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SUBJECT: ASSESSMENT OF ACUTE AQUATIC TOXICITY OF CURRENT-USE PESTICIDES IN CALIFORNIA, WITH MONITORING RECOMMENDATIONS

SUMMARY

The Department of Pesticide Regulation (DPR) conducts surface water monitoring for pesticide active ingredients (AIs) for which there are limited or no recent California monitoring data. The objective of this memorandum is to identify a prioritized list of candidate AIs and associated surface water monitoring locations based on detailed analysis of acute aquatic toxicity data and recent agricultural pesticide use data.

Approximately 125 agricultural use AIs served as the base set of pesticides for this surface water screening procedure. Sufficient aquatic toxicity data were available to classify 39 of these AIs into 5 broad relative aquatic toxicity categories ranging from "very low" to "very high." Spatial and temporal characteristics of agricultural pesticide use for the 23 AIs with the highest aquatic toxicity ranking were determined from analysis of recent agricultural use data. Prioritized monitoring recommendations were then developed for these 23 pesticide AIs.

Pesticide AIs currently undergoing reevaluation by DPR (pyrethroid insecticides, chlorpyrifos, and diazinon dormant spray use) are not included in this assessment.

PROCEDURE

Pesticide Use Assessment

Using DPR's Pesticide Use Reporting database (DPR 2006a), a list was developed of all AIs with at least 5,000 pounds of agricultural use in at least one county during 2003. The choice of this amount as a cut off point was chosen in order to capture all AIs with significant use, based on agricultural use patterns in California. Pesticide use in all counties statewide was included in this assessment. This initial list included approximately 125 AIs (Table A-1, Appendix A).

AIs with very low use rates were also considered. An alternate analysis of use data designed to identify AIs with widespread use but low use rates was completed. No additional AIs were identified for inclusion in the analysis. Note that the pyrethroid insecticides were not included in the assessment due to the fact that they are currently undergoing reevaluation by DPR.

Toxicity Assessment

For the 125 AIs on the current-use list, acute toxicity data for aquatic organisms were compiled from U.S. Environmental Protection Agency (EPA) databases (EPA 2006a, 2006b), directly and through the Pesticide Action Network pesticide database (Orme and Kegley, 2006). Due to a lack of adequate toxicity data for some AIs, the list of 125 was shortened to 39. For detail and discussion of AIs eliminated from the assessment, see Appendix A. The 39 AIs were assigned a toxicity score and a relative toxicity rank (very low to very high) to indicate acute toxicity to species in 4 different organism groups (Table 1). The assessment was limited to AIs with data for three of the four organism types in order to minimize the differences in the elements being compared. AIs with toxicity to fewer than the four organism groups are discussed in Appendix A.

Toxicity data from four different organism types (fish, crustaceans, aquatic insects, and zooplankton) were used in the toxicity assessment in order to estimate the overall impact the pesticide may have on aquatic systems. This approach provides a broader overall toxicity measure than single species LC50s.

Toxicity Scoring Process

Average species LC50 values were previously calculated by Orme and Kegley (2006) by averaging all LC50 values for a given species reported in the U.S. EPA ECOTOX database (U.S. EPA 2006a). These average species LC50 values were used in this assessment to calculate toxicity scores for each of the 39 AIs.

For each AI, a toxicity score was assigned for each average LC50 value utilizing the scheme described in Appendix A. Lower average LC50 values were assigned higher scores; a higher score is indicative of higher toxicity. For each AI, a total score for each organism group was then calculated by summing the scores for each species within that organism group. The overall total score for each AI was calculated by summing the scores for all four of the organism groups. These scores provide a relative estimate of the potential effects for each AI (Table 1).

All available toxicity data for all species were used. The data were pooled intentionally in order to provide as much information as possible about the toxicity of the AIs. Not all AIs had toxicity data for all species. Potentially, this could have resulted in a higher toxicity rank for those AIs with a higher number of tested species, based solely on the availability of data; in practice, this bias was minimal.

Degradation Product Toxicity

The acute toxicity of pesticide degradation products was also assessed utilizing currently available data (U.S. EPA 2006a, 2006b). Although toxicity data for pesticide degradation products are limited, a few notable issues were identified through this process. A few AIs with low agricultural use in California also form as degradates of other, higher use pesticides. For example, methamidaphos use in California agriculture is low, but use of acephate, which degrades in the environment to methamidaphos, is high in several regions of California. Methamidaphos is more acutely toxic to aquatic organisms than acephate. Naled, which degrades to the more toxic dichlorvos, also has relatively high agricultural use. The toxicity of these degradation products was taken into account in the toxicity ranking process. As such, the toxicity rank for acephate and naled are higher that they would be otherwise. Monitoring for such AI/degradate combinations may be warranted in some cases.

Fipronil degradation products also have reported high toxicity (U.S. EPA 2006b). Fipronil use is currently low in California agriculture, and as such was not included in this assessment. However, nonagricultural use is significant (DPR 2006a). DPR is currently developing a surface water monitoring plan for fipronil. The toxicity of nonagricultural AIs is being considered separately; see below. Additional efforts to assess the available toxicity data for pesticide degradation products are also currently underway.

Additional Toxicity Assessment Needs

AIs with few acute toxicity studies, or with acute toxicity studies in only one or two organism groups, may not be represented in this assessment. As such, all significantly toxic pesticides used in California may not be adequately assessed. Some herbicides and some newly registered pesticides may fit into this category. Alternate methods for assessment of these pesticides are under consideration.

The toxicity assessment presented here considers only the acute aquatic toxicity of the pesticides studied. Other toxic effects, including sublethal effects such as effects on endocrine-mediated processes, are not considered here. A similar assessment focusing on sublethal effects of current-use pesticides will be considered.

Additionally, the current assessment focuses on pesticides with significant agricultural use; nonagricultural use was not considered in the development of the list of AIs. Nonagricultural uses include applications for structural pest control and landscape and rights-of-way maintenance, among others. Consumer home and garden uses are not included in this designation. Since nonagricultural use can be considerable, a list of AIs with significant nonagricultural use (at least 5,000 pounds in at least one county in 2003) was also developed from DPR’s pesticide use report (PUR). This list was compared to the agricultural use list in order to identify AIs that do not have significant agricultural use, but may need to be assessed in terms of their toxicity. A toxicity assessment of these nonagricultural use AIs will be considered separately.

Chemical and Physical Properties

For the top 23 AIs from the toxicity assessment, the chemical and physical properties were reviewed and are presented in Appendix A, Table A-3. Based primarily on the water solubility and Koc data, it was concluded that none of the AIs under consideration should be eliminated from consideration based on these properties.

Recent California Pesticide Use and Surface Water Monitoring Data

For each of the top 23 AIs from the toxicity assessment, recent (2002-2004) agricultural use in California was assessed using data from DPR's PUR database (DPR 2006a).

Each AI was first assessed and ranked in terms of the total amount used statewide. The AIs were ranked from very low to very high use based on their average use over the years 2002-2004 (Table 2). A general monitoring priority was assigned based on this use ranking in conjunction with the toxicity ranking (Table 3). For ranking process details, see Appendix A.

A more detailed assessment of the recent agricultural use was then completed. For the 23 primary AIs, the agricultural use was mapped by county (Appendix B). From these maps, high use counties were determined. For each high use county, the use was then assessed by month to determine the timing of any peak use periods (Appendix C).

Recent surface water monitoring data (2000-2006) from DPR's surface water monitoring database (DPR 2006b) was also examined (Appendix C). For each county with high use, the number of samples collected in that county during the previously identified high-use period(s) and the number of detections in those samples was determined.
Monitoring results were used to identify high-use counties where additional monitoring may be needed. High-use areas with little or no historical monitoring data, or with frequent detections when monitoring occurred, were given the highest priority for future monitoring efforts.

For all pesticide use assessments, the average of the agricultural use over the years 2002-2004 was utilized. These were the most recent use data available. This approach assumes that the average of the historical use over the three-year period will provide a reasonable estimate of future use, at least in the short term. This estimate can serve as an aid when developing monitoring projects targeting high use areas.

The southern San Joaquin Valley region, which includes Madera, Fresno, Kings, Tulare, and Kern counties, was excluded from the high-use period assessment and from subsequent monitoring recommendations due to the general lack of surface water in close proximity to most of the agricultural pesticide use in the area. Nevertheless, due to the very high pesticide use in this area, a separate assessment of this region may be warranted.

RECOMMENDATIONS

Fifteen AIs are designated as high or medium monitoring priority, and are recommended for further investigation and/or monitoring (Tables 4 and 5). In some cases, additional assessment of the toxicity, use data, or other relevant factors may be necessary prior to initiating monitoring. Detailed results of the assessment are presented in Appendix D. For each AI in the high or moderate monitoring priority rank (Table 3), the high use regions and periods are given. Areas where DPR is currently conducting targeted monitoring are indicated in the “status” column.

REFERENCES

DPR 2006a. PUR Database. Available on DPR’s Web site at: <http://calpip.cdpr.ca.gov/cfdocs/calpip/prod/main.cfm>.

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Table 1. Assessment of acute toxicity of 39 pesticides to four general groups of aquatic organisms.

Chemical	Total Score	Crustaceans (4)	Fish	Insects	Zooplankton	Toxicity Rank
Methamidaphos	1100.00	1100.00	0.00	N/A	0.00	very high
Carbaryl	1007.55	2.46	0.01	1003.33	1.75	very high
Endosulfan	158.16	25.46	68.82	21.63	42.25	very high
Azinphos Methyl (1)	56.55	1.31	21.84	1.40	32.00	very high
Methyl Parathion	32.24	13.60	1.01	1.53	16.10	very high
Malathion	23.93	2.36	1.28	10.87	9.42	very high
Diazinon	19.31	0.31	0.30	4.39	14.31	high
Phorate	16.55	0.01	4.24	1.20	11.10	high
Carbofuran (1)	13.01	1.32	0.37	10.02	1.30	high
Thiram	11.39	0.00	11.35	0.01	0.03	high
Dichlorvos	10.16	5.32	0.1	1.42	3.32	high
Dimethoate	3.59	0.10	0.07	1.31	2.11	moderate
Trifluralin	3.19	0.11	2.75	0.00	0.33	moderate
Copper	2.82	0.24	1.00	0.03	1.55	moderate
Naled (2)	2.62	1.01	1.17	0.32	0.12	moderate
Chlorothalonil	2.18	1.32	0.85	0.00	0.01	moderate
Tribufos	2.04	0.01	1.00	0.00	1.03	moderate
Profenofos	1.81	0.10	0.61	0.10	1.00	moderate
Phosmet	1.68	0.11	0.26	0.01	1.30	moderate
Disulfoton	1.64	N/A	0.13	1.20	0.31	moderate
Methidathion	1.52	0.11	0.31	0.10	1.00	moderate
Methomyl	1.15	0.23	0.04	0.41	0.47	moderate
Acephate (3)	1.00	0.00	1.00	0.00	0.00	moderate
Piperonyl butoxide	1.02	1.00	0.00	0.00	0.02	low
Glyphosate	1.00	0.00	0.00	N/A	1.00	low
Aldicarb	0.81	0.01	0.45	0.32	0.03	low
Captan	0.72	0.00	0.72	0.00	0.00	low
Fenamiphos	0.32	0.10	0.12	N/A	0.10	low
Dicofol	0.31	0.03	0.27	0.00	0.01	low
Imidacloprid	0.30	N/A	0.00	0.20	0.10	low
Maneb	0.25	0.00	0.03	N/A	0.22	low
Thiobencarb	0.18	0.04	0.07	0.00	0.07	low
Atrazine	0.12	0.00	0.00	0.01	0.11	low
Oryzalin	0.02	0.01	0.00	N/A	0.01	low
Oxy-demeton	0.02	0.00	0.00	0.01	0.01	low
Molinate	0.02	0.01	0.00	0.01	0.00	low
Copper sulfate-penta	0.02	0.01	0.01	N/A	0.00	low
Diuron	0.02	0.00	0.00	0.00	0.02	low
Simazine	0.00	0.00	0.00	0.00	0.00	low

(1) Currently undergoing cancellation or phase-out by U.S. EPA.

(2) naled degrades to dichlorvos

(3) acephate degrades to methamidaphos

(4) The distinction between the zooplankton and crustacean groups is based on organism size; the division is sometimes unclear (Orme and Kegley, 2006).

N/A = no data available. Scores of 0.00 = all ave. LC50 values < 1000 ug/L

For scoring scheme, see Appendix A.

Table 2. Average annual California agricultural pesticide use (2002-2004) of top 23 toxicity ranked pesticides, with use rank.

Chemical	Pesticide Use	Use Rank
Trifluralin	646302	very high
Diazinon	391325	high
Malathion	374969	high
Chlorothalonil	354995	high
Dimethoate	214223	high
Methomyl	195335	high
Acephate	144346	high
Phosmet	102142	high
Carbaryl	85062	moderate
Thiram	54773	moderate
Naled	54656	moderate
Tribufos	54558	moderate
Disulfoton	44920	low
Carbofuran	41629	low
Azinphos-Methyl	41049	low
Methyl Parathion	38562	low
Phorate	36321	low
Methidathion	24269	low
Endosulfan	21761	low
Methamidaphos	17359	low
Copper	5052	very low
Profenofos	971	very low
Dichlorvos (DDVP)	0	very low

Statewide Pesticide Use Ranking Scheme

Pounds AI	Rank
< 15,000	very low
15,000 to 49,999	low
50,000 to 99,999	moderate
100,000 to 499,999	high
≥ 500,000	very high

Pesticide Use is average of use, 2002-2004, in pounds of active ingredient
Use assessment not completed for AIs with low toxicity rank (Table 1).

Table 3. General monitoring priority for top 23 pesticides, based on toxicity and use.

Chemical	**Toxicity**	**Use**	**Monitoring Priority**
Malathion	very high	high	high
Diazinon	high	high	high
Carbaryl	very high	moderate	high
Thiram	high	moderate	high
Trifluralin	moderate	very high	high
Acephate (1)	moderate	high	medium
Chlorothalonil	moderate	high	medium
Dimethoate	moderate	high	medium
Endosulfan	very high	low	medium
Methamidaphos (1)	very high	low	medium
Methomyl	moderate	high	medium
Methyl parathion	very high	low	medium
Phorate	high	low	medium
Dichlorvos (DDVP) (1)	high	very low	medium
Phosmet	moderate	high	medium
Naled (1)	moderate	moderate	medium
Tribufos	moderate	moderate	low
Disulfoton	moderate	low	low
Methidathion	moderate	low	low
Azinphos methyl (2)	very high	low	low
Carbofuran (2)	high	low	low
Copper	moderate	very low	very low
Profenofos	moderate	very low	very low

(1) Monitoring priority rank includes consideration of the high toxicity of a degradation product.
(2) Monitoring priority rank includes consideration of U.S. EPA cancellation / phase out currently in progress.

Monitoring Priority not determined for Low Toxicity AIs (Table 1).

Table 4. Five high priority pesticides recommended for monitoring.

Chemical	Region	Peak Use	Peak Use Amount (approx. lbs AI)	Monitoring Priority	Status
Carbaryl	NSJV	Spring-Summer	20000	high	
	Sac V	Summer	5000	high	
Trifluralin	NSJV	Winter/Spring	115000	high	
	SE Interior	Winter/Spring	215000	high	
	Sac V	Winter/Spring	45000	high	
Diazinon	NSJV	Spring	6000	high	
	Sac V	Spring	6500	high	
	Central Coast	Spring-Summer	15000	high	in progress
	SE Interior	Fall	35000	high	in progress
Malathion	NSJV	Spring-Summer	25000	high	
	Central Coast	Spring-Summer	95000	high	in progress
	SE Interior	Winter/Spring	70000	high	in progress
	South Coast	Spring-Summer	55000	high	in progress
Thiram	Central Coast	Spring-Summer	20000	high	in progress
	South Coast	Winter/Spring	17000	high	in progress

Region:
NSJV = North San Joaquin Valley, primarily San Joaquin, Stanislaus, and Merced counties
Sac V. = Sacramento Valley, primarily Sutter, Yolo, and Butte counties
SE Interior = Inland southeast, primarily Imperial, and Riverside counties
Central Coast = Santa Cruz, Monterey, San Benito, and San Luis Obispo counties
South Coast = Los Angeles, Orange, Santa Barbara, and Ventura counties
Status:
In progress: Targeted monitoring currently underway (DPR).

Table 5. Ten medium priority pesticides recommended for monitoring.

Chemical	Region	Peak Use	Peak Use Amount (approx. lbs AI)	Monitoring Priority	Status
Acephate	Central Coast	Spring-Summer	70000	medium	under dev.
(degrades to	South Coast	Spring-Summer, Fall	12500	medium	under dev.
methamidaphos)	SE Interior	Summer/Winter	11000	medium	under dev.
Chlorothalonil	NSJV	Summer	75000	medium	
	South Coast	all seasons	85000	medium	
	SE Interior	Spring	25000	medium	
	Sac V	Summer	21000	medium	
Dimethoate	Central Coast	Spring-Summer	40000	medium	
	NSJV	Summer	50000	medium	
	SE Interior	Winter/Spring	50000	medium	
Endosulfan	SE Interior	Summer	10000	medium	
	Sac V	Summer	3500	medium	
Methamidaphos	Sac V	Summer	5000	medium	under dev.
	North	Summer	4500	medium	under dev.
	SE Interior	Summer	1000	medium	under dev.
	South Coast	Summer	1000	medium	under dev.
Methomyl	Central Coast	Spring-Summer	50000	medium	in progress
	NSJV	Summer	38000	medium	
	SE Interior	Spring, Fall	23000	medium	in progress
	South Coast	Summer	5000	medium	in progress
Methyl parathion	NSJV	Summer	25000	medium	
	Sac V	Summer	6000	medium	
Phosmet	NSJV	Spring-Summer	30000	medium	
	Sac V	Spring-Fall	18000	medium	
Naled	Central Coast	Spring-Summer	21000	medium	
(degrades to	South Coast	Summer	5000	medium	
dichlorvos)	NSJV	Summer	7000	medium	
Phorate	SE Interior	Spring	8000	medium	
	NSJV	Spring	9000	medium	
	Sac V	Spring	4000	medium	
	North	Summer-Fall	3200	medium	

Region:
NSJV = North San Joaquin Valley, primarily San Joaquin, Stanislaus, and Merced counties
Sac V. = Sacramento Valley, primarily Sutter, Yolo, and Butte counties
SE Interior = Inland southeast, primarily Imperial, and Riverside counties
Central Coast = Santa Cruz, Monterey, San Benito, and San Luis Obispo counties
South Coast = Los Angeles, Orange, Santa Barbara, and Ventura counties
North = North State, primarily Modoc, Siskiyou, and Del Norte counties
Status:
In progress: Targeted monitoring currently underway (DPR).
Under dev.: Relevant environmental fate under review for possible monitoring project (DPR).
no entry: No targeted monitoring currently in progress or planned (DPR).