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Bioconcentration of Pesticides by Egg Masses of the Caddisfly, *Triaenodes tardus* Milne

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Extreme environmental persistence and high bioconcentration potential were important factors leading to the suspension of the widely used organochlorine insecticides, DDT and dieldrin. Bioconcentration processes have been well reviewed by KENAGA (1973, 1975); METCALF and coworkers (1971, 1975) have demonstrated the ecological magnification potential for a wide variety of chemicals in laboratory model ecosystems. Although many of the currently used pesticides are not nearly as persistent as DDT or the chlorinated cyclodienes, their water solubilities are quite low and consequently they exhibit relatively high bioconcentration potentials. Much work has been published recently regarding the relationship between physicochemical properties of pesticides (and other environmental contaminants) and bioconcentration potential (METCALF and SANBORN 1975; CHIOU et al. 1977; KENAGA 1980). Most researchers reported good correlations between log water solubility of a chemical and log bioconcentration factor when using fish as the test organism. Few studies reported on the use of aquatic invertebrates as test organisms and no studies that used the egg stages have been located.

BELLUCK et al. (in press) used *Triaenodes tardus* egg masses to develop a caddisfly egg toxicity bioassay; they found that the embryological development of this organism was highly sensitive to agrochemicals in the ppt to ppb range. The eggs of *T. tardus* are oviposited in masses in a gelatinous matrix that swells when exposed to water. It was hypothesized that the gelatinous matrix would provide an unique surface and/or barrier for the partitioning of environmental contaminants. The objective of the following study was to measure the bioaccumulation of 10 pesticides by caddisfly egg masses and to quantify the relationship between pesticide water solubility and bioconcentration factor.

METHODS

Triaenodes tardus eggs were collected as described by BELLUCK et al. (in press). Four egg masses (approximately 72 h after collection) were exposed to 50 mL of

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pesticide solution prepared in soft reconstituted fresh water[1] for 24, 72, 96, and 120 h. Each experiment was replicated twice. The ^{14}C-labelled pesticides and the nominal concentration of the water solutions used in the studies were: DDD, DDT, HCB (1 ppb); carbofuran (8 ppb); dieldrin (20 ppb); methoxychlor, terbufos, malathion, diflubenzuron, monuron (100 ppb).

After the appropriate exposure interval, the egg masses were removed and rinsed with distilled water; they were then blotted dry on filter paper and weighed. The egg masses were ground in a glass tissue homogenizer with a few grains of Na_2SO_4 and several mL hexane. Each extract was transferred to a scintillation vial with at least 2 rinses of hexane. The hexane was evaporated under a stream of N_2 and 15 mL of Aquasol® (New England Nuclear) were added. Aqueous solutions of most of the pesticides were pipetted directly (2 mL) into scintillation vials for analysis. Solutions of DDD, DDT, and HCB (20 mL) were extracted twice with an equal volume of hexane; the hexane was concentrated to a few mL and then transferred to vials. The hexane was evaporated prior to adding 15 mL aquasol.

Radioactivity was measured on a Packard Tri-Carb Series 3000 liquid scintillation spectrometer. Appropriate corrections were made for quenching in the aqueous samples. No corrections were made for degradation of the parent compound during the course of the study.

RESULTS AND DISCUSSION

Ten pesticides exhibiting a wide variability in water solubility were used in this study (Table 1). Bioconcentration factors (concentration of total ^{14}C-pesticide in egg mass/concentration in water) were determined at 24 through 120 h to determine if equilibrium was established under the conditions of the experiment. With the exception of dieldrin and methoxychlor, pesticide bioconcentration appeared to reach a relatively stable level by 120 h (Figure 1). The egg mass concentration of most of the pesticides studied reached the highest levels at 72 h after exposure and then declined to a lower, stable level (Figure 2). A similar pattern was observed when

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1/ Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians. The Committee on Methods for Toxicity Tests with Aquatic Organisms. Ecological Research Series. EPA-660/3-75-009. (1975).

Table 1. Selected properties of pesticides used in bioconcentration studies with *Triaenodes tardus* egg masses.

Pesticide	Molecular weight	Water solubility µg/L	Water solubility µmol/L	Log partition coefficient[a]
DDT	354	1.2[b]	0.003	6.69
DDD	320	4[c]	0.013	6.26
HCB	285	6[d]	0.021	6.12
Dieldrin	381	186[e]	0.488	5.21
Diflubenzuron	311	250[f]	0.804	5.06
Methoxychlor	346	620[g]	1.79	4.83
Terbufos	288	5000[h]	17.4	4.17
Malathion	330	145000[i]	439	3.23
Monuron	199	230000[j]	1156	2.95
Carbofuran	221	320000[k]	1448	2.88

a/ Calculated according to CHIOU et al. (1977)

b/ BOWMAN et al. (1960)

c/ HOLLIFIELD (1979)

d/ LU and METCALF (1975)

e/ PARK and BRUCE (1968)

f/ IVIE et al. (1980)

g/ KAPOOR et al. (1970)

h/ FELSOT and DAHM (1979)

i/ CHIOU et al. (1977)

j/ SANBORN et al. (1977)

k/ BOWMAN and SANS (1979)

bioconcentration factor was plotted relative to time (Figure 1). The water concentration of the pesticides remained fairly constant throughout the experiment.

The observed increase in bioconcentration factor over 72 h for many of the pesticides probably represented adsorption of the pesticide to the gelatinous matrix followed by absorption into the matrix and the eggs. The decline in bioconcentration factor may have

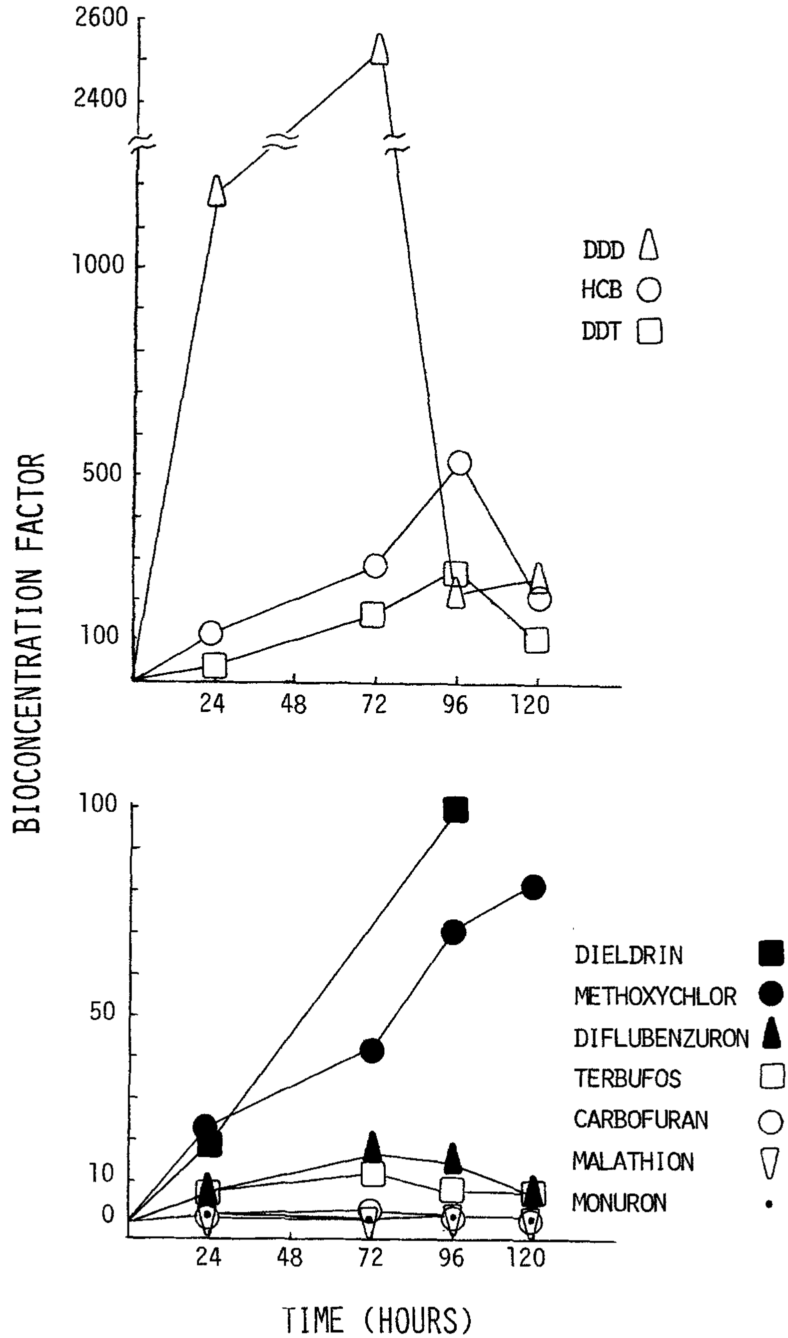

Figure 1. Effect of exposure time on measured bioconcentration factors in the _T. tardus_ egg mass-aqueous pesticide solution system.

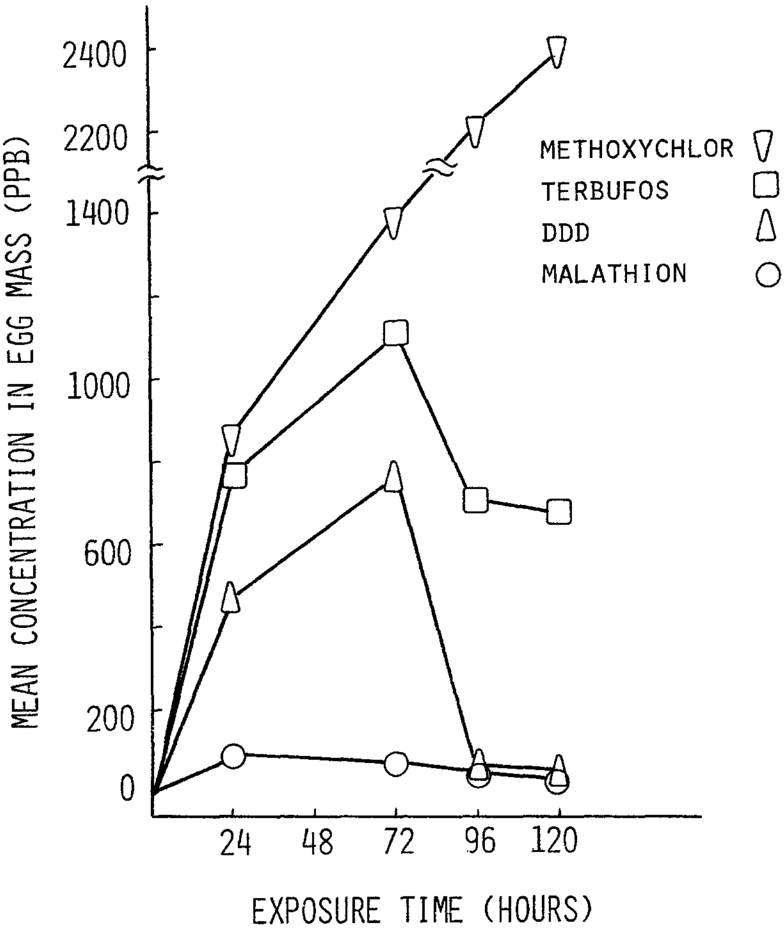

Figure 2. Effect of exposure time on the mean concentration of selected pesticides in *T. tardus* egg masses.

been due to rapid degradative loss of pesticide as CO_2, movement of water soluble pesticide metabolites out of the egg, or failure of the hexane solvent to extract all of the pesticide plus radiolabelled metabolites from the eggs at longer exposure intervals.

KENAGA (1973) has described bioconcentration as a two-stage phenomenon, i.e., adsorption of pesticide to biological surfaces followed by absorption into the tissue matrix. Since adsorption of various chemicals on soil surfaces has been shown to be well correlated with water solubilities and partition coefficients (BRIGGS

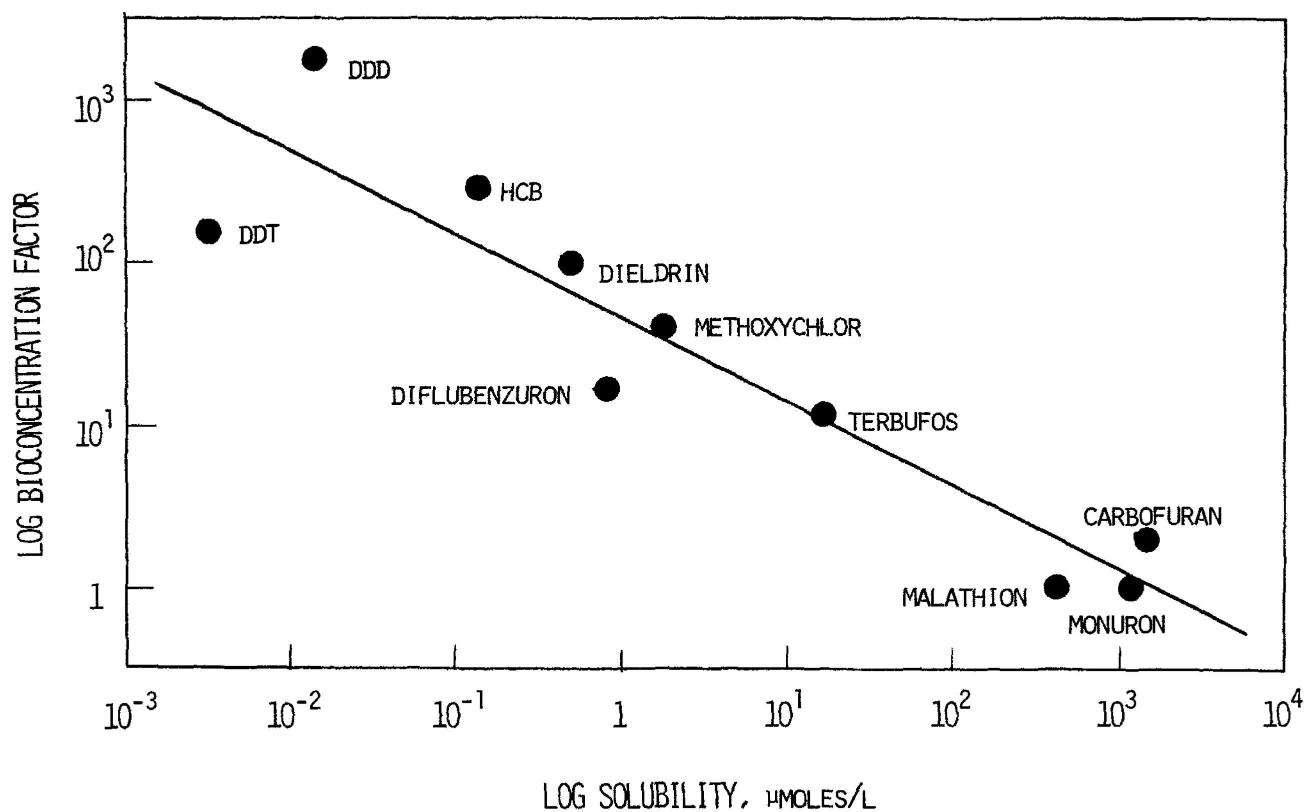

Figure 3. Relationship between log water solubility of pesticides and log bioconcentration factor for T. *tardus* egg masses.

1972; CHIOU et al. 1979; FELSOT and DAHM 1979), one would expect that bioaccumulation of pesticides with widely divergent physicochemical properties would also show a strong association with water solubility and partition coefficient. In fact, such a relationship has been well demonstrated by METCALF and SANBORN (1975) for the ecological magnification of many chemicals in mosquito fish. In the present study it was observed that a strong correlation existed between pesticide water solubility (WS) and 72 h bioconcentration factors (BF) in Triaenodes tardus egg masses ($\log BF = 1.67 - 0.52 \log WS$, $R^2 = 0.92$) (Figure 3). Bioconcentration factor was also well correlated with partition coefficient ($R^2 = 0.93$).

Although the bioconcentration factors for such compounds as DDT, DDD, dieldrin, and HCB in caddisfly eggs are 1 to 2 orders of magnitude lower than what has been reported for various fish species (CHIOU et al. 1977; KENAGA 1980; METCALF and SANBORN 1975), the magnitude of the values obtained compared favorably within one order of magnitude to ecological magnification factors calculated for Culex mosquito larvae (METCALF and SANBORN 1975). KENAGA (1973) has stressed the importance of considering surface area to mass ratios when comparing absolute pesticide accumulation among different organisms, but the effect of the protective gelatinous matrix around Triaenodes eggs on bioconcentration is unknown and requires further investigation. In conclusion, passive biological systems such as caddisfly eggs can accumulate significant quantities of pesticide from water, and the bioconcentration factor is correlated with the physicochemical properties of the pesticide.

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