L with distilled water and allowed to equilibrate for another 20 days. The four solutions had DOC concentrations of 0.57, 1.1, 1.7 and 2.8 mg/L, respectively. The remainder of the equilibrated stock solution was divided into three fractions and extracted using liquid-liquid extraction techniques with 100, 50 and 20 mL acetone:hexane solvent washings to quantify total solution concentrations.

After equilibration the 1 L solutions were transferred to the gas sparging column described in Chapter 3. The solutions were purged with nitrogen gas at flow rates of 300 mL/min. Three purge gas samples, collected by tenax traps at the outlet of the sparger column, were collected for each solution. The total purging period for all three traps ranged from 8 to 24 h and corresponded to total loss of less than 5% of polychlorinated dodecane from the system. The concentration of chemical in purge gas was determined using the mass of chemical extracted from the tenax trap and volume of purge gas passed through the trap. Tenax traps were extracted by eluting with 10 mL hexane at 1 mL/min. The eluant was analyzed directly by scintillation counting techniques.

### 5.5.3. Sorption Kinetics

The approach to equilibration was characterized more rigorously using a combination of batch experiments and gas sparging studies. In this set of experiments, 0.5 g of Lake 222 sediment was added to 1 L volumetric flasks. Two hundred mL of HPLC grade water saturated with the polychlorinated dodecane mixture using the generator column technique, was added to each flask and subsequently made up to volume using distilled water. The flasks were vigorously shaken at regular intervals, and allowed to equilibrate for time periods of 0.04, 0.08, 0.2, 0.3, 0.5, 1, 2, 4, 10, 12, 20, 40, 60 and 90 days. After the specified equilibration period, the batch system was added to the gas sparger column and purged at 300 mL/min to collect three air samples. Total purge duration ranged from 30 min for flasks equilibrated over short time intervals to 8 h for batch systems allowed to equilibrate over longer time periods.

The freely dissolved water concentrations were calculated according to Equation 8, and the sorbed concentrations were determined from Equation 9 by forcing the mass balance. Replicate batch systems were determined for the 12, 20, 60 and 90 d equilibration periods. Mass balance analysis was made on the two 60 d replicates and one 90 d replicate to check the validity of Equation 9. The sparged solutions were passed through a 0.22 μm filter to remove particulates and the sparger column rinsed with solvents to remove any chemical sorbed to glassware. The filter and particulates were soxhlet extracted for 8h using hexane:acetone solvent. The filtered water was passed through two conditioned $C_{18}$ reverse phase columns, and the eluant extracted by liquid-liquid extraction. The chemical adsorbed to the solid phase extraction column was recovered using the same procedures outlined for the batch studies. All extracts were quantified by scintillation counting techniques.

### 5.5.4. Desorption Kinetics

The equilibrated chemical-DOC solutions (Lake 222 water) employed for the $K_{DOC}$ determinations were purged in the gas sparging column at 300 mL·min$^{-1}$ for extended periods ranging from 10 to 21 d. Polychlorinated dodecane in the purge gas was monitored using tenax traps over 24 h intervals. In addition, the 40 d batch solution from the sorption kinetic study was purged over a period of 20 d and concentrations of chemical in purge gas monitored as described above. The various trials provided desorption rate data on solutions containing 5 organic carbon concentrations of 0.57, 1.1, 1.7, 2.8 and 13 mg·L$^{-1}$. Equations 10, 11 and 12 were then utilized to estimate desorption rates from total stripping rate of chemical from the sparger and mass balance equations.

## 5.6. Results

### 5.6.1. Batch Studies

The organic carbon contents of Lake 377, 239 and 222 sediments and total organic carbon concentrations in filtered lake water obtained from Lake 222 were determined by TOC analysis. The fraction of organic carbon from the three sediment types varied by a factor of 3.7 with values of 0.7, 1.8 and 2.6% for Lake 377, 239 and 222 sediments, respectively. The total organic carbon concentration of filtered lake water from Lake 222 water samples was 11.3 mg·L$^{-1}$, similar to the value of 10.7 mg·L$^{-1}$ reported by Servos and Muir (1989) for this lake. Table 5.1 summarizes the average % recoveries of activity from batch experiments of sediments from Lakes 377, 239 and 222. Mass balance calculations indicated acceptable recoveries of the order of 75 to 100% for most replicates, indicating

**Table 5.1** Average Recovery of $^{14}$C-Polychlorinated dodecane From Equilibrium Batch Experiments Utilizing Lake 377, 239 and 222 Sediments

| Time | Lake 377 | Lake 239 | Lake 222 |
|---|---|---|---|
| 20 | 76.1 | 90.2 | 84.5 |
| 33 | NA | 99.8 | 89.6 |
| 39 | NA | 75.2 | 76.9 |

Note: Percent Activity extracted from sediment + DOC associated activity + activity in the water phase relative to the amount spiked in each system at Day 0.

little loss of chemical during the 20 to 39 day equilibration periods. Three replicates from Lake 222 batch systems had lower recoveries of the order of 59 to 64%, and four replicates from Lake 239 had recoveries of the order of 59 to 67%. The individual $K_{OC}$s determined from these low recovery replicates were not significantly different ($p<0.05$; ANOVA) from $K_{OC}$s determined from batch systems with high recoveries and, therefore, all data were utilized in subsequent interpretations. In order to determine whether degradation occurred during the equilibration period and to assess the effect of determining the $K_{OC}$ on a mixture rather than a pure compound, radiochromatograms were obtained by HPLC analysis of sediment extracts and compared to the chromatographic behavior of the standard. Figure 5.1 summarizes the radiochromatograms from the HPLC characterization of 3 replicate standards and 4 sediment extracts from randomly chosen batch samples containing Lake 377 and Lake 222 sediments equilibrated for 20 d. Both standard and sediment extracts exhibited similar retention behavior on the reverse phase column yielding nearly identical chromatograms.

Figure 5.2 indicates the efficiency of the reverse-phase separation technique for distinguishing freely dissolved polychlorinated dodecane concentrations in the water from DOC associated chemical. The percent of chemical associated with DOC refers to the activity eluting from the reverse phase column relative to the total amount of chemical in the water which was separated from sediments by centrifugation. At the lowest particle concentrations, most of the activity (86 to 97%) was in the freely dissolved form and retained by the reverse phase column. DOC associated polychlorinated dodecane

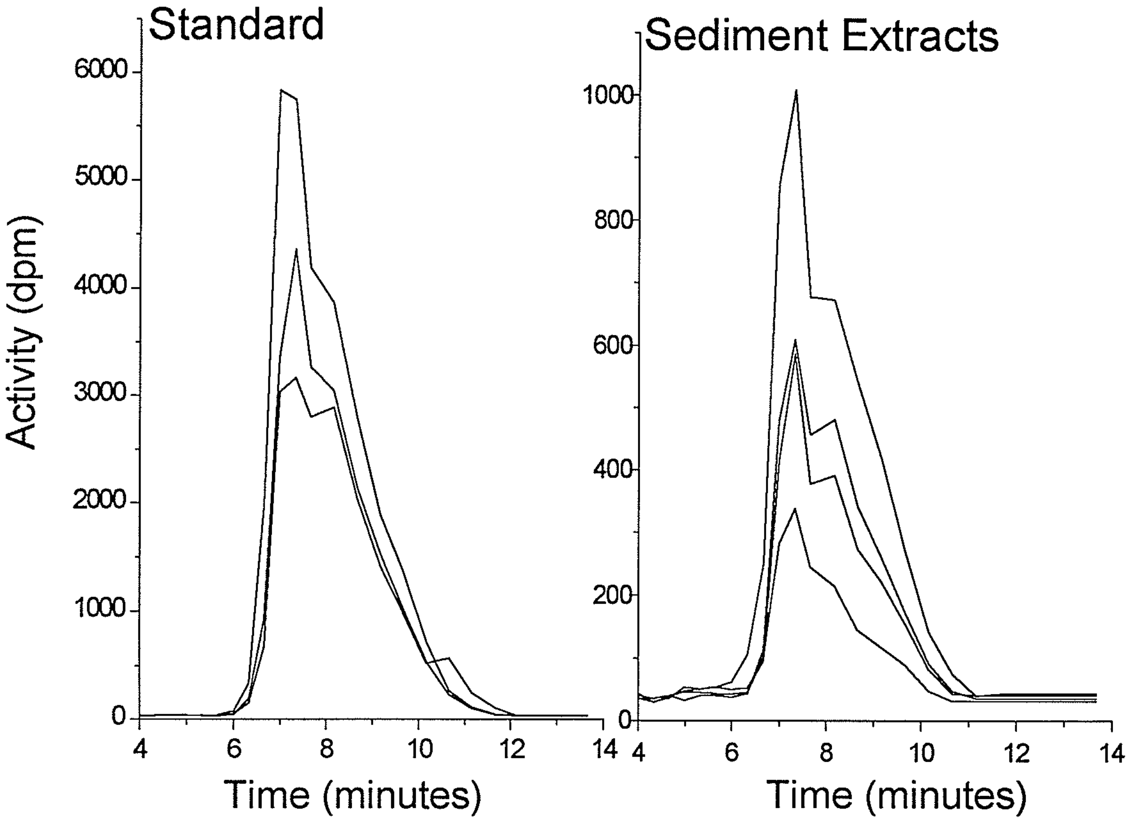

Figure 5.1 HPLC characterization of $^{14}$C-polychlorinated dodecane mixture in standard and sediment extracts. Different lines represent individual chromatograms for each sample injected.

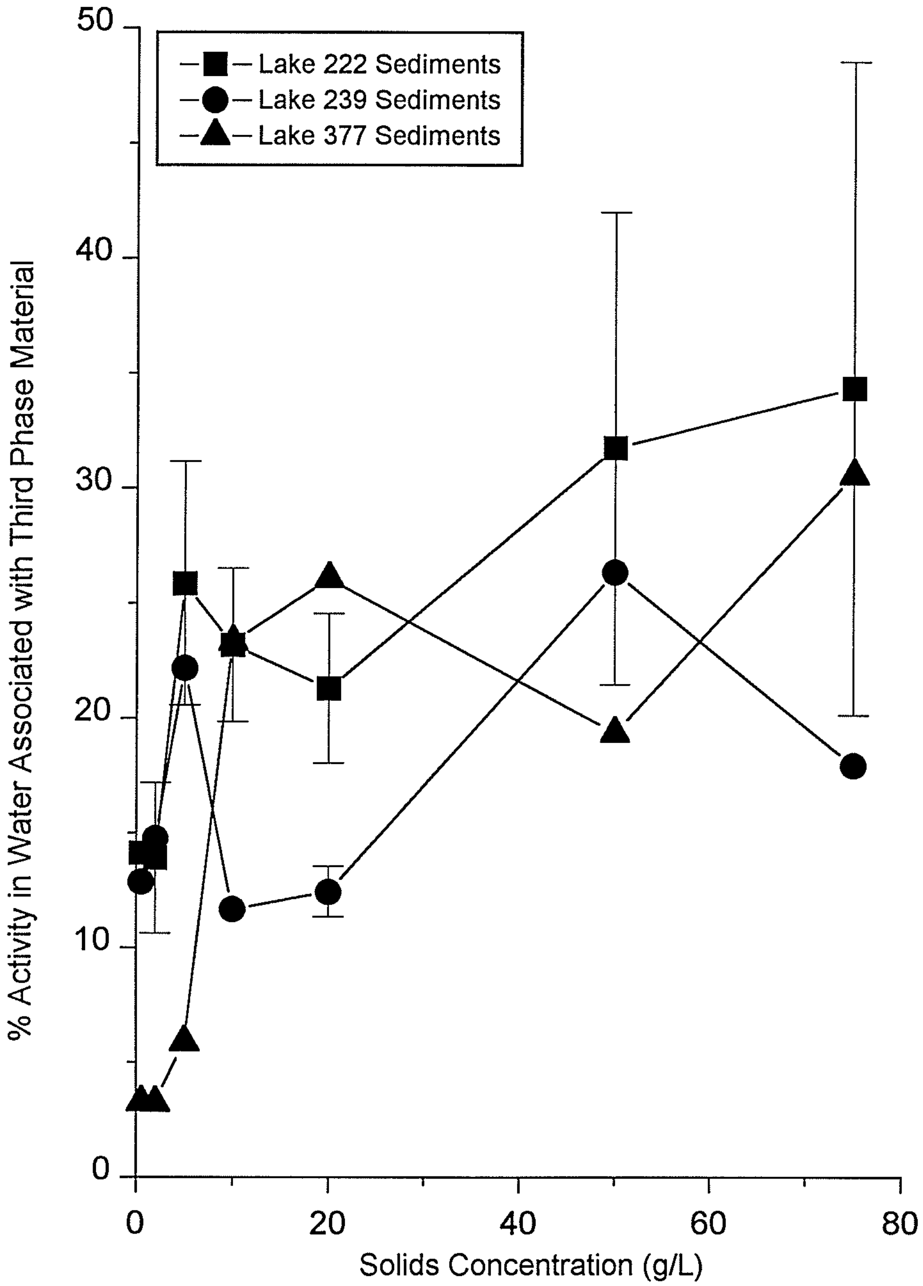

Figure 5.2 Third phase $^{14}$C-polychlorinated dodecane concentrations in batch studies as determined from the reverse phase separation technique. Data points are averaged over 20 and 39 d equilibration periods, error bars represent standard errors.

accounted for 17 to 48% of total mass of chemical in the water at the 75 g/L particle concentrations. The effect of solids concentration on freely dissolved chemical concentrations in the water was less apparent for Lake 239 sediments. All subsequent $K_{OC}$s were calculated using the freely dissolved activity in water, determined from the reverse-phase technique, *vs* the sum of chemical associated with third phase and with sediment organic carbon.

Log $K_{OC}$s determined for Lake 222 sediments, in which the polychlorinated dodecane mixture was added via 20% saturated water, were 4.81 and 4.94 for two replicates. The third replicate was lost during the sample preparation step. $K_{OCs}$ determined for these two batch systems were not significantly different (ANOVA; $p > 0.1$) from $K_{OC}$s determined from systems in which the compound was introduced by the spiking procedure (log $K_{OC}$s ranged from 4.65 to 5.51; $n = 10$). The fit to the Freundlich equation of the chemical in Lake 222 sediments was assessed by spiking various quantities of chemical in water among 5 batch replicates containing a constant solids concentration of 20 g/L. The results, summarized in Figure 5.3, show linear behavior consistent with Equation 1.

Figure 5.4 summarizes the average $K_P$ and organic carbon normalized distribution coefficients ($K_{OC}$) derived from batch studies over the three equilibration periods for systems containing Lake 239 and 222 sediments. Data were available only for the 20 d equilibration period for 1 batch system using lake 377 sediments. The mean distribution coefficient for Lake 222 batch studies appeared to be lower, but not significantly different

(ANOVA; $p>0.5$) at 20 d ($n=10$) from those observed for the day 33 ($n=3$) and day 39 ($n=3$) day replicates. The opposite trends were observed for Lake 239 sediments, which exhibited a slight decreasing trend with time. Expressing the distribution coefficient as $K_{OC}$ removed much of the sediment-to-sediment variability. When data from all three equilibration periods were combined, no significant differences (2-way ANOVA $p> 0.5$) in average $K_{OC}$ for the three sediment types were noted (Table A.7).

The relationship between $K_{OC}$ and the particle concentration employed in the batch system is outlined in Figure 5.5. All three sediments exhibit a log linear relationship between $K_{OC}$ and particle concentration. The relationship is much more variable for Lake 377 sediments, however, this relationship is based on a 20 d equilibration period rather than a 39 day equilibration period as utilized for the Lake 222 and 239 studies. Individual $K_{OC}$ values from all batch replicates were combined for analysis by two-way ANOVA and testing sediment type and particle concentration as potential sources of variation (Table A.7). Highly significant differences were observed among $K_{OC}$s for different particle concentrations (ANOVA; $p<0.01$). The model also indicated a non-significant sediment type x solids concentration interaction term, indicating that the slope of the particle concentration effect was similar for all three sediment types.

### 5.6.2. $K_{DOC}$

Table 5.2 summarizes the $K_{DOC}$ values determined for the 4 DOC solutions of diluted filtered Lake 222 water using the gas sparging technique. The $K_{DOC}$ was calculated from

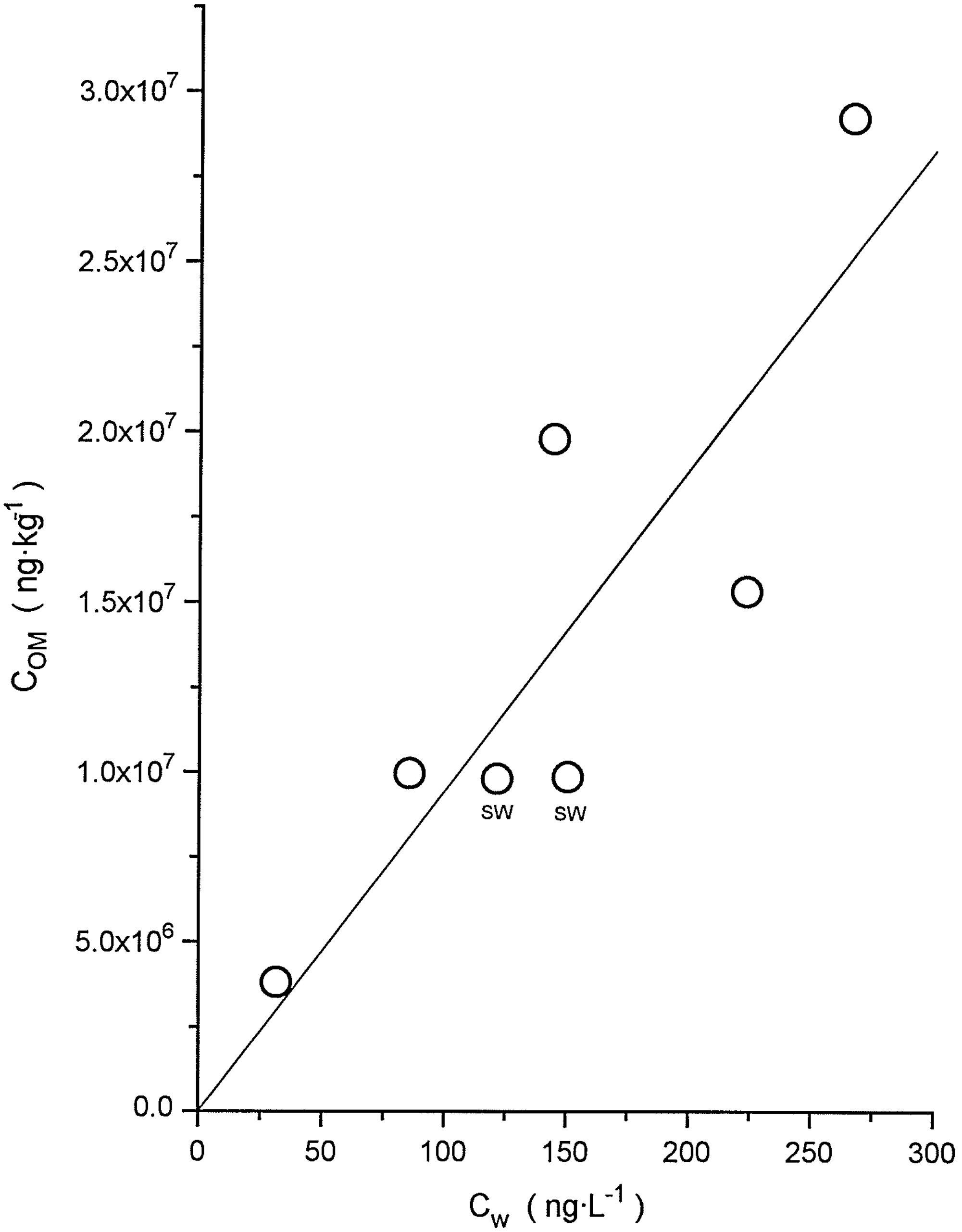

Figure 5.3. Freundlich isotherm for $^{14}$C-polychlorinated dodecane sorption to Lake 222 sediments. SW indicates data points from batch systems in which the chemical was added to water by the generator column technique. All points refer to a 20 d equilibration period with solids concentration of 20 g·L$^{-1}$. Solubility of $^{14}$C-polychlorinated dodecane in water = 36 μg·L$^{-1}$

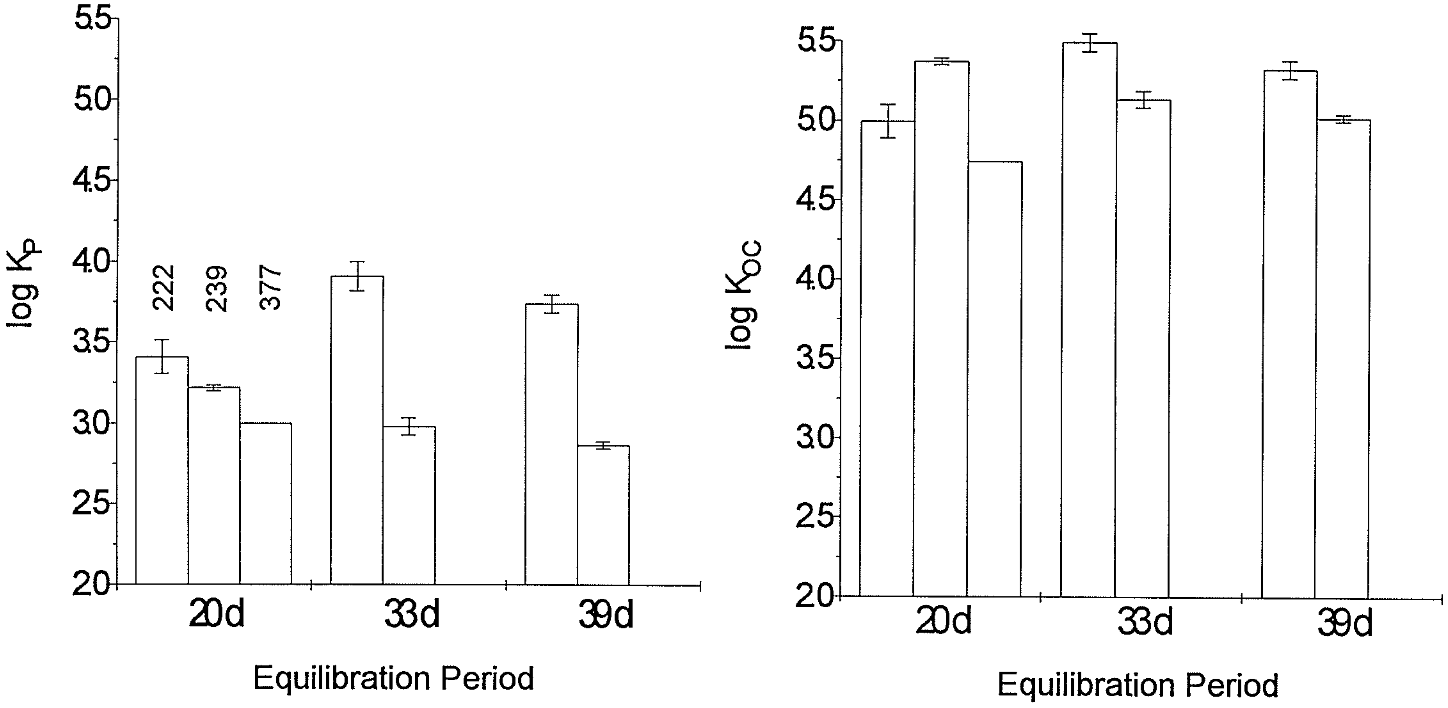

Figure 5.4. $K_P$ and $K_{OC}$ of $^{14}$C-polychlorinated dodecanes from batch studies utilizing different equilibration periods.

**Table 5.2** log $K_{DOC}$ Determined from Gas Sparging Studies on Filtered Lake 222 Water

| DOC Concentration (mg/L) | $m_{w(aq)}$[†] (ng) | Total Mass of Chemical in Sparger (ng) | $m_{DOC}$[‡] (ng) | log $K_{DOC}$ |
|---|---|---|---|---|
| 0.57 | 272±1.6 | 276±20 | NA | NA |
| 1.1 | 129±14 | 563±41 | 434 | 6.47±0.06 |
| 1.7 | 161±23 | 845±62 | 684 | 6.41±0.08 |
| 2.8 | 337±5.3 | 1408±103 | 1071 | 6.03±0.002 |

Note: [†] $m_{w(aq)}$ = mass of chemical in freely dissolved phase in sparger, calculated from Equation 8 and volume of water in sparger
[‡] $m_{DOC}$ = mass of chemical associated with DOC, calculated by mass balance (total mass in sparger – $m_{w(aq)}$)

the ratio of $C_{DOC}/C_w$, assuming sorptive equilibrium was achieved, as described by Equations 8 and 9. A $K_{DOC}$ value could not be determined for the solution of lowest DOC concentration, since calculated polychlorinated dodecane concentrations in the freely dissolved water phase (Equation 8) were not significantly different from the total amount of chemical added to the system. Addition of greater quantities of DOC into the water resulted in depression of calculated water concentrations despite increases in total mass of chemical added to the system. A weak, but significant ($p<0.01$; ANOVA slope = 0; $r^2=0.66$) relationship was observed for the effect of DOC concentrations on the determined log $K_{DOC}$.

### 5.6.3. Sorption Kinetics

Mass balance analysis was performed on one 90 d and two 60 d replicates to verify the assumptions of Equation 9. Total recovery of activity added to the sparger ranged from 94 to 95% for the 60 day equilibration period replicates and 84% for the 90 day equilibration period system. Based on the calculated freely dissolved water concentration from equation 8 and the forced mass balance of Equation 9, the predicted total mass of chemical on sediment was 310, 281 and 306 ng for the two 60 d replicates 90 d replicate, respectively. Measured mass of polychlorinated dodecane on sediments recovered by filtering the sparged water from the sparger column were 275, 258 and 239 ng for the three samples, respectively, and agreed closely with predicted values. The slight underestimates in measured *vs* predicted sediment associated chemical are likely due to

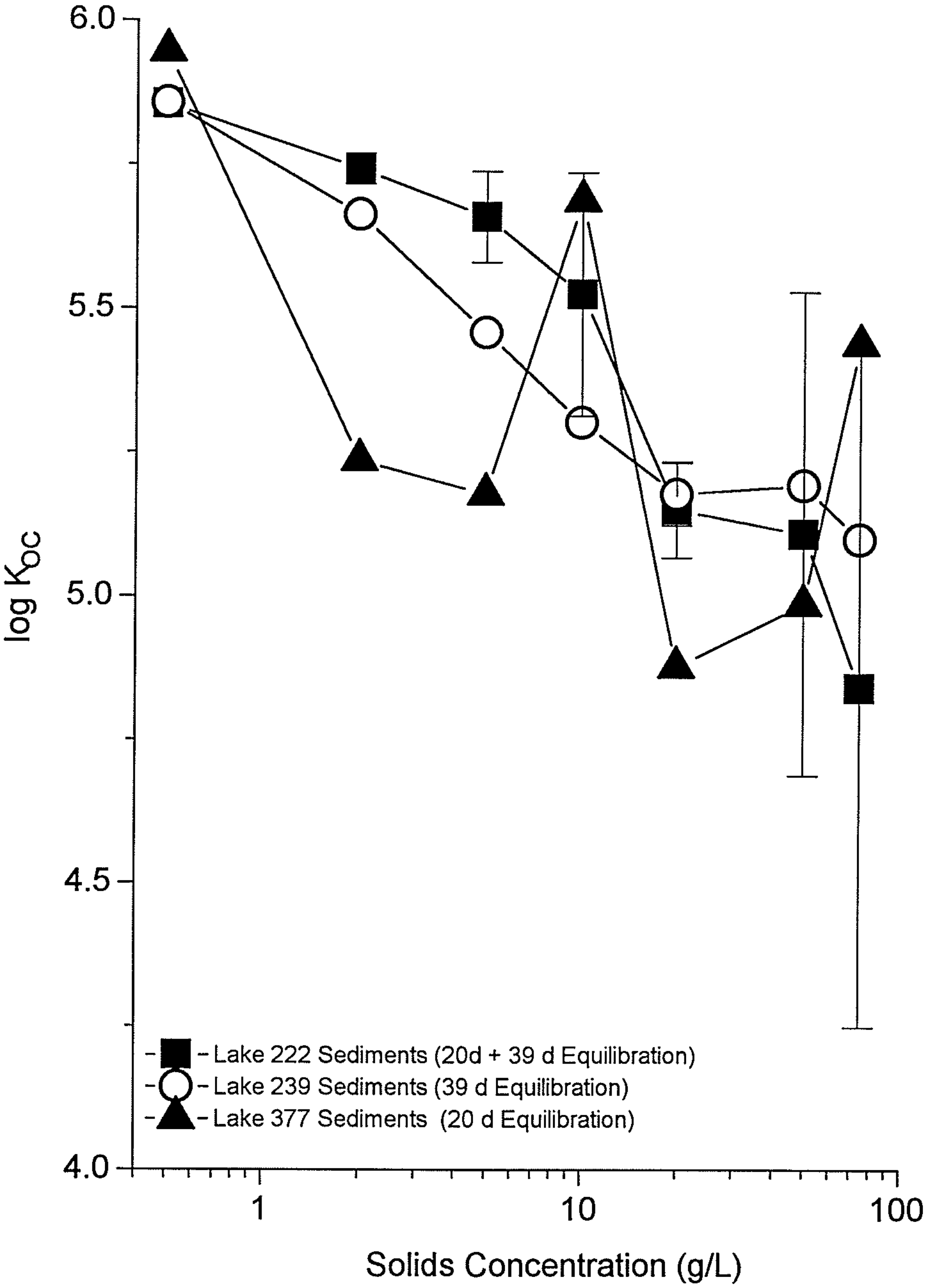

Figure 5.5 Effect of solids concentration on $K_{OC}$. Error bars for Lake 222 sediments refer to standard errors for data combined over two equilibration periods.

releases of DOC to the water during equilibration. This DOC-associated chemical would not have been retained by the 0.22 μm filter. The reverse-phase separation technique was utilized to quantify freely dissolved chemical in the filtered sparged water. However, the large volume of water (1L) passed through the reverse phase columns resulted in significant adsorption of third phase material to the $C_{18}$ stationary phase resulting in visible darkening of the SepPak cartridges and, as such, freely dissolved *vs* DOC associated chemical could not be distinguished in the mass balance study. The similarity in measured *vs* calculated sediment concentrations, does, however, indicate that the assumptions of mass balance were valid for the sorptive uptake studies.

Figure 5.6 outlines the decreasing trend in water concentrations with increasing equilibration period determined in the independent replicates. Although the data are variable over the first 20 days, there appears to be a rapid drop in water concentrations over the first 12 h, followed by a slower approach towards steady state conditions over the next 40 days. Equation 9 was utilized to calculate the concentration of chemical on organic carbon for each equilibration period. The data, however, exhibited too much scatter to be adequately fitted to a one compartment or multi-compartment models for estimation of the sorption rate constant. Figure 5.7 summarizes the $K_{OC}$ data over the various equilibration periods. Steady state conditions appear to have been reached after 40 d. Upper estimates of log $K_{OC}$ determined from the last three time points were in the range of 5.46 to 5.65 and were comparable to the single log $K_{OC}$ estimate of 5.85 derived

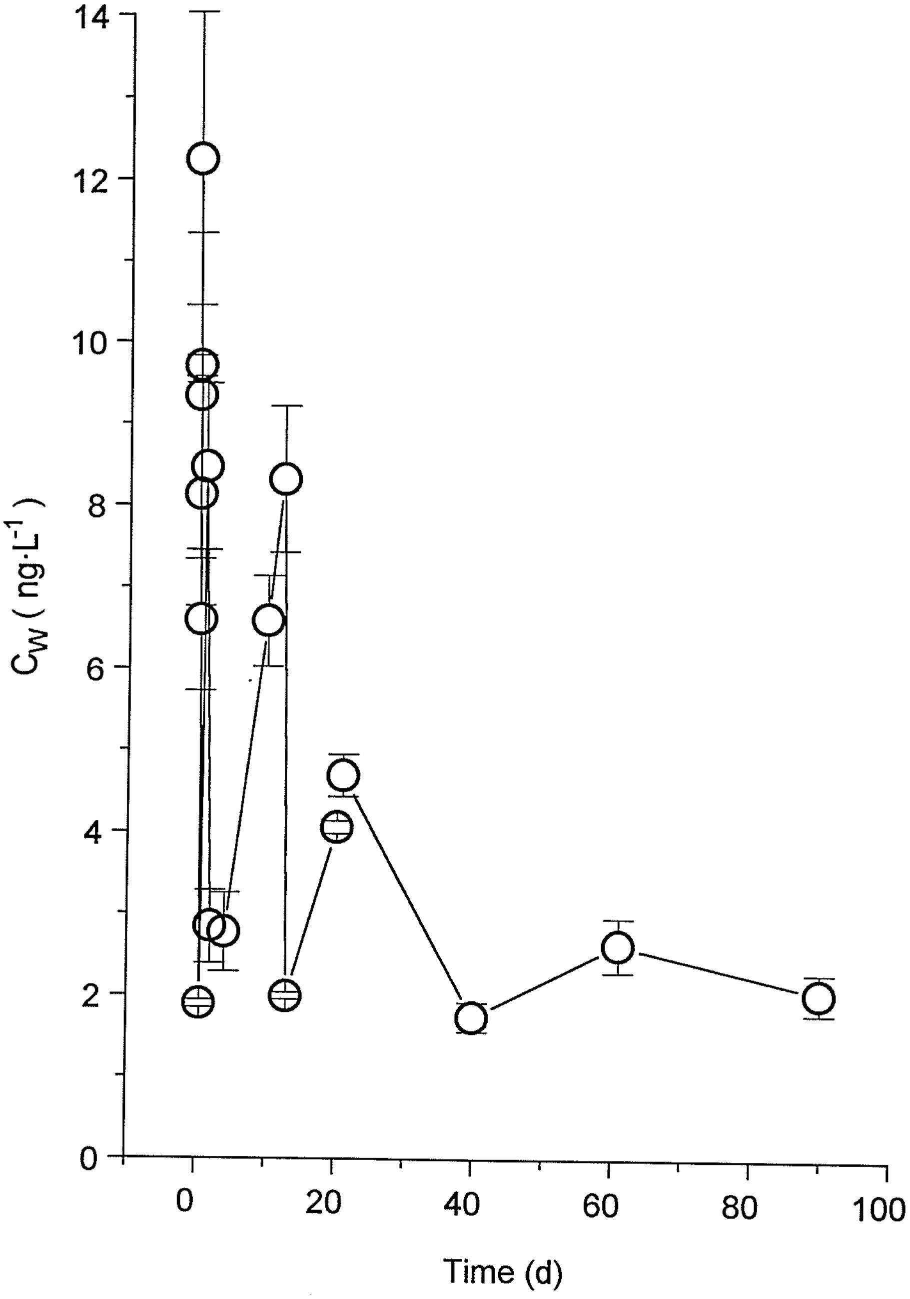

Figure 5.6. Changes in waterconcentrations of $^{14}$C-polychlorinated dodecane with time in sorption studies

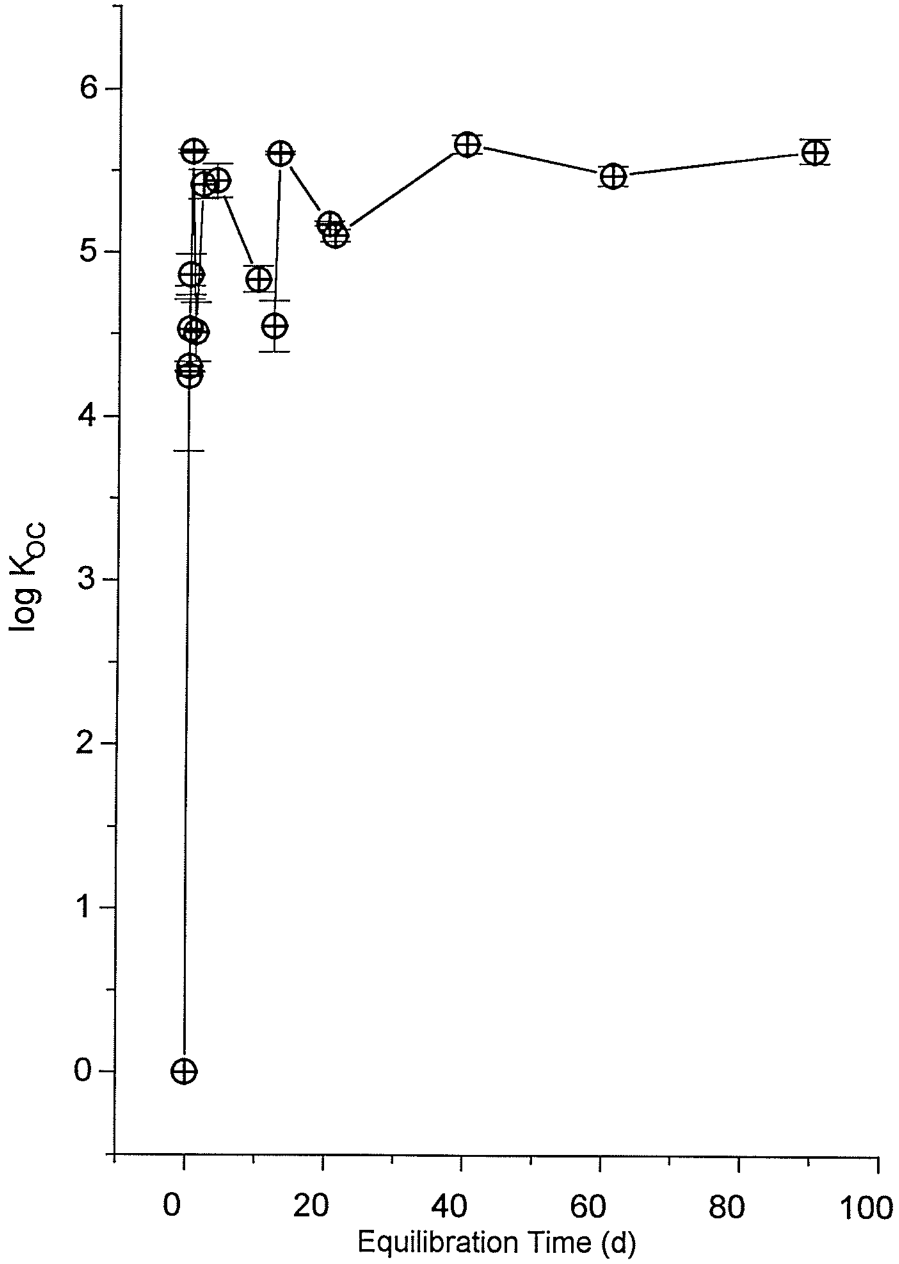

Figure 5.7. Changes in $K_{OC}$ for $^{14}$C-polychlorinated dodecane over time in sorption studies.

for the 0.5 g/L particle concentration utilizing the batch experiment for Lake 222 sediments.

### 5.6.4. Desorption Kinetics

The 0.57, 1.1, 1.7 and 2.8 $mg{\cdot}L^{-1}$ DOC solutions and a 13 $mg{\cdot}L^{-1}$ sediment OC solution (0.5 g of Lake 222 sediment added to 1 L of water), previously equilibrated with the polychlorinated dodecane mixture, were sparged over extended periods to obtain rate constants for desorption. Mass balance analysis was performed on the 0.57, 1.7 and 2.8 $mg{\cdot}L^{-1}$ solutions by comparing total mass of chemical added to the solution *vs* cumulative mass of chemical purged to air and mass of chemical extracted from the sparged solution at the end of the experiment. Percent recoveries for the three solutions were 105, 90.9 and 69%, respectively. The recovery efficiency of the equilibrated sediment/water solutions was described previously, ranging from 84 to 95% recovery. The recovery efficiencies were considered acceptable for utilization of Equation 12 to estimate mass of chemical associated with organic matter in the sparger column.

Figure 5.8 and Table 5.3 summarize the rate constants derived from the desorption experiments. No estimates were available for the desorption rate constant for the most dilute organic carbon solution (0.57 $mg{\cdot}L^{-1}$). Total stripping rates ($k_{total}$), measured as the total loss of chemical from the sparger with time, from the 0.57 $mg{\cdot}L^{-1}$ solution were not significantly different from stripping rates determined from control solutions (containing only pure water and chemical). In addition, initial estimates of water concentrations based

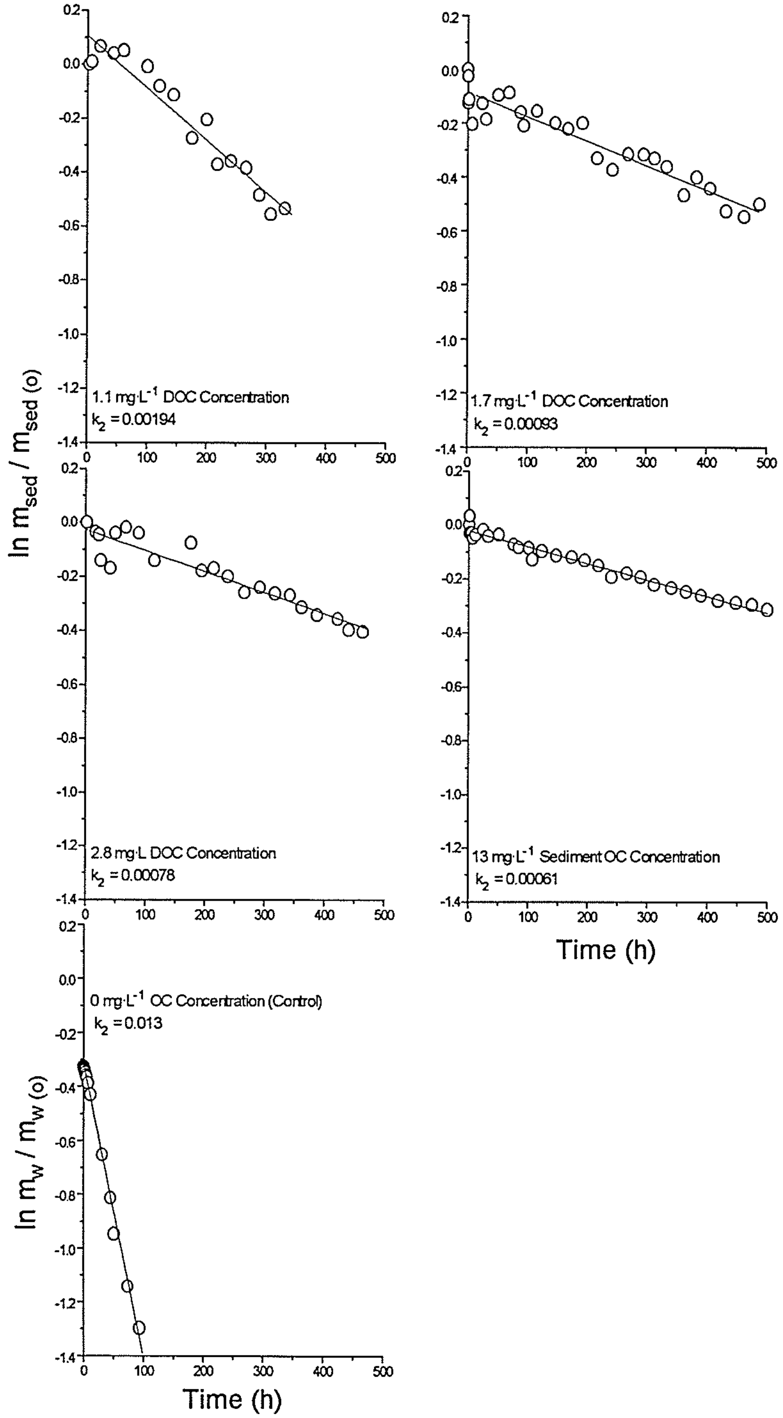

Figure 5.8 Desorption rates of 14C-polychlorinated dodecanes from DOC and sediment OC over varing OC concentrations.

on Equation 8 indicated that nearly all of the chemical was associated with the water phase. The inability to distinguish total stripping rates from this low OC containing solution and the control solutions indicate a limit in technique sensitivity for the method below organic carbon concentrations of approximately 1 mg·L$^{-1}$.

For solutions with OC concentrations greater than 1 mg·L$^{-1}$, most of the chemical was associated with organic carbon. The percent polychlorinated dodecane in the sparger associated with organic carbon ranged from 79.5 ± 1.0 to 91.8 ± 0.8% among the various solutions and exhibited an increasing trend with increasing OC concentration. Total mass of chemical stripped from the system ranged from 33.0 to 46.4% for the 14 to 21 day (336 to 500 h) sparging durations. Total stripping rates and the sediment desorption rates, calculated according to Equations 10 to 12, also exhibited a general decreasing trend with increasing organic carbon concentration (Table 5.3). Half-lives estimated from the desorption rate constants, assuming first-order kinetics, ranged from 14.9 days for the 1.1 mg·L$^{-1}$ organic carbon solution to 47.3 days for the 13 mg·L$^{-1}$ organic carbon solution. The first-order $t_{0.95}$ values (ln (1/0.05)/$k_2$), which indicate an estimated time to 95% equilibrium, ranged from 64 to 205 days. The slow desorption rates at the highest particle concentrations, which corresponded to the lowest particle concentration in the batch and sorption uptake studies, may indicate that the log $K_{OC}$ estimates from these experiments may not have reached true thermodynamic equilibrium over the relatively short 40 and 90 d experimental durations employed.

**Table 5.3** Summary of Desorption Rates from Equilibrated Solutions of $^{14}$C-Polychlorinated Dodecanes Associated With DOC and Sediment Organic Carbon

| Organic Carbon Concentration (mg·L$^{-1}$) | $k_{total}$[†] ($h^{-1}$) | $k_{sed}$[‡] ($h^{-1}$) | $t_{½}$[§] (d) |
|---|---|---|---|
| 0[*] | 0.0090±0.002 | NA | NA |
| 0.57 (DOC) | 0.0071 | NA | NA |
| 1.1 | 0.00186 | 0.00194 | 14.9 |
| 1.7 | 0.00115 | 0.00093 | 31.1 |
| 2.8 | 0.00122 | 0.00078 | 37.0 |
| 13 (Sediment) | 0.00082 | 0.00061 | 47.3 |

Note: [†] $k_{total}$ refers to the first-order rate constant describing the stripping rate of total chemical from the sparger system

[‡] $k_{sed}$ refers to the first-order rate constant describing the desorption rate

[§] refers to the first-order desorption half-life of sediment associated chemical (ln 2/$k_{sed}$ )

[*] % organic carbon in HPLC grade water assumed 0

## 5.7. Discussion

The similarity in radiochromatograms between $^{14}$C-polychlorinated dodecane standards and activity recovered from the batch sediment extracts by reverse phase HPLC indicates that little or no degradation of parent compound occurred during the 20 day incubation period using either Lake 222 or Lake 377 sediments. Degradation of parent material by hydrolysis or biodegradation would be expected to produce chromatograms significantly skewed towards the left relative to the standard. Of perhaps greater significance, however, is that the character of the mixture did not significantly change as a result of individual partitioning of congeners within the mixture. Significant differences in the distribution coefficients among individual congeners in the mixture may result in $K_D$s which are difficult to interpret since the partition coefficients were based on detection of total activity and not individual compounds. If, for example, the distribution coefficients for tetrachlorinated dodecane isomers in the mixture were substantially lower then the $K_D$ for heptachlorinated dodecane isomers, than the sediment extracts would have been expected to have radiochromatograms skewed towards the right relative to the standards. The similarity in the chromatographic retention behavior of standard and sediment extracts validates the assumption that the $K_{OC}$ determined for the polychlorinated dodecane mixture is representative of a hexachlorododecane isomer, the average isomer on a mass distribution basis in the mixture (Chapter 1.4).

Third phase components contributed to total water column chemical concentrations in both batch type systems and gas sparging experiments. The importance of the third phase became more pronounced at higher particle concentrations, indicating greater releases of DOC into water. At the highest particle concentrations in Lake 222 batch studies, 17 to 48% of total mass of chemical in the water was attributed to third phase contributions as measured by the reverse-phase separation technique. Servos and Muir (1989) found similar results for 1,3,6,8-TCDD in batch type $K_{OC}$ studies with 25% of total solution concentrations being attributed to third phase material. Correction for third phase associated chemical resulted in subsequent increases in $K_{OC}$ values by factors ranging from 1.1 to 5.4. The effect on $K_{OC}$ was most pronounced at the higher particle concentrations for sediments containing the lowest organic carbon content.

For filtered lake water solutions containing DOC concentrations ranging from 1.1 to 2.8 $mg \cdot L^{-1}$, from 75.3 to 80.1% of the total mass of polychlorinated dodecane was determined to be bound to DOM material. Such results are consistent with the observations of Yin and Hassett (1986) who found that up to 75% of mirex was associated with DOM phases when Aldrich humic acids were added to solution at 1.1 $mg \cdot L^{-1}$. Batch studies, in combination with reverse-phase techniques, and gas sparging studies yielded consistent results for $K_{OC}$ estimates at the 0.5 $g \cdot L^{-1}$ particle concentration for Lake 222 sediments. In the batch study, 89.7% of the total mass of chemical was estimated to be associated with OM phases compared to the estimate of 87.6% obtained from the gas sparging studies. Individual $K_{OC}$s estimated from the two techniques were within a factor of 1.6 to 2.5, in accord with technique-technique variability demonstrated by other investigators (Servos and Muir 1989; Hassett and Milicic 1985; Landrum et al. 1984).

The Freundlich isotherm summarized in Figure 5.3 was analyzed by linear regression, forcing the intercept through zero. The coefficient of determination for the equation was 0.94, with a slope of 94253 ± 10055 and corresponding log $K_{OC}$ estimate of 4.97. The results were also modeled using the Freundlich equation (Equation 3) by nonlinear regression using Systat statistical software. The fitted Freundlich capacity factor was 98875, corresponding to a log $K_{OC}$ of 5.00, and the best-fit Freundlich exponent was close to unity at 0.991 confirming linear behavior. Linearity in behavior, and the success of the OC normalization for eliminating sediment to sediment variability in $K_{OC}$s, indicated that partitioning to OM was the dominant mechanism of sorption for the polychlorinated dodecane compounds on bed sediment substrates. Log $K_{OC}$ estimates calculated from the slope of the isotherm were in accord with the $K_{OC}$ determinations from individual batch systems with 20 d equilibration periods for Lake 222 sediments, having an average value of 5.08 ± 0.09 (mean ± SE; n = 10).

There was considerable variability in individual $K_{OC}$ estimates among the 10 replicate batch studies at the 20 day equilibration period and 20 g/L particle concentration for Lake 222 sediments. Log $K_{OC}$s ranged from 4.65 to 5.51, varied by a factor of 7.3, and had a high coefficient of variation of 66%. However, evidence from both the three equilibration periods of the batch studies, and the sorption kinetic studies (for Lake 222 sediments), indicated that longer equilibration periods may be required to reach true equilibrium conditions. Therefore, the high variability among replicates at 20 days may reflect slight differences in sorption rates for individual batch systems resulting from differing degrees of particle aggregation, different amounts of perturbation or other factors. Indeed, when the replicates for the 33 and 39 d equilibration periods are combined for Lake 222 sediments, the coefficient of variation decreases to 24%, perhaps reflecting a closer approach to steady state conditions. Similarly, differences between $K_{OC}$ estimates at 20 and 39 d equilibration periods become more pronounced with increasing solids concentration (Table 5.4), further suggesting that the degree of non-equilibrium may be related to the solids concentration.

All three sediment types demonstrated log linear relationships between $K_{OC}$ and particle concentration. The three sediment types also exhibited similar slopes, as indicated by the non-significant interaction term in the two-way ANOVA which tested $K_{OC}$ values from different sediment types and solids concentrations (Table A.7), suggesting that a similar mechanism is involved in the solids concentration effect among the different OM types. O'Connor and Connolly (1980), however, noted that the solids concentration effect was found to vary among different sorbant types and different sediment sources. $K_{OC}$s decreased by factors ranging from 3.3 to 7 for the three sediment types over solids concentrations ranging from 0.5 to 75 g/L. Similarly, Tye et. al. (1996) and Horzempa and DiToro (1983) found decreases in steady-state HCB and PCB #153 distribution

**Table 5.4** Summary of $K_{OC}$ values for Polychlorinated Dodecanes Sorbed to Lake 222 Sediments Determined Over Various Equilibration Periods and Solids Concentrations

| Solids Concentration (g/L) | Equilibration Time, Experiment | log $K_{OC}$ ($L \cdot Kg^{-1} \pm SE$) |
|---|---|---|
| 0.5 | 20 d sp[†] | 5.13±0.03 |
| | 39 d batch[‡] | 5.85 |
| | 40 d sp | 5.65±0.06 |
| | 61 d sp | 5.46±0.06 |
| | 90 d sp | 5.61±0.08 |
| 2 | 20 d batch | 5.79 |
| | 39 d batch | 5.71 |
| 5 | 20 d batch | 5.60 |
| | 39 d batch | 5.77 |
| 10 | 20 d batch | 5.44 |
| | 39 d batch | 5.73 |
| 20 | 20 d batch | 5.10±0.09 |
| | 39 d batch | 5.32±0.03 |
| 50 | 20 d batch | 4.79 |
| | 39 d batch | 5.53 |
| 75 | 20 d batch | 4.58 |
| | 39 d batch | 5.43 |

Note: [†] SP indicates $K_{OC}$ determined from gas sparging experiment in the sorptive uptake study

[‡] Batch indicated $K_{OC}$ determined from equilibrium batch studies

coefficients ($K_P$) of the order of a factor of 4 to 5 when solids concentrations of 0.01 and 10 g/L, and 0.1 and 1 g/L were employed, respectively. In addition, the $K_{DOC}$ values derived from Lake 222 filtered water were found to be similar to $K_{OC}$ values when the organic carbon concentration was taken into account. The dependence of $K_{DOC}$ on organic carbon concentration was slightly stronger than observed for mirex and DDT in other studies, declining by a factor of 2.8 over organic carbon concentrations ranging from 1.1 to 2.8 mg/L. Landrum et al. (1984) and Yin and Hassett (1986) found decreases in $K_{DOC}$s by a factor of 3 over humic acid concentrations of <2 to 16 mg/L.

The sorption uptake study indicated rapid decreases in chemical concentrations in water over a period of 12 h followed by slower decreases over the next 40 days. $K_{OC}$ determinations were found to increase by a factor of 12 when comparing solutions equilibrated for only 24 h relative to systems equilibrated for 90 days. Several other studies have found sorption to exhibit a two-stage approach to equilibrium with 30 to 60% of the compound sorbing within minutes to hours followed by slower uptake over days to months (Brusseau et al. 1990; Karickhoff and Morris 1985). The data, however, exhibited too much scatter to be adequately fitted to a one compartment or multi-compartment sorption model for estimation of the sorption rate constant. Steady-state appears to have been reached within 40 days, although insufficient data are available to indicate whether or not true thermodynamic equilibrium has been achieved. Jepsen et al. (1995) found that HCB required equilibration periods of the order of 50 d. Karickhoff and Morris (1985) indicated that sorption studies should allow a minimum equilibration period on the order of $1/k_2$, where $k_2$ is the desorption rate constant. A $1/k_2$ estimate of 68 days, determined from the desorption rate experiment at 0.5 g/L solids concentration indicates that steady-state may have indeed occurred in the sorption kinetic study, but not in the batch studies which employed equilibration periods of only 39 days.

The desorption rate constants were found to decrease with increasing solids or DOC concentrations. The $t_{0.95}$ values, which indicate an estimated time to 95% equilibrium (assuming first-order kinetics), ranged from 64 to 205 days. Such values are likely underestimated, on account of the extremely slow desorption kinetics associated with the most resistant sorbed fractions, and enhanced perturbation encountered in the gas sparger system (Karickhoff and Morris 1985; Servos and Muir 1989). The desorption rates indicate much longer time to equilibrium than estimated from sorption data. Harmon and Roberts (1994), however, cautioned that one of the most prevalent causes of sorption/desorption rate nonsingularity was failure to achieve equilibrium during the sorptive uptake phase of the experiment.

Only 33 to 46% of the total mass of polychlorinated dodecane was stripped from the sparged solution over the 14 to 21 day sparging durations. Oliver (1985) also found that only 39-65% of sorbed anthropogenic chemicals (average of 13 compounds) were desorbed from gas stripping experiments performed over 39 d durations. Karickhoff and Morris (1985) indicated that generally 25 to 60% of sorbed chemical is labile with only 10% of compound comprising the resistant fraction. As such, the desorption rates estimated in this study likely reflect labile fraction desorption rates. Further sparging experiments, of the order of 68 to 207 days would be required in order to adequately model desorption rates using multi-box models as described by Karickhoff and Morris (1985) and Kolemans et al. (1993).

Several authors have reported a general relationship between $K_P$ and $k_2$ (Brusseau et al. 1990; Kolemans et al. 1993; Hu et al. 1995). The relationships reported by Brusseau et al. (1990) and Kolemans et al. (1993) predicted $k_2$ values of the order of 1.05 to $0.86 \times 10^{-5}$ $h^{-1}$ which are slightly lower than observed in this study ($k_2 = 6.1 \times 10^{-5}$ $h^{-1}$ ; particle concentration = 0.5 g/L; log $K_P$ = 4.27). The $k_2$ value predicted by the Hu et al. (1995) relationship was in better agreement at $5.9 \times 10^{-5}$ $h^{-1}$. Since the observed desorption rates were found to be a function of the solids concentrations, differences in observed *vs* predicted results likely reflect differences in experimental conditions used to derive $K_P$ and $k_2$ values among the various studies.

The observed decreases in desorption rates with increasing solids concentration strongly indicate that at least a portion of the mechanism responsible for the solids concentration effect is due to kinetic factors. The results do not support the particle mediated desorption hypothesis set forward by DiToro (1985) and Mackay and Powers (1987) which predict higher net desorption rates with increasing solids loading. Other investigators have noted the trend of decreasing desorption rates with increasing solids concentration (Karickhoff and Morris 1985). Tye et al. (1996) found that the time to steady-state for HCB was short (< 1 d) at low solids concentrations compared to 30 to 40 d for high solids concentrations. Jepsen et al. (1995) and Tye et al. (1996) hypothesized that the solids concentration loading is directly related to the size and density of aggregates formed in batch systems. Jepsen et al. (1995) and Tye et al. (1996) observed that high solids loadings in experimental batch systems resulted in the formation of more stable and dense aggregates relative to fluffy, 'open' aggregates, typically formed at lower solid concentrations. The more dense aggregates associated with the highest solids concentrations are hypothesized to exhibit slower sorption/desorption kinetics as a result of diffusion constraints due to aggregate packing.

Karickhoff and Morris (1985) found that addition of dispersants to the aqueous phase, which prevented formation of aggregates, eliminated much of the solids concentration effect. Other investigators found that sonication of particles to break apart aggregates resulted in more rapid desorption kinetics and increased chemical bioavailability to mineralizing microorganisms (Wu and Gschwend 1986; Hatzinger and Alexander 1995). Further studies, which involve near quantitative desorption of chemical over wider particle concentration ranges in conjunction with long term sorption experiments (of the order of a year or more), are required in order to determine if the solids concentration effect can be eliminated by ensuring true thermodynamic equilibrium.

## 5.8. Conclusions

$K_{OC}$, $K_{DOC}$, and desorption kinetics were determined for the 1-$^{14}$C-polychlorinated dodecane mixture utilizing batch experiments in combination with reverse-phase separation techniques and gas sparging methods. Natural sources of organic matter were obtained from sediments and filtered lake water samples from three lakes within the Experimental Lakes Area. Results from the two independent techniques, designed to distinguish freely dissolved chemical concentrations from chemical associated with third phase material, yielded equivalent results having $K_{OC}$ estimates within a factor of 2.5. Both $K_{OC}$ and $K_{DOC}$ were significantly dependent on the solids concentration employed in the experimental study and required relatively long sorptive equilibration periods, of the order of 40 to 90 d, to reach steady state conditions. No significant differences in $K_{OC}$ estimates were observed among different sediment types for a given particle concentration and equilibration period (when equilibration periods > 20 d were compared). In addition, $K_{DOC}$ was found to be equivalent to $K_{OC}$ for natural OM derived from filtered lake water and sediment samples from Lake 222. The log $K_{OC}$ under dilute organic carbon concentrations was calculated at 6.44, a value thought to represent the true thermodynamic equilibrium partition coefficient. Desorption rates were found to decrease with increasing particle concentration, supporting the hypothesis that the solids concentration effect is at least partially due to different sorption/desorption kinetics over varying solid loadings. The solids concentration may, therefore, reflect an artifact of comparing $K_P$s which are at different states of non-equilibrium in the sorptive process.

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# 6. Appendix

**Table A.1** 2-Way ANOVA of Vapor Pressures at 25°C for Chlorinated Alkanes of Different Carbon Chain Length and Chlorine Content

| Source of Variation | D.F. | MS | F |
|---|---|---|---|
| Carbons | 2 | 0.71 | 19.9*** |
| Chlorine | 2 | 1.97 | 55.7*** |
| Carbon · Chlorine | 5 | 0.024 | 0.68 |
| error | 9 | 0.035 | |

Note: ANOVA performed using SYSTAT statistical software, SYSTAT Inc., 1800 Sherman Ave., Evanston, IL, U.S.A., on log transformed data

D.F. = Degrees of Freedom
MS = Mean Square
F = F-Test
*** = Indicates highly significant differences ($p < 0.001$) at the 99% confidence level

**Table A.2** Summary of Mass Balance Study for the September 28 Sparging Trial Utilizing the Polychlorinated Decanes

| | Cumulative Mass Sparged (μg) | | |
|---|---|---|---|
| Time (h) | $T_4C_{10}$ | $P_5C_{10}$ (a+b) | $P_5C_{10}$ (c+d) |
| 0 | 0 | 0 | 0 |
| 3.14 | 1.65 | 0.06 | 0.03 |
| 14.51 | 2.84 | 0.51 | 0.39 |
| 28.41 | 3.06 | 0.74 | 0.67 |
| 38.39 | 3.14 | 0.78 | 0.72 |
| 49.67 | 3.61 | 0.87 | 0.89 |
| 72.89 | 3.70 | 0.91 | 0.97 |
| $m_{wat(sp)}$ | 0.94 | 0.20 | 0.18 |
| $m_{wat(total)}$ | 4.64 | 1.11 | 1.15 |
| $m_{w(o)meas}$ | 4.30 | 0.90 | 1.05 |
| $m_{w(iterative)}$ | 3.27 | 1.17 | 1.23 |

**Table A.3** Summary of Mass Balance Study for The March 12 Sparging Trial Utilizing the Polychlorinated Undecanes

| | Cumulative Mass Purged (μg) | | |
|---|---|---|---|
| Time (h) | $T_4C_{11}$ | $P_5C_{11}$ (a+b) | $P_5C_{11}$ (c+d+e) |
| 0 | 0 | 0 | 0 |
| 0.81 | 0.24 | N.D. | N.D. |
| 1.76 | 0.95 | 0.035 | 0.025 |
| 3.72 | 2.09 | 0.087 | 0.037 |
| 4.77 | 3.92 | 0.212 | 0.119 |
| 5.65 | 4.67 | 0.242 | 0.122 |
| 8.36 | 6.71 | 0.348 | 0.166 |
| 14.95 | 11.93 | 0.722 | 0.445 |
| 22.22 | 14.96 | 0.989 | 0.638 |
| 39.24 | 19.42 | 1.522 | 0.947 |
| 53.78 | 21.51 | 1.841 | 1.182 |
| 72.28 | 24.37 | 2.512 | 1.708 |
| $m_{wat(sp)}$ | N.D. | 1.432 | 3.25 |
| $m_{wat(total)}$ | 24.37 | 3.944 | 4.95 |
| $m_{w(o)meas}$ | 19.00 | 5.58 | 8.95 |
| $m_{w(iterative)}$ | 25.67 | 5.243 | 7.673 |

**Table A.4** Summary of Experimental Conditions and Measured HLCs for Individual Sparging Runs

| Date | Compound | Model Fit[†] | Mo | k2 | R2 | T | Vol. (L) | G (L/hr) | H (Pa.m3/mol) |
|---|---|---|---|---|---|---|---|---|---|
| 26-Sep | $C_{10}H_{18}Cl_4$ | linear | 5.21 | 0.12 | 0.99 | 294.7 | 1.00 | 24.00 | 11.81 |
| 28-Sep | $C_{10}H_{18}Cl_4$ | nonlinear | 3.27 | 0.20 | 0.96 | 296.7 | 1.00 | 24.00 | 20.92 |
| 5-Oct | $C_{10}H_{18}Cl_4$ | nonlinear | 2.77 | 0.15 | 1.00 | 297.3 | 0.50 | 24.00 | 7.45 |
| 3-Dec | $C_{10}H_{18}Cl_4$ | nonlinear | 1.15 | 0.11 | 1.00 | 294.8 | 1.00 | 24.00 | 10.91 |
| 18-Apr | $C_{10}H_{18}Cl_4$ | nonlinear | 5.61 | 0.13 | 0.97 | 297.1 | 0.50 | 18.00 | 9.18 |
| 28-Feb | $C_{10}H_{18}Cl_4$ | non-linear | 2.70 | 0.21 | 0.95 | 292.7 | 1.00 | 18.00 | 28.74 |
| 13-Apr | $C_{10}H_{18}Cl_4$ | non-linear | 4.23 | 0.64 | 1.00 | 297.1 | 0.50 | 18.00 | 43.90 |
| 19-Oct | $C_{10}H_{18}Cl_4$ | non-linear | 2.21 | 0.17 | 1.00 | 297.3 | 0.50 | 24.00 | 8.48 |
| 28-Sep | $C_{10}H_{17}Cl_5$ ab | nonlinear | 0.94 | 0.05 | 0.99 | 296.7 | 1.00 | 24.00 | 5.23 |
| 26-Sep | $C_{10}H_{17}Cl_5$ ab | linear | 1.17 | 0.04 | 0.99 | 294.7 | 1.00 | 24.00 | 4.02 |
| 5-Oct | $C_{10}H_{17}Cl_5$ ab | nonlinear | 0.50 | 0.03 | 0.94 | 297.3 | 0.50 | 24.00 | 1.34 |
| 19-Oct | $C_{10}H_{17}Cl_5$ ab | nonlinear | 0.69 | 0.14 | 1.00 | 297.3 | 0.50 | 24.00 | 7.35 |
| 3-Dec | $C_{10}H_{17}Cl_5$ ab | nonlinear | 0.62 | 0.05 | 1.00 | 294.8 | 1.00 | 24.00 | 4.89 |
| 13-Apr | $C_{10}H_{17}Cl_5$ ab | nonlinear | 1.85 | 0.10 | 1.00 | 297.1 | 0.50 | 18.00 | 7.05 |
| 18-Apr | $C_{10}H_{17}Cl_5$ ab | nonlinear | 2.19 | 0.04 | 0.98 | 296.5 | 0.50 | 18.00 | 2.46 |
| 7-Feb | $C_{10}H_{17}Cl_5$ ab | nonlinear | 0.61 | 0.06 | 0.99 | 294.8 | 0.50 | 24.00 | 3.26 |
| 20-Feb | $C_{10}H_{17}Cl_5$ ab | nonlinear | 0.54 | 0.10 | 0.99 | 296.4 | 0.50 | 24.00 | 5.17 |
| 28-Feb | $C_{10}H_{17}Cl_5$ ab | linear | 2.23 | 0.06 | 0.99 | 292.7 | 1.00 | 18.00 | 8.41 |
| 28-Sep | $C_{10}H_{17}Cl_5$ cd | Linear | 1.14 | 0.03 | 0.99 | 296.7 | 1.00 | 24.00 | 2.74 |
| 26-Sep | $C_{10}H_{17}Cl_5$ cd | Linear | 1.23 | 0.03 | 0.96 | 294.7 | 1.00 | 24.00 | 3.34 |
| 5-Oct | $C_{10}H_{17}Cl_5$ cd | nonlinear | 0.58 | 0.03 | 0.94 | 297.3 | 0.50 | 24.00 | 1.34 |
| 19-Oct | $C_{10}H_{17}Cl_5$ cd | nonlinear | 0.80 | 0.14 | 1.00 | 297.3 | 0.50 | 24.00 | 7.35 |
| 3-Dec | $C_{10}H_{17}Cl_5$ cd | nonlinear | 1.01 | 0.01 | 0.99 | 294.8 | 1.00 | 24.00 | 1.43 |
| 13-Apr | $C_{10}H_{17}Cl_5$ cd | nonlinear | 3.29 | 0.04 | 1.00 | 297.1 | 0.50 | 18.00 | 2.67 |
| 18-Apr | $C_{10}H_{17}Cl_5$ cd | nonlinear | 5.96 | 0.02 | 0.99 | 296.5 | 0.50 | 18.00 | 1.03 |
| 7-Feb | $C_{10}H_{17}Cl_5$ cd | nonlinear | 0.44 | 0.03 | 1.00 | 294.8 | 0.50 | 24.00 | 1.58 |
| 20-Feb | $C_{10}H_{17}Cl_5$ cd | nonlinear | 0.77 | 0.04 | 0.99 | 296.4 | 0.50 | 24.00 | 2.10 |
| 27-Jun | $C_{11}H_{20}Cl_4$ | linear | 12.25 | 0.05 | 0.91 | 296.5 | 0.50 | 18.00 | 3.53 |
| 29-Aug | $C_{11}H_{20}Cl_4$ | nonlinear | 12.27 | 0.20 | 1.00 | 296.5 | 0.50 | 18.00 | 13.33 |
| 2-Mar | $C_{11}H_{20}Cl_4$ | linear | 29.02 | 0.04 | 0.98 | 296.5 | 1.00 | 18.00 | 5.61 |
| 4-Mar | $C_{11}H_{20}Cl_4$ | nonlinear | 30.02 | 0.03 | 0.99 | 296.5 | 1.00 | 18.00 | 4.10 |
| 12-Mar | $C_{11}H_{20}Cl_4$ | nonlinear | 25.67 | 0.04 | 0.99 | 296.5 | 1.00 | 18.00 | 5.06 |
| 27-Jun | $C_{11}H_{19}Cl_5$ ab | linear | 7.23 | 0.01 | 0.97 | 296.5 | 0.50 | 18.00 | 0.69 |
| 29-Aug | $C_{11}H_{19}Cl_5$ ab | nonlinear | 7.25 | 0.04 | 1.00 | 296.5 | 0.50 | 18.00 | 2.60 |
| 2-Mar | $C_{11}H_{19}Cl_5$ ab | linear | 5.58 | 0.01 | 0.98 | 296.5 | 1.00 | 18.00 | 1.09 |
| 4-Mar | $C_{11}H_{19}Cl_5$ ab | linear | 6.83 | 0.01 | 0.99 | 296.5 | 1.00 | 18.00 | 1.70 |
| 12-Mar | $C_{11}H_{19}Cl_5$ ab | nonlinear | 5.24 | 0.01 | 0.99 | 296.5 | 1.00 | 18.00 | 1.23 |
| 27-Jun | $C_{11}H_{19}Cl_5$ cde | linear | 6.90 | 0.01 | 0.98 | 296.5 | 0.50 | 18.00 | 0.81 |
| 29-Aug | $C_{11}H_{19}Cl_5$ cde | nonlinear | 6.87 | 0.02 | 0.99 | 296.5 | 0.50 | 18.00 | 1.37 |
| 2-Mar | $C_{11}H_{19}Cl_5$ cde | linear | 7.95 | 0.00 | 1.00 | 296.5 | 1.00 | 18.00 | 0.19 |
| 4-Mar | $C_{11}H_{19}Cl_5$ cde | linear | 8.95 | 0.00 | 0.99 | 296.5 | 1.00 | 18.00 | 0.60 |
| 12-Mar | $C_{11}H_{19}Cl_5$ cde | nonlinear | 7.67 | 0.00 | 0.99 | 296.5 | 1.00 | 18.00 | 0.41 |
| 6-Oct | $^{14}C_{12}H_{20}Cl_6$ | nonlinear | 0.72 | 0.01 | 0.99 | 296.5 | 1.00 | 18.00 | 1.77 |
| 10-Oct | $^{14}C_{12}H_{20}Cl_6$ | linear | 0.25 | 0.01 | 1.00 | 296.5 | 1.00 | 18.00 | 1.09 |
| 16-Oct | $^{14}C_{12}H_{20}Cl_6$ | nonlinear | 0.47 | 0.01 | 0.99 | 296.5 | 1.00 | 18.00 | 0.84 |

**Table A.4** (Cont.). Summary of Experimental Conditions and Measured HLCs for Individual Sparging Runs

| | | | | | | |
|---|---|---|---|---|---|---|
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point‡ | 40cm Col | 1.00 | 18.00 | 0.93 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 40cm Col | 1.00 | 18.00 | 1.27 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 40cm Col | 1.00 | 18.00 | 1.39 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 40cm Col | 1.00 | 18.00 | 1.33 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 50 cm Col | 1.00 | 18.00 | 1.08 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 50 cm Col | 1.00 | 18.00 | 1.07 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 50 cm Col | 1.00 | 18.00 | 1.35 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 50 cm Col | 1.00 | 18.00 | 1.47 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 50 cm Col | 1.00 | 18.00 | 1.40 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 60 cm Col | 1.00 | 18.00 | 1.33 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 60 cm Col | 1.00 | 18.00 | 1.78 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 60 cm Col | 1.00 | 18.00 | 1.66 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 60 cm Col | 1.00 | 18.00 | 1.66 |
| 12-Feb | $^{14}C_{12}H_{20}Cl_6$ | single point | 60 cm Col | 1.00 | 18.00 | 1.83 |

**Note:** †Denotes model of experimental fit. Non-linear refers to data analyzed according to Equation 8, linear refers to data analyzed according to Equation 7.
‡HLC determined from single sample point, assuming no change in water concentration over time.

**Table A.5** Variability in Apparent Solubility Data for Chlorinated Alkanes at 25°C From Different Generator Column Experiments

| Chemical | Trial | Average | SE | CV | n |
|---|---|---|---|---|---|
| $T_4C_{10}$ | 1 | 140.58 | 4.62 | 6.57 | 4 |
| | 2 | 141.29 | 9.74 | 13.79 | 4 |
| $P_5C_{10}$ a | 1 | 27.90 | 1.18 | 8.47 | 4 |
| | 2 | 24.09 | 2.35 | 19.54 | 4 |
| $P_5C_{10}$ b | 1 | 30.64 | 1.30 | 8.47 | 4 |
| | 2 | 26.46 | 2.59 | 19.54 | 4 |
| $P_5C_{10}$ c | 1 | 28.35 | 1.20 | 8.47 | 4 |
| | 2 | 24.48 | 2.39 | 19.54 | 4 |
| $P_5C_{10}$ d | 1 | 27.84 | 1.18 | 8.47 | 4 |
| | 2 | 24.04 | 2.35 | 19.54 | 4 |
| $H_6C_{10}$ a | 1 | 1.64 | 0.07 | 8.63 | 4 |
| | 2 | 1.87 | 0.06 | 6.78 | 4 |
| $H_6C_{10}$ b | 1 | 4.01 | 0.17 | 8.63 | 4 |
| | 2 | 5.04 | 0.17 | 6.78 | 4 |
| $T_4C_{11}$ | 1 | 24.98 | 2.32 | 24.60 | 7 |
| | 2 | 23.41 | 1.54 | 14.69 | 5 |
| | 3 | 26.82 | 1.66 | 16.33 | 7 |
| | 4 | 35.97 | 2.00 | 14.75 | 7 |
| $P_5C_{11}$ c | 1 | 12.74 | 0.88 | 18.31 | 7 |
| | 2 | 5.18 | 0.24 | 10.36 | 5 |
| | 3 | 12.05 | 0.76 | 16.65 | 7 |
| | 4 | 21.08 | 1.42 | 17.85 | 7 |
| $P_5C_{11}$ d | 1 | 12.93 | 0.90 | 18.31 | 7 |
| | 2 | 7.10 | 0.33 | 10.36 | 5 |
| | 3 | 12.60 | 0.79 | 16.65 | 7 |
| | 4 | 23.10 | 1.56 | 17.85 | 7 |
| $P_5C_{11}$ e | 1 | 21.48 | 1.49 | 18.31 | 7 |
| | 2 | 10.96 | 0.51 | 10.36 | 5 |
| | 3 | 20.89 | 1.31 | 16.65 | 7 |
| | 4 | 27.45 | 1.85 | 17.85 | 7 |
| $H_6C_{11}$ a | 1 | 1.63 | 0.15 | 24.39 | 7 |
| | 2 | 0.77 | 0.05 | 16.30 | 6 |
| | 3 | 1.60 | 0.09 | 14.28 | 7 |
| | 4 | 2.66 | 0.21 | 20.96 | 7 |
| $H_6C_{11}$ b | 1 | 7.61 | 0.70 | 24.40 | 7 |
| | 2 | 3.59 | 0.24 | 16. 30 | 6 |
| | 3 | 7.43 | 0.40 | 14.28 | 7 |
| | 4 | 12.36 | 0.98 | 20.96 | 7 |

**Table A.6** Two-Way ANOVA Results Testing Solubilities Determined by The Correction of the Apparent Solubilities to True Solubilities and by Calculation from $P_{(sub)}/H$ data for the Tetra- and Pentachlorodecanes

| Source of Variation | DF | MS | F |
|---|---|---|---|
| Chemical | 2 | 26157 | 3.13 |
| Technique | 1 | 435957 | $5.22^*$ |
| Chemical x Technique | 2 | 80432 | 0.963 |
| Error | 39 | 83498 | |

Note: ANOVA performed using SYSTAT statistical software on log transformed data

D.F. = Degrees of Freedom

MS = Mean Square

F = F-Test

*** = Indicates highly significant differences ($p < 0.001$) at the 99% confidence level

**Table A.7** Two-Way Analysis of Variance of $K_{OC}$s determined For Batch Studies Among Three Sediment Types and 7 Solids Concentration

| Source of Variation | DF | MS | F |
|---|---|---|---|
| Solids Concentration | 6 | 0.303 | 4.03*** |
| Sediment Type | 2 | 0.043 | 0.57 |
| Solids Conc. x Sed Type | 12 | 0.042 | 0.56 |
| Error | 28 | 0.075 | |

Note: ANOVA performed using SYSTAT statistical software on log transformed data

D.F. = Degrees of Freedom

MS = Mean Square

F = F-Test

*** = Indicates highly significant differences ($p < 0.001$) at the 99% confidence level

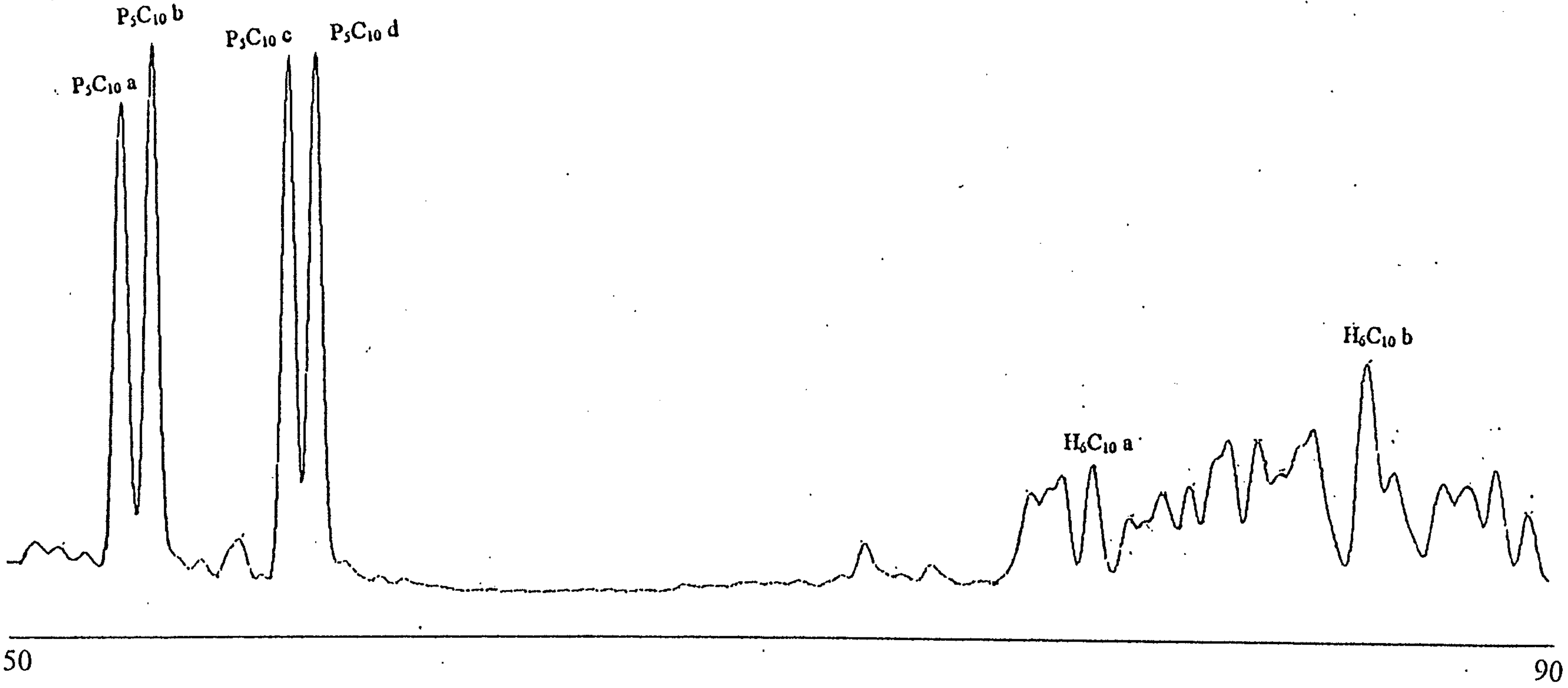

Figure A.1. GC-ECD analysis of penta- and hexachlorodecane isomers from the polychlorinated decane mixture using an extended oven program. Time on x-axis in min. Oven program: 80°C for 1.5 min, 10°C/min to 150°C, 0.6°C/min to 250°C.

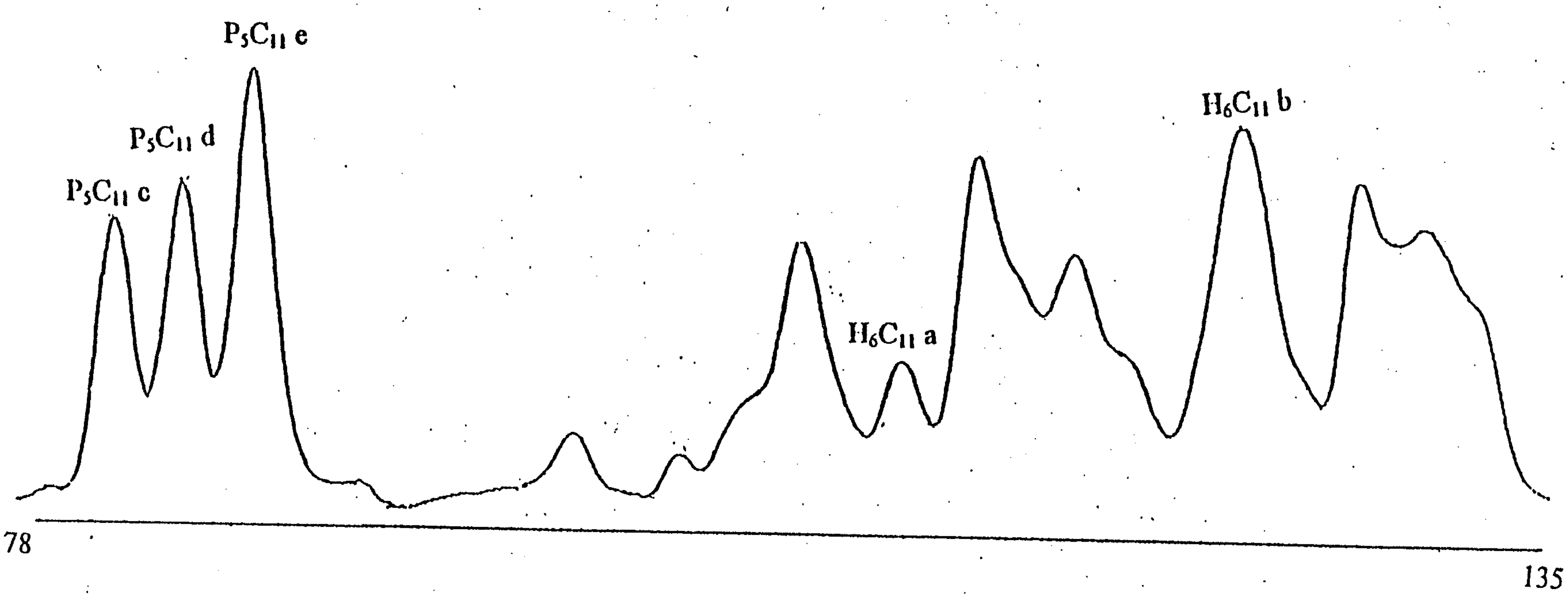

Figure A.2. GC-ECD analysis of penta- and hexachloroundecane isomers from the polychlorinated undecane mixture using an extended oven program. Time on x-axis in min. Oven program: 80°C for 1.5 min, 10°C/min to 150°C, 0.6°C/min to 250°C.

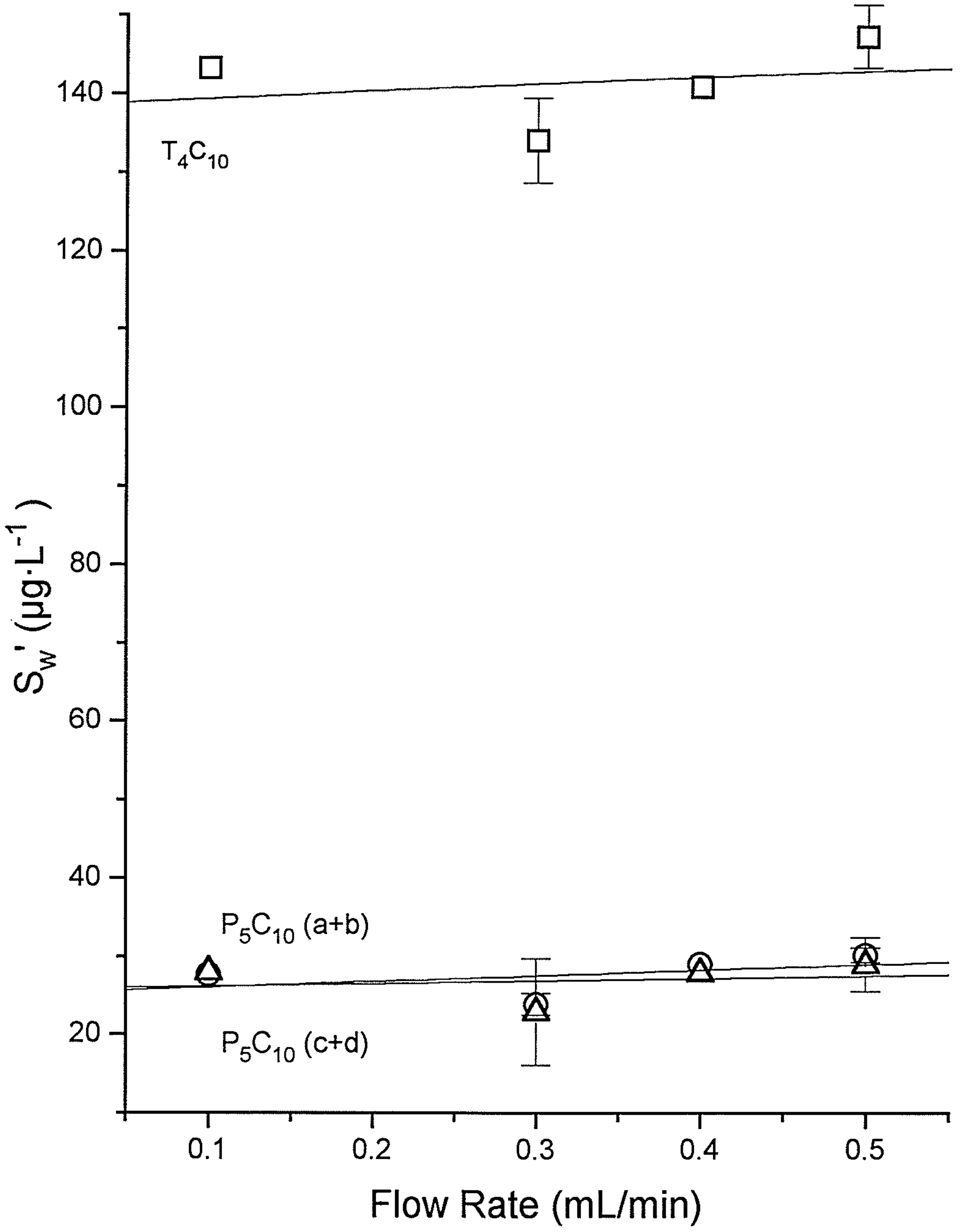

Figure A.3. Apparent solubility of polychlorinated decanes at 25°C *vs* flow rate of water through the generator column. Linear regression analysis yielded slopes not significantly different from zero ($p>0.5$) for all three components.