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Determination of Octanol-Water Partition Coefficients for the Major Components of Technical Chlordane

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Data obtained from the measurement of physicochemical properties for contaminant chemicals can be used to help understand the fate and distribution of such chemicals in the environment. Parameters such as aqueous solubility, vapor pressure and various partition coefficients have been incorporated into quantitative structure-activity relationships (QSARs) which can be used to predict the toxicity or environmental persistence of a given chemical (Saito et al. 1993).

In particular, the octanol-water partition coefficient (K_{ow}) has been shown to correlate strongly with the bioconcentration factor (BCF) for many different hydrophobic organic compounds (Veith et al. 1979; Mackay 1982), and has been used for the prediction of LC50 values in several organisms (Hermens 1990; De Bruijn and Hermens 1991). K_{ow} can also be used to describe sorption of pollutants to sediment if the organic carbon content of the sediment is known (Karickhoff 1981; Di Toro 1985). Hence K_{ow} values are useful tools for determining appropriate sediment quality criteria.

Several methods have been used to detemine K_{ow} values.(Noble 1993; Niimi 1991; Mabey et al. 1982) The most common direct technique is the shake flask method in which the test chemical is added to a vessel containing octanol and water which is then shaken vigorously to facilitate equilibration of the analyte between the two phases (Sanborn et al. 1976). This method is not suitable for compounds with K_{ow} values greater than about 4 since the water phase becomes contaminated with an octanol emulsion. This causes a significant error in determining the concentration of analyte in the water phase, and underestimates the true K_{ow}. This problem is overcome in the slow stirring method. Equilibration of the analyte between the two phases is achieved by gentle agitation of the reaction mixture with a stirring bar, rather than by vigorous shaking, so emulsions are not formed. A reverse-phase HPLC method is often used to determine K_{ow} values indirectly (Veith et al. 1979). Reference compounds of known K_{ow} are run through the HPLC system, and calibration curves of K_{ow} against retention time or capacity factor are produced from which Kow can be determined for an unknown. This method was deemed inappropriate for the present study largely because the structural diversity of the chlordane components would make a direct correlation between retention time and K_{ow}. Numerical methods which calculate K_{ow} from fragment constants and π-values have been used also (Hansch and Leo 1979), however these techniques are generally less accurate than direct determinations and in some cases require that K_{ow} of an appropriate parent compound is known.

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Technical chlordane is a multi-component chlorinated hydrocarbon pesticide formulation containing in excess of 140 different compounds (Dearth and Hites 1991). Chlordane residues are very persistent in the environment. Some minor components of the mixture are especially resistant to degradation and accumulate in biota to potentially toxic levels (Shigenaka 1990). Accurate, compound specific K_{ow} values for chlordane components would improve our understanding of the fate and effect of trace contamination by chlordane residues. Unfortunately, K_{ow} values have only been determined for the major components, and those values presented in the literature are not all in agreement, creating confusion as to what the correct values are.

In this study the slow stirring method of De Bruijn et al. (1989) is used to determine K_{ow} values for 13 of the major components of technical chlordane.

MATERIALS AND METHODS

The reaction vessel used was a 1L conical flask with a dual outlet ground glass stopper which permitted sampling of both phases without disturbing the interface between the phases. 900mL of glass distilled water which had been stored under octanol was added to the reaction vessel. The central stem of the stopper was lowered well into the water, and a Teflon coated magnetic stirring rod placed in the bottom of the flask. 20mL of water-saturated octanol was carefully poured onto the water through a glass pasteur pipette, the tip of which was just in contact with the surface of the water. The two phase system was then allowed to thermally equilibrate in a water bath at 25° C for 24 hrs. After equilibration a solution of technical chlordane in octanol was added to the octanol layer via a glass pasteur pipette. The stirring rate was adjusted to approximately 200rpm so that a depression could just be seen at the surface of the octanol layer.

After several days water samples (80mL) were removed by applying a positive pressure to the outer sampling tube and collecting the water forced up through the central tube. A synthetic quantitation standard (2-chlorononachlor in isopropanol) was weighed into a volumetric flask and the water sample added to it. The mixture was thoroughly shaken, then 10mL of petroleum ether was added to the flask, which was shaken overnight to extract the analytes. A portion of the petroleum ether was taken for analysis using an HP5890 gas chromatograph equipped with an electron capture detector.

The octanol layer was sampled directly. Approximately 0.1g of octanol was weighed accurately into a volumetric flask containing the 2-chlorononachlor standard and made up to 50mL with petroleum ether. A portion was removed and analyzed in the same manner as the water extract.

RESULTS AND DISCUSSION

The water layer was sampled successively over several days to confirm that equilibrium partitioning of the analytes between the two phases had been established. The concentration of chlordane components in the water layer attained a steady state after approximately three days.

The experiment was performed using two different concentrations of technical chlordane in octanol (1745mg/L, 435mg/L). Both solutions yielded the same K_{ow} values, confirming that the K_{ow} values were independent of chlordane concentration. The results are presented in Table 1. (The two compounds, unkown one and unknown two, have been identified and their structures characterised as heptachlor and octachlordane isomers respectively. However the trivial names unknown one and unknown two are still commonly used in the literature.)

Table 1: Log K_{OW} values determined for the major components of technical chlordane

Compound	Log K_{OW} (±1SD)*	Compound	Log K_{OW} (±1SD)*
compound C	5.56 (0.31)	unknown 2	5.91 (0.07)
heptachlor	6.10 (0.18)	*cis*-chlordane	6.10 (0.11)
α-chlordene	5.66 (0.05)	nonachlor III	6.06 (0.12)
γ-chlordene	5.44 (0.23)	*trans*-nonachlor	6.35 (0.14)
β-chlordene	5.62 (0.20)	*cis*-nonachlor	6.08 (0.19)
unknown 1	5.47 (0.16)	compound K	6.09 (0.16)
trans-chlordane	6.22 (0.10)		

* mean of four determinations

The K_{OW} values were determined using a solution of technical chlordane. It is possible that matrix effects due to the presence of more than one analyte species in the reaction vessel may influence the measured K_{OW} values such that the values determined in this experiment may be different from those that would be obtained for pure compounds. However, since these compounds, with the exception of heptachlor, are always used as part of the technical formulation, it is the K_{OW} values obtained in the technical chlordane matrix that would be applicable to environmental contamination by Chlordane.

Table 2: Literature values of K_{OW} for some components of technical chlordane

Compound	Log K_{OW}	Source
heptachlor	4.41	Mabey et al. (1982)
	5.36	Cited in Niimi (1991)
	5.27	Cited in Noble (1993)
	5.44	Cited in Noble (1993)
	6.06	Cited in Noble (1993)
chlordane (*cis* and *trans* mixture)	2.78	Sanborn et al (1976)
	5.48	Mabey et al. (1982)
trans-chlordane	6.00	Veith et al. (1979)
cis-chlordane	6.00	Veith et al. (1979)

The literature values that do exist for Chlordane components are listed in Table 2 for comparison. The only value that is a direct measurement is that of Sanborn et al. (1976) who measured a K_{OW} value of 2.78 for a 3:1 mixture of *cis*- and *trans*-chlordane using the shake flask method. The value they determined is particularly low when compared to the other values published, and lower than would be predicted from other physicochemical properties of chlordane which correlate with K_{OW}. This result probably reflects the unsuitability of the shake flask method for use with extremely hydrophobic chemicals, as discussed earlier. The other values in Table 2 were either determined using the indirect HPLC method (data from Veith et al. 1979) or were calculated using numerical methods. The data from the present work are somewhat higher than these previously published values.

Previous work has shown that, for groups of related compounds (e.g. polychlorinated biphenyls, chlorobenzenes), K_{OW} and BCF increase with increasing degree of chlorine substitution (De Bruijn et al. 1989; Oliver and Niimi 1983). To assess whether this relationship holds for the components of technical chlordane also, the values in Table 1 were plotted against chlorine number. The results are presented in Figure 1.

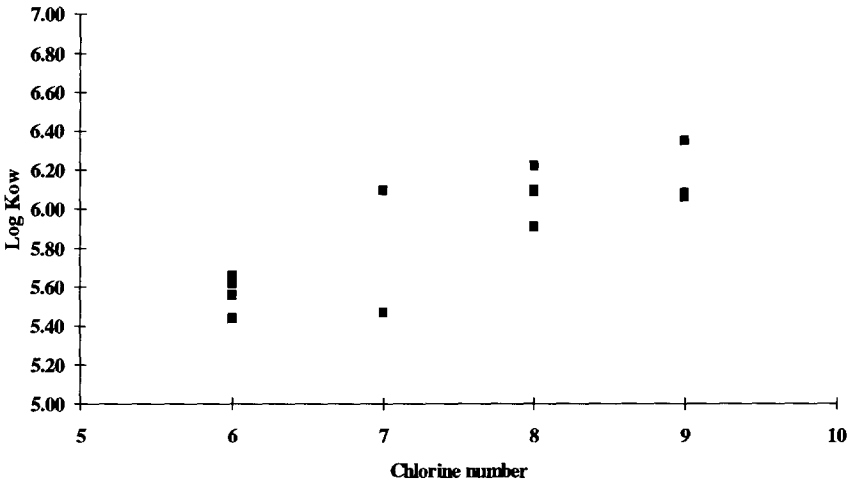

Figure 1: Relationship between number of chlorine atoms per molecule and Log K_{ow}

The data do exhibit a clear positive correlation. A linear regression on the data yields a positive slope of gradient 0.21 and a correlation coefficient (r) of 0.826. A two tailed students t-test was used to confirm that the correlation was indeed significant ($t_{crit.} = 3.11$, $t_{calc.} = 4.86$, $P = 0.01$).

There is, however, a large amount of scatter around the regression line. The authors attribute this in large part to the structural diversity of the compounds analysed. Structural features such as conformational effects, and differences in charge distribution due to the number and spatial disposition of double bonds and chlorine atoms would no doubt affect K_{ow}.

The scatter in Figure 1 illustrates potential difficulties arising from the use of simple structural relationships to predict K_{ow} values for structurally diverse compounds. Our results confirm that the slow stirring method provides reliable K_{ow} values for very hydrophobic organic chemicals. These values will help to further our understaniding of the fate and effect of techinical chlordane contamination in the environment.

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