Pergamon

Chemosphere, Vol. 39, No. 14, pp. 2549-2562, 1999

0045-6535/99/ $ - see front matter

PII: S0045-6535(99)00157-5

OCTANOL/WATER PARTITION COEFFICIENTS OF TOXAPHENE CONGENERS DETERMINED BY THE "SLOW-STIRRING" METHOD

Aaron T. Fisk[1,2], Bruno Rosenberg[2], Chris D. Cymbalisty[2], Gary A. Stern[2] and Derek C.G. Muir [3*]

[1]Department of Soil Science, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

[2]Freshwater Institute, Department of Fisheries and Oceans, 501 University Crescent, Winnipeg, Manitoba R3T 2N6, Canada

[3]National Water Research Institute, Environment Canada, 867 Lakeshore Road, Burlington, Ontario L7R 4A6, Canada

[*] to whom correspondence should be addressed (e-mail address: derek.muir@cciw.ca). Current address of A.T. Fisk is: NWRC, Environment Canada, Hull, Quebec K1A 0H3, Canada (afisk@ccs.carleton.ca)

(Received in USA 23 February 1999; accepted 26 April 1999)

Abstract

The octanol/water partition coefficients (K_{ow}) for a series of technical toxaphene peaks and congeners (n = 36) and organochlorines (pentachlorobenzene (PClBz), hexachlorobenzene (HClBz), mirex and polychlorinated biphenyl congeners (CB) 105, 153 and 209) were determined using the "slow-stirring" technique with two different concentrations at 25°C. K_{ow}s of the organochlorines were consistent with published values and results from the two treatments were in good agreement, suggesting the toxaphene congener K_{ow}s are accurate and precise. Log K_{ow} of toxaphene components / congeners ranged from 4.77 ± 0.076 to 6.64 ± 0.074, and were significantly related to chlorine number (log K_{ow} = 3.4 + [0.28 * # Cl], r^2 = 0.44, $p < 0.001$). Additional variation in toxaphene congener K_{ow}, and likely other physical chemical properties, is due to chlorine position and the structure of the carbon skeleton. These results represent some of the first physical-chemical properties of individual toxaphene congeners.

Introduction

Toxaphene has been one of the most heavily used pesticide in the United States and Canada and other parts of the world during the past 40 years [1], with a cumulative world use between 1950-1993 of 1.33 megatonnes [2]. Due to its toxicity and environmental persistence, it was banned in North America in the early 1980s but use continued until the 1990's in Central and South America, Africa, Eastern Europe and parts of Asia. Toxaphene is ubiquitous and one of the major organochlorine contaminants found in the environment. Components of toxaphene have been measured in water [3], sediment [4], fish [5], marine mammals [6] and seabirds [7], and in remote areas such as the Arctic and Antarctic [8,9].

Technical toxaphene is a complex mixture of chemicals consisting mainly of polychlorinated bornanes, but also of polychlorinated camphenes and camphadienes. Although there are 32,768 possible toxaphene isomers [10], technical toxaphene is believed to contain approximately 300 congeners, ranging from pentachloro to decachloro [11]. Recent advancements in analytical techniques have provided methods to separate and quantify individual toxaphene congeners [12], and characterize the chemical structure of many of these congeners [13,14,15]. Analytical techniques have revealed that the relative abundance of individual toxaphene congeners varies between technical toxaphene and in environmental matrices, such as sediment and fish. This is due to different degradation [4, 16], biotransformation [17], and bioaccumulation [18] of individual congeners, which result from differences in the number and position of chlorine atoms. For example, higher trophic level organisms in the arctic selectively accumulated the more highly chlorinated components of toxaphene [9,14,19].

The octanol/water partition coefficient (K_{ow}) is one of the most commonly used physical-chemical properties to describe the behavior and fate of hydrophobic organic contaminants in the environment. It is a key parameter in many bioaccumulation models [20,21], and is used to describe the partition behavior of contaminants between water and aquatic organisms [22]. Despite the presence and persistence of toxaphene in the environment, and the importance of K_{ow}, there are few data on the K_{ow} of toxaphene and to date no attempts to experimentally measure the K_{ow} of individual toxaphene congeners. The objective of this work was to determine the K_{ow} of a range of toxaphene congeners found in technical toxaphene using the "slow-stirring" technique. This technique has been shown to be an accurate method for determining the K_{ow} of hydrophobic chemicals [23,24]. As a reference, the K_{ow}s of pentachlorobenzene (PClBz); hexachlorobenzene (HClBz); mirex; 2,3,3',4,4'-pentachlorobiphenyl (CB 105); 2,2',4,4',5,5'-hexachlorobiphenyl (CB 153); and 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (CB 209) were also determined and their values compared to known literature values, including those determined by the "slow-stirring" technique.

Methods

Chemicals, octanol spiking and water saturation

Technical toxaphene was purchased from Radian International (Vancouver, BC, Canada), and PClBz, HClBz, mirex and the PCB congeners from Ultra Scientific (North Kingston, RI, USA). All chemicals were purchased at the highest purity, and were used without further purification.

300 ml of octanol was spiked with a known quantity of PClBz, HClBz, mirex, CBs 105, 153 and 209 (concentration range = 20 - 300 $\mu g \cdot ml^{-1}$). One half of the volume was then spiked with a known quantity of technical toxaphene (low treatment total toxaphene concentration = 43 $\mu g \cdot ml^{-1}$) the other half with 10 times the quantity of toxaphene (high treatment total toxaphene concentration = 430 $\mu g \cdot ml^{-1}$).

Octanol saturated water was prepared by adding octanol (50 ml) to the surface of distilled water in 20 L glass carboys. A Teflon stirring bar slowly mixed the water, without disturbing the octanol surface film, for 48 hours. Saturation of water by octanol has been shown to take less than 48 hrs [24].

Experimental Procedure

The reaction vessels consisted of Pyrex glass 6 L flasks, fitted with glass taps and Teflon stopcocks approximately one cm from the bottom of the flasks (similar to de Bruijn et al. [24]. Following the addition of a Teflon stirring bar and 3.5 L of octanol saturated water to each flask, 20 ml of the toxaphene-spiked-octanol was carefully added by allowing the octanol to run slowly down the side of the flask. This avoided any mixing of the spiked octanol and the octanol-saturated water. Careful not to cause any mixing, a slow vortex, one cm height, was created with the stirring bar.

All reaction vessels were kept in a climate controlled room at a constant temperature of 25°C. There were five and four replicates (flasks) per low and high treatment, respectively, and the low and high treatments were carried out sequentially. On days 2, 7, 10 and 14, 500 ml of water was removed from each treatment and spiked with recovery standard (CB 30 and octachloronaphthalene (OCN)). CB 30 and OCN recoveries were uniformly greater than 80%, and concentrations were not corrected for recoveries. 20-30 ml of water was allowed to run from the tap prior to sample collection. After each collection the vortex height in each reaction vessel was corrected to 1 cm.

Extraction and Analysis

Toxaphene, PClBz, HClBz, mirex and the PCB congeners were extracted from water by shaking the water with 75 ml of DCM in a sealed 1 L separatory funnel for 15 min. The water/DCM slurry was allowed to stand, the DCM was drawn off, and the procedure was repeated a second time. The DCM extracts were combined and exchanged for hexane prior to fractionation. Octanol samples were diluted by 1000 in hexane prior to fractionation. The water extracts and diluted octanol samples were fractionated by applying them to a Florisil column (8 g, 1.2% deactivated). The toxaphene and other organochlorines were recovered by consecutive elution with 35 mL hexane (F1) and 38 mL of 85% hexane: 15% DCM (F2) (Table 1). All fractions were evaporated, transferred to 2,2,4-trimethyl pentane and were evaporated to 0.2 ml for the low treatment samples and 1.5 ml for the high treatment and octanol samples. Aldrin and/or tribromobenzene were added as volume corrector(s).

Samples were analyzed on a Varian 3600 gas chromatograph (GC) equipped with a 60 m X 0.25 mm DB-5 column and an ^{63}Ni-electron capture detector (ECD). The carrier gas was H_2, and N_2 was used as the make-up gas for the ECD. A total of 36 toxaphene congeners were quantified (Table 1 and Figure 1) by using the "Parlar 22 Components Standard" standard. Additional characterization of components in the ECD chromatograms were carried out by mass spectrometry using a HP 5973 MSD in electron-capture negative ion mode (CH_4 moderating gas). Technical toxaphene (40 $pg \cdot \mu l^{-1}$) was analyzed on a 30 m x 0.25 mm DB-5 MS column (0.25 μm film thickness).

Table 1: The relative retention time to T2 and T12, percent fractionation between Florisil fractions F1 and F2, chemical structure and common names of the 36 toxaphene congeners and 6 organochlorines identified for K_{ow}.

	Relative retention time to:		Florisil Fraction. (%)			
Chemical^A	T2	T12	F1	F2	chemical structure (reference)	common names
Toxaphene congeners						
Parlar 11	0.86	0.73	3	97	2,2,3-exo,8,9,10-hexachlorocamphene	
Parlar 12	0.87	0.74	0	100	2-exo,3-endo,8,8,9,10 α-hexachlorocamphene	
Parlar 15	0.90	0.77	48	52	2-exo,3-endo,7,8,9,10 α-hexachlorocamphene	
B7-499	0.95	0.80	17	83	2.2,5,5,9c,10a,10b-heptachlorobornane	TSE, Parlar 21
Parlar 25	0.99	0.84	0	100	2,2,3-exo,8b,8c,9c,10μ-heptachlorocamphene	
B8-1413	1.00	0.85	45	55	2-exo,3-endo,5-exo,6-endo, 8,8,10,10 -octachlorobornane	Parlar 26, Tox 8, T2, 169-603
CTT-UNK1	1.02	0.87	0	100	octachlorobornane	
Parlar 31	1.04	0.88	8	92	2,2,3-exo,8a,8b,9b,9c,10-α-octachlorocamphene	
B7-515	1.04	0.89	1	99	2,2,5-endo,6-exo,8b,9c,10a-heptachlorobornane	Toxicant b, Parlar 32
CTT-UNK2	1.05	0.89	1	99	heptachlorobornane	
CTT-UNK3	1.06	0.90	10	90	octachlorobornane	
CTT-UNK4	1.08	0.92	4	96	octachlorobornane	
B8-789	1.09	0.92	100	0	2,2,5,5,9b,9c,10a,10b-octachlorobornane	Parlar 38
CTT-UNK5	1.09	0.93	0	100	nonachlorobornane	
B8-531	1.11	0.94	3	97	2-exo,3-endo,5-exo,6,6,8b,9c, 10c (or 10a)-octachlorobornane	TS2, Parlar 39
CTT-UNK6	1.11	0.94	0	100	octachlorobornane	
B8-1414	1.12	0.95	0	100	2-endo,3-exo,5-endo,6-exo,8c, 9b,10a,10c (or 10b)- octachlorobornane	Parlar 40, TS3, 297-243
B8-1945	1.12	0.95	0	100	2-exo,3-endo,5-exo,8c,9b,9c, 10a,10b-octachlorobornane	Parlar 41, 41-643
B8-806/809	1.13	0.96	0	100	2-exo,3-endo,6,6,8b,8c,9c,10c (or 10a)-octachlorobornane / 2-exo,3-endo,6,6,8b,9b,9c,10a (or 10b)-octachlorobornane	Parlar 42, Toxicant A, TS4
B8-2229	1.14	0.96	0	100	2-exo,5,5,8c,9b,9c,10a,10b-octachlorobornane	Parlar 44, 97-643
CTT-UNK7	1.15	0.98	4	96	nonachlorobornane	
B9-1679	1.18	1.00	43	57	2-exo,3-endo,5-exo,6-endo, 8,8,9,10,10-nonachlorobornane	Parlar 50, Toxicant Ac, Tox 9, T12, 297-303
B8-786	1.19	1.01	0	100	2,2,5,5,8c,9b,10a,10b-octaclorobornane	Parlar 51
CTT-UNK8	1.20	1.02	0	100	octachlorobornane	
CTT-UNK9	1.22	1.03	4	96	nonachlorobornane	

Table 1 cont'd

B9-1046	1.23	1.04	13	87	2,2,5-endo,6-exo,8b,8c,9c,10a,10c-nonachlorobornane	Parlar 56
B9-715	1.24	1.06	80	20	2,2,3-exo,5,5,8b,9c,10a,10b-nonachlorobornane	Parlar 58
B9-1049	1.25	1.06	12	88	2,2,5-endo,6-exo,8c,9b,9c,10a, 10b-octachlorobornane	Parlar 59
B9-1025	1.28	1.09	6	94	2,2,5,5,8c,9b,9c,10a,10b-nonachlorobornane	Parlar 62, 99-643
CTT-UNK10	1.29	1.10	7	93	octachlorobornane	
B9-2206	1.30	1.10	0	100	2-exo,3-endo,5-exo,6-exo,8b, 8c,9c,10,10-nonachlorobornane	Parlar 63
CTT-UNK11	1.32	1.12	0	100	nonachlorobornane	
CTT-UNK12	1.34	1.14	100	0	nonachlorobornane	
CTT-UNK13	1.37	1.16	0	100	nonachlorobornane	
B10-1110	1.42	1.20	77	23	2,2,5,5,6-exo,8c,9b,9c,10a,10b-decachlorobornane	Parlar 69
CTT-UNK14	1.42	1.21	34	66	decachlorobornane	
Organochlorines						
PClBz	0.36	0.30	95	5	pentachlorobenzene	
HClBz	0.51	0.44	90	10	hexachlorobenzene	
mirex	1.31	1.11	90	10	1,3,4-metheno-1H-cyclobuta-(cd)pentalene,1,1a,2,2,3,3a,4,5,5,5s,5b, 6-dodecachloro-octahydro	
CB 105	1.07	0.91	100	0	2',3,3',4,4'-pentachlorobiphenyl	
CB 153	1.07	0.91	100	0	2,2',4,4',5,5'-hexachlorobiphenyl	
CB 209	1.63	1.38	100	0	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	

[A] Toxaphene congener numbers are based on those described in Andrews and Vetter [34] or by the "Parlar numbers" which have been assigned by their elution [35,36]. Unknown peaks are identified as CTT-UNK#, the # is assigned by elution order.

Toxaphene congener selection

Selection of peaks from the technical toxaphene for quantification were based on the 22 toxaphene congeners in the "Parlar 22 Components Standard" (Dr. Ehrenstorfer, GnbH Augsburg, Germany) and predominant peaks in the technical standard that are also observed in environmental samples [25]. The components of these "predominant peaks" have not been characterized and there are no chemical names. These unidentified peaks have been labeled CTT-UNK (component(s) of technical toxaphene-unknown) followed by a number based on their order of elution off the GC-column.

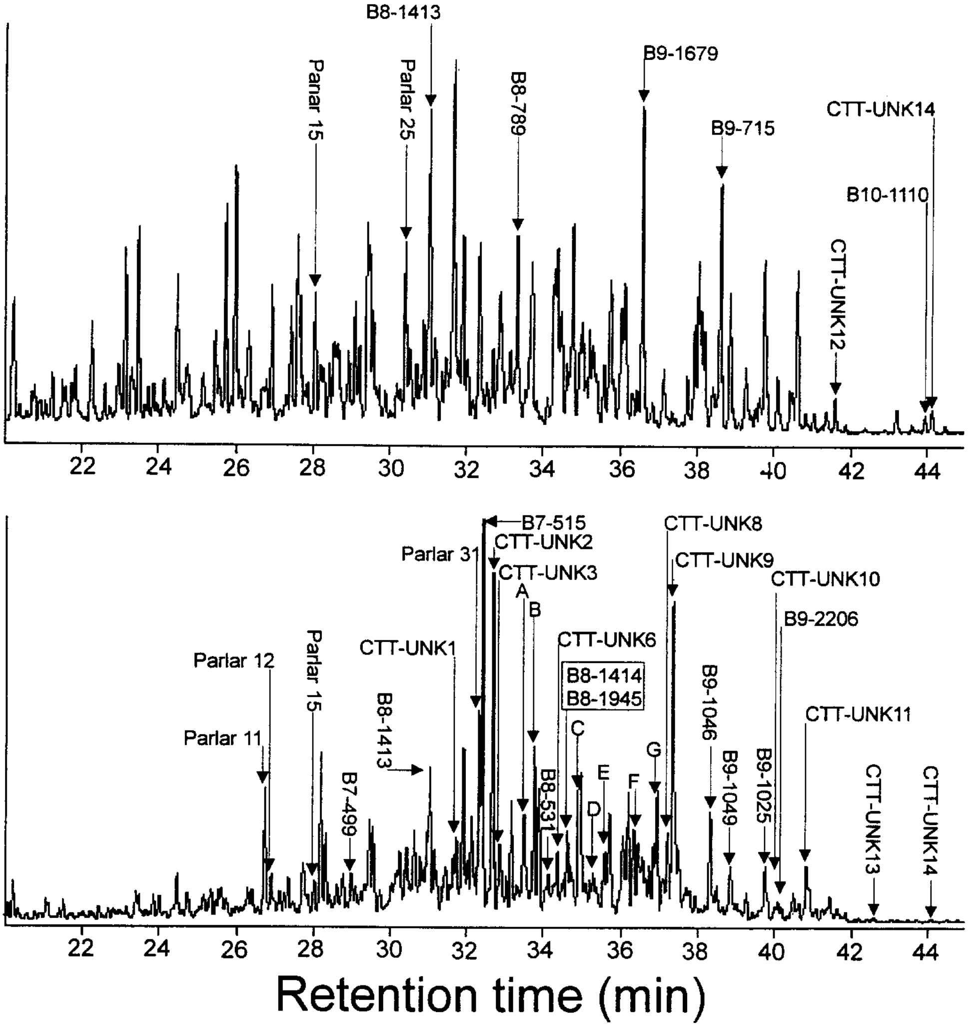

Figure 1: GC-ECD chromatograms of F1 and F2 water samples collected on day 14. Peaks identified by a letter are: A - CTT-UNK4; B - CTT-UNK5; C - B8-806/809; D - B8-2229; E - CTT-UNK7; F - B9-1679; G - Parlar 51.

Data Analysis

K_{ow}s were calculated using the equation:

$$K_{ow} = [\text{CTT octanol}] / [\text{CTT water}]$$

for equal sample volumes after the system had come to equilibrium. Octanol concentrations were determined from octanol collected on day 14. ANOVA and linear regressions were performed with Systat for Windows (Version 5, Systat, Evanston, IL, USA).

Results and Discussion

Equilibrium Time

The concentrations of all chemicals reached equilibrium between the water and octanol by day 7 of the experiment (Figure 2). For many compounds, including PClBz and HClBz, equilibrium was reached by day 2. This is consistent with de Bruijn et al. [24] who reported that di- and penta-chlorobenzenes reached equilibrium between water and octanol in slow-stir experiments within 24 hours, and *p,p*-DDT within 3-4 days.

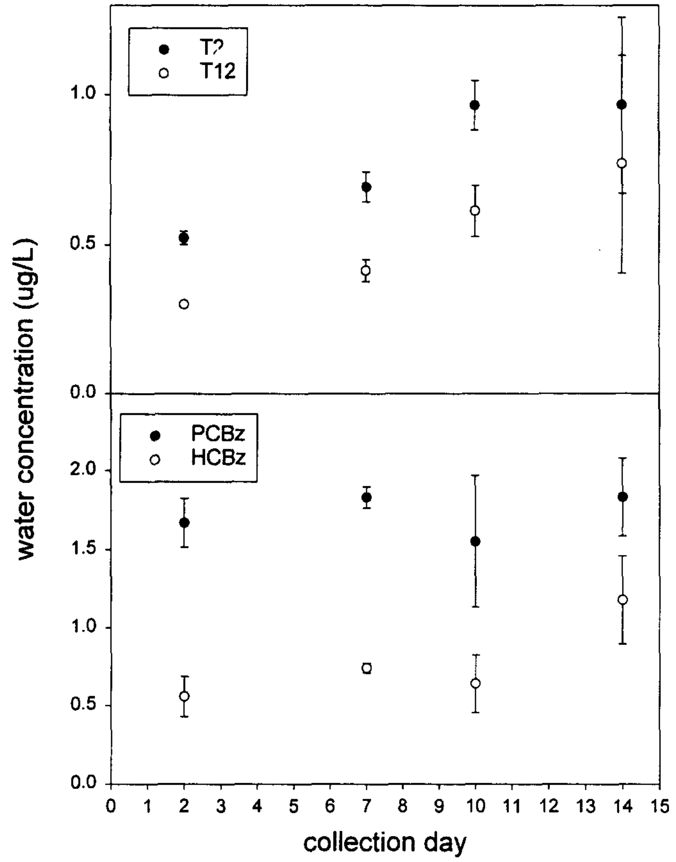

Figure 2: Water concentrations of T2, T12, PClBz and HClBz on collection days 2, 7, 10 and 14.

Accuracy

Log K_{ow} values for PClBz, HClBz, mirex and CB 105 agreed well with the literature values, but values for CB 153 and 209 were lower (Table 2). There has been a range of log K_{ow} values reported for PCB congeners (see Mackay et al. [26]), which vary to a certain extent by the method used. The log K_{ow}s of CB

153 and 209 reported in this paper fall within the low end of the range reported in Mackay et al. [26]. The log K_{ow} value for CB 209 is also lower than that reported using the slow-stirring method [24]. However, octanol concentrations of CB 153 and 209, both of which are extremely hydrophobic, were low (20 $\mu g \cdot ml^{-1}$) compared to the other chemicals, resulting in water concentrations that were below detection limits for many samples. Only 6 water samples from the high treatment had measurable amounts of CB 209, and CB 209 was not quantifiable in any of the low treatment water samples. Discrepancies between the K_{ow}s of CBs 153 and 209 reported in this work and published literature can most likely therefore be attributed to the detection limits problems and not due to problems with this experiment or the method. Water concentrations of all toxaphene congeners were well above detection limits.

Table 2: Slow-stir determined (mean ± 1 SE for days 7, 10 and 14) and literature log K_{ow} values for PClBz, HClBz, mirex and CB congeners 105, 153 and 209. Day 7, 10 and 14.

Chemical	low treatment log K_{ow} (n)	high treatment log K_{ow} (n)	literature log K_{ow} slow-stir	literature log K_{ow}
PClBz	5.10 ± 0.071 (n = 12)	4.97 ± 0.118 (n = 10)	5.18 ± 0.021^{A}	5^{B}
HClBz	5.67 ± 0.082 (n = 12)	5.78 ± 0.077 (n = 10)	5.73 ± 0.009^{A}	5.5^{B}
mirex	7.24 ± 0.096 (n = 12)	7.13 ± 0.041 (n = 9)	-	6.9^{C}
CB 105	6.02 ± 0.052 (n = 12)	5.67 ± 0.100 (n = 10)	-	6^{B}
CB 153	6.58 ± 0.117 (n = 8)	5.61 ± 0.096 (n = 10)	-	6.9^{B}
CB 209	nd	7.59 ± 0.178 (n = 3)	8.27 ± 0.001^{A}	8.26^{B}

^{A} - [24]; ^{B} - [26]; ^{C} - [37]

Despite the discrepancy for PCB K_{ow} values, relationships between K_{ow}s from this work and published values were highly significant (Figure 3), suggesting that the accuracy of the K_{ow} values reported for the toxaphene congeners are high. For the low treatment experiment the relationships had an intercept near 0 and a slope near 1, but the intercept and slope from the high treatment were not as close to 0 and 1, respectively (Figure 3). The relationship for the high treatment appeared to be driven by the low K_{ow} values of CBs 153 and 209 determined by the slow-stir method. Furthermore, the K_{ow}s for toxaphene congeners were generally in the range of CB 105 and HClBz and thus in a window where excellent agreement was found between K_{ow} of known compounds and literature values.

Precision

Log K_{ow} values determined in the low and high treatments are in good agreement for the PClBz, HClBz, mirex, PCB congeners and toxaphene congeners (Tables 2 and 3, Figure 4). For all toxaphene congeners, treatment (i.e., low and high) and congener X treatment (ANOVA, p = 0.01) did not have a significant effect on K_{ow}. The close agreement between the low and high treatments and the low variation between treatments suggest that the results of this work are precise.

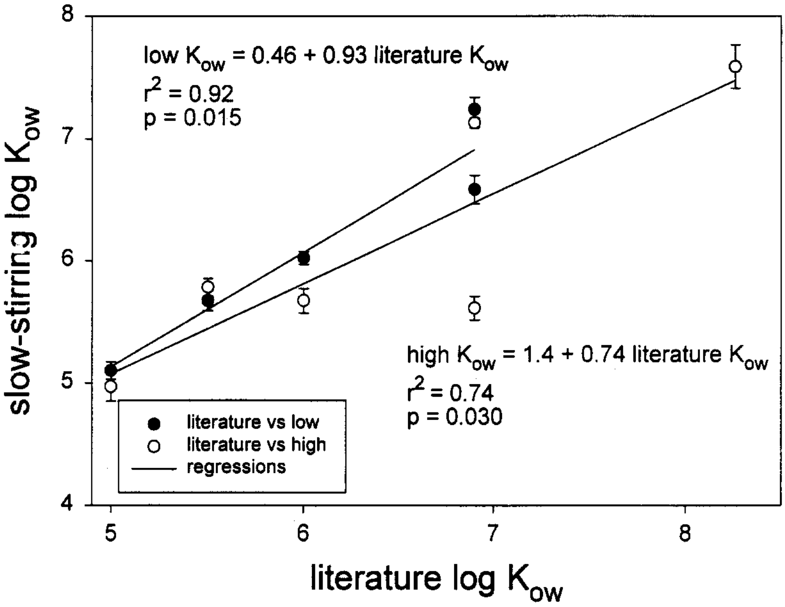

Figure 3: Relationships between slowing-stir K_{ow} for the low and high treatment and literature K_{ow} for PClBz, HClBz, CB 105, 153 and 209, and mirex (see table 1 for references).

Toxaphene congener K_{ow}s

Log K_{ow}s of the 36 toxaphene components / congeners ranged from 4.77 ± 0.076 to 6.64 ± 0.74 (Table 3), and fall within the range of the two log K_{ow}s, 4.82 [27] and 6.4 [28], published for toxaphene as a single group. Geyer et al. [29] estimated the log K_{ow} of 6 toxaphene congeners (B8-1413, B8-1414, B8-1945, B8-2229, B9-1679 and B9-1025) using a computer program that estimates log K_{ow} based on chemical structure. For all congeners, the estimates of Geyer et al. [29] were 0.39 to 1.76 fold higher than our "slow-stir" determined log K_{ow}s. Fisk et al. [18] estimated the log K_{ow}s of Parlar 21, B8-1413 and B9-1679 by the fragment constant method and by the relationship between log K_{ow} and half life in juvenile rainbow trout determined for a series of recalcitrant organochlorines. The fragment constant estimates for Parlar 21, B8-1413 and B9-1679 were higher (6.2, 6.5 and 6.6, respectively) but the log K_{ow}-half life relationship estimates (5.4, 5.8 and 5.8, respectively) were similar to those determined by the "slow-stir" method.

Log K_{ow} had a positive linear relationship with chlorine number (log K_{ow} = 3.4 + [0.28 * # Cl], r^2 = 0.44, $p < 0.001$). This is not surprising because increases in chlorine result in higher K_{ow} for other organic compounds, such as PCBs and chlorinated paraffins [30,31]. The remaining variation in toxaphene K_{ow} is likely due to chlorine position and the structure of the carbon skeleton (i.e., bornanes, camphenes and camphadienes). However, the limited number of characterized toxaphene congeners makes it difficult to assess which chlorine substitution patterns have the greatest effect on K_{ow}. Removing the five chlorinated camphenes from the regression analysis produced a similar regression result (log K_{ow} = 2.5 + [0.38 * # Cl], $r^2 = 0.46$, $p < 0.001$), suggesting that chlorine position plays a more important role in toxaphene congener K_{ow}s than carbon skeleton structure.

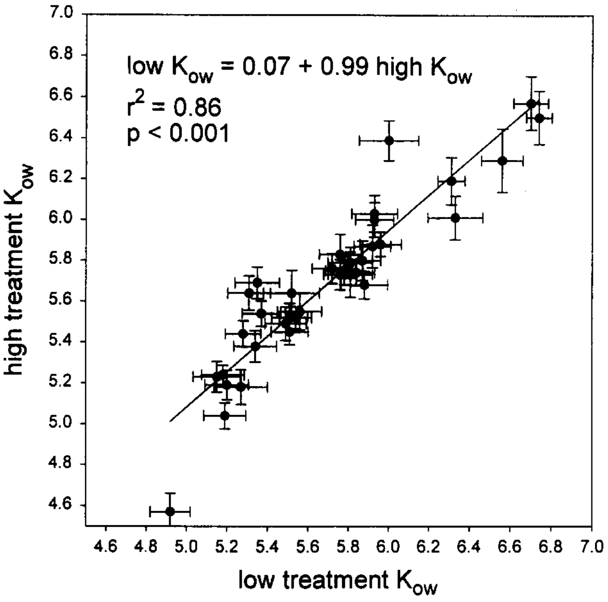

Figure 4: Relationship between low treatment K_{ow} and high treatment K_{ow} for 36 components of technical toxaphene.

Using technical toxaphene to determine the K_{ow} of individual congeners is problematic. Estimates on the number of compounds in technical toxaphene range from 300 [11] to 670 [32], although this latter number of compounds has not been resolved by high-resolution gas chromatography [12]. Most GC peaks in technical toxaphene, when analyzed by multidimensional GC, represent more than one compound [33]. For example, Zhu et al. [11] found that T2 and T12, congeners commonly found in the environment and quantified in this work, co-elute with several other congeners in technical toxaphene. However, retention time can be correlated to log K_{ow} for a series of similar chemicals, although this is not commonly done with GC [26], and co-eluting toxaphene congeners are likely to have a similar K_{ow}. A significant relationship between log K_{ow} and retention time (log K_{ow} = 3.2 + [0.07 * retention time], $r^2 = 0.59$, $p < 0.001$) was observed for the toxaphene congeners. This is because the lower chlorinated compounds generally elute of the column first and we know K_{ow} is correlated with chlorine number.

Table 3: Log K_{ow} (mean ± 1 SE) values of toxaphene congeners based on data from days 7, 10 and 14.

Chemical	low treatment log K_{ow} (mean ± 1 SE, n = 14)	high treatment log K_{ow} (mean ± 1 SE, n = 11)	mean (low and high) log K_{ow} (mean ± 1 SE, n = 25)
Parlar 11	5.18 ± 0.105	5.24 ± 0.047	5.20 ± 0.062
Parlar 12	5.31 ± 0.105	5.64 ± 0.084	5.45 ± 0.076
Parlar 15	5.28 ± 0.088	5.44 ± 0.064	5.35 ± 0.058
B7-499	5.51 ± 0.091	5.45 ± 0.062	5.49 ± 0.057
Parlar 25	5.37 ± 0.096	5.54 ± 0.063	5.44 ± 0.062
B8-1413	5.51 ± 0.088	5.52 ± 0.070	5.52 ± 0.057
CTT-UNK1	5.34 ± 0.106	5.38 ± 0.077	5.36 ± 0.067
Parlar 31	5.49 ± 0.102	5.49 ± 0.082	5.49 ± 0.066
B7-515	5.27 ± 0.131	5.18 ± 0.085	5.23 ± 0.081
CTT-UNK2	5.20 ± 0.108	5.19 ± 0.072	5.20 ± 0.067
CTT-UNK3	5.54 ± 0.078	5.52 ± 0.055	5.53 ± 0.049
CTT-UNK4	4.92 ± 0.100	4.57 ± 0.090	4.77 ± 0.076
B8-789	5.92 ± 0.091	5.87 ± 0.104	5.90 ± 0.067
CTT-UNK5	5.19 ± 0.104	5.04 ± 0.064	5.13 ± 0.065
B8-531	5.72 ± 0.099	5.76 ± 0.074	5.74 ± 0.063
CTT-UNK6	5.93 ± 0.114	6.03 ± 0.090	5.97 ± 0.374
B8-1414	5.52 ± 0.138	5.64 ± 0.112	5.57 ± 0.091
B8-1945	5.15 ± 0.116	5.23 ± 0.075	5.19 ± 0.072
B8-806/809	5.81 ± 0.110	5.73 ± 0.111	5.78 ± 0.078
B8-2229	5.76 ± 0.081	5.73 ± 0.074	5.75 ± 0.055
CTT-UNK7	5.35 ± 0.110	5.69 ± 0.077	5.50 ± 0.077
B9-1679	5.87 ± 0.091	5.80 ± 0.098	5.84 ± 0.066
B8-786	5.76 ± 0.104	5.83 ± 0.099	5.79 ± 0.072
CTT-UNK8	5.56 ± 0.109	5.55 ± 0.089	5.56 ± 0.071
CTT-UNK9	6.00 ± 0.148	6.39 ± 0.098	6.17 ± 0.100
B9-1046	5.84 ± 0.091	5.74 ± 0.064	5.80 ± 0.058
B9-715	6.31 ± 0.067	6.19 ± 0.116	6.26 ± 0.063
B9-1049	5.78 ± 0.093	5.75 ± 0.069	5.77 ± 0.059
B9-1025	5.93 ± 0.095	6.00 ± 0.085	5.96 ± 0.064
CTT-UNK10	5.88 ± 0.117	5.68 ± 0.067	5.79 ± 0.073
B9-2206	5.96 ± 0.103	5.88 ± 0.060	5.93 ± 0.063
CTT-UNK11	5.81 ± 0.111	5.79 ± 0.076	5.80 ± 0.069
CTT-UNK12	6.56 ± 0.101	6.29 ± 0.155	6.44 ± 0.091
CTT-UNK13	6.33 ± 0.135	6.01 ± 0.107	6.19 ± 0.093
B10-1110	6.74 ± 0.063	6.50 ± 0.130	6.64 ± 0.070
CTT-UNK14	6.70 ± 0.085	6.57 ± 0.130	6.64 ± 0.074

In summary, K_{ow}'s have been determined for 36 component peaks of technical toxaphene. The identity of 22 of these peaks can be assigned based on retention time matching Parlar standards while the remaining 14 are characterized by chlorine content (via GC-MS) and relative retention times. While there is still uncertainty about the true K_{ow}'s of each congener, because there are numerous co-elution of many of the congeners with unknown or partially characterized components, we believe these results represent a major improvement over the previous situation in which there were no K_{ow} measurements of individual purified toxaphene congeners.

Acknowledgments

Funding for this work was provided in part by the DFO-Toxic Chemicals Program (Mike Whittle) and a University of Manitoba graduate fellowship awarded to Aaron Fisk. We thank the Freshwater Institute, Department of Fisheries and Oceans Canada for use of lab facilities and Sean Backus (NWRI, Environment Canada, Burlington, ON) for GC-MSD work on technical toxaphene.

References

[1] M.A. Saleh. Toxaphene: Chemistry, biochemistry, toxicity and environmetal fate. *Rev. Environ. Toxicol. Chem.* **118**, 1-8 (1991).

[2] E.C. Voldner, and Y.F. Li. Global usage of toxaphene. *Chemosphere* **27**, 2073-2078 (1993).

[3] J.R. Kucklick, T.F. Bidleman, L.L. McConnell, M.D. Walla, and G.P. Ivanov. Organochlorines in the water and biota of Lake Baikal, Siberia. *Environ. Sci. Technol.* **28**, 31-37 (1994).

[4] B.M. Miskimmin, D.C.G. Muir, D.W. Schindler, G.A. Stern, and N.P. Grift. Chlorobornanes in sediments and fish 30 years after toxaphene treatment of lakes. *Environ. Sci. Technol.* **29**, 2490-2495 (1995).

[5] S.T. Glassmeyer, D.S. de Vault, T.R. Myers and R.A. Hites. Toxaphene in great lakes fish: A temporal, spatial, and trophic study. *Environ. Sci. Technol.* **31**, 84-88 (1997).

[6] D.C.G. Muir, C.A. Ford, R.A. Stewart and T.F. Bidleman. Organochlorine contaminants in narwhal (*Monodon monoceros*) from the Canadian arctic. *Environ. Pollut.* **75**, 307-316 (1992).

[7] U. Wideqvist, B. Jansson, M. Olsson, T. Odsjo, L. Reutergardh and U-B. Uveno. Temporal trends of PCC on guillemot eggs from the Baltic. *Chemosphere* **27**, 1987-2001 (1993).

[8] H-R. Buser and M.D. Muller. Isomer- and enantiomer-selective analyses of toxaphene components using chiral high-resolution gas chromatography and detection by mass spectrometry/mass spectrometry. *Environ. Sci. Technol.* **28**, 119-128 (1994).

[9] B.T. Hargrave, D.C.G. Muir and T.F. Bidleman. Toxaphene in amphipods and zooplankton from the arctic ocean. *Chemosphere* **27**, 1949-1963 (1993).

[10] W. Vetter and B. Luckas. Theoretical aspects of polychlorinated bornanes and the composition of toxaphene in technical mixtures and environmental samples. *Sci. Total Environ.* **160/161**, 505-510 (1995).

[11] J. Zhu, M.J. Mulvihill and R.J. Norstrom. Characterization of technical toxaphene using combined high-performance liquid chromatography-gas chromatography-electron capture negative ionization mass spectrometry techniques. *J. Chromat.* **669**, 103-117 (1994).

[12] D.C.G. Muir and J. de Boer. Recent developments in the analysis and environmental chemistry of toxaphene with emphasis on the marine environment. *Trends Anal. Chem.* **14**, 56-66 (1995).

[13] M.D. Loewen, G.A. Stern, J.B. Westmore, D.C.G. Muir and H. Parlar. Characterization of three major toxaphene congeners in arctic ringed seal by electron ionization and electron capture negative ion mass spectrometry. *Chemosphere* **36**, 3119-3135 (1998).

[14] G.A. Stern, D.C.G. Muir, C.A. Ford, N.P. Grift, E. Dewailly, T.F. Bidleman and M.D. Walla. Isolation and identification of two major recalcitrant toxaphene congeners in aquatic biota. *Environ. Sci. Technol.* **26**, 1838-1840 (1992).

[15] G.A. Stern, M.D. Loewen, B.M. Miskimmin, D.C.G. Muir and J.B. Westmore. Characterization of two major toxaphene components in treated lake sediment. *Environ. Sci. Technol.* **30**, 2251-2258 (1996).

[16] H. Parlar, D. Schulz-Jander, G. Fingerling, G. Koske, D. Angerhofer and J. Burhenne. The role of biotic and abiotic degradation processes during the formation of typical toxaphene peak patterns in aquatic biota. *Organohalogen Comp.* **35**, 221-224 (1998).

[17] P.D. Delorme, D.C.G. Muir, W.L. Lockhart, K.H. Mills and F.J. Ward. Depuration of toxaphene in lake trout and white suckers in a natural ecosystem following a single I.P. dose. *Chemosphere* **27**, 1965-1973 (1993).

[18] A.T. Fisk, R.J. Norstrom, C.D. Cymbalisty and D.C.G. Muir. Dietary accumulation and depuration of hydrophobic organochlorines: Bioaccumulation parameters and their relationship with octanol/water partition coefficient. *Environ. Toxicol. Chem.* **17**, 951-961 (1998).

[19] T.F. Bidleman, M.D. Walla, D.C.G. Muir and G.A. Stern. Selective accumulation of polychlorocamphenes in aquatic biota from the Canadian arctic. *Environ. Toxicol. Chem.* **12**, 701-709 (1993).

[20] R.V. Thomann. Bioaccumulation model of organic chemical distribution in aquatic food chains. *Environ. Sci. Technol.* **23**, 699-707 (1989).

[21] M.C. Barber, L.A. Suarez and R.R. Lassiter. Modelling bioaccumulation of organic pollutants in fish with an application to PCBs in Lake Ontario salmonids. *Can. J. Fish. Aquat. Sci.* **48**, 318-337 (1991).

[22] J. Devillers, S. Bintein and D. Domine. Comparison of BCF models based on log P. *Chemosphere* **33**, 1047-1065 (1996).

[23] D. Brooke, I. Nielsen, J. de Bruijn and J. Hermens. An interlaboratory evaluation of the stir-flask method for the determination of ocatnol-water partition coefficients. *Chemopshere* **21**, 119-133 (1990).

[24] J. de Bruijn, F. Busser, W. Seinen and J. Hermens. Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the "slow-stirring" method. *Environ. Toxicol. Chem.* **8**, 499-512 (1989).

[25] D.C.G. Muir, N.P Grift and C.A. Ford. Toxaphene quantification using individual response factors: Method description and application to fish and marine mammal extracts. *Presented at the Toxaphene Workshop*, Feb. 4-6, Burlington, ON, Canada (1993).

[26] D. Mackay, W.Y. Shiu and K.C. Ma. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals.* Vol. I. Lewis Publishers, Chelsea, MI, USA (1993).

[27] P.H. Howard. *Handbook of environmental fate and exposure data for organic chemicals. Vol. III. Pesticides.* Lewis Publishers Inc., Chelsea, MI, USA. 684 p (1991).

[28] J.R. Sullivan and D.E. Armstrong. *Toxaphene status in the Great Lakes. Sea Grant Institute, Priority Pollutants Status Rep. No. 2.*, University of Wisconsin, Madison, WI, USA (1985).

[29] H.J. Geyer, A. Kaune, K-W. Schramm, G. Rimkus, W. Vetter, A. Kettrup and D.C.G. Muir. Bioconcentration factors (BCFs) of specific persistent polychlorinated bornane (toxaphene) congeners in fish and comparison with bioaccumulation factors (BAFs) of biota from the marine environment. *Organohalogen Comp.* **35**, 263- 268 (1998).

[30] D.W. Hawker and D.W. Connell. Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **22**, 382-387 (1988).

[31] D.T.H.M. Sijm and T. L. Sinnige. Experimental octanol/water partition coefficients of chlorinated paraffins. *Chemosphere* **31**, 4427-4435 (1995).

[32] B. Jansson and U. Wideqvist. Analysis of toxaphene (PCC) and chlordane in biological samples by NCI mass spectrometry. *Intern. J. Environ. Anal. Chem.* **13**, 309-322 (1983)

[33] J. De Boer, H-J. de Gaus and U.A.T. Brinkman. Multidimensional gas chromatographic analysis of toxaphene. *Environ. Sci. Technol.* **31**, 873-879 (1996).

[34] P, Andrews and W. Vetter. A systematic nomenclature system for toxaphene congeners Part 1: Chlorinated bornanes. *Chemosphere* **31**, 3879-3886 (1995).

[35] J. Burhenne, D. Hainzl, L. Xu, B. Veith, L. Alder and H. Parlar. Preparation and structure elucidation of high-chlorinated bornane derivatives for the quantification of toxaphene residues in environmental samples. *Fresenius. J. Anal. Chem.* **346**, 779-785 (1993).

[36] D. Hainzl, J. Burhenne and H. Parlar. Spectroscopic characterization of environmentally relevant C10-chloroterpenes from a photochemically modified standard. *Fresenius. J. Anal. Chem.* **351**, 271-285 (1995).

[37] L.R. Suntio, W.Y. Shiu, D. Mackay, J.N. Seiber and D. Glotfelty. Critical review of Henry'sLaw Constants for pesticides. *Rev. Environ. Contam. Toxicol.* **103**, 1-59 (1988).