The Effect of a Sublethal Concentration of LAS on the Acute Toxicity of Various Phosphate Pesticides to the Fathead Minnow (*Pimephales promelas* Rafinesque)

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For the past three years we have been investigating the toxic interaction of linear alkyl benzene sulfonate detergent (LAS) and a selected number of pesticides in relation to their combined acute toxic effects on the Fathead Minnow (Pimephales promelas Rafinesque). This study was initiated from the original work published by Dugan et. al. (1,2) which indicated that goldfish, preconditioned to alkyl benzene sulfonate (ABS) or linear alkyl benzene sulfonate (LAS) are more susceptible to the toxic effects of DDT and dieldrin than goldfish with no previous exposure to the detergents. It was hypothesized that these compounds may act synergistically in their toxic action on fish.

The U.S. detergent industry began using LAS in place of ABS in their household detergents in 1965 and thus we felt that it would be of more environmental significance to study the possible toxic interaction of LAS and pesticides.

In a recent article, we reported the TLm values of separate 96 hour exposures of the fathead minnow to endrin, DDT and parathion both in the presence and absence of LAS (3). These studies indicated no synergistic toxic effect between endrin and LAS but a statistically significant synergistic effect was noted between parathion and LAS. The results of the DDT and DDT in combination with LAS experiments were inconsistent and the variability of DDT toxicity appeared to be too great to accurately determine any synergistic action with LAS.

We would like to report the results of 96 hour TLm tests which we have conducted on 8 phosphorus insecticides in the presence and absence of LAS. Representatives from the phosphorothionate, phosphorodithioate and phosphonothionate groups were tested. It was our intention in this study to determine if the apparent synergism observed between LAS and parathion also exists between LAS and compounds structurally analagous to parathion.

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MATERIALS & METHODS

A standard bioassay procedure as recommended by the U.S. Department of Interior Fish and Wildlife Service Pesticides Review Staff (4) was used for all tests. The fathead minnows were exposed to the toxicants in pickle jars containing 10 1. of water. Each jar was supplied with a continuous flow of toxicant solution by means of a delivery apparatus developed in our laboratory (5). Because of the low solubility of the pesticides in water, an appropriate concentration of each compound was dissolved in a small quantity of acetone to facilitate introduction into the continuous flow system. A detergent and an acetone control was included in each test. TLm values were determined by plotting percent survival vs. log mean measured pesticide concentration for each insecticide by itself, and in combination with 1.0 mg/l concentration of LAS. This concentration of LAS was found to be sublethal for a 96 hour exposure period.

The test water was analyzed periodically to determine the actual exposure concentration of pesticide. The method of analysis is that described in our original study (3). The mean of the measured concentrations were used in computing the TLm values. A list of the compounds tested, their purity, and their source is given in Table 1.

TABLE 1
Source and Purity of the Compounds Tested

| Compound | % Purity | Source | | |
|-------------------------------|--------------|---|--|--|
| Parathion Methyl Parathion | 98.5 98.5 | American Cyanamid Co. Monsanto | | |
| Ronnel | 98.5 | Dow Chemical Co. | | |
| Dicapthon Guthion | 99.8 99.9 | American Cyanamid Co. Chemagro Corp. | | |
| Trichion | 94.6 | Stauffer Chemical Co. | | |
| EPN Trichloronat | 99.5 95.0 | Dupont Chemagro Corp. | | |
| LAS | 85.0 | Monsanto Co. | | |

RESULTS & DISCUSSION

Four phosphorothionate insecticides were tested - parathion, methyl parathion, ronnel and dicapthon. The 48 and 96 hour TLm values for these compounds are given in Table 2.

TABLE 2

Toxicity of Four Phosphorothionate Insecticides in the Presence and Absence of 1 PPM LAS

| | | TLm (| ルタ ル タ/1 |
|---|------------------|---------|--------------------|
| Compound | <u>LAS</u> | 48 hour | 96 hour |
| Parathion S | + | 860 | 720 |
| $(C_2H_5O)_2 - P - O - $ | o ₂ - | 1490 | 1410 |
| Methyl Parathion S | + | 7400 | 3750 |
| $(CH_3O)_2 - P - O - $ | 2 - | 7900 | 7850 |
| Ronnel S C1 C1 CH ₃ O) ₂ - P - 0 - C1 | + | 337 | 265 |
| (CH ₃ O) ₂ - P - 0 - C1 | - | 475 | 305 |
| Dicapthon S | + | 1890 | - |
| $(CH_3O)_2 - P - O - $ | - | 1600 | - |
| Cı | | | |

The difference between the 48 and 96 hour TLm values of parathion exposures in the presence and absence of LAS are 32 and 49% respectively. Since a sublethal concentration of LAS was used, we have

accepted any realistic decrease in the TIm value as indicating synergism. Similar decreases in the TIm values for methyl parathion and ronnel were noted. No synergism was noted for dicapthon. Thus, the toxicity of the majority of phosphorothionate compounds tested is enhanced in the presence of LAS. Dicapthon, a metachloro substituted methyl parathion is an exception, although the absolute TIm is about 5 fold greater than with the parent methyl parathion.

The results of tests with guthion and trithion--both of the phosphordithioate structure--are shown in Table 3. No change in guthion toxicity was noted when LAS was present. Trithion on the other hand, showed a 40% increase in toxicity over 96 hours in the presence of LAS.

TABLE 3

Toxicity of Two Phosphorodithioate Insecticides in the Presence and Absence of 1 PPM LAS

| | | TLm mg /1 | |
|---|-----|----------------------|---------|
| Compound | LAS | | 96 hour |
| Guthion S O | + | _ | 1600 |
| (CH ₃ O) ₂ -P-S-CH ₂ C | - | - | 1600 |
| Trithion | + | 200 | 130 |
| $(C_2H_5O)_2-P-S-CH_2-S-$ | 1 - | 240 | 220 |

In tests with two phosphonothionate compounds, EPN and trichloronat, the former shows no apparent synergism with LAS whereas trichloronat toxicity was found to be synergistically enhanced in the presence of LAS. (Table 4).

TABLE 4

Toxicity of Two Phosphothionate Insecticides in the Presence and Absence of 1 PPM LAS

| | | <i>从</i> TLm a g∕l | |
|--|-----|------------------------------|---------|
| Compound | LAS | 48 hour | 96 hour |
| EPN S | + | 185 | 130 |
| "P-0- \\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ | - | 130 | 110 |
| C2H50 | | | |
| Trichloronat | + | _ | 135 |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | | | |
| C_2H_5 | - | - | 225 |

From the results reported in Tables 2, 3 and 4, there appears to be no consistent relationship between synergistic activity with LAS and structure. Parathion, methyl parathion, ronnel, trithion and trichloronat all contain a substituted phenyl ring and each appears to act synergistically with LAS. EPN and Dicapthon also contain a substituted phenyl ring yet neither exhibits synergism with LAS. The synergistic relationship does not appear to be exclusive with one general structural group. Synergism was noted in representatives from the phosphorothionate, phosphorodithioate and phosphonothionate groups.

A number of possible explanations exist for the synergism noted in this study. These include biochemical interaction in which the LAS is activating the enzymes responsible for oxidation of the thiophosphate compounds to their oxygen analogues or deactivating the enzymes responsible for detoxification as well as purely physical interaction in which the LAS is increasing the solubility of the pesticides on

the gill or skin membrane. Because of the low solubility of all the phosphate insecticides tested, the second hypothesis involving a physical interaction is more appealing to us. Both possibilities need to be determined.

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