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Molecular Structure and Acute Toxicity of Different Insecticides to Three Marine Fish Species

By

Ali A.H. Elsebae
Dept. of Environment Sciences,
Faculty of Environ. Agric Sciences,
Suez Canal Univ. Alareesh, North Sinai

ABSTRACT

Ten insecticides representing the more widely used compounds during the last twenty years were selected for studying there acute toxicity hazard to the three marine fish species: *Dicentrarachus labrex* (sea bass); *Sparus auratus* (sea breem); and *Solea vulgaris*. The 96 hr LC_{50} values revealed a wide variation in susceptibility of the three marine fish species. *Dicentrarachus labrex* (sea bass) was the most sensitive followed by *Sparus auratus* and *Solea vulgaris* in a descending order. The ten insecticides include four synthetic pyrethroids, four organophosphorous compounds and two oxime carbamates. The wide range variation in the molecular weight (e.g. 3 fold between methomyl and deltamethrin), required molar correction by converting LC_{50} to molar LC_{50} to give equal chances for comparing molecular toxicity. Molecular correction changed the magnitude of relative acute toxicity hazard for some compounds. Permethrin was the most hazardous compound, followed by deltamethrin, and triazophos for the three fish species. This correction will be helpful for more precise structure activity relationships. The hazards of tested insecticides to the highly sensitive sea bass, indicates the inportance of including fish toxicity data in the registeration of pesticides.

INTRODUCTION

Wong and Dixon (1995) reported that the acute toxicity test with fish is the major tool for estimating the adverse effects of toxic chemicals in the aquatic environment. Acute lethality tests are now also used in effluent monitoring and in comparing the relative toxicity of large numbers of chemicals in predictive models relating toxicity to chemical structure. (Sprague, 1973) and (Ali Elsabae 1994) conducted a comparative susceptibility study of the shrimp *Penaeus japonicas* and the brine shrimp *Artemia salina* to different insecticides and heavy metals.

Fairchild *et al.*, (1992) evaluated the aquatic hazard of the organophosphorous insecticide fonofos by measuring the acute oral 96 hr-LC_{50} to rainbow trout and the blue gill fish. Anderson (1992), indicated that the acute LD_{50} values decrease with increasing exposure time. Hashimoto (1982) tested marine fish for evaluation of pesticide hazards to the aquatic systems. He concluded that marine fish were found to be more sensitive than carp especially to organophosphorous insecticides. Le Blanc (1984) concluded that different groups of organisms respond differently to the effects of pesticides. The effect of a pesticide on one phylum should not be extrapolated to other phylums.

Rubin and Soderlund (1992) stressed that the acute toxicity of the pyrethroid insecticides varies greatly across phylogenic lines with fish being marked by hypersensitivity to pyethroid intoxication. Webber *et al.*, (1992) described a laboratory ecosystem-level testing of a synthetic pyrethroid insecticide in aqueous mesocosms. (Coats and Jeffery 1979); studied the toxicity of four experimental photostable synthetic pyrethroids to fingerling rainbow trout. A comparison of technical and formulated products was included to determine the effects of the emulsifiers on toxicity. Alabaster and Abram (1965) had developed a standardized procedure for estimating the toxicity of pesticides to fish.

MATERIAL AND METHODS

Tested Insecticides

Technical pure samples of the following insecticides were provided by the Central Lab of Pesticides, Agric. Res. Center, Dokki, Cairo .-

Azinphos methyl, chlorpyrifos, profenofos, triazophos, cypermethrin, deltamethrin, fenvalerate, permethrin, aldicarb and methomyl. They represent the main three chemical groups in large scale use in the Egyptian environment at least for the last twenty years.

Bioassay Organism:

Larval stage of age 25 days fry of each of the three species of the marine fish, (sea bass) *Dicentrarachus labrex*, (sea breem) *Sparus auratus* ,and *Solea vulgaris*, were made available by the Marine Culture Center at Alareesh.

Acute Toxicity Testing:

Sea water solutions with series of concentrations of each of the tested insecticides stock solutions in acetone were prepared and then diluted with water, were used for acute toxicity testing in three replicates each of 200 ml water solution in 500 ml. glass beaker and for each concentration 10 fry larvae of each species of 25 days old fry were added. control tests were included.

The tests were repeated twice and the average mortality counts were recorded after 96 hrs. By using the concentration / mortality probits, relationships were expressed in log/probit regression lines. The coresponding 96 hrs LC_{50}'s with their confidense limits and slope of regression lines were computed according to Finney (1971).

The adopted acute toxicity procedure complies with all the specifications stated by the standard practices for conducting toxicity tests reported by the American Society for Testing and Materials (ASTM) (Anonymous, 1980).

RESULTS AND DISCUSSION

The 96hr LC_{50} acute toxicity data for the ten tested insecticides on the three marine fish species are tabulated in tables 1,2 and 3 with the corresponding regression lines slopes and confidence limits. The results in Table (1) indicates that the LC_{50} values of the tested insecticides on the *Dicentrarachusus labrex* fish ranged from 1.5 to 9.4 ug/l (ppb), while the LC_{50} values of the same compounds on *Sparus auratus* ranged from 2.5 to 19.4 ug/l Table (2), and those of the third fish species *Solea vulgaris* the LC_{50} ranged from 3.5 – 50 ug/l Table (3). Accordingly, the first species *Dicentrarachus labrex* can be considered highly susceptible to insecticides acute toxicity hazards followed by *Sparus auratus* and then *Solea vulgaris* in a descending order with a wide variation of LC_{50} values of more than 3 fold in some cases Table (4).

Table (1): Acute Toxicity of Tested Insecticides To (25 days old fry) of *Dicentrarachus labrex* (sea bass) fish

Insecticide	96 hr LC_{50} $\mu g/l^{-1}$ p.p.b	Slope	Confidence limits
Azinphos methyl	9.40	0.236	9.1×10^{-2} -4.63×10^{-2}
Chlorpyrifos	6.20	0.203	2.6×10^{-2} -3.05×10^{-2}
Profenofos	0.42	0.208	8.53×10^{-3} -2.07×10^{-2}
Triazophos	1.6	0.160	3.05×10^{-3} -4.78×10^{-3}
Aldicarb	3.0	0.463	6.09×10^{-3} -1.48×10^{-3}
Methomyl	2.4	0.289	4.88×10^{-3} -1.18×10^{-3}
Cypermethrin	8.0	0.177	1.8×10^{-4} -3.9×10^{-3}
Deltamethrin	2.3	0.303	4.67×10^{-3} -1.13×10^{-3}
Fenvalerate	5.4	0.136	0.9×10^{-2} -2.6×10^{-3}
Permethrin	1.5	0.102	3.05×10^{-3} -0.74×10^{-3}

Table (2): Acute Toxicity of Tested Insecticides To (25 days old fry) of *Sparus auratus* (sea breem) fish

Insecticide	96 hr LC_{50} $\mu g/l^{-1}$ p.p.b	Slope	Confidence limits
Azinphos methyl	19.8	0.1800	8.3×10^{-2} - 39.0×10^{-2}
Chlorpyrifos	8.4	0.287	8.44×10^{-3} - 8.36×10^{-3}
Profenofos	4.8	0.297	4.9×10^{-3} - 4.68×10^{-3}
Triazophos	2.7	0.456	2.5×10^{-3} - 0.6×10^{-3}
Aldicarb	5.8	0.212	6.9×10^{-1} - 1.25×10^{-3}
Methomyl	3.6	0.175	6.7×10^{-2} - 0.78×10^{-3}
Cypermethrin	17.0	0.219	7.87×10^{-2} - 0.37×10^{-2}
Deltamethrin	3.4	0.212	5.7×10^{-2} - 0.73×10^{-3}
Fenvalerate	11.0	0.270	5.09×10^{-2} - 0.24×10^{-2}
Permethrin	2.5	0.206	1.58×10^{-2} - 0.54×10^{-3}

Table (3): Acute Toxicity of Tested Insecticides To (25 days old fry) of *Solea vulgaris* fish

Insecticide	96 hr LC_{50} $\mu g/l^{-1}$ p.p.b	Slope	Confidence limits
Azinphos methyl	27.0	0.313	2.8×10^{-2} - 2.6×10^{-2}
Chlorpyrifos	18.0	0.274	1.85×10^{-2} - 1.75×10^{-2}
Profenofos	7.2	0.236	7.4×10^{-3} - 7.0×10^{-3}
Triazophos	4.5	0.260	4.6×10^{-3} - 4.4×10^{-3}
Aldicarb	7.0	0.333	7.2×10^{-3} - 6.8×10^{-3}
Methomyl	6.2	0.206	6.4×10^{-3} - 6.0×10^{-3}
Cypermethrin	50.0	0.214	5.14×10^{-2} - 4.9×10^{-2}
Deltamethrin	6.0	0.223	6.2×10^{-3} - 5.8×10^{-3}
Fenvalerate	25.0	0.236	2.6×10^{-2} - 2.4×10^{-2}
Permethrin	3.5	0.274	3.6×10^{-3} - 3.9×10^{-3}

Molecular Structure and Acute Toxicity

The data in tables 4 and 5 include the ranks of hazard for each chemical insecticide to each of the three marine fish species. The LC_{50} values were corrected to Molar concentrations to give equal chances for equimolar concentrations. The low molecular weight compounds, particularly aldicarb and methomyl, changed their rank of acute hazard effect. On the other hand the relatively high molecular weight compounds such as deltamethrin gained higher potency rank in terms of molar levels. Permethrin proved to be the more hazardous compound in all comparisons on the three fish species. This implies high affinity of permethrin to induce some fish mortality to fish fry larvae. On molar levels the first two hazardous compounds were permethrin and deltamethrin. They were followed by the two organophosphorous insecticides triazophos and profenofos . Azinphosmethyl was the least toxic to the three fish species. The LC_{50} values reveal that the sea bass was the more sensitive than other two slecies, while *Solea vulgaris* was the least susceptible. The LC_{50} of azinphosmethyl to the sea bass of 9.4 ug/l is in the range reported by Johnson and Finley (1980) (5 ug/l) for the large mouth bass.

According the Rubin and Soderlund (1992) fish and crustacea are very sensitive to synthetic pyrethroids. The present findings support such conclusion. The fish hypersensitivity to synthetic pyrethroids is attribeted to the fact that the metabolic and detoxification rate is not as efficient as occuring in other organisms.

The present results show clearly that pesticide residues are highly hazardous to aquaculture fish farms. This is why Le Blanc (1984) stated that both acute and chronic fish toxicity data should be required when the pesticides are used in the vicinity of marine estuaries and agricultural run off at coastal areas. Our data shows also that there is a wide range in the fish susceptibility to various pesticides. This is why more than one species of marine fish should be used to predict more precisely the level of actual environmental hazards to fish cultures. The wide variation between different molecular structures of pesticides which reaches more than three fold in molecular weight requires also a molar correction of the LC_{50}

Table (4):Malar Comparative Susceptibility of The Three fish species To The tested Insecticides

Insecticide	96 hr LC_{50} $\mu g/l^{-1}$ (p.p.b.)			Mol wt	Molar LC_{50} X 10^{3}		
	Dicentrara chus labrex	*Sparus auratus*	*Solea vulgaris*		*Dicentrara chus labrex*	*Sparus auratus*	*Solea vulgaris*
Azinphos methyl	9.4	19.8	27.0	317.1	2.9644	5.3355	8.5147
Chlorpyrifos	6.2	8.4	18.0	350.6	1.7684	2.3959	5.1341
Profenofos	4.2	4.8	7.2	373.6	1.1242	1.2848	1.9272
Triazophos	1.6	2.7	4.5	313.3	0.5107	0.8618	1.4363
Aldicarb	3.0	5.8	7.0	190.3	1.5765	3.0478	3.6784
Methomyl	2.4	3.6	6.2	162.5	1.4769	2.2154	3.8154
Cypermethrin	8.0	7.0	50.0	416.3	1.9217	4.0865	12.0048
Deltamethrin	2.3	3.4	6.0	505.2	0.4553	0.6730	1.1876
Fenvalerate	5.4	11.0	25.0	419.9	1.2860	2.6197	5.9538
Permethrin	1.5	2.5	3.5	391.3	0.3833	0.6389	0.8945

Table (5):Malar Comparative Susceptibility of The Three Marine fish species To The Acute Hazard of the Tested Insecticides

Insecticide	Mol wt.	*Dicentrarachus labrex*		*Sparus auratus*		*Solea vulgaris*	
		acute hazard rank	Molar acute hazard rank	Acute hazard rank	Molar acute hazard rank	acute hazard rank	Molar acute hazard rank
Azinphos methyl	317.1	10 *th*	10 *th*	10 *th*	10 *th*	9 *th*	9 *th*
Chlorpyrifos	350.6	8 *th*	8 *th*	7 *th*	6 *th*	7 *th*	6 *th*
Profenofos	373.6	6 *th*	4 *th*	5 *th*	4 *th*	6 *th*	4 *th*
Triazophos	313.3	2 *nd*	3 *rd*	2 *rd*	3 *rd*	2 *nd*	3 *rd*
Aldicarb	190.3	5 *th*	7 *th*	6 *th*	8 *th*	5 *th*	5 *th*
Methomyl	162.5	4 *th*	6 *th*	4 *th*	5 *th*	4 *th*	7 th
Cypermethrin	416.3	9 *th*	9 *th*	9 *th*	9 *th*	10 *th*	10 *th*
Deltamethrin	505.2	3 *rd*	2 *nd*	3 *rd*	2 *nd*	3 *rd*	2 *nd*
Fenvalerate	419.9	7 *th*	5 *th*	8 *th*	7 *th*	8 *th*	8 *th*
Permethrin	391.3	1 *st*	1 *st*	1 *st*	1 *st*	1 *st*	1 *st*

values to give much accurate criteria in studying structure activity relationship between the molecules which vary much in their molecular weights (El-Sebae, 1963), especially when they overlap in their range of acute toxicity. Our data are also important to draw the attention to the expected impact of increased agricultural areas in North Sinai and the hazard of pesticides used on marine aquacultures at Bardaweel brackish lake and other coastal areas.

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الملخص العربــى

التركيب الجزيئى والسمية الحادة للمبيدات الحشرية المختلفة على ثلاثة أنواع من الاسماك البحرية

د. على عبد الخالق السباعى
قسم علوم البيئه – كلية العلوم الزراعية البيئية
جامعة قناة السويس العريش – شمال سيناء

وقع الاختيار على عشرة من المبيدات الحشرية التى تستخدم على نطاق واسع فــى البيئة المصرية فى السنوات الاخيرة – منها اربعة مبيدات مــــن البيريــثرويدات المحضــرة صناعيا – واربعة مبيدات فوسفورية عضوية ومبيدين من الاوكسيم كاربامات . وقد تم اختيار سميتها الحادة على ثلاثة انواع من الاسماك البحريــة وقــد تبيــن ان الاســماك مــن نــوع *Dicentrarachus labrex* كانت اعلى الانواع حساسية للتأثر بالمبيدات الحشرية . بينمــا كان السمك من نوع *Solea vulgaris* هو الاقل تأثرا بالمبيدات المختبرة بينما كــان نــوع السمك من *Sparus auratus* ذو حساسية متوسطة. وعند محاولة ايجاد مدى الارتباط بيــن التأثير الضار بالاسماك وبين التركيب الكيميائى للمبيدات العشرة المختبرة وجد تباينا كبيرا بين المبيدات العشرة وكان اشدها سمية حادة ضد الاسماك هو مبيد Permethrin وكــان أقلــها سمية نسبيا هو المبيد الفوسفورى Azinphos-methyl أما ترتيب المبيدات الكميائية الاخــوى حسب الخطورة النسبية فى قتل الاسماك فقد اقتضى الامر تحويل الجرعات المتوسطة للمــوت لنظائرها من الجرعات الجزيئية المتوسطة للموت ويكفى كمثال ان مبيــد الميثوميــل وزنــه الجزيئى ٢ر١٦٢ – بينما ان مبيد الدلتامثرين وزنه الجزيئى ٢ر٥٠٥ اى حوالى ثلاثة اضعــاف الميثوميل ولذلك فان استخدام التركيزات بدلالة القيم الجزيئيـــة يعطــى ترتيبــا أدق لســمية المركبات ضد الاسماك حيث تفوق الدلتامثرين على الميثوميل. وهكذا فان تقييم السمية النسبية

المرتبطة بالتركيب الكيميائي للتحدي استخدام الجرعات الجزيئية المتوسطة للموت. كما يلزم استخدام أكثر من نوع من الأسماك في تقدير مخاطر السمية الحادة للمبيدات للتفاوت الكبير في حساسيتها للسموم.