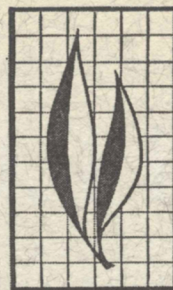# Apparent Solubility of Organochlorine Insecticides in Water at Various Temperatures
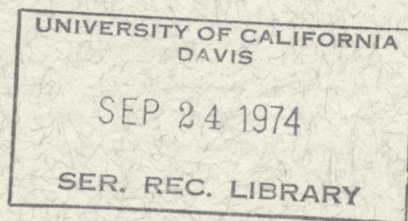
J. W. Biggar and R. L. Riggs

The apparent solubility in water of several organochlorine insecticides has been examined and found to vary, depending upon the rate of centrifugation of the samples prior to analysis. Samples centrifuged at rates calculated to produce equivalent particle diameters based on Stokes' law of 0.01, 0.05 and 5.0 microns showed increases of the average concentration in solution for all compounds investigated. The tendency of these slightly soluble organic compounds to form colloidal aggregates and to accumulate at air-water interfaces may be partly responsible for changes in concentration. This tendency may be important to physio-chemical and biological reactions that occur in the environment.

Of no less importance is the change in apparent solubility with temperature. As the temperature was increased from 15°C to 45°C, the apparent solubility increased for all compounds investigated. Three- to ten-fold increases in concentration were measured for some compounds when the temperature was increased from 15°C to 45°C. These changes in temperature and the corresponding changes in concentration are considered to have important implications relative to pesticide interactions with soil, water, and biological activity in the environment.

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J. W. Biggar and R. L. Riggs

Apparent Solubility of Organochlorine Insecticides in Water at Various Temperatures[1]

INTRODUCTION

THE BEHAVIOR OF ORGANOCHLORINE PESTICIDES in water should be understood in order to determine the interrelation between solubility (or lack of it) and various adsorption-desorption reactions that occur during the movement and mixing of waters in streams and soils. Such information would also help researchers to assess solubility effects on biological activity and degradation of the material, since solubility, organism response, and degradation or leaching may be significant factors in the disappearance of many of these materials from soil and water.

Of no less importance—from a biological as well as a physiochemical point of view—is the effect that temperature has on the concentration of pesticidal compounds in water. The variability of apparent pesticide content of lakes, streams, and drainage waters may sometimes be attributed to changes in temperature. Such changes require new equilibria to be established for suspended particulate matter, solid phase or adsorbed pesticides, and solutions.

Solubility data for a number of the organochlorine pesticides reported here are available for particular temperatures but not in relation to changes of temperature. Other solubility data obtained by chemical analysis and bioassay methods have been reviewed by Gunther *et al.* (1968).

One of the most commonly used pesticides, DDT, has been the subject of most of the research conducted on organochlorine pesticide solubilities in water. Richards and Cutkomp (1946) reported a solubility of from 0.2–1.0 ppb at 15°C, determined by bioassay with mosquito larvae. Gavaudan and Poussel (1947) estimated 100 ppb at 18°C by a nephelometric technique. Roeder and Weiant (1946) estimated the solubility of DDT in water to be 10–100 ppb at room temperature by observing nerve reactions in cockroaches. Using radiometric techniques, Babers (1955) reported solubility values of 5.9 ppb, 37 ppb, and 45 ppb, at temperatures of 2°C, 25°C, and 37°C, respectively. Sazonov, Bogdarina, and Gudkova (1956) determined the solubility of DDT to be less than 1.0 ppm. Bowman, Acree, and Corbett (1960) used C^{14}-labeled DDT and ultracentrifugation to determine the concentration of a saturated solution. They pointed out the probable existence of particles in the solution and gave a value of 1.2 ppb as the solubility in water. Biggar, Dutt, and Riggs (1967) reported a value of 1.7 ppb for DDT as determined by ultracentrifugation and analysis by electron capture gas chromatography.

The solubility of lindane in water was determined by Slade (1945) to be 10 ppm. Hancock and Laws (1955) and Ivanov (1956) reported values of 7.0 ppm and 8.0 to 8.5 ppm, respectively.

[383]

A solubility of 31.8 ppm was reported by Sazonov, Bogdarina, and Gudkova (1956).

Richardson and Miller (1960) determined the solubilities of several pesticides at various temperatures by means of UV spectrophotometry and, in the case of lindane, polarography.

Robeck *et al.* (1965) determined the solubility of five pesticides and one herbicide at 25°C and at particle sizes ranging from 0.04 to 5 microns.

A second factor prompted the need for solubility-temperature data: In studying the energetics of adsorption-desorption reactions in soils, the effect of temperature on the concentration should be known in order to calculate certain thermodynamic quantities. Such a need prompted an investigation of the temperature-solubility interaction for the range of temperature encountered in the adsorption-desorption experiments.

The true solubility in water of many of these only-slightly soluble organochlorine pesticides is difficult to ascertain because they are hydrophobic in nature and because of the analytical problems associated with such low concentrations. The possibility that compounds with very few hydrophilic groups will concentrate at the air-water interface has been shown to occur for some compounds (Davies and Rideal, 1963). The presence of contaminants in small quantities may significantly change the solubility of compounds by emulsification that are normally slightly soluble in water.

Bowman, Acree, and Corbett (1960) pointed out that groups of molecules or a colloidal phase, as well as individual species of the organochlorine pesticide, may exist in the solution. Therefore, determination of the solubility of these materials is complicated by the tendency to form colloidal suspensions and accumulate at interfaces.

In our study, much effort was expended to dissolve or disperse the compounds in such a way as to form individual molecular species. This has involved dispersion by shaking—and ultrasonic treatment, filtering, and centrifuging at different velocities.

PROCEDURE

Samples of the chemicals in powder form, all greater than 99.9 per cent purity, passing a 200-mesh sieve were stirred into 1 liter of distilled water (double distilled in glass) at concentrations of 25 ppm. The samples were treated ultrasonically (Riggs and Biggar, 1965) and shaken for two weeks in a constant temperature bath at 15°, 25°, 35° and 45°C ± 0.05°C. They were filtered through a sintered glass filter of 4.5 to 5.5 micron porosity. All samples were centrifuged at the above temperatures for one-half hour at three velocities, which are expressed in terms of equivalent particle diameters based on uniform spherical particles and the application of Stokes' law. Aliquots of 100 and 200 ml, depending upon the particular pesticide, were taken after centrifuging. The aliquots were combined (600 to 700 ml) and extracted three times with nanograde hexane (redistilled over Na) using 100 and 50 ml volumes. Extracts were combined, eluted through a column of anhydrous Na_2SO_4, and concentrated to 0.2 to 1.0 ml using Kuderna-Danish evaporative concentrators. Extraction and recovery efficiencies (99 to 100 per cent) were determined by adding known amounts of pesticide before sampling. Calibration curves were prepared for each pesticide in nanograde hexane. In some instances, aldrin was added as an internal standard. No analysis was made on unfiltered samples.

One to 5 microliters aliquots of concentrate were chromatographed using a Varian Aerograph 600-B, employing

TABLE 1.

CONCENTRATIONS (PPB) IN WATER AT 25°C OF SELECTED ORGANOCHLORINE
INSECTICIDES EXPRESSED IN PARTICLE SIZES

Pesticide	Concentration in following particle size :		
	0.01μ	0.05μ	5.0μ
	ppb	*ppb*	*ppb*
Lindane	150	600	6,800
Aldrin	13	140	180
Dieldrin	22	150	195
Endrin	24	180	250
Heptachlor	30	125	180
Heptachlor epoxide	25	120	200
p,p'–DDT	1.7	6	25
o,p'–DDT	4	12	85
p,p'–TDE (DDD)	5	15	90
p,p'–TDEE*	------	------	140
p,p'–DDE	10	40	120
o,p'–DDE*	15	40	140
Tech B–DDT†	10	17	40
Methoxychlor	3	10	45
Nemagon‡	------	------	1,150

* Synthesized by dehydrohalogenating parent compounds.
† Mixture of 76% p,p'–DDT; 22% o,p'–DDT, o,o'–DDT,p,p'–TDE; 2% p,p'–DDE.
‡ Concentration in ppm. All other ppb.

a concentric 250 mc H^3 electron capture detector operated at 90 V. Other gas-liquid-chromatography parameters were as follows: the columns employed were 5 feet × ⅛ inch borosilicate glass packed with 5 per cent Dow 11, 5 per cent DC 200, and 5 per cent QF-1, on 60- to 80-mesh Chromosorb W; the carrier gas was molecular sieve purified N_2 at a flow rate of 50 ml per minute. Injector, column, and detector temperature were 225°, 180°, and 200°C, respectively. The chromatograms were recorded on a Honeywell-Brown Electronik 15 recorder equipped with a 201-B Disc integrator. Nemagon was

determined using the following conditions: injector, oven, and detector temperatures were 100°, 90°, and 100°C, respectively; column flow rate was 30 ml per minute.

A Dohrmann C-200 microcoulometer and T-300-S halide titration cell were also used for samples of high solubility, such as lindane. Retention times and sensitivities for these systems have been generally noted (Bonelli, Hartman, and Dimick, 1964; Burchfield and Johnson, 1965) and need not be listed here. Each value reported represents the average of at least three determinations.

RESULTS

Previous work on the dispersion of p,p'–DDT in water indicated the difficulties and dangers of assuming completely uniform molecular distribution of the slightly soluble hydrocarbons. Despite the rigorous methods employed to obtain true solution of the materials investigated, it was still considered desirable to centrifuge the suspensions at two or three velocities until concentra-

tion changes with time were small. The results of the analyses are presented as the concentration for these three velocities expressed as equivalent particle size, assuming Stokes' law and the appropriate temperature and density of the solute and solvent.

Table 1 shows a summary of the concentration of all compounds measured at 25°C and suggests, as has been

TABLE 2.
CONCENTRATIONS OF SELECTED PESTICIDES IN WATER AFTER
CENTRIFUGATION AS AFFECTED BY TEMPERATURE

Pesticide*	Concentration (ppb) at following temperature:			
	15°C	25°C	35°C	45°C
Lindane	2,150	6,800	11,400	15,200
Aldrin	105	180	350	600
Dieldrin	90	195	400	650
Endrin	130	250	420	625
Heptachlor	100	180	315	490
Heptachlor epoxide	110	200	350	600
p,p'–DDT	17	25	37	45
o,p'–DDT	50	85	135	200
p,p'–TDE (DDD)	50	90	150	240
o,p'–TDE (DDD)	60	100	280	315
p,p'–TDEE†	65	140	260	510
p,p'–DDE	55	120	235	450
o,p'–DDE†	...	140	...	...
Methoxychlor	20	45	95	185

* Particle sizes 5 μ or less.
† Synthesized by dehdyrohalogenating the parent compound.

stated elsewhere in this paper, that a colloidal phase, as well as individual species may be present in the solvent. Aldrin, dieldrin, and endrin having somewhat similar molecular characteristics, behaved similarly, with endrin proving to be the most soluble. In hexane, both dieldrin and endrin are much less soluble than aldrin, the range being from 7 to 98 grams per ml, but considerably higher than in water as expected. It is interesting to note from this limited table and other reports (Edwards, 1966) that the compound of lowest solubility, namely p,p'–DDT, is also the pesticide reported to be the most persistent in the environment. The others more or less follow in the order of their solubility, although this is not the only factor important in the degradation of these insecticides. In some cases, lindane, the most soluble of the group with the exception of nemagon, has shown more persistence than aldrin. Aldrin, however, is oxidized to dieldrin, which is more persistent than lindane.

The temperature range in the present investigation corresponds to fluctuations that are found in nature. Table 2 presents data for a number of materials expressing the concentration changes

with temperature for particle size equal to or less than 5 microns. The compounds reported may be present in true solution, as well as subject to colloidal distribution, as previously noted.

In all cases investigated, the temperature had a significant effect on the saturation concentration of the insecticides in water. Increases ranged from 2.5-fold for p,p'–DDT to > nine-fold for Methoxychlor. The changes in concentration of the constituents in the solvent with temperature for some of the compounds are illustrated in figures 1 and 2. The wide differences in the effect of temperature on the concentration is quite evident by comparing p,p'–DDT and Heptachlor epoxide. None of the compounds exhibited a linear change with temperature.

Figure 2 shows that the cyclodiene compounds related to aldrin respond similarly, there being a six-fold change in the concentration over the 30°C temperature change.

In table 3, the changes in concentration at saturation with changes in particle diameter and temperature are given for selected compounds. It should be recalled that the designated particle
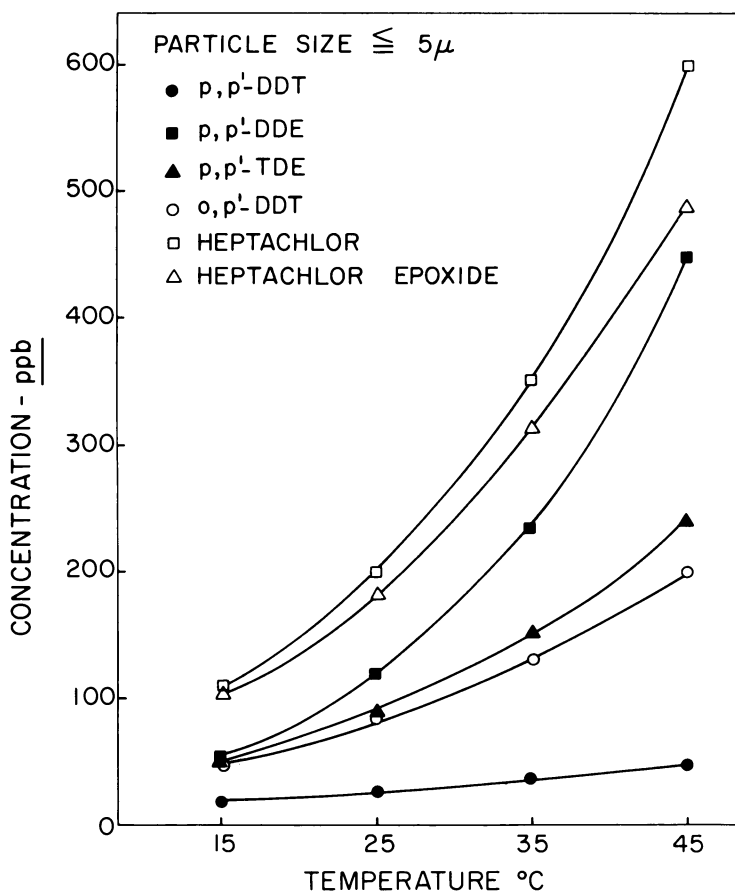
Fig. 1. Temperature effects on the concentration of aqueous solutions of organochlorine pesticides with particle sizes equal to or less than 5.0 μ in diameter.

sizes of 5.0, 0.05, and 0.01 microns represent upper limits of particle sizes present in the solvent as calculated for Stokes' law. They do not imply that the particles are spherical or that particles of this size are necessarily present. The occurrence of individual molecular species cannot be ruled out.

For the smallest size, the change in concentration with temperature exceeded ten-fold for compounds such as aldrin and endrin, while for p,p'–DDT it barely exceeds a two-fold change. In figure 2, these changes are given for the aldrin group for the largest and smallest equivalent particle diameter. It is

apparent for these compounds that the changes of concentration are nonlinear, both with respect to temperature and with respect to equivalent particle size, within a given compound. In general, the temperature effects on concentration show that the 0.05 micron size is between the 0.01 and 5.0 micron size.

While the authors of the present paper do not wish to extrapolate from the available data, it is worthwhile to make some additional comments concerning the temperature interactions.

For the data shown in figures 1 and 2, the concentration as a function of temperature appears to follow the solu-
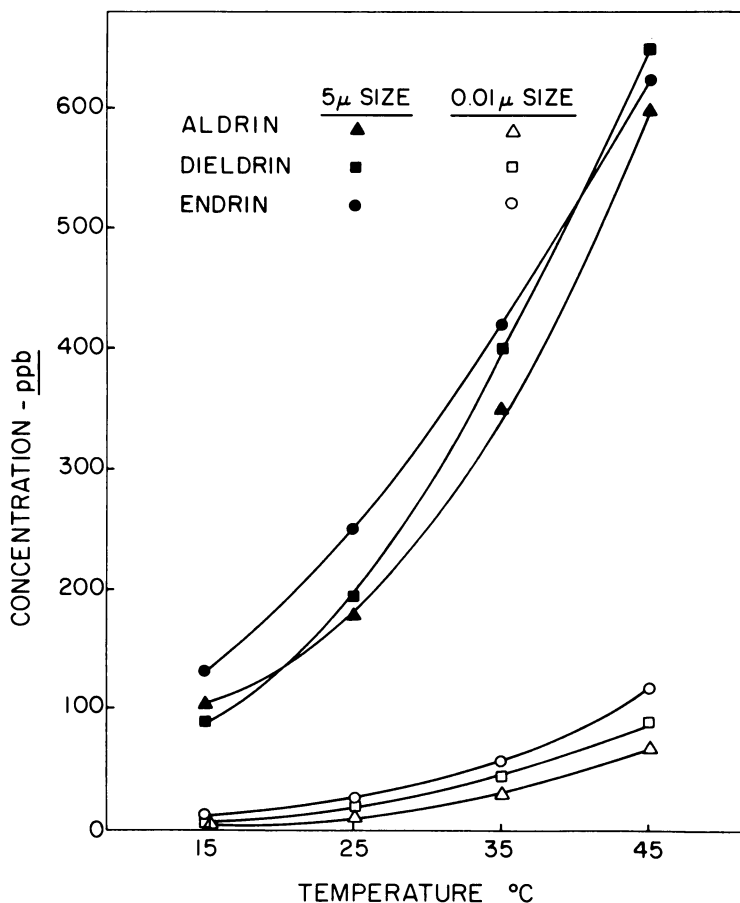
Fig. 2. Temperature effects on the concentration of aldrin, dieldrin, and endrin in saturated aqueous solutions with particle sizes equal to or less than 5.0 and 0.01μ.

bility-temperature equation given in many text books.

$$\ln \frac{1}{X_A} = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \quad (1)$$

where X_A is the mole fraction of compound A, ΔH, the heat of fusion, T, temperature, T_f, the temperature of melting and R the universal gas constant.

Figure 3 presents data for the aldrin group and DDT according to equation 1 and suggests that the effect of tem-

perature on the concentration of these compounds is predictable and should not be ovelooked. More extensive investigation should consider the fugacity of the solution, including temperature effects, so that increased colloidal dispersion of a compound may be differentiated from increased solubility, since both phases may co-exist at any time. Measurement of heats of fusion, the triple-point temperature, temperature of melting, and the like, represent possible areas of research.
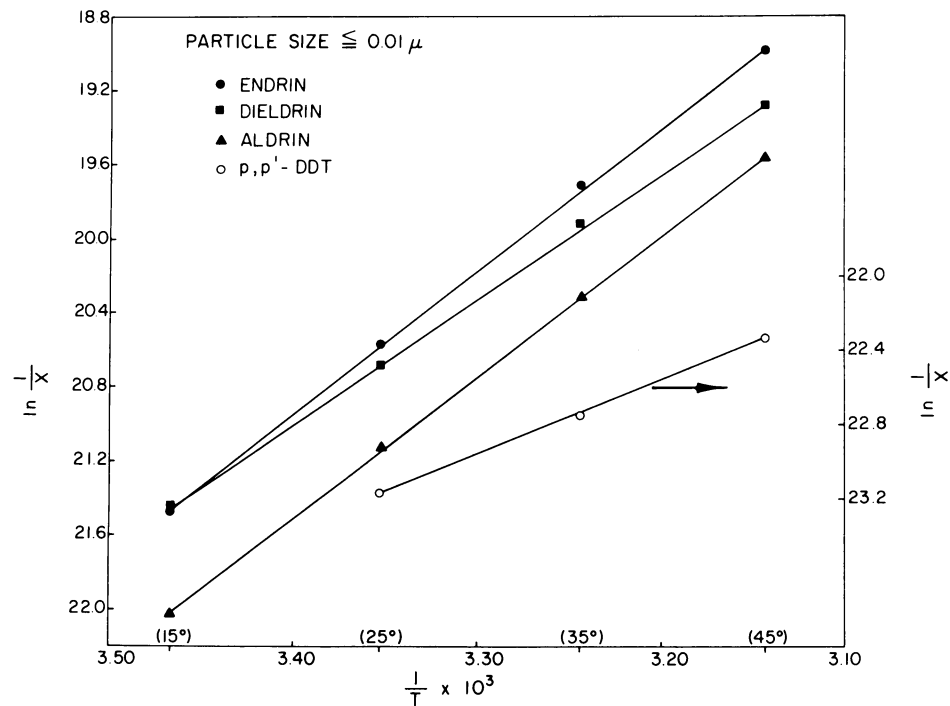
Fig. 3. Changes in the mole fraction of selected pesticides in relation to reciprocal of the absolute temperature for saturated aqueous solution and particle diameter equal to or less than 0.01μ.

TABLE 3

CONCENTRATIONS OF SELECTED PESTICIDES AT THREE DIFFERENT
PARTICLE SIZES IN WATER AT FOUR DIFFERENT TEMPERATURES

Pesticide and particle size*	Concentration at following temperature:			
	15°C	25°C	35°C	45°C
μ	*ppb*	*ppb*	*ppb*	*ppb*
Lindane:				
0.01	75.0	150.0	315.0	575.0
0.05	330.0	600.0	950.0	1,450.0
5.0	2,150.0	6,800.0	11,400.0	15,200.0
Aldrin:				
0.01	5.5	13.5	30.0	65.0
0.05	52.0	140.0	235.0	455.0
5.0	105.0	180.0	350.0	600.0
Dieldrin:				
0.01	10.0	22.0	47.0	90.0
0.05	65.0	150.0	270.0	480.0
5.0	90.0	195.0	400.0	650.0
Endrin:				
0.01	10.0	24.5	58.0	120.0
0.05	90.0	180.0	315.0	518.0
5.0	130.0	250.0	420.0	625.0
p,p'–DDT:				
0.01	1.0	1.7	2.6	3.9
0.05	2.5	6.0	13.0	27.5
5.0	17.0	25.0	37.0	45.0

* Particle sizes represent upper limits of sizes present in solvent as calculated for Stokes' law.

CONCLUSION

While the relationship between the colloidal and solution phases of various pesticidal compounds in aqueous solution is beyond the scope of this paper, it would appear that an organism or plant might be subject to varying concentrations which would depend upon the temperature of the environment. These concentrations may change as much as ten-fold for a 30°C change in temperature. It should not be surprising then that the amount of pesticide in solution in relation to particulate matter, or in its absence may change as samples of water are withdrawn from drains, streams, lakes and other water bodies. Consequently, differences in adsorption and desorption of pesticides by soils or sediments may be affected not only by their near-insolubility in aqueous media, but more significantly by variations in temperature.

This temperature variable, together with the tendency of the organic compound to concentrate at the air-water interface, deserves additional investigation.

ACKNOWLEDGMENT

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