APPENDIX B

MEMORANDUM

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD - CENTRAL VALLEY REGION

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DATE: 26 October 1989

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SUBJECT: CARBOFURAN, MALATHION AND METHYL PARATHION

Regional Board staff review of information on carbofuran, malathion and methyl parathion in Sacramento Valley waters has found that these insecticides are present at concentrations that adversely impact aquatic organisms. Since the discharges of these materials are in violation of Basin Plan toxicity objectives, a control program should be initiated.

The highest concentrations of these materials are being found in the Colusa Basin Drain, and therfore they are most likely discharged from treated fields with irrigation return flows. Water quality monitoring has already found both carbofuran and methyl parathion in rice field tailwater. Irrigation runoff from other crops and/or other activities such as mosquito abatement, are the probable sources of malathion.

These chemicals are being detected at low part per billion (ppb) levels in the late spring. Peak concentrations observed in the Colusa Basin Drain have been 13, 6 and 14 ppb for carbofuran, methyl parathion and malathion respectively. Sampling dates and results are presented in Tables 1 and 2.

For comparison purposes , the information on these chemicals will be contrasted with that for molinate, a herbicide that has been subject to a special regulatory program since 1984 to reduce discharges from treated rice fields.

The greatest risk of these insecticides is not to municipal drinking water supplies. The concentrations, even in the drains, remain below the human health criteria (see Table 3).

The chemicals, however, clearly pose a risk to aquatic organisms. For malathion, EPA's recommended criterion for protection of freshwater aquatic life is 0.1 ppb, whereas Department of Fish and Game's guideline for molinate (in the absence of thiobencarb) is 90 ppb for drain waters; comparable criteria are not available for the other two pesticides. The LC50 value (or other impact level) of the most sensitive organisms, divided by a safety factor, can be used to estimate levels that will provide protection of aquatic species. Ceriodaphnia LC50 for methyl parathion, carbofuran, malathion and molinate is 2.6, 2.6, 1.4 and >5000 ppb, respectively (personal communication Ms. Teresa Norberg-King of EPA to Christopher Foe). Similarly, the 96 hour channel catfish LC50 is 5.2, 0.248 8.97, and 33.24 ppm, respectively. Reported LC50 values for several other important classes of organisms are listed in Table 4. Note that concentrations of the insecticides in Colusa Basin Drain (Tables 1 and 2) often exceed the LC50 for Ceriodaphnia, let alone safe levels. A surprisingly small amount of toxicological pesticide data exists for crustaceans in view of their relative importance as aquatic forage organisms and their known sensitivity.

One method of evaluating the relative hazard posed by the compounds detected in Sacramento Valley waters is to divide concentration data by reported LC50 values. The result is an index of the risk posed by each in terms of toxic units. The highest concentration reported for each chemical in CBD was employed in making these calculations. This procedure probably underevaluated the relative threat posed by the insecticides in comparison with herbicides. This is because it is doubtful that the peak concentrations of the insecticides were measured in either year whereas the peak herbicide concentration probably was. Figures 1 and 2 suggest that the insecticides, rather than molinate, are the more serious threat to aquatic life. The change between years in the relative threat posed by each of the pesticides is the result of the large amount of variation in their measured concentrations at CBD.

It is difficult to evaluate the past environmental aquatic impact of discharges of carbofuran, methyl parathion and malathion as little analytical sampling work was done until recently. One method of estimating the potential relative impact posed by past applications is to divide the number of pounds of active ingredients applied each year in rice cultivation by the reported LC50 concentration of representative aquatic organisms. The major limitation of this method is that it assumes that the rate of degradation and the environmental fate of each chemical is similar. This is not correct. However, Figures 3 and 4 clearly indicate that carbofuran and methyl parathion pose a greater risk to aquatic organisms than does molinate even if movement of these compounds from treated fields is only a fraction of the molinate movement. These figures, as well as data to be presented later, also show that the use of the insecticides on rice has increased dramatically since the mid 1970s.

Additional information on the toxicity and environmental fate of the three insecticides is presented in Appendix 1. It is important to also realize that carbofuran, methyl parathion and malathion probably have additive type of toxicity to fish and invertebrates as each is an acetocholinesterase inhibitor.

SOURCES

Additional work is needed to determine all of the sources of these pesticides. Unlike the herbicides addressed by the Rice Herbicide Program, the three insecticides are used on a wide variety of crops. The top five uses for each chemical, as reported in Department of Food and Agriculture's 1985 Pesticide Use Report, are presented in Table 5. The DFA data will be particularly helpful in identifying the sources of the restricted materials carbofuran and methyl parathion since all applications must be reported. Malathion applications by growers do not have to be reported to DFA and thus additional sources will have to be consulted to get a full picture of the uses of this chemical.

Studies by the Regional Board (file data) and DFA[1] have detected carbofuran and methyl parathion respectively in rice field irrigation return flows. Use of these two chemicals on rice fields is not nearly as extensive as herbicide use and the rates of application are relatively low. For example, 25%, 18% and 74% of the California rice acreage was treated with carbofuran, methyl parathion and molinate, respectively, in 1985. Acreage treated has increased significantly since the mid 1970s (Figures 5 and 6), increasing the risk of off target impacts. For comparison, the acreage of rice grown in the Sacramento Valley from 1960 through 1988 is presented in Figure 7.

We have not determined the exact reason for the increased use of carbofuran and methyl parathion on rice. It could be the result of increased tolerance of the insects to the products, growth of varieties that are less resistant to insect damage, changes in cultural practices , loss of other products or a combination of these and other factors. For future reference, the use of the insecticides on rice is discussed below:

Carbofuran (Furadan) is used to control rice water weevil, an insect whose larvae feed on rice plant roots. The product is applied in granular form at a rate of one half pound active ingredient per acre. Preplant applications are by ground rig or by air and post plant applications are made exclusively by air to drained fields. Since the heaviest damage to the crop usually occurs near the soil/water interface, only the sections of fields within 40 feet of a berm or edge are typically treated. The material is incorporated into the soil in the top checks after preplant applications to reduce the risk to waterfowl. Post flood applications are made from two and one half to eight weeks after seeding as a result of observed damage. Carbofuran is a restricted use material which requires a permit from the Agricultural Commissioner before each use.

Methyl Parathion is used to control tadpole shrimp and also has a secondary impact of reducing crawfish populations. The tadpole shrimp begin hatching a few days after the field is flooded and chew on seedling roots and coleoptiles. They can also stir up the mud and thereby slow growth of young seedlings. Crayfish can also stir up mud, but their major threat is to levees and irrigation systems as a result of their burrowing activities.

Methyl parathion is typically applied during the first two weeks after the field is flooded. It is flown on in liquid form at a rate of 0.6 lb. active ingredient per acre.It is a restricted use material and there is a mandatory three day holding time for the water in the field at the time of application.(Information on pesticide use on rice was obtained from "Integrated Pest Management for Rice" by the University of California Statewide Integrated Pest Management Project and through personal communication with Steve Scardaci, Cooperative Extension, Colusa County.)

Efforts to identify potential sources of malathion have been unsuccessful. Agricultural Commissioners and Cooperative Extension staff serving the Colusa Basin Drain area were contacted and it was determined that the product was applied to wheat and alfalfa during the early spring months, however the timing of this use did not coincide with the detections in the drain. The Colusa County

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[1] 22 February 1989 memorandum from Susan Nicosia to Ron Oshima. The study also detected carbofuram in irrigation tailwater from treated sugar beet fields.

C-029864

Mosquito Abatement District rarely uses this insecticide and was not using it at the time it was found.

CONTROL PROGRAM

A water quality control program is already in place for other pesticides detected in Sacramento Valley waters and this program could serve as the framework for controlling carbofuran, malathion and methyl parathion. The existing program, DFA's Rice Herbicide Program, has addressed water quality impacts resulting from the use of molinate, thiobencarb and bentazon on rice fields and should be able to help control the discharges of carbofuran and methyl parathion from these same fields. Determining the source(s) and best control measures for the malathion discharges could be handled in a similar cooperative effort with DFA and other interested agencies.

The environmental fate data in Appendix 1 can be used to help evalucate the potential effectiveness of various control options.

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FIGURE 1

PREDICTED RELATIVE TOXICITY OF CARBOFURAN, METHYL PARATHION, MOLINATE, AND MALATHION TO CERIODAPHNIA BASED UPON THE MAXIMUM DETECTED CONCENTRATION IN COLUSA BASIN DRAIN

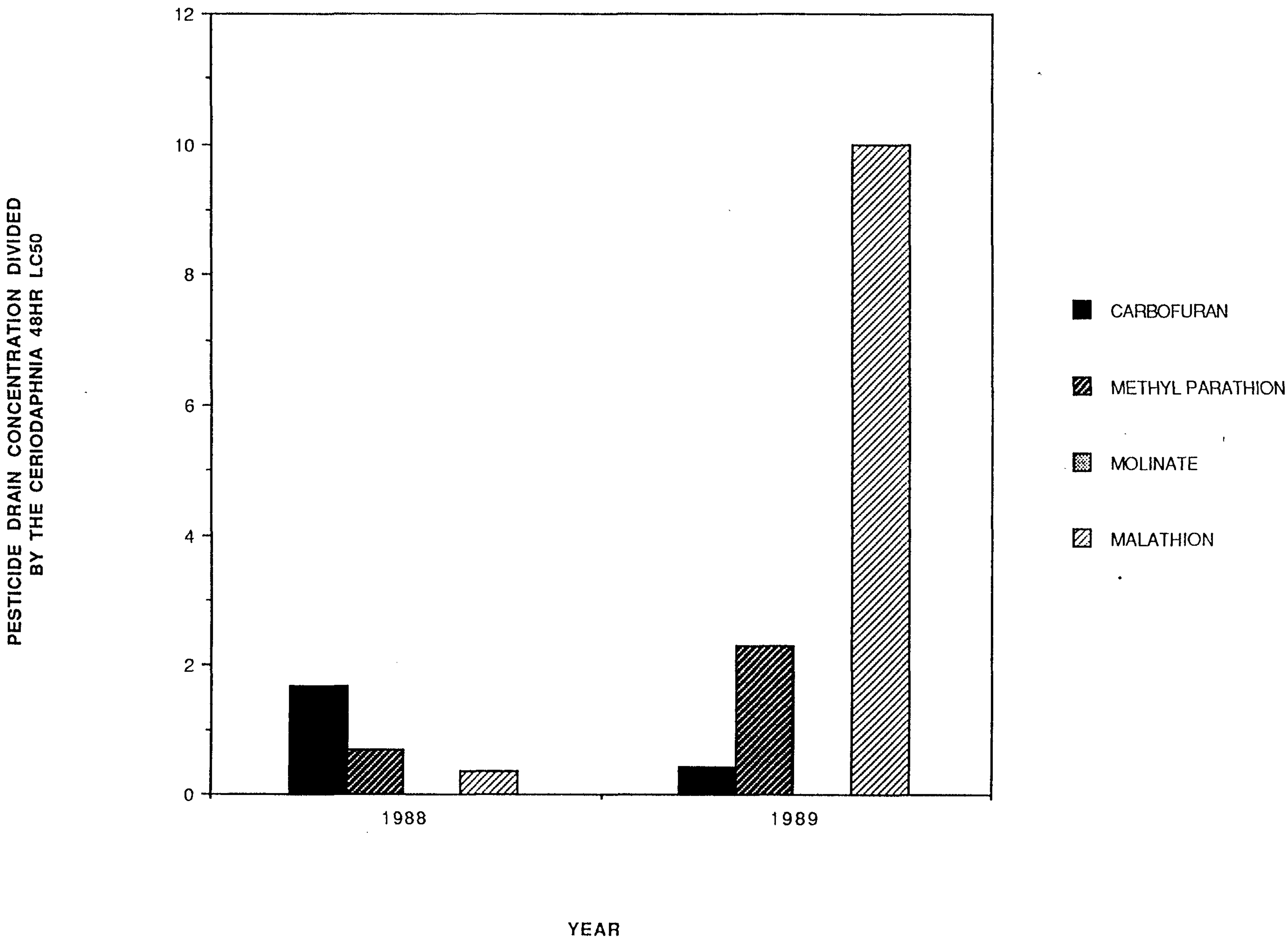

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FIGURE 2

PREDICTED RELATIVE TOXICITY OF CARBOFURAN, METHYL PARATHION, MOLINATE, AND MALATHION TO CHANNEL CATFISH BASED UPON THE MAXIMUM DETECTED CONCENTRATIONS IN COLUSA BASIN DRAIN

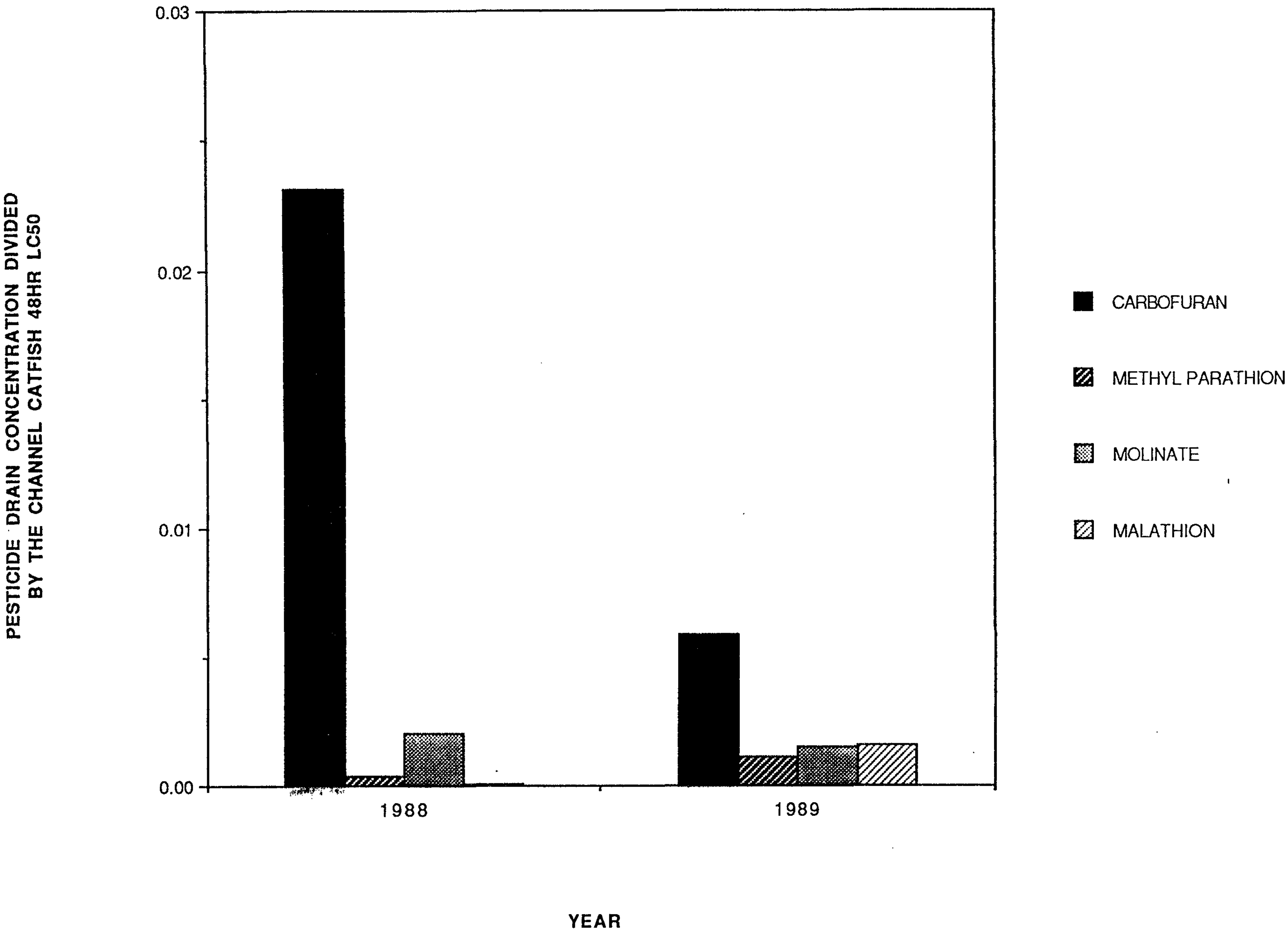

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FIGURE 3

PREDICTED RELATIVE TOXICITY OF CARBOFURAN, METHYL PARATHION, MOLINATE, AND MALATHION TO CERIODAPHNIA BASED UPON THE POUNDS APPLIED TO RICE

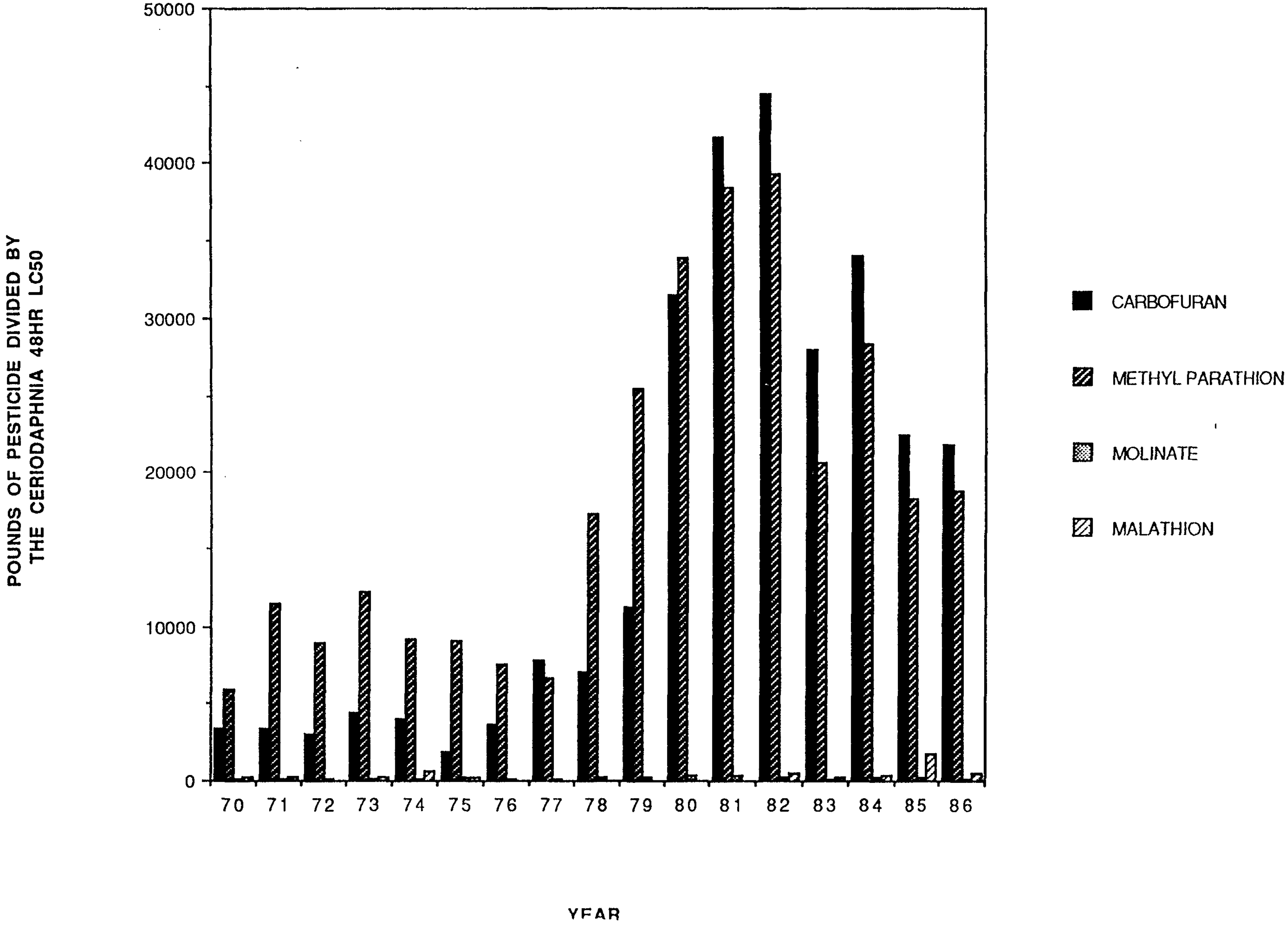

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FIGURE 4

PREDICTED RELATIVE TOXICITY OF CARBOFURAN, METHYL PARATHION, MOLINATE, AND MALATHION TO CHANNEL CATFISH BASED UPON THE POUNDS APPLIED TO RICE

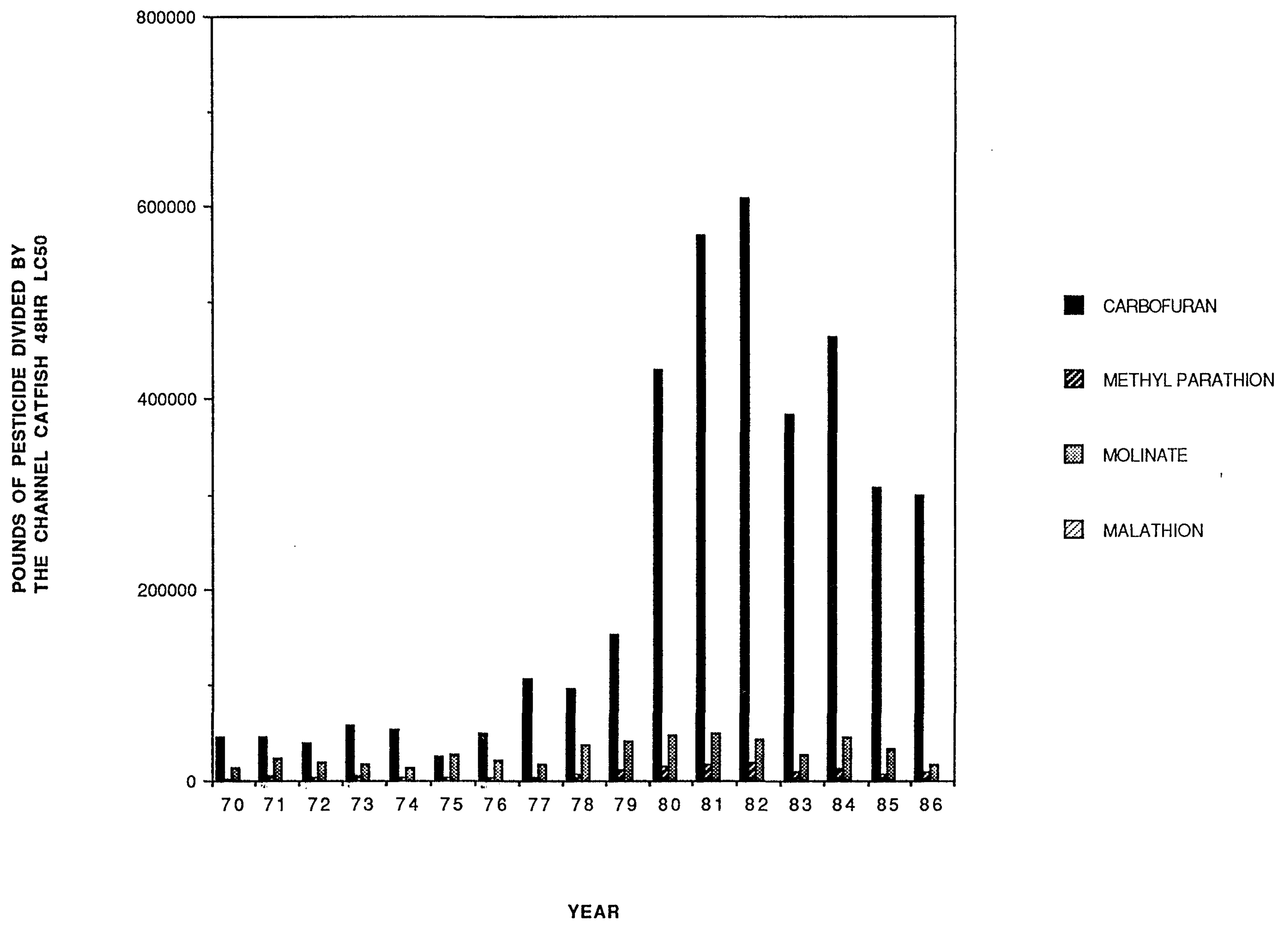

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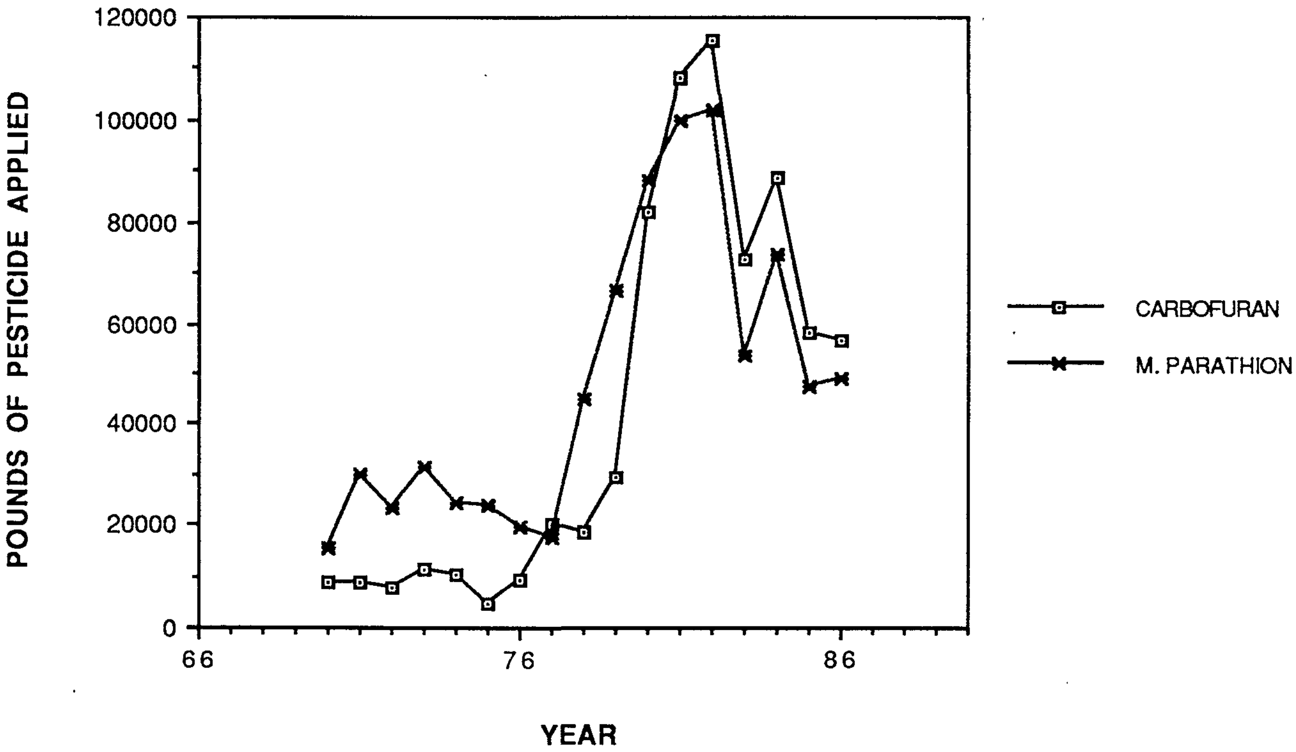
FIGURE 5

POUNDS OF CARBOFURAN AND METHYL PARATHION APPLIED ON RICE



C —0 2 9 8 7 0

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FIGURE 6

POUNDS OF ORDRAM AND METHYL PARATHION APPLIED ON RICE

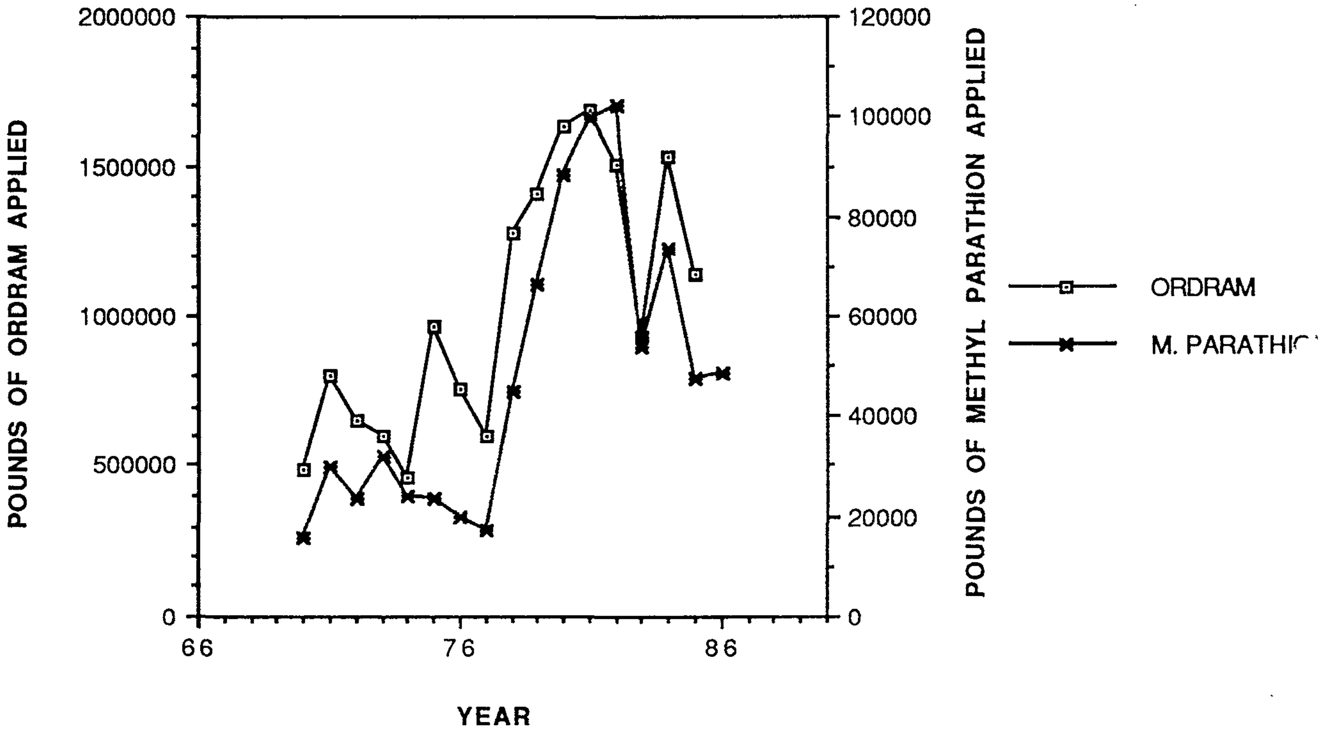

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FIGURE 7

SACRAMENTO VALLEY RICE ACREAGE

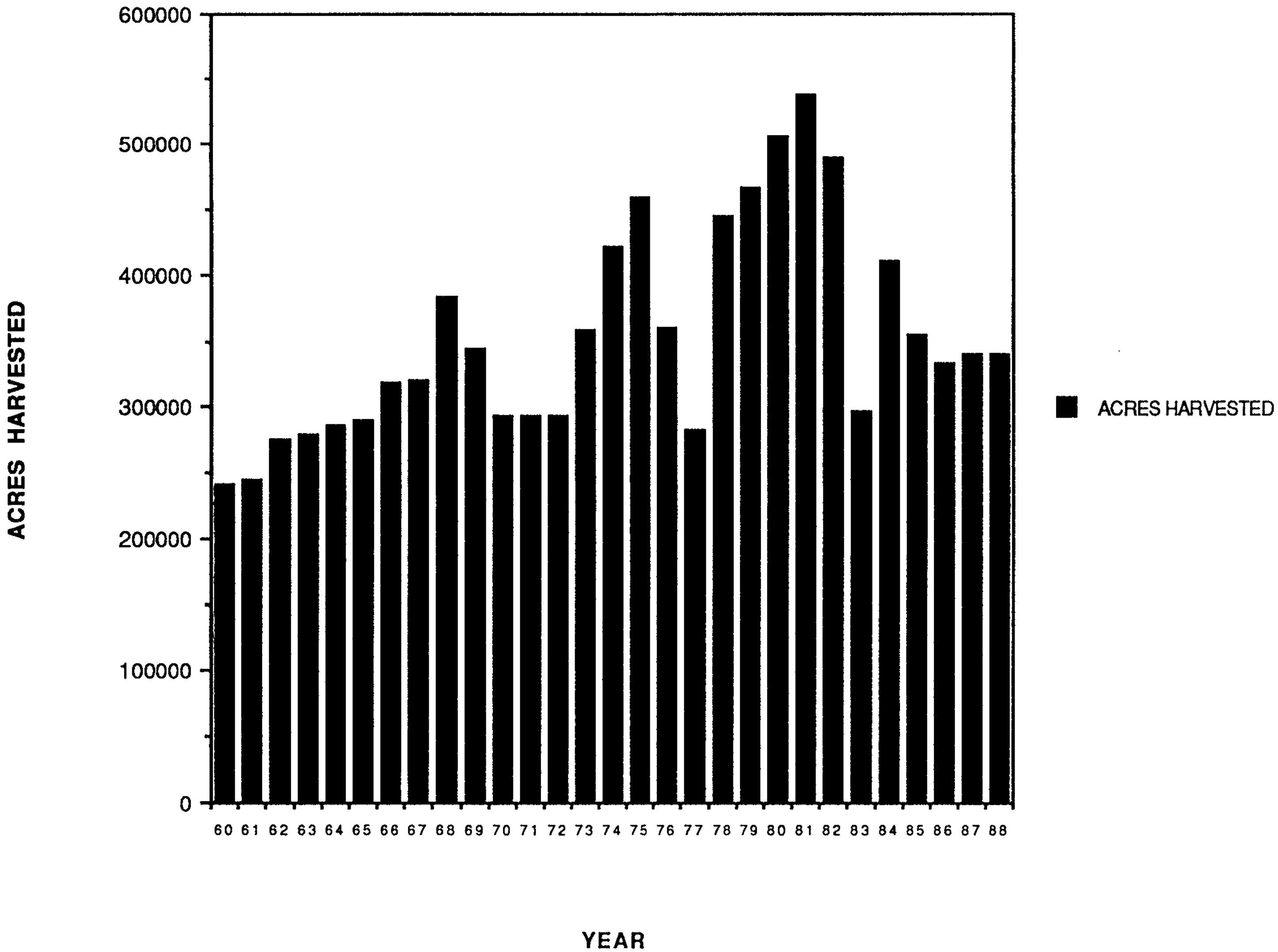

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Table 5

Major Reported Uses for Carbofuran, Malathion and Methyl Parathion in 1985

	No. of Apps.	Pounds Applied	Acres Treated
CARBOFURAN			
alfalfa	1370	65,435	134,581
rice	1290	58,262	97,304
grapes	99	22,647	2,826
turf	220	19,546	23,179
artichoke	13	935	869
total all crops		167,744	
MALATHION			
structural pest cont.	2682	104,299	
alfalfa	837	94272	73,732
landscape maintenance	1743	43,894	
date	913	35,257	10,363
pasture/rangeland	32	19,193	30,962
lettuce(head)	208	18,218	10,194
total all crops		431,365	
METHYL PARATHION			
rice	647	47,543	71,076
alfalfa	1081	43,454	112,944
lettuce	650	23,977	29,408
tomato	353	23,882	28,042
cotton	207	15,574	24,517
total all crops		208,736	

Source: California Department of Food and Agriculture's 1985 Pesticide Use Report.

Table 1. Summary of carbofuran (C), methyl parathion (MP), and malathion (M) concentrations (ppb) in Colusa Basin Drain water samples collected during May and June of 1989.

	Eureka[1]			CDFA[2]			EPA[3]		
Date	C	MP	M	C	MP	M	C	MP	M
April 27				1.2[5]					
May 4				1.5[5]					
May 15				1.5[5]					
May 15				1.12	1.6	<0.1[4]	0.8	0.46	
May 17	0.77	6.04	0.66	0.71	2.7	0.2	0.16	0.58	
May 18				1.0[5]					
May 18				0.55	0.8	<0.1	0.23	0.21	
May 21	0.56	0.47	3.30						
May 22				1.1[5]					
May 22	<0.2	0.38	0.89	0.62	0.4	1.3			
May 23	0.54	1.78	0.21						
May 24	0.53	3.90	<0.2						
May 25				1.1[5]					
May 31	0.72	0.16	1.18				0.83	0.09	1.22
June 1	0.53	0.5	1.1						
June 6	<0.2	<0.4	14.0				0.96	0.53	0.53

1. Eureka Laboratories, Inc., 6790 Florin Perkins Rd., Sacramento, CA.

2. California Department of Food and Agriculture, Sacramento, CA.

3. U.S. EPA, Environmental Research Laboratory, Duluth, MN, 55804

4. Detection limit.

5. Special carbofuran study (personal communication Mr. Marshall Lee).

Table 2. Reported carbamate and organophosphorus pesticide concentrations (ppb) in water samples collected from Colusa Basin Drain and the Sacramento River at Village Marina (City of Sacramento) during previous years.

		Drain			River			Reference
Date	Year	C[1]	MP[2]	M[3]	C	MP	M	
June 16	1980		0.8					Finlayson et al., 1982
June 27			<0.1					
July 3			2.3					
July 7			1.9					
July 15			2.0					
July 22			1.5					
September 8			0.2					
April 30	1981		<1.0					
May 18			3.0					
May 21			2.9					
May 26			1.8					
May 28			1.9					
June[4]			<1.0					
July[5]			<1.0					
August[6]			<1.0					
May 29	1986		0.7					Shaner, S. 1986
May 6	1987	2.0			<1.0			CDFA, 1987 (draft)
May 11		3.5			<1.0			
May 14		5.4			<1.0			
May 18		7.7			<1.0			
May 21		6.2			<1.0			
May 25		13.0			1.4			
May 28		9.9			2.1			
June 1		7.2			1.7			
June 4		2.0			<1.0			
June 8		<1.0			<1.0			
June 15		<1.0			<1.0			
April 25	1988	4.4						Nicosia, S. 1989
April 28		3.8						
May 2		2.7						
May 5		1.6						
May 9		3.2						
May 12		2.0						
May 16		1.4						
May 19		1.4						
May 23		ND[7]						
May 26		ND						
May 30		ND						
June 2		ND						
June 6		ND						

Table 2. (continued).

Date	Year	Drain C	Drain MP	Drain M	River C	River MP	River M	Reference
May 17	1988	>0.33	>1.8					Norberg-King et al., 1989 (appendix A)
June 1		>0.12	>1.4					
April 19	1988	1.74	0.41	0.01	0.40	0.32	ND	Keydel et al., 1988
May 15		0.92	0.21	0.50	0.25	0.08	ND	
June 1		0.34	0.110	0.211	0.05	0.06	ND	
June 13		0.14	0.20	ND	0.01	0.01	ND	

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[1] Carbofuran
[2] Methyl parathion
[3] Malathion
[4] Five sampling dates
[5] Four sampling dates
[6] Two sampling dates
[7] Non detected

Table 3

Human Health Water Quality Goals for
Carbofuran, Methyl Parathion and Malathion

	DHS[2] Primary MCL[3]	DHS Action Level
Carbofuran	18 ppb	
Malathion		160 ppb
Methyl Parathion		30 ppb

[2] DHS = Department of Health Services

[3] MCL = Maximum Contaminant Level

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TABLE 4
AQUATIC SPECIES TOXICITY DATA SUMMARY

	SPECIES	CHEMICAL	96 HR. LC50	REFERENCES
INVERTEBRATES	DAPHNIA MAGNA	CARBOFURAN	48 PPB	Johnson, 1986
		MALATHION	1 PPB	Johnson and Finley, 1980
		METHYL PARATHION	.14 PPB	Johnson and Finley, 1980
		MOLINATE	>600 PPB	Sanders, 1970
	PINK SHRIMP	CARBOFURAN	4.6 PPB	US Env Resrch Lab, 1986
	(Penaeus	MALATHION	280 PPB	US Env Resrch Lab, 1986
	duorarum)	METHYL PARATHION	1.2 PPB	US Env Resrch Lab, 1986
		MOLINATE	>1000 PPB	US Env Resrch Lab, 1986
	CERIODAPHNIA	CARBOFURAN	2.6 PPB (48HR.)	Norberg-King, et al., 1989a
	DUBIA	MALATHION	1.4 PPB	Norberg-King, 1989
		METHYL PARATHION	2.6 PPB (48 HR.)	Norberg-King, et al., 1989a
		MOLINATE	>5000 PPB	Norberg-King, et al., 1989a
FISH	SPOT	CARBOFURAN	N/A	
	(Leiostomus	MALATHION	320 PPB	US Env Resrch Lab, 1986
	xanthrus)	METHYL PARATHION	59 PPB	US Env Resrch Lab, 1986
		MOLINATE	>1000 PPB	US Env Resrch Lab, 1986
	SHEEPSHEAD	CARBOFURAN	1386 PPB	Verschueren, 1983
	MINNOW	MALATHION	51 PPB	Verschueren, 1983
	(Cyprindon	METHYL PARATHION	>800 PPB	US Env Resrch Lab, 1986
	variegatus)	MOLINATE	N/A	
	LAKE TROUT	CARBOFURAN	164 PPB	Johnson and Finley, 1980
	(Salvelinus	MALATHION	76 PPB	Johnson and Finley, 1980
	namaycush)	METHYL PARATHION	3.7 PPM	Johnson and Finley, 1980
		MOLINATE	.21 PPM	Mayer and Ellersieck, 1986
	YELLOW PERCH	CARBOFURAN	147 PPB	Johnson and Finley, 1980
	(Perca	MALATHION	263 PPB	Johnson and Finley, 1980
	flavescens)	METHYL PARATHION	3.06 PPM	Johnson and Finley, 1980
		MOLINATE	N/A	
	CHANNEL CATFISH	CARBOFURAN	.248 PPM	Johnson and Finley, 1980
	(Ictalurus	MALATHION	8.97 PPM	Johnson and Finley, 1980
	punctatus)	METHYL PARATHION	5.2 PPM	Johnson and Finley, 1980
		MOLINATE	33.24 PPM	Brown, et al., 1979
	STRIPED BASS	CARBOFURAN	N/A	
	(Morone	MALATHION	.039 PPM	Mayer and Ellersieck, 1986
	saxatilis)	METHYL PARATHION	14.0 PPM	Mayer and Ellersieck, 1986
		MOLINATE	8.10 PPM	Mayer and Ellersieck, 1986
	COHO SALMON	CARBOFURAN	530 PPB	Mayer and Ellersieck, 1986
	(Oncorhynchus	MALATHION	170 PPB	Mayer and Ellersieck, 1986
	kisutch)	METHYL PARATHION	5300 PPB	Mayer and Ellersieck, 1986
		MOLINATE	N/A	
MOLLUSKS	EASTERN OYSTER	CARBOFURAN	>1000 PPB	US Env Resrch Lab, 1986
	(Crassostrea	MALATHION	>1000 PPB	US Env Resrch Lab, 1986
	virginica)	METHYL PARATHION	12 PPM	US Env Resrch Lab, 1986
		MOLINATE	>1000 PPB	US Env Resrch Lab, 1986

N/A=DATA NOT AVAILABLE

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