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R. Stevens 5/12/81

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESEARCH LABORATORY
SABINE ISLAND
GULF BREEZE, FLORIDA 32561

February 17, 1981

SUBJECT: Results of Pesticide Testing by the Experimental Environments Branch, ERL, Gulf Breeze

FROM: Jack I. Lowe *Jack I. Lowe*
Chief, Experimental Environments Branch

THRU: Dr. Henry Enos *Henry F. Enos*
Director, ERL, Gulf Breeze

TO: Mr. Clayton Bushong
Chief, Ecological Effects Branch, OPTS (TS-769C)

The attached data are summaries and abstracts of research which we have conducted in the areas of Methods Development and Effects Assessment. Pesticides used in most of these studies were selected on the basis of communications with your staff. Most of these data will be published in scientific journals or reports at a later date, and must go through our manuscript clearance/peer review process.

These materials are being supplied to you at the request of Dr. Henry F. Enos, the Laboratory Director, in anticipation of, and in preparation for, the upcoming program review to be held March 10-11. These are selected materials intended to provide a background for discussion. Greater detail or a more comprehensive review of these materials can be provided upon request.

A summary of the attachments follows:

Annex A: Acute Toxicity, Bioconcentration, and Persistence of AC 222,705, Benthiocarb, Chlorpyrifos, Fenvalerate, Methyl Parathion, and Permethrin in the Estuarine Environment (summary of manuscript in editorial review).

Annex B: Acute Static Toxicity Tests.

Annex C: Chronic Toxicity Tests with Estuarine Fishes.

Annex D: Methods Development with Estuarine Fishes.

Annex E: Methods Development in Determining Chronic Effects of Toxicants on Marine Invertebrates.

<u>Annex F</u>: Effects of Fenvalerate on Field- and Laboratory-developed Estuarine Benthic Communities.

<u>Annex G</u>: Effects of Dursban on Laboratory-developed Estuarine Benthic Communities.

<u>Annex H</u>: A Flow-through System for Exposure of Seagrass to Pollutants (abstract of manuscript in editorial review).

<u>Annex I</u>: A Sand Filtration/Activated Carbon Treatment System for Removal of Pesticide Residues from Flowing Aquatic Toxicity Tests (abstract of manuscript in editorial review).

<u>Annex J</u>: Acephate, Aldicarb, Carbophenothion, DEF, EPN, Ethoprop, Methyl Parathion, and Phorate: Their Acute and Chronic Toxicity, Bioconcentration Potential, and Persistence as Related to Marine Environments. (Cover page of special report on subject pesticides, approximately 120 pages. Final draft being typed.)

Attachments - 10

cc: Allan Hirsch (RD-682) w/o attachments
William Murray (RD-682) w/o attachments
Darwin Wright (RD-682) w/o attachments
Peter McGrath (TS-769C) w/o attachments

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Annex A: Acute Toxicity, Bioconcentration, and Persistence of AC 222,705, Benthiocarb, Chlorpyrifos, Fenvalerate, Methyl Parathion, and Permethrin in the Estuarine Environment (summary of manuscript in editorial review).

ANNEX A

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ACUTE TOXICITY, BIOCONCENTRATION, AND PERSISTENCE OF AC 222,705, BENTHIOCARB, CHLORPYRIFOS, FENVALERATE, METHYL PARATHION, AND PERMETHRIN IN THE ESTUARINE ENVIRONMENT

by

Steven C. Schimmel, Richard L. Garnas,
James M. Patrick, Jr., and James C. Moore

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PESTICIDE CHEMISTRY

TOXICITY, BIOCONCENTRATION, AND PERSISTENCE OF PYRETHROID INSECTICIDES IN THE MARINE ENVIRONMENT.

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Paper to be presented at the 181st National Meeting of the American Chemical Society to be held in Atlanta, Georgia, March 29-April 3, 1981.

TOXICITY, BIOCONCENTRATION, AND PERSISTENCE OF PYRETHROID INSECTICIDES IN THE MARINE ENVIRONMENT. R.L. Garnas and S.C. Schimmel, U.S. Environmental Protection Agency, Environmental Research Laboratory, Gulf Breeze, Florida 32561.

Although the synthetic pyrethroids, fenvalerate{cyano(3-phenoxyphenyl)methyl-4-chloro-α-(1-methylethyl)benzeneacetate} and permethrin{*cis* and *trans* (3-phenoxyphenyl)-methyl-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate}, have received conditional registration by the U.S. Environmental Protection Agency, serious questions remain concerning their effects on aquatic environments. We report here the results of toxicity, bioconcentration, and persistence tests using organisms and substrates from the marine environment.

The 96-hour LC50 value of fenvalerate and permethrin for the estuarine fish, *Menidia menidia*, was 0.31 and 2.2 ug/L respectively; the 96-hour LC50 value for the mysid shrimp, *Mysidopsis bahia*, was 0.008(fenvalerate) and 0.020(permethrin)ug/L. The octanol/water partition coefficient(Log P) was 6.5(fenvalerate) and 6.2(permethrin); the bioconcentration factor at steady state for the oyster, *Crassostrea virginica*, was 4,700(fenvalerate) and 1,900(permethrin). In estuarine sediment/water systems, the disappearance rate for fenvalerate and permethrin was first order, with half-lives of 23 and <0.05 days respectively. Degradation was attributed to biological activity associated with the sediment. Outdoor photolysis studies using natural seawater displayed first order disappearance rates with half-lives of 8(fenvalerate) and 6.4(permethrin)days. Hydrolysis and volatility were not significant factors in this study. Similarities and differences are apparent for these pyrethroids and must be considered in an environmental hazard assessment.

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Table I. Pesticide Sources, Purities, Recoveries, and Limits of Detection

Parameter	Permethrin[a]	Fenvalerate[b]	AC 222,705[c]	Benthiocarb[d]	Methyl Parathion[e]	Chlorpyrifos[f]
Technical Material Source	ICI Americas, Inc.	Shell Development Co.	American Cyanamid Co.	Chevron Chemical Co.	Chem Services	Dow Chemical Co.
Purity (%)	83	98	77	90	99	92
GCMS-Base Peak (M/E)	184	125	199	100	109	97
GCMS-Molecular Ion (M/E)	391	420	451	258	263	351
Analytical Standard (ng/uL)	0.50	0.30	0.30	1.0	0.10	0.03
Water Recovery (%)	94	95	97	96	95	96
Tissue Recovery (%)	97	92	88	--	--	--
Sediment Recovery (%)	82	88	91	88	90	95
Lower Limit of Detection[g]	0.25	0.15	0.15	0.50	0.05	0.015

[a] cis and trans (3-phenoxyphenyl)methyl-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-carboxylate
[b] cyano(3-phenoxyphenyl)methyl-4-chloro-α-(1-methylethyl)benzeneacetate
[c] cyano(3-phenoxyphenyl)methyl-4-(difluoromethoxy)-α-(1-methylethyl)benzeneacetate
[d] S-(4-chlorophenyl)methyl diethyl carbamothioate
[e] O,O-dimethyl-O-4-nitrophenyl phosphorothioate
[f] O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate
[g] For 1L of seawater; 1g of sediment (dry weight); and 1g/mL of tissue (wet weight)

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Table II. Acute Toxicity of AC 222,705, Benthiocarb and Chlorpyrifos to Estuarine Animals in Flowing Seawater Acute (96-h) Lethality Tests.

Pesticide	Species	96-hour LC50 µg/ℓ* (95% confidence interval)	Test Temperature ($\bar{x}$, ^{o}C)	Test Salinity ($\bar{x}$, $^{o}/oo$)
AC 222,705	Mysidopsis bahia, estuarine mysid	0.008** (0.006-0.01)	26.0	19.5
	Penaeus duorarum, pink shrimp	0.22 (0.15-0.70)	25.1	24.2
	Cyprinodon variegatus, sheepshead minnow	1.1 (0.38-1.3)	29.4	20.0
Benthiocarb	M. bahia	330 (260-410)	27.6	25.5
	C. variegatus	1,370 (1,350-1,380)	25.6	25.5
Chlorpyrifos	M. bahia	0.035 (0.029-0.043)	26.8	26.7
	C. variegatus	136 (113-153)	31.4	10.3
	Fundulus similis, longnose killifish	4.1 (2.8-6.9)	30.0	25.9
	Menidia menidia, Atlantic silverside	1.7 (1.4-2.0)	27.5	24.3
	Mugil cephalus, striped mullet	5.4 (4.0-6.9)	24.8	24.7

*LC50 values based on measured concentrations.
**LC50 values based on nominal concentrations.

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Table III. Acute toxicity of fenvalerate, methyl parathion and permethrin to estuarine animals in flowing seawater acute (96-hour) lethality tests.

Pesticide	Species	96-hour LC50, µg/ℓ* (95% confidence interval)	Test Temperature ($\bar{x}$, °C)	Test Salinity ($\bar{x}$, ‰)
Fenvalerate	*Mysidopsis bahia*, estuarine mysid	0.008** (0.005-0.01)	25.4	25.3
	Penaeus duorarum, pink shrimp	0.84 (0.66-1.2)	24.8	24.9
	Cyprinodon variegatus, sheepshead minnow	5.0 (4.8-5.3)	30.0	26.5
	Menidia menidia, Atlantic silverside	0.31 (0.21-0.40)	24.1	25.0
	Mugil cephalus, striped mullet	0.58 (0.41-1.0)	25.9	25.8
Methyl parathion	*M. bahia*	0.78 (0.58-1.1)	19.5	14.0
	P. duorarum	1.2 (0.91-1.4)	24.8	21.6
Permethrin →	*M. bahia*	0.02** (0.017-0.024)	26.0	22.6
	P. duorarum	0.22 (0.06-0.79)	24.9	25.0
	C. variegatus	7.8 (6.2-10.)	30.0	22.1
	M. menidia	2.2 (1.2-6.4)	25.5	25.0
	M. cephalus	5.5 (4.1-7.4)	24.5	19.0

*LC50 values based on measured concentrations.
**LC50 values based on nominal concentrations.

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Table V. Octanol/Water Partition Coefficient[a] (Log P), Solubility[b], and Steady-state Bioconcentration Factor[c] (BCF).

Pesticide	Log P	Solubility(ug/L)	BCF
Methyl Parathion	1.8	>1000	--
Benthiocarb	3.4	>1000	--
Chlorpyrifos	5.2	73.	--
AC 222,705	6.2	49.	2,300
Fenvalerate	6.2	24.	4,700
Permethrin	6.5	50.	1,900

[a] $\text{Log } \frac{\text{concentration pesticide in octanol}}{\text{concentration pesticide in water}}$

[b] in seawater.

[c] $\frac{\text{concentration pesticide in tissue}}{\text{concentration pesticide in water}}$

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Table VI. Persistence Studies. Regression[a] of Pesticide Concentration on Sampling Time in Sediment/Water Systems[b].

Pesticide	N	b	a	r^2	Half-life (Days)	95% C.I.[d]
Methyl Parathion[c]	12	-0.30	0.78	0.94	1.2	0.60-2.0
Benthiocarb[c]	8	-0.048	0.90	0.85	6.4	4.0-9.0
Chlorpyrifos[c]	10	-0.013	0.81	0.91	24.	20.-29.
AC 222,705[c]	10	-0.019	0.61	0.88	16.	13.-21.
Fenvalerate[c]	9	-0.014	-0.22	0.87	34.	27.-42.
	5	-0.011	0.43	0.94	27.	20.-35.
Permethrin	--	--	--	--	<2.5	--

[a] $\hat{y} = a + bx$; $\hat{y}$ = Log concentration; x = Time.

[b] Ten grams of sediment and 100 ml of a pesticide/seawater solution.

[c] Analysis of variance performed; the null hypothesis was rejected at $\alpha=0.01$ level of significance.

[d] 95% confidence interval.

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Table VII. Persistence Studies. Pesticide Half-lives for Different Experimental Conditions. Except for untreated sediment/water systems, sufficient numbers of samples were not analyzed for statistical validation.

Pesticide	Half-life (Days)				
	Sediment/Water[c]		Water[e]		
	Untreated	Sterile[d]	Indoor-light[f]	Outdoor-light[g]	Outdoor-dark[h]
Methyl Parathion	1.2	>28.[a]	>28.[a]	6.3	18.
Benthiocarb	6.4	>28.[a]	8.7[b]	>14.[a]	>14.[a]
Chlorpyrifos	24.	>28.[a]	<2.0[b]	4.6	7.1
AC 222,705	16.	>28.[a]	26.	6.1	38.
Fenvalerate	34.	>28.[a]	>28.[a]	8.0	>14.[a]
Permethrin	<2.5	>28.[a]	>21.[a]	14.	>14.[a]

[a]Within experimental error, no significant change in pesticide concentration.
[b]Pesticide volatilized, as determined by analysis of XAD resin traps.
[c]Ten grams of sediment and 100 ml of a pesticide/seawater solution.
[d]One-half milliliter formalin/gram sediment.
[e]One hundred milliliters pesticide/seawater solution.
[f]$25^{o}C$ with 12h photoperiod white fluorescent light.
[g]Stoppered, Pyrex flasks exposed to ambient sunlight and temperature (22-$45^{o}C$).
[h]Foil-covered flasks.

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Table IX. Comparative acute toxicity of four classes of pesticides tested at the Environmental Research Laboratory, Gulf Breeze, 1960-1980.

Pesticide Class (No. Pesticides Tested) [$\bar{x}$ No. Species Tested]	Most Sensitive Species	Most Toxic Pesticide	96-Hour LC50 (µg/ℓ)	Reference
Organochlorine (>24) [>3]	*Penaeus duorarum*, Pink shrimp	Analytical-grade heptachlor	0.03	Schimmel et al., 1976
Organophosphate (>26) [>3]	*Penaeus aztecus*, Brown shrimp	Baytex (Bayer 29493)	0.024*	Butler, 1963
Carbamate (>10) [>3]	*P. aztecus*,	Carbaryl	2.5*	Butler, 1963
Synthetic Pyrethroid (3) [4]	*Mysidopsis bahia*, Mysid shrimp	AC 222,705 and Fenvalerate	0.008	Present study

*48-hour EC50.

ANNEX B

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ACUTE STATIC TOXICITY TESTS
FY 79-80

Patrick W. Borthwick

Static testing to estimate the acute toxicity of pesticides to estuarine and marine animals continued in FY 79-80. In addition to "cookbook" static tests with laboratory reared, uniform aged sheepshead minnows (Cyprinodon variegatus) and mysid shrimp (Mysidopsis bahia), we have successfully tested laboratory spawned embryos of the Eastern oyster (Crassostrea virginica), the stone crab (Menippe mercenaria), and fry of the Atlantic silversides (Menidia menidia). Variable success in static tests with wild-caught pink shrimp (Penaeus duorarum) and pinfish (Lagodon rhomboides) support the decision to replace them with other test species for static testing. Also, the ASTM 48-hr EC50 tests with oyster larvae were not sensitive to the pesticides tested, and may not be as valuable as the flow-through 96-hr acute shell deposition test with adult oysters. Conversely, static test results with stone crab larvae and silversides have been promising.

Periodically we conduct tests with new species to seek and identify additional test organisms based on availability, importance, sensitivity to pesticides, and potential for rearing and culture. The goal is to develop static tests for representatives of major phyla emphasizing early life-stages and animals of small size.

This progress report summarizes data in tabular form on:

1. Static acute toxicity test results on seven OPP pesticides.

2. Toxicity and deactivation tests with marine-grade creosote.

3. Results to date on two OPP pesticides (AC 217,300 and AC 222,705).

Special attention should be paid to the high toxicity of the three synthetic pyrethroids ambush, pydrin, and payoff (AC 222,705). Amdro (AC 217,300) does not seem to be acutely toxic at or below the limits of solubility in seawater (50 ppb), consequently derivation of 96-hr LC50's may not be feasible.

NOTE: Data in this summary are not yet published and should not be cited.

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Table Progress summary (February 4, 1981) of acute static toxicity tests with 7 OPP pesticides to 4 species estuarine animals. Values are 96-hr LC50's (95% confidence interval) or *48-hr EC50 (based on abnormal development) expressed in units of parts per billion (micrograms/liter).

OPP Pesticide	**Crassostrea virginica* <2-hr. larvae	*Mysidopsis bahia* 1-day juveniles	*Menippe mercenaria* zoea larvae	*Cyprinodon variegatus* 28-day fry
Ambush	>1,000	0.046(0.032-0.056)	0.018(0.010-0.032)	88.4(81.7-95.5)
Bolero	1,000<X<10,000	370(317-433)	--	>1,000
Bux	--	1.0 by graphical interpolation	--	46(41-51)
Dursban	1,991(1,505-2,809)	0.056(0.032-0.100)	--	270(235-309)
Fentrifanil	--	0.01<X<0.10	--	9(8-10)
Larvin	--	263(229-298)	--	>1,000
Pydrin	>1,000	0.021(0.019-0.024)	--	120.9(95.9-149.3)

NOTE: No testing is planned for bolstar. No further static tests are planned for bux or fentrifanil.
Greater than (>) values are the result of confirmatory tests.
Ranges (<X<) indicate results of range-finder tests.

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ANNEX C

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CHRONIC TOXICITY TESTS
WITH ESTUARINE FISHES
FY-1980

David J. Hansen and Larry R. Goodman

Research conducted in FY-80 emphasized the development of chronic toxicity test methods and testing of pesticides of particular interest to OPP.

Previous to FY-80, the sheepshead minnow (Cyprinodon variegatus) was the only estuarine fish that could be tested in early life-stage or in complete life-cycle toxicity tests. This absence of chronic test methods prevented generation of data needed to establish the variability in sensitivity of marine fishes and made extrapolations from chronic test results from one fish to other fishes tenuous. In the last twelve months, we developed methods for conducting early life-stage toxicity tests with the Atlantic silverside (Menidia menidia) and the gulf toadfish (Opsanus beta).

Early life-stage toxicity tests have emphasized the pyrethroid insecticides fenvalerate, permethrin, and payoff and the insecticides chlorpyrifos and endosulfan. Sheepshead minnows have been exposed to all five insecticides, silversides to fenvalerate and chlorpyrifos, and toadfish to fenvalerate. This data is summarized below and on the attached tables.

Results of Early Life-stage Toxicity Tests
with Estuarine Fishes

Species	Pesticide	96-hour LC50, µg/ℓ	Chronic Limits, µg/ℓ	
			Lower	Upper
Sheepshead minnow	fenvalerate	5.0	0.56	2.0
" "	permethrin	7.8	10.	22.
" "	payoff	1.1	0.03*	0.06*
" "	chlorpyrifos	136	--	<1.4
" "	endosulfan	0.83	0.27	0.60
Atlantic silversides	fenvalerate	0.31	0.06*	0.2*
" "	chlorpyrifos	1.7	0.28	0.48
Gulf toadfish	fenvalerate	5.4	>1.2	--

*Based on nominal concentrations.