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Insecticide Market Trends and Potential Water Quality Implications

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PREFACE

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INSECTICIDE MARKET TRENDS AND POTENTIAL WATER QUALITY IMPLICATIONS

EXECUTIVE SUMMARY

The entire market for urban-use insecticides is changing as a result of the U.S. EPA phase out of most urban uses of diazinon and chlorpyrifos (Dursban), two of the most commonly used urban insecticides. Both diazinon and chlorpyrifos were linked to toxicity in urban runoff and surface waters throughout California. With funding from the San Francisco Bay Regional Water Quality Control Board, TDC Environmental assessed the possibility that pesticides entering the marketplace to replace diazinon and chlorpyrifos may cause adverse impacts to aquatic ecosystems receiving urban runoff.

Of the 45 insecticides that are possible replacements for urban uses of diazinon and chlorpyrifos, ten insecticides and one synergist (bifenthrin, carbaryl, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, imidacloprid, malathion, permethrin, pyrethrins, and piperonyl butoxide) appeared to be most likely to gain significant market share in the coming years and may pose concerns for water quality; these were selected for detailed review.[1]

Conclusions

This report summarizes environmental information relevant to the 10 insecticides and the synergist, such as chemical and physical properties, environmental fate data, commercial product characteristics, sales, use, regulatory status, chemical analysis methods, and aquatic toxicity. Using this information, the report assesses possibility that pesticides entering the marketplace to replace diazinon and chlorpyrifos may cause adverse impacts to aquatic ecosystems receiving urban runoff. The assessment uses all available environmental monitoring data, together with a qualitative review of use, transport and fate of each pesticide in the urban environment. Conclusions, based on the weight of the available evidence, are as follows:

1. **Use of bifenthrin, carbaryl, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, malathion, and permethrin as replacements for urban uses of diazinon and chlorpyrifos may cause adverse effects in aquatic ecosystems receiving urban runoff.**
2. **Depending on application locations, use of imidacloprid and pyrethrins as replacements for urban uses of diazinon and chlorpyrifos may cause adverse effects in aquatic ecosystems receiving urban runoff. Extensive data gaps preclude a more definitive conclusion.**
3. **Use of piperonyl butoxide as a synergist in pesticide products that replace urban uses of diazinon and chlorpyrifos has the potential to contribute to adverse effects caused by other pesticides in aquatic ecosystems receiving urban runoff.**
4. **While sufficient data were identified to support a weight-of-evidence evaluation, critical data gaps exist for study list pesticides.**

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[1] Since the initial evaluation was completed, lambda cyhalothrin products entered the urban retail marketplace at a level that may be equivalent to the selected pesticides.

Recommendations

This report recommends several actions in response to these conclusions. The recommendations, listed below, address critical data gaps, monitoring needs, regulatory shortcomings, and education and outreach imperatives.

Data Gaps

Data gaps are barriers to understanding the potential effects of pesticides on aquatic ecosystems. The following actions are recommended to address the most critical data gaps identified in this report:

1. Fill toxicity testing data gaps.
2. Evaluate potential for pyrethroid pesticides to accumulate in surface water body sediments at concentrations that may cause toxicity to benthic organisms.
3. Assess water quality implications of the use of synergists other than piperonyl butoxide in products that replace diazinon and chlorpyrifos urban use products.
4. Assess water quality implications of use of the pyrethroid insecticide lambda cyhalothrin as a replacement for urban uses of diazinon and chlorpyrifos. Lambda cyhalothrin has growing agricultural use and began entering the residential retail market as this study neared completion.
5. Make all information necessary to evaluate and prevent surface water quality impacts from pesticides publicly available for every registered pesticide.

Monitoring

Since adverse effects may occur in aquatic ecosystems receiving urban runoff, water quality monitoring is recommended. Unfortunately, a full suite of monitoring methods is not currently readily available for the investigated insecticides. Recommendations include feasible monitoring activities and development of methods to improve monitoring capabilities:

6. Develop practical methods for monitoring urban surface waters and sediments to identify the presence of and to measure possible environmental effects of diazinon and chlorpyrifos replacement pesticides.
7. Develop methods for chemical analysis of bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, imidacloprid, and permethrin suitable for use by commercial laboratories with detection limits below environmentally relevant concentrations.
8. Monitor urban surface waters to identify the presence of and to measure possible environmental effects of diazinon and chlorpyrifos replacement pesticides.
9. Monitor sales and use of diazinon and chlorpyrifos replacement pesticides in urban areas.
10. Develop specific plans to respond to findings of toxicity in surface waters or sediments.
11. Establish a monitoring network to characterize the presence of pesticides in California surface waters.

Pesticide Regulatory Activities

California and Federal regulatory processes should, in theory, be able to prevent future water quality impacts from pesticides. Modifications are recommended to fill gaps in current pesticide regulatory processes that have allowed adverse impacts to occur in aquatic ecosystems receiving urban runoff:

12. Maximize the ability of the pesticide registration process to prevent potential water quality problems associated with pesticide use.
13. Use California and Federal water quality agency expertise during the pesticide registration process to ensure that pesticide applications comply with the Clean Water Act and the Porter-Cologne Water Quality Control Act.
14. Develop a California or Federal "surface water protection list" similar to the California Department of Pesticide Regulation's ground water protection list.
15. Identify and/or develop methods appropriate for ecological risk assessment of surface water quality impacts of pesticides.
16. Make regulatory changes to facilitate efforts to promote pest management methods that use non-chemical and least-toxic chemical alternatives to pesticides to manage urban pest problems.

Education and Outreach

Since any regulatory changes to address potential adverse effects of diazinon and chlorpyrifos replacement insecticides will not occur quickly, education and outreach are recommended to minimize surface water impacts from urban pesticide use:

17. Discourage use of bifenthrin, carbaryl, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, malathion, and permethrin as replacements for urban uses of diazinon and chlorpyrifos.
18. Until further information is available, refrain from recommending imidacloprid and pyrethrins (particularly products with piperonyl butoxide) as substitutes for urban uses of diazinon and chlorpyrifos.
19. Strengthen efforts to promote pest management methods that use non-chemical and least-toxic chemical alternatives to pesticides to manage urban pest problems.
20. Minimize pesticide wash-off by minimizing use of uncontained chemical pesticides.

1.0 INTRODUCTION

1.1 Background

Until the 1990s, water quality managers generally did not actively consider the potential for urban pesticide use to harm surface water quality. In the mid-1990s, California water quality agencies found widespread toxicity in water bodies receiving urban runoff. The toxicity was linked to two commonly used pesticides—diazinon and chlorpyrifos. A national water quality survey conducted by the U.S. Geological Survey (USGS) frequently detected the insecticides diazinon, chlorpyrifos, carbaryl, and malathion in urban streams, and often at concentrations that exceeded water quality criteria (Gilliom *et al.*, 1999). The USGS survey found that urban surface water insecticide levels are similar to—and in some cases higher than—insecticide concentrations in agricultural surface waters (Hoffman et al., 2000). These surprising findings have caused water quality managers to redesign urban runoff management programs to address potential surface water impacts from urban pesticide use.

In 2000**,** the U.S. Environmental Protection Agency (U.S. EPA) announced agreements with manufacturers to phase out most urban uses of diazinon and chlorpyrifos. While the planned phase out is likely to end most (if not all) of the previously identified toxicity, it brings new water quality management challenges as different insecticides enter the urban pesticide marketplace.

The purpose of this report is to assess the possibility that pesticides entering the marketplace to replace diazinon and chlorpyrifos may cause adverse impacts to aquatic ecosystems receiving urban runoff. This analysis is intended to help the California State and Regional Water Quality Control Boards, local urban runoff management programs, and other interested parties focus on potential future sources of pesticide-related urban surface water toxicity. Using the information in this report, water quality managers can determine prudent management actions while setting priorities for future investigations.

1.2 Scope of This Report

Ideally, the water quality impacts of the use of a chemical can be evaluated with environmental measurements of the chemical concentration and the observance of adverse effects (*e.g.*, aquatic toxicity) from the substance in a real-world situation. This ideal approach has a major down side—waiting until such measurements can be made for pesticides now entering the marketplace eliminates opportunities to prevent adverse impacts. Since a primary goal of this project is to provide information for water quality managers to use to prevent potential impacts, the report relies on existing, available information from the scientific literature to form the basis of the evaluation of potential for future environmental harm.

Because the insecticides in this study are just now gaining significant market share, information about their real-world impacts is extremely limited. This analysis relies on the weight of the evidence in existing environmental information to assess the potential for each of the pesticides evaluated to cause adverse impacts on aquatic ecosystems.

This study specifically focuses on urban insecticide use. For purposes of the study, "urban" was broadly defined to include facilities and activities commonly found in California urban and suburban areas, like residences, commercial buildings, institutions, parks, golf courses, nurseries, greenhouses, and rights-of-way. Agricultural activities are not addressed in this report.

1.3 Report Organization

This report contains the following major elements:

- <u>Identification of the “New” Urban Insecticides</u>. Section 2 presents the results of the first phase of the project, which was to identify those pesticides most likely to gain significant market share in the coming years. The remainder of the analysis focuses on the eleven selected pesticides, called the “study list pesticides.”
- <u>Compilation of Data Relevant to the Analysis</u>. Sections 3 through 11 summarize relevant information about the pesticides, such as chemical and physical properties, environmental fate data, commercial product characteristics, sales, use, regulatory status, chemical analysis methods, and aquatic toxicity.
- <u>Development of Significance Thresholds</u>. In Section 12, water quality criteria (where available) and toxicity data (where no water quality criterion exists) are compiled to develop a set of “environmentally relevant concentrations” for each study list pesticide for both fresh and salt water. For purposes of this report, exceeding the “environmentally relevant concentration” indicates that adverse effects on aquatic ecosystems are likely.
- <u>Analysis of Potential Impacts</u>. Section 13 presents the assessment of the possibility that pesticides entering the marketplace to replace diazinon and chlorpyrifos may cause adverse impacts to aquatic ecosystems receiving urban runoff. The assessment uses all available environmental monitoring data, together with a qualitative review of use, transport and fate of each pesticide in the urban environment. Conclusions are based on the weight of the available evidence.

Section 14 contains conclusions and recommendations for future actions to prevent and manage surface water impacts from urban pesticide use.

2.0 SELECTION OF PESTICIDES FOR DETAILED REVIEW

The goal of the first phase of the project was to identify up to ten pesticides that are replacing diazinon and chlorpyrifos in the urban marketplace and that are likely to gain significant market share. On the basis of a review of pesticide usage trend indicators, it was clear that many more than 10 insecticides are gaining meaningful market share. Because budget limitations preclude detailed review of more than about 10 pesticides, the first phase was expanded to include limited review of available surface water quality data, aquatic toxicity data, product formulations, and U.S. Environmental Protection Agency (U.S. EPA) registration documents in order to ensure that those pesticides with greatest potential to be of concern for water quality were included in the detailed review.

2.1 Insecticide Candidate List

The initial list of insecticides for review (the "candidate list") was created from U.S. EPA lists of alternatives to diazinon and chlorpyrifos (U.S. EPA, 2000). All listed chemical products for non-agricultural uses were included, except one veterinary product that is not registered as a pesticide. During the review process, several insecticides identified in pesticide product surveys were added to the candidate list.

The identified insecticides fall into the following classes:

- Pyrethroids—a family of synthetic insecticides that are chemically similar to the natural insecticide pyrethrins, which come from chrysanthemums.
- Carbamates—a group of synthetic insecticides that are esters of carbamic acids.
- Other organophosphorous pesticides—other synthetic insecticides in the same chemical class as diazinon and chlorpyrifos.
- Other types of pesticides—botanicals, synthetic insecticides in new chemical classes (like chloronicotinyl pesticides), and other miscellaneous insecticides.
- Synergists—substances (like piperonyl butoxide) that enhance the toxicity of the pesticide active ingredient in a product.

2.2 Usage Trend Indicators

Usage trend indicators were explored for insecticides that control the same target pests on the formerly common urban sites of use for diazinon and chlorpyrifos. The usage investigation relied primarily on two types of data sources:

- California Department of Pesticide Regulation (DPR) pesticide usage data—information reported to the State of California by professional pesticide applicators, whose urban use of insecticides is primarily for structural pest control and landscaping.
- Pesticide product surveys—information from retail shelf surveys, manufacturer product promotion materials and Internet sites, and interviews with those knowledgeable about pesticide sales and use patterns.

The information obtained from these sources is described below.

Professional Applicator Pesticide Use

California requires professional pesticide applicators to report pesticide use to the County Agricultural Commissioners. Each calendar year, DPR compiles pesticide use reports. The most recent data available at the time of this analysis was for calendar year 2000, which is prior to the initiation of regulatory changes for diazinon and chlorpyrifos.

To address the problem that available pesticide use reports are unlikely to reflect changes in insecticide use due to diazinon and chlorpyrifos regulatory changes, several interviews were conducted with people working in the field who are familiar with trends in insecticide use.

The major urban reported uses of insecticides fall into two categories in DPR's compilation of pesticide use reports: structural pest control and landscape maintenance.[2] Since previous investigation of the water quality impacts of diazinon and chlorpyrifos found that outdoor structural pest control applications were most likely to release the applied pesticide to surface waters (TDC Environmental, 2001), insecticide use for structural pest control insecticide use was explored in more detail than insecticide use on landscaping.

Structural Pest Control. Table 2-1 (on the next page) lists pesticides with more than 10,000 pounds of active ingredient reported applied for structural pest control in 1996, 1997, 1998, 1999, and 2000 (DPR, 1999, 2000, and 2001). These data do not show clear trends for most pesticides. Diazinon and chlorpyrifos usage do not show downward trends within this time period. Of the listed pesticides that are likely alternatives to diazinon and chlorpyrifos, only cypermethrin shows a meaningful trend toward increased use. In 2000, two alternatives to diazinon and chlorpyrifos had more than 100,000 pounds of reported use: cypermethrin and permethrin.

Participants in the Pest Control Operator IPM Evaluation Alliance Team have noted common use of cyfluthrin, deltamethrin, hydramethylnon, permethrin, and various containerized baits for structural pest control (Quarles *et al.*, 2002). Informally, it was noted that diazinon (which can be used until 2004) continues to be used by structural pest control companies (Brandenburg, 2002). An informal survey of San Mateo County termite control companies found use of fipronil, imidacloprid, and permethrin for control of subterranean termites, which were a common target pest for chlorpyrifos (Moran, April 2002).

Landscape Maintenance. Table 2-2 (on page 9) lists the reported use for landscape maintenance of diazinon, chlorpyrifos, and alternatives on the candidate list in 2000 (DPR, 2001). Diazinon and chlorpyrifos use far exceed reported use of any alternative. Of the alternatives on the candidate list, only three non-traditional pesticides are in the top 10: bifenthrin, imidacloprid, and permethrin.

Since trend analysis was not particularly informative for structural pest control insecticides, only a limited trend analysis of insecticides reported applied for landscape maintenance was conducted. Table 2-3 (on page 10) shows the reported use from 1996 through 2000 of diazinon, chlorpyrifos, and the alternatives on the candidate list for which more than 1,000 pounds were reported used in 2000 (DPR, 1999, 2000, and 2001). Again, no clear trend in use of most of these pesticides exists—even for diazinon and chlorpyrifos. Only bifenthrin and boric acid show steady trends of increased use. Given the variability in the data, it is not clear if the significant jump in imidacloprid use in 2000 is meaningful.

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[2] For urban pesticide use, DPR categorizes reported uses in a relatively granular manner that provides the ability to obtain a general understanding of the use location for a pesticide. Public reports do not currently match the more detailed sites of use list used by DPR's registration group.

Table 2-1. Reported Use of Structural Pest Control Pesticides (Pesticides with California Reported Use Greater than 10,000 Pounds)

Pesticide	**Reported Use (Pounds of Active Ingredient)**				
	2000	**1999**	**1998**	**1997**	**1996**
Chlorpyrifos	*428,918*	*526,298*	*462,288*	*506,945*	*521,480*
Diazinon	*519,136*	*345,528*	*291,878*	*308,775*	*286,854*
Bifenthrin	10,728	--	--	--	--
Boric Acid	87,472	84,439	237,071	313,069	143,162
Carbon Dioxide	--	--	--	18,235	--
Copper Sulfate Pentahyd.	--	--	28,022	--	--
Cyfluthrin	14,438		20,505	33,072	31,910
Cypermethrin	126,098	114,130	120,514	88,497	73,708
Deltamethrin	10,607	--	--	--	--
Disodium Octaborate Tetrahydrate	302,046	385,804	402,056	232,198	180,920
Dodecylbenzene Sulfonic Acid	11,379	--	--	--	--
Fenvalerate	--	--	--	27,155	33,929
Formaldehyde	49,336	72,469	244,642	322,435	134,470
Glyphosate, Isopropylamine Salt	--	10,887	30,227	--	--
Imidacloprid	27,473	32,424	--	--	--
Isoparaffinic Hydrocarbons	--	--	--	--	61,556
Lambda Cyhalothrin	10,925	10,543	--	--	--
Limonene	31,034	18,690	17,005	--	--
Malathion	17,607	36,239	22,945	29,999	36,312
Methyl Bromide	275,793	314,749	306,618	504,221	596,830
Nitrogen, Liquified	391,469	392,121	1,003,749	422,101	423,124
Octyl Phenyl Polyethoxyethanol	14,187	--	--	--	--
Permethrin	240,988	158,232	191,700	153,804	168,296
Petroleum Distillates	23,053	12,002	39,626	43,830	60,609
Petroleum Distillates, Aromatic	--	89,497	26,742	--	--
Piperonyl Butoxide	--	--	--	10,305	10,632
Potassium Dimethyldithiocarbamate	--	--	24,795	--	--
Propetamphos	--	--	--	17,280	23,089
Silica Aerogel	10,796	--	--	10,416	16,082
Sodium Chloride	--	11,095	23,706	14,469	--
Sulfur Dioxide	11,290	16,031	--	27,474	13,611
Sulfuryl Fluoride	2,406,133	2,566,707	2,170,746	1,935,677	1,799,946
Xylene Range Aromatic Solvent	--	--	--	16,329	--

"--" indicates less than 10,000 pounds reported used.
Source: DPR Annual Pesticide Use Reports (DPR, 1999, 2000, and 2001).

Table 2-2. Reported Use of Insecticides for Landscape Maintenance, 2000

Insecticide	Reported Use (Pounds of Active Ingredient)
Chlorpyrifos	*13,566*
Diazinon	*24,665*
Carbaryl	10,096
Acephate	8,425
Imidacloprid	7,999
Naled	7,049
Permethrin	4,329
Boric Acid	4,061
Malathion	3,566
Trichlorfon	2,879
Bifenthrin	1,258
Piperonyl Butoxide	885
Cyfluthrin and Beta-Cyfluthrin	832
Cypermethrin and (S)-Cypermethrin	769
Clarified Hydrophobic Extract Of Neem Oil	322
Propoxur	313
Tau-Fluvalinate	249
Deltamethrin	197
Tetrachlorvinphos	163
Lambda Cyhalothrin	118
Spinosad	109
Pyrethrins	82
Diflubenzuron	55
n-octyl bicycloheptene dicarboximide	44
Hydramethylnon	33
Fenoxycarb	24
Propetamphos	9
Avermectin	7
Methoprene and S-Methoprene	5
Pyriproxyfen	5
Phosmet	3
Allethrin (family)	2
Esfenvalerate	2
Fipronil	2
Hydroprene	2
Phenothrin	2
Resmethrin	1
Tralomethrin	1
Tetramethrin	0.4
Fenvalerate	0.1
Hexaflumuron	0.1
Sulfluramid	0.1
Aldicarb, Fenthion, Halofenozide, and Temephos	No reported use

Note: Table only includes insecticides on candidate list.
Source: DPR Annual Pesticide Use Reports (DPR 1999, 2000, and 2001).

Table 2-3. Reported Use of Insecticides for Landscape Maintenance, 1996-2000 (Pesticides with California Reported Use Greater than 1,000 Pounds in 2000)

Insecticide	Amount Reported Used (Pounds of Active Ingredient)				
	2000	1999	1998	1997	1996
Chlorpyrifos	*13,566*	*158,187**	*18,725*	*21,560*	*22,926*
Diazinon	*24,665*	*20,566*	*30,155*	*29,770*	*28,810*
Carbaryl	10,096	8,896	11,120	13,694	15,558
Acephate	8,425	5,351	4,577	5,737	5,708
Imidacloprid	7,999	2,252	3,013	3,201	5,696
Naled	7,049	6,425	2,401	6,137	3,999
Permethrin	4,329	2,229	1,937	1,372	3,899
Boric Acid	4,061	251	123	153	402
Malathion	3,566	3,310	4,777	4,078	5,122
Trichlorfon	2,879	1,640	1,576	3,016	2,626
Bifenthrin	1,258	222	90	0.5	1

*Value is unusually high, apparently due to reported use recording errors in 3 counties (Singhasemanon, 2003).
Source: DPR Annual Pesticide Use Reports (DPR 1999, 2000, and 2001).

The Pesticide Distributor Project[3] involves interaction with San Francisco Bay Area pesticide distributors and attendance at trade shows in the region. Common alternatives observed by the technical consultant to that project include bifenthrin, cyfluthrin, deltamethrin, and trans-allethrin (in aerosols). The granular form of deltamethrin is particularly being promoted to professional landscapers (Joseph, 2002).

Pesticide Product Surveys

While California requires pesticide use reporting by professional applicators, no tracking mechanism exists for residential pesticide use. Since unreported use comprises about half of urban pesticide use, it can be very important for water quality. In addition to looking at current unreported urban use of insecticide substitutes for diazinon and chlorpyrifos, the pesticide product survey sought information that would indicate future market trends.

Retail shelf surveys. Surveys of insecticide products displayed for retail sale were conducted at two of the three San Francisco Bay Area retail chains that have previously been documented as selling the largest volumes of home-use insecticides (Cooper, 1996; Scanlin and Cooper, 1997). (The third major retailer only carries large volumes of insecticide products in the summer season, and thus could not be surveyed within the project schedule.) The surveys (see Appendix A) found major shifts in insecticide product mix, likely the result of the phase-out of most urban diazinon and chlorpyrifos uses. Pyrethroid products dominated the observed substitutes, which included a wide mix of chemicals.

Retail product surveys. On the basis of current and past retail product surveys, Ortho, Scotts, Bayer Advanced, Spectracide, and Real-Kill were identified as the major product lines for residential-use insecticides. Internet sites for the manufacturers of these products were consulted to identify formulation trends for insecticide products (other than containerized baits and aerosols), with the following results:

- Ortho and Scotts (Ortho is owned by Scotts)—Diazinon and chlorpyrifos products have been replaced by bifenthrin, esfenvalerate, and permethrin. Some new

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[3] Managed by the Marin County Stormwater Pollution Prevention Program.

products contain pyrethrum. Carbaryl is more prominently displayed and available in more formulations.

- <u>Spectracide and Real-Kill</u> (both owned by Spectrum Brands)—Spectracide chlorpyrifos products have been replaced by permethrin. (Both stores and the Internet site had these products highlighted by a "Looking for Dursban?" logo.) While Real-Kill products are not described on Spectrum Brand's Internet site, the shelf survey showed that diazinon and chlorpyrifos products have been replaced with permethrin and, to a lesser extent, tralomethrin. Real-Kill malathion products were also prominently displayed.
- <u>Bayer Advanced</u>—Diazinon and chlorpyrifos products have been replaced primarily by cyfluthrin and imidacloprid. Similar products include one with beta-cyfluthrin and one with trichlorfon.

The following insecticides on the candidate list were not identified in these retail product surveys: aldicarb, avermectin, diflubenzuron, fenoxycarb, fenthion, fenvalerate, halofenozide, hexaflumuron, lambda cyhalothrin,[4] naled, phosmet, propetamphos, propoxur, pyriproxyfen, spinosad, sulfuramid, taufluvalinate, temephos, tetrachlorvinphos, and trichlorfon.

Other Resources

Three other data sources were explored, but did not provide data that was particularly helpful in distinguishing potential future market leaders among the alternatives to diazinon and chlorpyrifos:

- <u>DPR weekly registration notices</u>—DPR issues two weekly notices: the "Materials Entering Evaluation Process" and the "Notice of Proposed and Final Decisions." These notices list pesticides entering the registration process and pesticides actually registered. No trend toward any specific insecticides was apparent from review of notices from 2001 and early 2002. New and modified registrations for pyrethroids and new types of broad-spectrum insecticides were common.
- <u>Pesticide Sales in California</u>—DPR compiles statewide pesticide sales data based on proceeds of DPR's funding source, the "mill tax." Public data are only available for pesticides for which more than 3 companies have registered products. While statewide sales figures for the years 1997 through 2000 were examined (DPR, 1998, 1999, 2000, and 2001), they did not prove informative primarily because sales for agricultural uses dominate sales of many insecticides, making analysis difficult. (An analysis of the unreported sales of selected pesticides will be included in the next phase of the project.)
- <u>Residential Pesticide Sales and Use Surveys</u>—Previous California residential pesticide sales and use surveys all predate the diazinon and chlorpyrifos regulatory changes (initiated in 2001), and thus do not indicate the market shifts currently underway (Cooper, 1996; Scanlin and Cooper 1997; URS, 2000; Wilen, 2001). The most recent of these surveys (Wilen, 2001) estimated calendar year 2000 retail sales of several insecticides in the San Diego Creek (Orange County) watershed. Because it estimated that sales of clarified hydrophobic extract of Neem oil (an insecticide for some of the same target pests as diazinon and chlorpyrifos) were higher than sales of any other insecticide active ingredient in the study watershed, it was added to the candidate list.

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[4] Since these surveys were conducted, lambda cyhalothrin products have entered the retail marketplace. For example, it is marketed as "Triazicide" under the Spectracide brand name.

Modifications to Candidate List Based on Usage Trend Indicators

On the basis of the review of current insecticide products and sales trends, several insecticides and two synergists were added to the candidate list: acephate, aldicarb, allethrin and related pesticides (d-allethrin, d-trans allethrin, S-bioallethrin, prallethrin, and esbiothrin), clarified hydrophobic extract of Neem oil, lambda cyhalothrin, tetramethrin, tralomethrin, n-octyl bicycloheptene dicarboximide, and piperonyl butoxide (PBO).

2.3 Indicators Of Environmental Importance

To avoid omitting a particularly environmentally important insecticide from detailed review, three indicators of environmental importance were explored for insecticides on the candidate list: screening surface water quality data, basic toxicity information, and U.S. EPA classification of pesticides as "botanicals" or "reduced risk" pesticides. The limited data described below were used for screening the candidate list of insecticides; a more thorough review will be conducted for selected pesticides in the next phase of the project.

<u>Surface Water Quality Data</u>. Data on surface water detections from the U.S. Geological Survey National Water Quality Assessment (USGS NAWQA) and DPR was reviewed. The USGS NAWQA studies, which are currently in progress, provide the most complete available urban surface water data set. The following NAWQA results are particularly relevant to this investigation:

- The insecticides diazinon, chlorpyrifos, carbaryl, and malathion were the ones most commonly detected in urban streams (Gilliom *et al.*, 1999).
- Malathion was found in more than 20% of urban surface water samples; more than 50% of sampled urban streams had at least one sample exceeding a North American aquatic life criterion (Gilliom *et al.*, 1999; Hoffman *et al.*, 2000).
- Carbaryl was found in about 40% of urban stream samples and exceeded a North American aquatic life criterion in 10% of samples from 8 urban streams (Gilliom *et al.*, 1999; Hoffman *et al.*, 2000).
- Early NAWQA investigations did not detect cis-permethrin (the only pyrethroid on the NAWQA analyte list) (Hoffman *et al.*, 2000); however, recent data only available on the Internet shows it was detected in four urban watersheds at concentrations up to 0.011 µg/l (USGS, 2002).
- Aldicarb was not detected (Hoffman *et al.*, 2000)
- Propoxur was found in surface water (Hoffman *et al.*, 2000).

Although an attempt to utilize the DPR Surface Water Quality Database did not provide useful results,[5] search of the DPR internet site identified a presentation summarizing results of a recent DPR-funded surface water study that found diazinon and chlorpyrifos alternatives in surface water (Kim *et al.*, 2001). That study, which explored pesticides used for red imported fire ant control in Southern California, had the following results relevant to this investigation:

- Use of bifenthrin and malathion at nurseries was linked to surface water runoff toxicity measured in the study.

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[5] DPR is working to expand the database and to improve data accessibility. These changes should reduce the primary limitations encountered in this search, which were that urban runoff and stream studies and data from San Francisco Bay area counties were not included in the online database at the time of the search; and the online interface precluded searches for detections of specific pesticides.

- Malathion in runoff from urban and integrated sites was linked to surface water runoff toxicity measured in the study.
- Fenoxycarb was detected in nursery runoff, but detection itself was not definitely linked to toxicity in surface water runoff.
- Hydramethylnon and pyriproxyfen were detected once each in runoff; neither detection was linked to toxicity in surface water runoff.

Toxicity Data. The Pesticide Action Network Pesticide Database (PAN Database)[6] contains a compilation of data on pesticide properties and toxicity. This database has a very convenient interface that provides a way to quickly identify and review available aquatic toxicity data for pesticides. It did not, however, contain any aquatic toxicity data for avermectin, clarified hydrophobic extract of Neem oil, fipronil, halofenozide, hydroprene, or spinosad. While the National Library of Medicine's Toxnet Hazardous Substances Data Bank (HSDB)[7] was also explored, it contained toxicity data for fewer pesticides than the PAN database and the data format makes focus on aquatic species very inconvenient for a screening review. In general, the aquatic toxicity data confirmed that most of the insecticides on the candidate list are very toxic to one or more aquatic species. Even some insecticides labeled "reduced risk" by U.S. EPA (*e.g.*, diflubenzuron, hexaflumuron, pyriproxyfen) can be quite toxic to certain aquatic species. For boric acid, the data confirmed the general view that it is a "least toxic" insecticide.

Pesticide classification. Certain classes of pesticides are less likely to be environmentally harmful than ordinary broad-spectrum insecticides. Two possible indicators of lower toxicity were checked:

- U.S. EPA "Reduced Risk" Classification—For registration purposes, U.S. EPA has classified certain pesticides as "reduced risk" due to their potential to be less toxic replacements for common pesticides. While this classification focuses on human health, it may be an indicator of relative environmental importance of a pesticide. The reduced-risk pesticides on the candidate list are: fipronil, hexaflumuron, pyriproxyfen, spinosad, and tebufenozide.
- Botanicals—Pesticides derived from plants or bacteria are often—but not always—less environmentally problematic than synthetic pesticides. The botanicals on the candidate list are: avermectin, clarified hydrophobic extract of Neem oil, hydroprene, pyrethrins, and spinosad.

2.4 Other Factors

Assembled usage trend data showed that diazinon and chlorpyrifos are being replaced with a mix of products, rather than just one or two substitutes. To create a list of products that would be feasible to review in detail within the project budget, additional information needed to be considered that would differentiate among the insecticides on the candidate list. An evaluation of the potential for each of the insecticides to be released to surface water proved quite useful in differentiating the insecticides, as did considering information developed by U.S. EPA in its pesticide registration and re-evaluation processes.

Potential for release to surface water. Insecticide applications on certain sites of use and using certain formulations are more likely than others to release the insecticide to surface water (TDC Environmental, 2001). Using pesticide product information from DPR's Product/Label database, it was possible to determine that products containing

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[6] http://www.pesticideinfo.org
[7] http://toxnet.nlm.nih.gov/

several of the insecticides on the candidate list are primarily in two types of formulations that are unlikely to release meaningful quantities of the insecticide to surface water:

- Baits—product design prevents most environmental release of the active ingredient. Hydramethylnon and methoprene are primarily formulated into baits.
- Aerosols—low active ingredient concentrations combined with typical application behaviors result in relatively small quantities of insecticide release. The synergist n-octyl bicycloheptene dicarboximide, and the insecticides allethrin (and family), resmethrin, tetramethrin, and tralomethrin are primarily formulated into aerosol products.

Information from U.S. EPA pesticide re-evaluation process. U.S. EPA must review and approve any pesticide before it can be offered for sale in the U.S. This process is called "registration." Many of the currently popular pesticides were first approved for sale decades ago, when scientific understanding of human health and environmental effects of pesticides was far less complete than it is today. In response to concerns about the inadequate environmental review of older pesticides, Congress has put in place two regulatory review requirements for pesticides:

- Reregistration—under 1988 amendments to the nation's primary pesticide law, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), all pesticides initially registered prior to November 1, 1984 must be re-reviewed and reregistered.
- Food Quality Protection Act (FQPA) Review—the 1996 FQPA requires U.S. EPA to review all pesticides with a focus on protecting human health. Reviews, which must be completed by 2011, must consider cumulative human exposures and common modes of action among multiple pesticides. FQPA also requires U.S. EPA to continue to review and reregister all pesticides every 15 years.

The U.S. EPA FIFRA registration and reregistration and the FQPA review processes generate technical documents that contain useful information about the potential for environmentally meaningful releases of a pesticide to surface waters. These documents may include preliminary and revised environmental risk assessments, cumulative risk assessments (for pesticides that are part of a group with a common mode of action) and Registration Eligibility Documents (REDs). For pesticides that are part of a group with a common mode of action, an "Interim RED" (IRED) is generated until the results of the cumulative risk assessment are available to be incorporated into a final RED.

Since passage of FQPA, U.S. EPA has worked to combine FIFRA-required pesticide reregistrations with FQPA reviews, focusing first on the pesticides with the highest potential risks to human health. To facilitate compliance with the requirement to consider cumulative effects of pesticides with common modes of action, U.S. EPA is reviewing pesticides in groups. Currently, the focus is organophosphorous pesticides. In the next year or so, the focus will shift to carbamate pesticides. Future reviews will include pyrethroid pesticides. Table 2-4 provides the status of insecticides on the candidate list in U.S. EPA's reregistration and FQPA review processes as of April 2002 (see Table 10-2 [on page 60] for more recent information for study list pesticides).

Reregistration documents provided a wealth of information about potential for environmentally important surface water releases from organophosphorous pesticides on the candidate list. In addition, REDs for pesticides registered in the 1990s and pesticides considered in special reviews during that time period also provided some valuable information. Appendix B presents a summary of the relevant findings from these U.S. EPA documents.

Table 2-4. U.S. EPA Registration Status for Diazinon and Chlorpyrifos Alternatives (as of April, 2002)[8]

Pesticide	**U.S. EPA Registration Status**
Pyrethrins and Pyrethroids	*Pyrethroids that are candidates for reregistration are likely to be evaluated cumulatively as well as individually. U.S. EPA has not announced a timeline for pyrethroid reregistrations.*
Allethrin and family (D-Allethrin, D-Trans Allethrin, S-Bioallethrin, Prallethrin, and Esbiothrin)	Allethrin family will be reviewed for reregistration (except prallethrin, which is not subject to reregistration*)
Bifenthrin	Not subject to reregistration*
Cyfluthrin and Beta-Cyfluthrin	Not subject to reregistration*
Lambda Cyhalothrin	Not subject to reregistration*
Cypermethrin and (S)-Cypermethrin	Will be reviewed for reregistration
Deltamethrin	Not subject to reregistration*
Esfenvalerate	Not subject to reregistration*
Fenvalerate	Will be reviewed for reregistration
Permethrin	Will be reviewed for reregistration
Phenothrin	Will be reviewed for reregistration
Pyrethrins	Will be reviewed for reregistration
Resmethrin	Will be reviewed for reregistration
Tau-Fluvalinate	Will be reviewed for reregistration
Tetramethrin	Will be reviewed for reregistration
Tralomethrin	Not subject to reregistration*
Carbamates	*A cumulative risk assessment for carbamate pesticides is planned; it must be completed before the final REDs for the carbamates below can be completed.*
Aldicarb	Preliminary risk assessment not yet prepared; Candidate for 2002 IRED
Carbaryl	Preliminary risk assessment in preparation; IRED must be completed by June 30, 2003 in accordance with NRDC lawsuit settlement
Fenoxycarb	Preliminary risk assessment not yet prepared
Propoxur	RED completed in 1997.
Organophosphorous Pesticides	*A cumulative risk assessment for organophosphorous pesticides is in progress; it must be completed before the final REDs for the organophosphorous pesticides below can be completed.*
Acephate	IRED completed 2001
Fenthion	IRED completed 2000
Malathion	Revised risk assessment completed 2000; IRED in preparation
Naled	Revised risk assessment completed 1999; IRED in preparation
Phosmet	IRED completed 2001
Propetamphos	IRED completed 2000

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[8] See Table 10-2 for more detailed recent information on study list pesticides.

Table 2-4. U.S. EPA Registration Status for Diazinon and Chlorpyrifos Alternatives (As of April, 2002, Continued)

Pesticide	U.S. EPA Registration Status
Temephos	IRED completed, apparently in 2000 (undated)
Tetrachlorvinphos	RED completed 1995; revised risk assessment completed 2000; IRED in preparation
Trichlorfon	RED completed 1995; reregistration revised risk assessment 2000; IRED in preparation
Other pesticides	
Avermectin	Not subject to reregistration*
Boric Acid	RED completed 1993
Clarified Hydrophobic Extract Of Neem Oil	Not subject to reregistration*
Diflubenzuron	RED completed 1997
Fipronil	Not subject to reregistration*
Halofenozide	Not subject to reregistration*
Hexaflumuron	Not subject to reregistration*
Hydramethylnon	RED completed 1998
Hydroprene	Not subject to reregistration*
Imidacloprid	Not subject to reregistration*
Methoprene and S-Methoprene	Methoprene RED completed 1991; S-Methoprene not subject to reregistration*
Pyriproxyfen	Not subject to reregistration*
Spinosad	Not subject to reregistration*
Sulfluramid	Not subject to reregistration*

*Pesticides originally registered after November 1, 1984 are not subject to reregistration
Source: U.S. EPA registration status information (U.S. EPA, April 2002).

For several pesticides, regulatory changes from this process make it unlikely that they will see increased use in response to the diazinon and chlorpyrifos regulatory changes. Specifically, for acephate, fenthion, phosmet, propetamphos, and temephos, regulatory changes proposed in the REDs will greatly reduce future urban uses. For naled and tetrachlorvinphos, findings of significant risks in reregistration risk assessments suggest that uses are likely to be curtailed in the future.

2.5 Selection of Insecticides for Study List

Table 2-5 (on pages 18 and 19) summarizes the information gathered in the investigation described above for the 45 insecticides identified as possible substitutes for urban uses of diazinon and chlorpyrifos. Columns were marked as follows:

- Surveys predict more urban use—Insecticides found frequently in shelf surveys, formulated into most diazinon and chlorpyrifos replacement products by the three major consumer retail product manufacturers, or reportedly frequently used or highly promoted to professional applicators were marked with an "X."
- Documented concern in surface water—If USGS NAWQA found the pesticide above a North American aquatic life criterion or if DPR linked the pesticide to toxicity in urban surface water it received an "X."
- Reported urban use greater than 10K, greater than 100K, or less than 100 pounds—Three columns were used to indicate relatively large or relatively small reported urban use of insecticides (structural pest control, landscaping pest control, and other minor urban uses). If reported urban use exceeded 10,000

(10K) pounds, exceeded 100,000 (100K) pounds, or was less than 100 pounds, the pesticide was marked with an "X" in the appropriate column.

- U.S. EPA may reduce use—This column was marked if a U.S. EPA RED document indicates plans to reduce or eliminate urban uses or if a risk assessment found significant risks that may be mitigated by urban use reductions.
- Primarily in low-release formulations—Insecticides primarily formulated as baits and aerosols were marked.
- Botanical or reduced risk—Insecticides classified by U.S. EPA in either of these groups were marked.
- Not found in surveys—insecticides not found in the pesticide product surveys were marked.

Columns on the left side of the table list factors that make an insecticide a priority for more detailed review. Columns on the right side (shaded) list factors that make an insecticide a lower priority for detailed review at this time. Based on the frequency of markings in the left and right columns and information in the "Notes" column, the insecticides were divided into four groups:

- Pesticides and synergist to be reviewed in detail—These substances will be the focus of the remainder of this project. Piperonyl butoxide (PBO) was included in this group because of its frequent appearance in surface water, where it can increase environmental toxicity of pyrethroids other than ones in the product that resulted in the release of the PBO.
- Recommended priorities for future detailed review—These insecticides were separated from the remaining ones because currently available information suggests that they may contribute to urban surface water toxicity in the future. For hydramethylnon, its formulation into uncontainerized bait granules for application around structures is of concern—a concern that is exacerbated by DPR's finding it in nursery runoff (Kim *et al.*, 2001). For n-octyl bicycloheptene dicarboximide, the primary concern is that it (like PBO) has the ability to increase pyrethroid toxicity. For naled and tetrachlorvinphos, the outcome of U.S. EPA reregistration processes are uncertain—U.S. EPA may not select risk management measures that eliminate aquatic toxicity identified in risk assessments.
- Recommended for future screening—The urban insecticide market is still in a state of flux in response to diazinon and chlorpyrifos regulatory changes. Some of the remaining pesticide may gain significant market share as market changes continue. The market should be reviewed in several years to determine if any additional insecticides have developed meaningful market share.
- Least likely to pose future problems—Three pesticides are unlikely to be of future concern to water quality. For boric acid, low aquatic toxicity makes surface water problems unlikely. Phasing out of all urban uses will (in the long term) eliminate future urban releases of fenthion and temephos to surface waters.

Table 2-5. Insecticide Replacements for Diazinon and Chlorpyrifos: Summary of Prioritization Review Results[9]

Insecticide	Surveys predict more urban use	Documented concern in surface water	Reported urban use >100K lbs	Reported urban use >10K lbs	Reported urban use <100 lb.	U.S. EPA may reduce use	Primarily in low-release formulations	Botanical or Reduced-Risk	Not found in surveys	Notes
Pesticides and Synergists to be Reviewed in Detail										
Bifenthrin	X	X		X						
Cyfluthrin	X			X						
Cypermethrin and (S)-Cypermethrin	X		X	X						
Deltamethrin	X			X						
Esfenvalerate	X									
Permethrin	X		X	X						
Pyrethrins	X									
Carbaryl	X	X		X						
Malathion	X	X		X						
Imidacloprid	X			X						
Piperonyl Butoxide (PBO)*				X						USGS found frequently in surface water; synergizes pyrethroid toxicity
Recommended Priorities for Future Detailed Review										
Hydramethylnon	X						X			
n-octyl bicycloheptene dicarboximide*							X			Synergizes pyrethroid toxicity
Naled				X		X			X	
Tetrachlorvinphos						X			X	
Recommended for Future Screening										
Allethrin and family* (D-Allethrin, D-Trans Allethrin, S-Bioallethrin, Prallethrin, and Esbiothrin)	X						X			
Beta-Cyfluthrin					X					
Lambda Cyhalothrin*				X					X	

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[9] See text for detailed documentation for each category.

Table 2-5. Insecticide Replacements for Diazinon and Chlorpyrifos: Summary of Prioritization Review Results (Continued)

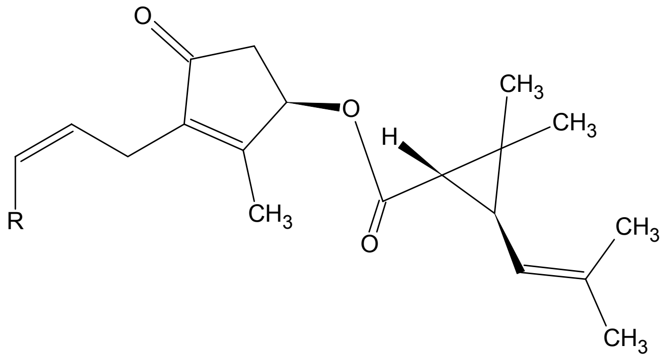
Insecticide	Surveys predict more urban use	Documented concern in surface water	Reported urban use >100K lbs	Reported urban use >10K lbs	Reported urban use <100 lb.	U.S. EPA may reduce use	Primarily in low-release formulations	Botanical or Reduced-Risk	Not found in surveys	Notes
Fenvalerate									X	
Tau-Fluvalinate									X	
Phenothrin					X					
Resmethrin							X			
Tetramethrin*							X			
Tralomethrin*							X			
Aldicarb*									X	
Fenoxycarb					X				X	
Propoxur									X	
Acephate*				X		X				
Phosmet						X			X	
Propetamphos						X			X	
Trichlorfon									X	
Avermectin					X			X	X	
Clarified Hydrophobic Extract Of Neem Oil*								X		
Diflubenzuron								X	X	
Fipronil	X							X		Growing use is for under-ground injection
Halofenozide					X				X	
Hexaflumuron					X			X	X	
Hydroprene								X		
Methoprene and S-Methoprene				X			X			
Pyriproxyfen					X			X	X	
Spinosad								X	X	
Sulfluramid					X				X	
Pesticides Least Likely to Pose Future Problems										
Boric Acid								X		
Fenthion					X	X			X	
Temephos					X	X			X	

*Not on U.S. EPA lists of alternatives for diazinon and chlorpyrifos
Source: TDC Environmental analysis (see text).

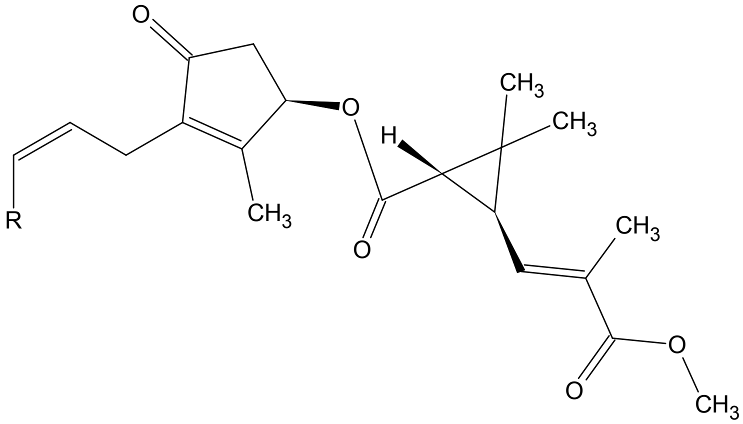
3.0 BACKGROUND INFORMATION FOR SELECTED INSECTICIDES

3.1 Pyrethrins and Pyrethroids[10]

Pyrethrins are naturally occurring pesticidal chemicals that are the active component of "pyrethrum," which is a powder made by drying and breaking up the flower heads of chrysanthemums. Pyrethrins are a mixture of chemicals: three esters of chrysanthemic acid (known as "pyrethrins I"), and three esters of pyrethric acid (called "pyrethrins II"). Generic structures for the pyrethrins are shown below.[11]



Pyrethrins I



Pyrethrins II

Pyrethroids are a family of chemical insecticides that are synthetic analogs of the pyrethrins. This project includes a detailed evaluation of six pyrethroids, the structures for which are shown on the next two pages.

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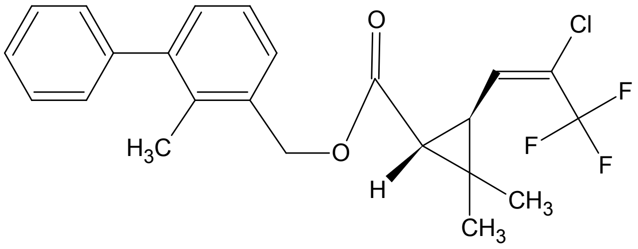
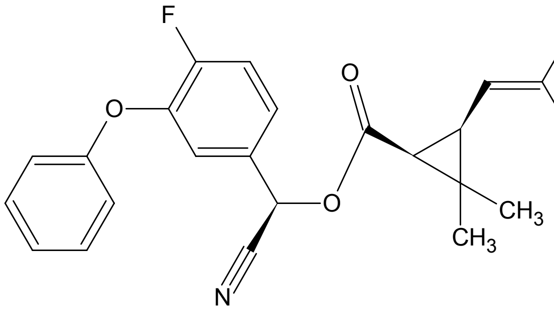
[10] Background information on pyrethroids obtained from Kamrin, 1997; Olkowski et al., 1991; and Casida and Quistad, 1995.

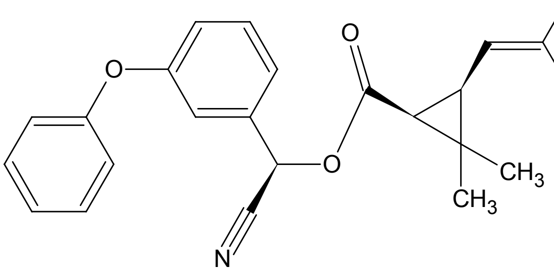
[11] "R" represents methyl (cinerin I and II), ethyl (jasmolin I and II), or ethylene (pyrethrin I and II).



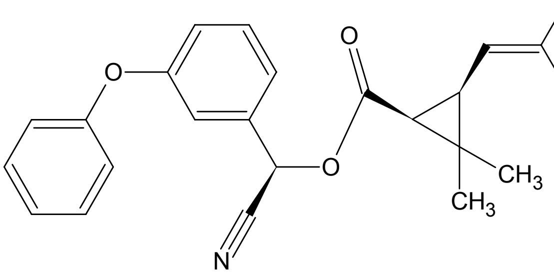
Bifenthrin



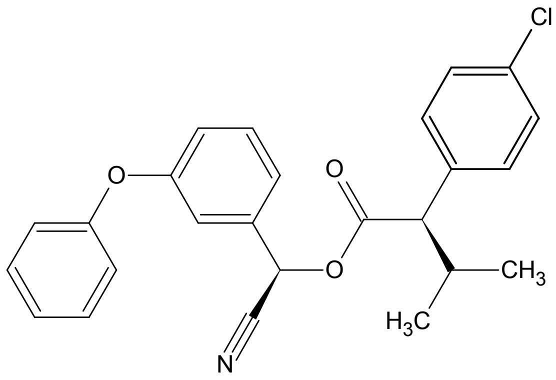
Cyfluthrin



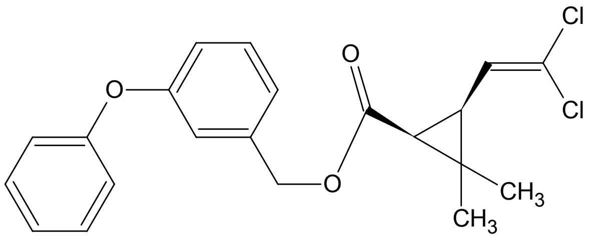
Cypermethrin



Deltamethrin



Esfenvalerate

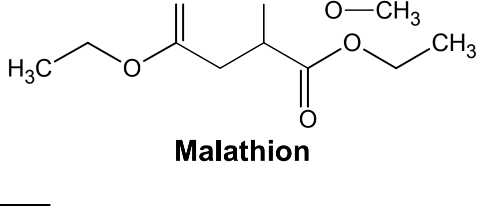


Permethrin

In general, the synthetic pyrethroids are more chemically stable and more toxic than the naturally occurring pyrethrins. Both pyrethrins and pyrethroids interfere with the function of the nervous system, specifically the sodium channel. Humans and other mammals are generally less sensitive to pyrethrins and pyrethroids than are insects because mammals have the ability to break down pyrethrins and most pyrethroid molecules relatively quickly.[12] Although pyrethrins have been sold for more than a century and pyrethroids have been marketed since the 1960s, their use has increased greatly in recent years to fill the market openings created by regulatory restrictions on other types of pesticides.

3.2 Malathion[13]

Like diazinon and chlorpyrifos, malathion is one of the organophosphorous pesticides (which are often called "organophosphates" even though all members of the class do not have a phosphate chemical group). Developed from compounds first created in wartime nerve gas research, organophosphorous pesticides became common when more environmentally persistent chlorinated pesticides fell out of favor in the 1970s and 1980s.



Malathion

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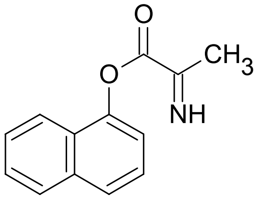
[12] By metabolism by oxidative and hydrolytic pathways.

[13] Background information on malathion obtained from Kamrin, 1997.

Organophosphorous pesticides control insects (and can affect humans and other mammals) by inhibiting a neural enzyme called acetylcholinesterase. Until recent regulatory changes reduced their use, organophosphorous pesticides were the most common insecticides used in the U.S. Since the 1940s, commercial producers have sold organophosphorous pesticides for a wide range of urban and agricultural uses.

3.3 Carbaryl[14]

Carbaryl is probably the most well known member of a class of pesticides known as carbamates. The carbamates are synthetic analogs of pesticidal chemicals found in the extracts of the West African calabar bean. Most carbamates (including carbaryl) are esters of carbamic acid.

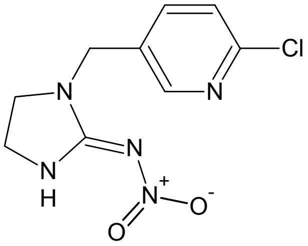


Carbaryl

While some carbamates serve as herbicides and fungicides, their primary application is to control insects. Like organophosphorous pesticides, carbamates control insects (and can affect humans and other mammals) by inhibiting the neural enzyme acetylcholinesterase. Since the 1950s, carbamates have been sold commercially in the U.S. for both urban and agricultural uses. Carbaryl is most often recognized by consumers under its most common retail name, "Sevin."

3.4 Imidacloprid[15]

Imidacloprid is the first member of a relatively new group of pesticides—the cloronicotinyl nitroguanidines—to be developed for commercial use. The cloronicotinyl nitroguanidines are part of a larger family of insecticides, the "nicotinoids," which are chemically similar to nicotine, a natural insecticide in tobacco.



Imidacloprid

Imidacloprid affects insect (and to a lesser extent human and other mammal) neural systems by blocking signals passed through the neural system. (Specifically, acetylcholine receptors are blocked by competitive inhibition.) Imidacloprid was commercially developed in the early 1990s and first registered by the U.S. Environmental Protection Agency (U.S. EPA) in 1994. Imidacloprid has been marketed

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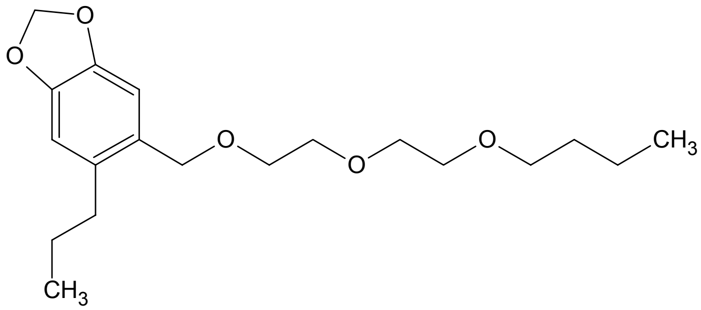
[14] Background information on carbaryl obtained from Kamrin, 1997.

[15] Background information on imidacloprid obtained from NPTN, 1998; U.S. EPA, 1994; and Cox, 2001.

commercially since the mid-1990s, first for urban uses and then later for both urban and agricultural insect control.

3.5 Piperonyl Butoxide[16]

Although it is technically registered as a pesticide, piperonyl butoxide's primary function in commercial pesticides is as a synergist—a substance that enhances the pesticidal activity of another ingredient in the formulation. In the late 1940s, piperonyl butoxide (PBO) was derived from safrole, a pesticidal component of oils from a variety of natural sources like black pepper and sassafras root bark.



Piperonyl Butoxide

PBO functions by inhibiting the mechanism that insects and other organisms use to detoxify pyrethroids and certain other pesticides, enhancing or prolonging the toxic response. Specifically, PBO inhibits a group of enzymes called mixed-function oxidases that—when operating normally—break down many insecticides, including pyrethroids. PBO is the most common synergist used in insecticides, appearing in more than 750 California-registered urban and agricultural use pesticide products. PBO appears in products with many different active ingredients such as pyrethrins, pyrethroids, rotenone, limonene, and linalool. Piperonyl butoxide is the most common pesticide used in households.

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[16] Background information on piperonyl butoxide obtained from Olkowski et al., 1991; Cox, 2002; Zimmerman *et al.*, 2001; and U.S. EPA, 2000.

4.0 CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE DATA

4.1 Data Sources

Most chemical property data was obtained from the U.S. Department of Agriculture (USDA) Agricultural Research Service's (ARS's) Pesticide Properties Database, managed by the USDA's Alternate Crops & Systems Laboratory. A review of other commonly referenced data sources (*e.g.*, EXTOXNET, National Library of Medicine Hazardous Substances Data Bank, Pesticide Action Network Pesticide Database, *The Pesticide Manual*) revealed that the ARS Pesticide Properties Database is the most complete and current of the publicly available databases. According to ARS, the ARS Pesticide Properties Database was "developed to provide water quality modelers and managers with a list of the pesticide properties most important for predicting the potentials of pesticides to move into ground and surface waters" (ARS, 2002). The ARS database also has two major advantages over other sources: references are given for all values, and all data have been verified by the manufacturers to confirm that they are the latest and most reliable values. Where data were not available from the ARS Pesticide Properties Database, information was taken from other reliable sources, with preference given to California Department of Pesticide Regulation and U.S. EPA peer-reviewed publications.

The review of commonly referenced data sources demonstrated reason to be concerned about the quality of chemical property and environmental fate data for pesticides. In some cases various sources reported widely differing values for the same parameters. To the extent that references are provided, many of the commonly referenced data sources cite each other, lending confusion as to the original source of a particular value, and making it impossible to examine the quality of the methods used to make the reported measurement.[17] A recent USGS review of chemical property data for DDT and its metabolite DDE identified "egregious errors in reporting data and references and poor data quality and/or inadequate documentation of procedures" within the pesticide chemical characterization literature (Pontolillo and Eganhouse, 2001). On the basis of these findings, caution should be exercised in the use of the values reported in this section, and values from high-quality reports from the peer-reviewed literature should be sought for use in any detailed modeling of pesticide fate and transport.

4.2 Chemical Properties

Table 4-1 (on the next page) lists the molecular formula, molecular weight, common synonyms (generally commercial brand names), and the unique identifying number for each chemical assigned by the American Chemical Society's Chemical Abstract Service. Table 4-2 (on page 27) provides basic chemical properties for each pesticide: solubility in water, vapor pressure, octanol-water partition coefficient, and organic carbon sorption coefficient.

4.3 Environmental Fate Data

In Table 4-3 (on page 28), the half-lives for various environmental decomposition pathways are provided.

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[17] Evaluation of the values presented in this chapter would be a major effort that was beyond the scope of this project. Since this analysis takes a weight-of-evidence approach, any inaccuracies in this data are unlikely to alter the report's conclusions.

Table 4-1. Basic Information About Study List Pesticides

Name	Chemical Abstracts Service Number	Synonyms and Trade Names	Molecular Formula	Molecular Weight
Bifenthrin	82657-04-3	Biphenthrin, Bifenthrine, Brigade, Capture, Talstar	$C_{23}H_{22}ClF_3O_2$	422.9
Carbaryl	63-25-2	Sevin	$C_{12}H_{11}NO_2$	201.2
Cyfluthrin	68359-37-5	Baythroid, Tempo	$C_{22}H_{18}Cl_2FNO_3$	434.3
Cypermethrin	52315-07-8	Stockade, Cymbush, Ammo, Cynoff, Demon	$C_{22}H_{19}Cl_2NO_3$	416.3
Deltamethrin	52918-63-5	Decamethrin	$C_{22}H_{19}Br_2NO_3$	505.2
Esfenvalerate	66230-04-4	(S)-Fenvalerate Asana	$C_{25}H_{22}ClNO_3$	419.9
Imidacloprid	105827-78-9 and 138261-41-3	Merit, Admire, Advantage, Pre-Empt, Premise,	$C_9H_{10}ClN_5O_2$	255.7
Malathion	121-75-5	Cythion	$C_{10}H_{19}O_6PS_2$	330.4
Permethrin	52645-53-1	Ambush, Nix, Pounce	$C_{21}H_{20}Cl_2O_3$	391.3
Piperonyl Butoxide	51-03-6	PBO	$C_{19}H_{30}O_5$	338.4
Pyrethrins	121-21-1 121-21-9	Pyrethrins I Pyrethrins II	$C_{21}H_{28}O_3$ $C_{22}H_{28}O_5$	328.4* 372.4*

*Pyrethrins are a mixture of substances; the molecular weight is the average for the mixture.
Sources: Data from the ARS Pesticide Properties Database (ARS, 2002); synonyms compiled from those frequently mentioned in literature sources (see reference list).

Table 4-2. Chemical Properties

Name	Solubility in Water (ppb)*	K_{ow}	K_{oc}	Vapor Pressure (torr)
Bifenthrin	100[a]	1,000,000	240,000	1.80×10^{-07}
Carbaryl	110,000	204	288	1.17×10^{-06}[a]
Chlorpyrifos	*1,180*	*100,000*	*9,930*	1.06×10^{-04}
Cyfluthrin[g]	20	891,251	31,000	3.30×10^{-08}
Cypermethrin	4	3,981,072	61,000	1.30×10^{-09}[a]
Deltamethrin	2[c]	269,153[c]	46,000 to 1,630,000[b]	1.50×10^{-08}[c]
Diazinon	*60,000*	*2,000*	*1,520*	1.88×10^{-05}
Esfenvalerate	0.2*	10,000	5,273	1.50×10^{-09}
Imidacloprid	514,000[a]	3.7[f]	132 to 310[a]	1.00×10^{-07}[a]
Malathion	130,000	501	1,200	3.40×10^{-06}
Permethrin	6	1,258,925	39,300	2.20×10^{-08}
Piperonyl Butoxide	14,000[d]	56,234[e]	1,810[d]	2.60×10^{-07}[b]
Pyrethrins I	200[b]	794,328[b]	39,000 (predicted)[b]	2.03×10^{-05}[b]
Pyrethrins II	9,000[b]	19,953[b]	5,200 (predicted)[b]	3.98×10^{-07}[b]

Notes: Solubility At 20° C to 25° C. Where data give a range of K_{oc}, ARS calculates an average.
*May be low; reported concentrations (*e.g.*, in the aquatic toxicity databases) exceed this value.
Sources: All data from the ARS Pesticide Properties Database (ARS, 2002) unless marked as follows:
[a] DPR Environmental Fate Reviews (Casjens, 2002; Fecko, 1999; Goh, 1990: Jones, 1999; Xu, 2000).
[b] NLM, 2002. [c] WHO *et al.*, 1989. [d] PAN, 2002. [e] Tomlin, 2000. [f] Bacey, 2000. [g] ARS Pesticide Properties Database (ARS, 2002) designated "selected values" are listed here as they are the only available peer-reviewed data source. A manufacturer representative has stated that the following values from DPR (Casjens, 2002) are more appropriate: solubility–2 ppb; K_{ow}–458,000 - 640,000; K_{oc}–62, 400 (Meier, 2002).

Table 4-3. Environmental Fate Data—Pesticide Decomposition Half-Lives (Days)

Name	Aqueous Photolysis Half-Life	Hydrolysis Half-Life	Soil Photolysis Half-Life	Soil Anaerobic Half-Life	Soil Aerobic Half-Life
Bifenthrin	210	Stable	Stable	97 to 156[a]	65 to 95
Carbaryl	45	11	41[a]	46	4 to 27[a]
Chlorpyrifos	*30*[h]	*29*	*Stable*[h]	*39 to 51*[h]	*30*
Cyfluthrin	12	193	2 to 16	34[a]	63[a]
Cypermethrin	56	Stable	165	<14 to 60	6 to 60
Deltamethrin	Stable[b]	Stable[b]	9[b]	31 to 36[b]	11 to 19[b]
Diazinon	*140*	*5*	*5*	*17*	*39*
Esfenvalerate	25	Stable	Stable	77	74
Imidacloprid	0.04[a]	>30[a]	39[a]	27[a]	997[i]
Malathion	94 to 143[c]	6	173[c]	Not available[c]	<1 to 3[c]
Permethrin	30	Stable	33	108	30
Piperonyl Butoxide	0.35[d]	Stable[d]	1[d]	927[g]	14[f]
Pyrethrins	Unstable[d]	Stable[d]	Unstable (predicted)[e]	14 to 60 (predicted)[e]	Unstable (predicted)[d]

*Half-life decreases as pH increases. Value is for pH 7.

Sources: All data from ARS Pesticide Properties Database (ARS, 2002) unless marked as follows: [a]DPR Environmental Fate Reviews (Casjens, 2002; Fecko, 1999; Goh, 1990; Jones, 1999; Xu, 2000). [b]U.S. EPA, Undated. [c]U.S. EPA, 2000. [d]Jones, 1998. [e]Casida and Quistad, 1995. [f]Tomlin, 2000. [g]Kollman and Segawa, 1995. [h]U.S. EPA, 2000. [i]Bacey, 2000; a manufacturer representative has stated that this value is artificially high (Meier, 2002), but a literature review did not identify any peer-reviewed data source with any other value.

Table 4-4 (on the next page) gives the commonly referenced “field dissipation half-life” for each pesticide. The field dissipation half-life is a measure of the overall rate of disappearance of a pesticide from field soil—it is not necessarily a measure of the environmental degradation of the pesticide. “Dissipation” may include leaching, runoff, hydrolysis, photolysis, microbial degradation, and vaporization. Field dissipation half-life data typically have wide ranges, as they are a function of the site, climate, and soil as well as the chemical characteristics of the pesticide. While field dissipation values are commonly used in descriptions of the environmental fate of pesticides (and therefore have been tabulated for the study list pesticides), they are not particularly relevant to a surface water quality analysis, since they may reflect losses due to pesticide runoff to surface waters.

Table 4-4. Field Dissipation Data

Name	**Reported Field Dissipation Half-Life (Days)**
Bifenthrin	7 to 62; 122 to 345[a]
Carbaryl	4 to 22; 1 to 11[a]
Chlorpyrifos	*4 to 139*
Cyfluthrin	4 to 90; about 13.5[a]
Cypermethrin	7 to 82; 4 to 12[a]
Deltamethrin	6 to 209[b]
Diazinon	*3 to 13*
Esfenvalerate	22 to 75
Imidacloprid	27 to 229[a]
Malathion	0.2 to 25
Permethrin	6 to 106
Piperonyl Butoxide	about 4[c]
Pyrethrins	about 12

Note: Where data from two reliable sources differed significantly, both values were included.
Sources: All data from the ARS Pesticide Properties Database (ARS, 2002) unless marked as follows: [a]DPR Environmental Fate Reviews (Bacey, 2000; Casjens, 2002; Fecko, 1999; Jones, 1999; Xu, 2000). [b]U.S. EPA, Undated. [c]Cox, 2002.

5.0 PRODUCTS CONTAINING STUDY LIST PESTICIDES

5.1 Data Sources

Data about pesticide products was obtained from the California Department of Pesticide Regulation (DPR). The DPR Pesticide Product/Label database (DPR, 2002) provided pesticide product registration information.

5.2 Pesticide Products

Pesticides on the study list have been formulated into hundreds of commercial products. This section describes the active ingredient composition of these products.

Table 5-1 provides basic facts about the pesticide products that contain each of the study list pesticides: number of California-registered products, most common formulations, and the identity of the "basic manufacturer" (the manufacturer that takes the lead in preparing technical data necessary for registration of products containing the pesticide).

Table 5-1. Product Data

Name	Number of California Registered Products	Most Common Formulation(s)	Basic Manufacturer
Bifenthrin	47	Granules, Ready-to-use liquids	FMC Corporation
Carbaryl	94	Dust, Granules	Rhone Poulenc
Cyfluthrin	53	Aerosols. Ready-to-use liquids	Bayer
Cypermethrin	36	Emulsifiable concentrates	Zeneca
Deltamethrin	48	Dust, Granules	AgrEvo
Esfenvalerate	49	Aerosols	DuPont
Imidacloprid	57	Granules, Ready-to-use liquids	Bayer
Malathion	47	Emulsifiable concentrates	Cheminova Agro
Permethrin	625	Aerosols, Ready-to-use liquids	Zeneca
Piperonyl Butoxide	783	Aerosols, Ready-to-use liquids	Endura SpA
Pyrethrins	750	Aerosols, Ready-to-use liquids	Pyrethrin Task Force (several manufacturers)

Sources: Product registration and formulation data from DPR Pesticide Product/Label Database as of July 1, 2002 (DPR, 2002); basic manufacturer information from EXTOXNET Pesticide Information Profiles (EXTOXNET, 1994-1996) except for piperonyl butoxide (Jones, 1998).

California-registered pesticide products containing study list pesticides are available in a wide range of concentrations, as shown in Table 5-2.[18] Most products formulated with bifenthrin, deltamethrin, esfenvalerate, permethrin, piperonyl butoxide, and pyrethrins contain less than 1% active ingredient.[19] Products with cyfluthrin and imidacloprid have slightly higher concentrations, with about half having concentrations of about 2.5% or less. Just over half of carbaryl products contain between 5 and 10% active ingredient. Cypermethrin and malathion products contain much higher active ingredient concentrations—half of cypermethrin products have active ingredient concentrations exceeding 24% and more than 80% of malathion products contain more than 20% malathion.

Table 5-2. Study List Pesticide Product Active Ingredient Concentrations

Name	Lowest	Highest[a]	Most Common Concentrations
Bifenthrin	0.1%	25.1%	<1% (31 of 47 products)
Carbaryl	0.126%	99%	≥5% (84 of 94 products)
Cyfluthrin	0.003%	25%	<2% (37 of 53 products)
Cypermethrin	0.5%	40%	>24% (23 of 46 products)
Deltamethrin	0.02%	98%[b]	<1% (37 of 48 products)
Esfenvalerate	0.0033%	35%	<1% (39 of 49 products)
Imidacloprid	0.011%	98%	≤2.5% (28 of 57 products)
Malathion	2%	97%	>20% (40 of 47 products)
Permethrin	0.02%	99.5%	<1% (413 of 625 products)[c]
Piperonyl Butoxide	0.02%	90%	<1% (475 of 782 products)[d]
Pyrethrins	0.01%	30%	<1% (637 of 751 products)

[a] Some high concentration products are used primarily to formulate other products.
[b] Only 1 product >5%.
[c] Most products <3% (503 of 625 products).
[d] Most products <2% (597 of 782 products).
Source: DPR Pesticide Product/Label Database (DPR 2002).

Some of these active ingredients are commonly formulated with other pesticides prior to sale in commercial products, as shown in Table 5-3 (on the next page). Nearly every pyrethrins product and nearly every piperonyl butoxide product contains at least one other active ingredient. More than half of permethrin products contain another active ingredient. In contrast, bifenthrin, deltamethrin, imidacloprid, and malathion are rarely formulated into products containing other active ingredients.

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[18] New products containing the pesticides on the study list are registered or are removed from registration almost weekly. This report evaluates the pesticide products registered by the state of California as of July 1, 2002.

[19] All percentages in this report are on a weight basis.

Table 5-3. Products Formulated with Other Active Ingredients

Name	% of Products	Other Active Ingredients
Bifenthrin	0%	--
Carbaryl	24%	Metaldehyde, butoxy polypropyleneglycol, PBO, pyrethrins, and silica aerogel
Cyfluthrin	30%	Prallethrin, imidacloprid, PBO, n-octyl dicycloheptene dicarboximide, tetramethrin, pyrethrins, chlorpyrifos, and propoxur
Cypermethrin	17%	Tetramethrin, PBO, chlorpyrifos, butoxy polypropyleneglycol, pyrethrins, dipropyl isocinchomeronate, esbiothrin, and imiprothrin
Deltamethrin	10%	S-bioallethrin and imiprothrin
Esfenvalerate	32%	PBO, imiprothrin, d-trans allethrin, prallethrin, tetramethrin, pyrethrins, n-octylbicycloheptene dicarboximide
Imidacloprid	6%	Cyfluthrin
Malathion	6%	DDVP, pyrethrins, and PBO
Permethrin	56%	S-methoprene, Z-11-tetradecen-1-yl acetate, S-bioallethrin, d-trans allethrin, pyriproxyfen, prallethrin, d-allethrin, myclobutanil, hydroprene, linalool, (R,Z)-5-(1-decenyl) dihydro-2-(3h)-furanone, phenothrin, E,E-8,10-dodecadien-1-ol, tetramethrin, petroleum distillates, dipropyl isocinchomeronate, pyrethrins, PBO, ortho-phenylphenol, n-octyl bicycloheptene dicarboximide, chlorpyrifos, butoxy polypropyleneglycol
Piperonyl Butoxide	98%	S-methoprene, esbiothrin, S-bioallethrin, d-trans allethrin, pyriproxyfen, (S)-cypermethrin, esfenvalerate, lambda cyahlothrin, d-allethrin, fenoxycarb, linalool, cyfluthrin, cypermethrin, resmethrin, (R,Z)-5-(1-decenyl) dihydro-2-(3h)-furanone, phenothrin, permethrin, fenvalerate, tetramethrin, limonene, petroleum distillates, dipropyl isocinchomeronate, silica aerogel, rotenone, pyrethrins, propylene glycol, ortho-phenylphenol, n-octyl bicycloheptene dicarboximide, malathion, chlorpyrifos, diazinon, diatomaceous earth, DDVP, butoxy polypropylene glycol, carbaryl, fenthion, propoxur, allethrin
Pyrethrins	98%	Canola oil, S-methoprene, d-trans allethrin, pyroproxyfen, esfenvalerate, fenoxycarb, linalool, cyfluthrin, cypermethrin, resmethrin, phenothrin, permethrin, fenvalerate, tetramethrin, potash soap, petroleum distillates, dipropyl isocinchomeronate, silica aerogel, rotenone, PBO, ortho-phenylphenol, n-octyl bicycloheptene dicarboximide, malathion, chlorpyrifos, diazinon, diatomaceous earth, DDVP, butoxy polypropylene glycol, carbaryl, propoxur

Source: DPR Pesticide Product/Label Database, 2002.

6.0 FORMULATIONS

6.1 Background

Few pesticides contain only the pesticide active ingredient. Instead, manufacturers formulate pesticide products by mixing the active ingredient with other chemicals to dilute the pesticide to an appropriate application concentration and to improve properties like storage life, ease of handling, ease of application, effectiveness, or safety. The added ingredients are called “inert” ingredients to differentiate them from the active ingredient. (The term “inert” does not imply “slow to move” or “without active properties.”) Because of the inert ingredients, each pesticide product formulation has unique physical and chemical characteristics that may affect its potential for release to surface waters (Wauchope, 1980; Willis, 1980; Cohen, 1986). Some pesticide inert ingredients are themselves environmental pollutants.

Because the formulation may change the active ingredient’s performance and use, the U.S. Environmental Protection Agency (U.S. EPA) and the California Department of Pesticide Regulation (DPR) obtain lists of all pesticide ingredients from manufacturers and both agencies are required to register each formulated pesticide individually. In practice, U.S. EPA and DPR generally only conduct formulation-specific evaluations of pesticides in regard to worker safety—and such analyses look at formulation types (*e.g.*, wettable powder, concentrates), rather than individual pesticide products.[20] Because evaluating each individual formulation for the more than 10,000 registered pesticide products would be impractical, U.S. EPA and DPR rely on separate evaluations of pesticide active ingredients to consider surface water impacts.

6.2 Purposes Of Inert Ingredients In Pesticide Products

Inert ingredients appear in pesticide products for one of three reasons:

1. The ingredient has a specific function in the product—for example, to dilute it, preserve it, or increase its effectiveness..
2. The ingredient is an impurity in the active ingredient or a functional ingredient—like crystalline silica in a talc carrier for a dust product.
3. The ingredient is a component of a commercially available form of one of the functional ingredients in the formulation—such as a solvent or a preservative for an anti-foaming agent.

Common functions for inert ingredients in pesticides include:

- <u>Dissolving</u> the active ingredient into a stable liquid form.
    - Solvents are often petroleum-based solvents; however, water can also serve as a solvent for some pesticides.
    - Emulsifiers allow petroleum-based pesticides to mix with water.
    - Invert emulsifiers allow water-based pesticides to mix with a petroleum carrier.
    - Compatibility agents aid in combining two or more pesticides.

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[20] Certain formulation-specific toxicity data—including aquatic toxicity data—must be submitted by pesticide manufacturers prior to registration of each formulation. Unfortunately, such data are not made public, nor are they typically used in environmental risk assessments (which typically explore only active ingredients).

- Diluting the active ingredient to a desirable concentration for shipment or application.
- Carrying the active ingredient to the application site.
    - Carriers like clay powder, talc, chalk, ash, or clay, corn, or walnut granules or pellets facilitate handling of the pesticide.
    - Tiny plastic beads can be used to microencapsulate a pesticide.
- Stabilizing the pesticide to prevent its decomposition.
    - Buffers decrease the breakdown of a pesticide caused by exposure to acidic or alkaline conditions and allow pesticides to be mixed with diluents or other pesticides of different acidity or alkalinity.
    - Preservatives prevent biological growth in the pesticide material (for example, in the aqueous phase of a ready-to-use product).
- Controlling foam levels in products to make them more convenient to handle.
    - Foaming agents and thickeners reduce pesticide drift by foaming or by increasing droplet size.
    - Anti-foaming agents reduce foaming of spray mixtures that require vigorous agitation.
- Serving as "adjuvants," which are a special class of inert ingredients that increase the effectiveness of the active ingredient and make application easier or safer.
    - Stickers help a pesticide stay on the treated surface, particularly preventing washing by rainfall or irrigation.
    - Synergists increase the activity of insecticides, making the product more effective at controlling the target pest.
    - Penetrants help active ingredients penetrate the surface to which the pesticide is applied (*e.g.*, into the leaves of a plant).
    - Attractants (like food) draw pests to baits.
    - Wetting agents (some of the most common adjuvants) alter the dispersing, spreading, and wetting properties of spray droplets or wettable powders.
- Hiding odors with another fragrance.
- Increasing the safety of the product by reducing the toxicity of a pesticide formulation to the pesticide handler or to the treated surface (*e.g.*, a plant being protected from insects).

6.3 Common Pesticide Product Formulations

The physical mixture of inert and active ingredients into a commercial pesticide product creates its formulation. For example, granules, dust, ready-to-use liquids and concentrates are all types of pesticide formulations. Some formulations include gaseous propellants, like aerosols and foggers. Table 6-1 (on the next page) lists common formulations and examples of urban pesticide products for each formulation.

Table 6-1. Pesticide Product Formulations

Formulation Type	Urban Product Examples
Aqueous Concentrate	Water-based concentrate for mixing insect sprays
Dry Flowable	Fungicides and algaecides
Dust/Powder	Insect control dusts
Emulsifiable Concentrate	Solvent-based concentrate for mixing insect sprays (dilute with water)
Flowable Concentrate	Powder or slurry concentrate for mixing insect sprays
Gel/Paste/Cream	Roach and ant baits
Granular/Flake	Turf weed control products
Impregnated Material	Pet flea collars
Microencapsulated	Aerosol spray for "controlled release" of insecticide
Oil	Tree treatment, rose dormant spray
Other (Dry)	Pesticide for manufacturing and formulation
Other (Liquid)	Pesticide for manufacturing and formulation
Paint/Coating	Paints for sewer manholes
Pellet/Tablet/Cake/Briquet	Ant and rat baits
Pressurized Dust	Cockroach powder
Pressurized Gas	Home termite treatments
Pressurized Liquid/Spray/Fogger	Aerosols, flea foggers
Soluble Powder	Wood preservatives
Solution/Liquid (Ready-To-Use)	Home use insect sprays with pump handles
Suspension	Concentrate or ready-to-use insect spray requiring agitation during use
Wettable Powder	Professional applicator products for insect control (mixed with water)

Source: Based on products in DPR Pesticide Product/Label database (DPR, 2002).

6.4 Data Sources

To date, information about inert ingredients in pesticides has been considered confidential business information that is not provided to customers and cannot generally be disclosed by state or Federal government staff. For this reason, pesticide inert ingredients are almost never listed on product labels and cannot be readily obtained from any source.

A 1996 court decision requires U.S. EPA to disclose inert ingredients in specific products under certain conditions, when such information is requested under the Freedom of Information Act. Almost all of the inert ingredient information included in this report was obtained from U.S. EPA, which provided copies of all previously sent Freedom of Information Act responses regarding study list pesticide products (Furlow, 2002).[21] A few additional ingredients were identified from lists on product labels. The DPR Pesticide Product/Label database (DPR, 2002) provided pesticide product registration information.

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[21] This project does not include a Freedom of Information Act request—such requests take months or even years to complete, particularly when they involve a relatively large number of products. The study list pesticides are in more than 2,000 products. No inert ingredient information was obtained from DPR, whose employees are not allowed to disclose such information.

6.5 Study List Pesticide Products: Inert Ingredients and Formulations

The data sources listed in Section 6.5 disclosed the identities of as few as six 6 and as many as 42 inert ingredients in products containing individual study list pesticides. No information was found regarding inert ingredients in cypermethrin or esfenvalerate products. The list of inert ingredients developed through this data assembly process is not comprehensive, but it does provide an indication of the types of inert ingredients present in study list pesticide products. The types of ingredients found in study list pesticide products are similar to those identified for diazinon and chlorpyrifos products (TDC Environmental, 2001).

Table 6-2 (on the next page) gives an overview and Appendix C lists the inert ingredients identified in products containing each of the study list pesticides. The tables in Appendix C include the type of product that contained the identified ingredient and identify the likely function of that ingredient, based on the ingredient's chemical characteristics and its use in similar products (obtained from ingredient manufacturer and distributor information available on the Internet). As expected, the types of inert ingredients depended on the product formulation (*e.g.*, propellants in aerosol sprays and surfactants in emulsifiable concentrates and wettable powders).

Study list pesticides are available in 19 formulations, as shown in Table 6-3 (on page 38).

6.6 Water Quality Evaluation of Inert Ingredients

Although available information is too limited to allow quantification of the significance of various inert ingredients, it suggests that there are two major issues to consider with regard to water quality:

- Inert ingredients modify the transport of the study list pesticides to surface waters. These modifications may involve chemical or physical features of inert ingredients:
    - *Chemical enhancement of pesticide wash-off*. Ingredients that facilitate dissolution or suspension of pesticides in water (like surfactants and emulsifiers) are likely to facilitate dissolution or suspension of active ingredients into storm water runoff.
    - *Chemical reduction of pesticide wash-off.* Adjuvants like penetrants and stickers that help a pesticide stay on the treated surface are likely to reduce off-site transport of the active ingredient.
    - *Physical enhancement of pesticide wash-off*. Carriers composed of fine particles or tiny capsules can facilitate environmental transport of the pesticide because fine particles are quite mobile in the environment.
    - *Physical reduction of pesticide wash-off.* Formulation in containerized baits or blocks reduces a pesticide's exposure to surface water, thereby reducing the environmental mobility of the active ingredient.
- Some inert ingredients in study list pesticide products are water pollutants. The compiled lists of inert ingredients contain many water pollutants (*e.g.*, hydrocarbon solvents and chlorinated solvents). Since inert ingredient concentrations are not disclosed under the Freedom of Information Act process, it is impossible to gauge the significance of these releases in regard to surface water concentrations of such substances.

Table 6-2. Inert Ingredient Overview

Pesticide	Examples of Inert Ingredients Identified	Functions of Inert Ingredients Identified
Bifenthrin	Alkyl phenol ethoxylate, Attaclay LVM, Corn cob, Naphthalene Depleted Aromatic 200, Paper, Polyoxypropylene-polyoxyethylene block copolymer, Sunspray 6N	Carrier, Flow agent, Horticultural oil, Solvent, Surfactant
Carbaryl	1,2-Benziothiazoline-3-one, Amorphous synthetic silica, Butyl benzyl phthalate, Ethanol, Gypsum, Kaolin clay, Silicone emulsion, Soap, Sponto N-140, Talc, Tenneco T 500-100, Water, Xanthan gum	Carrier, Dispersant, Emulsifier, pH adjustment, Preservative, Solvent, Surfactant
Cyfluthrin	Corn cob, Glycerin, Organic solvent (unnamed), Surfactants (unnamed)	Antifreeze, Carrier, Solvent, Surfactant
Cypermethrin	None identified	--
Deltamethrin	Acetyl tri-n-butyl citrate, Ammonium phosphate urea, Ammonium sulfate, Dimethyl polysiloxane derivative, Magnesium chloride, Propylene glycol, Sodium lauryl sulfate, Sulfur-coated urea	Anti-foaming agent, Carrier, Electrolyte, pH adjustment, Preservative, Solvent
Esfenvalerate	None identified	--
Imidacloprid	Carbopol resin 2984, Ethylene glycol, Limestone granules, Peanut shells, Pyla-cert oil amber XA MS-166A, Tetrahydrofurfuryl alcohol	Carrier, Emulsion stabilizer, Fertilizer, Solvent, Surfactant
Malathion	Calsoft F-90, Marasperse N-22, Paper, Sponto N-140, Talc, Tenneco T 500-100, Triton X-155	Carrier, Dispersant, Emulsifier, Solvent, Surfactant,
Permethrin	Agent X-2084-40A emulsifier blend, Brij 96, Corrosion inhibitors (unspecified), Fragrance, Hydrocarbon propellant (butane/isobutane/propane), Mineral seal oil, Nonylphenoxypoly (ethyleneoxy) ethanol, SAG 30, Sodium benzoate	Carrier, Defoamer, Emulsifier, Fragrance, Propellant, Solvent, Surfactant,
Piperonyl Butoxide	1,1,1-Trichloroethane, Aromatic 150 Petroleum Solvent, Carbon dioxide, Fragrance, Freon 22, Isopar M, Isopropanol, Odorless mineral spirits, Soltrol 170, Solvent 529-66 Low Odor, Water	Carrier, Corrosion Inhibitor, Defoamer, Emulsifier, Fragrance, Preservative, Propellant, Solvent, Surfactant
Pyrethrins	Chlorodifluoromethane, Freon 22, Monooleate ester of sorbitan monostearate, Propane, Silica gel, Silicone emulsion, Vista LPA, Water	Carrier, Corrosion Inhibitor, Emulsifier, Fragrance, Preservative, Propellant, Solvent, Surfactant

Source: Appendix C.

Table 6-3. Product Formulations

Name	Dust/Powder	Emulsifiable Concentrate	Flowable Concentrate	Gel, Paste, Cream	Granular/Flake	Impregnated Material	Microencapsulated	Oil	Paint/Coatings	Pellet/Tablet/ Cake/Briquet	Pressurized Gas	Pressurized Liquid/Sprays/ Foggers	Soluble Powder	Solution/Liquid (Ready-to-use)	Wettable Powder	Suspension	Aqueous Concentrate	Other (Liquid)	Other (Dry)
Bifenthrin	0	2	8	0	18	0	1	2	0	0	0	2	0	12	1	1	0	0	0
Carbaryl	25	2	7	2	27	5	1	1	0	4	0	1	2	5	6	1	5	0	0
Cyfluthrin	4	2	0	0	4	1	0	0	0	0	0	17	0	11	8	2	4	0	0
Cypermethrin	0	19	0	1	0	1	0	0	0	0	0	8	0	3	4	0	0	0	0
Deltamethrin	13	2	0	0	12	0	0	0	0	0	0	5	0	8	2	6	0	0	0
Esfenvalerate	0	9	1	0	0	0	0	0	0	0	1	23	0	5	3	0	7	0	0
Imidacloprid	1	2	6	1	17	2	0	0	0	2	0	0	0	12	9	0	5	0	0
Malathion	4	28	4	0	0	0	0	0	0	0	0	2	0	7	2	0	0	0	0
Permethrin	27	39	10	3	22	8	1	0	1	1	1	271	1	172	3	1	59	5	0
Piperonyl Butoxide	50	58	7	12	0	11	1	4	0	2	6	290	0	266	3	1	59	11	2
Pyrethrins	48	59	7	11	0	2	1	4	0	2	4	282	0	262	3	1	55	8	2

Note: No products were in the “dry flowable” or “pressurized dust” formulations.
Source: DPR Pesticide Product/Label database, data from July 1, 2002 (DPR, 2002).

6.7 Water Quality Evaluation of Formulations

The physical and chemical differences among formulations greatly affect the transport of a pesticide in the environment. At one extreme, pesticides formulated as impregnated materials or briquets can only enter the environment if leached from a solid carrier. At the other extreme, water-soluble solid or liquid pesticides can readily be washed off of an outdoor surface (if they do not decompose prior to rainfall or washing of the application location).

A review of the literature did not identify any systematic investigation of the relationship of pesticide formulation type to runoff. Some individual investigations comparing two formulations exist in the literature, as described below:

- An investigator compared runoff of liquid and granular diazinon formulations from turf test plots, finding 0.7 to 1.15% of applied diazinon washed off in relatively light irrigation (1.3 cm). Twice as much diazinon washed off from an emulsifiable concentrate application than from application of granules. The difference in wash-off between the two formulations was attributed to surfactants in the emulsifiable concentrate facilitating wash-off and the need for dissolution out of the carrier material (paper) before diazinon from the granular formation could wash-off (Evans *et al.*, 1998).
- A study of dithiopyr granule compared to emulsifiable concentrate applications to a simulated golf course fairway found that about 2% of an emulsifiable concentrate formulation and 1% of a granular formulation was washed off (Hong and Smith, 1997).
- A review of pre-1980 pesticide wash-off studies found that emulsifiable concentrates were more resistant to removal by rain than dusts or wettable powders, perhaps because the emulsifiable concentrate formulation is capable of penetrating vegetation surfaces (unlike powders, which sit on the surface) (Willis, 1980).
- In diazinon turf wash-off experiments conducted on laboratory test plots, 1.5% of a granular formulation was washed off, while 21.8% of an emulsifiable concentrate formulation was washed off (Spurlock *et al.*, 2002).[22]
- Formulation had a small effect on imidacloprid wash-off from turf plots. Mean wash-off fractions for a total of four model storms were 1.46% for the wettable powder and 1.92% for granules. In the same tests, 2,4-D had a reverse pattern, with 3% of the wettable powder application washed off as compared to 2.2% of the granular formulation (Ambrust and Peeler, 2002).
- Mixing with adjuvants both enhanced and reduced bifenthrin wash-off from cotton leaves in a 12 mm model storm. Adjuvants classified as “spreaders” and “wetters” increased bifenthrin runoff, while adjuvant “stickers” reduced wash-off Mulrooney and Elmore, 2000).

A frequently cited literature review compiled information showing some consistency in runoff fractions of various pesticides in the same formulation. The reviewer found that water insoluble pesticides applied in emulsion formulations runoff more than water-soluble pesticides; he also concluded that about 2% of the active ingredient from a

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[22] Wash-off was initiated immediately after application, which probably accounts for the relatively high runoff fraction. While the report calls the liquid “aqueous,” diazinon is not water soluble and a check of the product label confirmed that it is an emulsifiable concentrate that contains some water as packaged for sale.

typical wettable powder application would be carried off the application site by storm water runoff (Wauchope, 1978). Another reviewer suggested that as much as 5% of the active ingredient in wettable powder formulations run off of the application site in storm water (Evans, 1998).

While the literature on this topic continues to grow, without a systematic study of the effects of formulation on pesticides and without evaluations of impervious surface runoff, there is not sufficient information to provide the basis for a quantitative evaluation of the effects of formulation on the runoff of study list pesticides.

7.0 URBAN SITES OF USE OF STUDY LIST PESTICIDES

A "site of use" is a location where a pesticide may be applied. During pesticide registration, the U.S. Environmental Protection Agency (U.S. EPA) and the California Department of Pesticide Regulation (DPR) determine the allowable sites of use for each pesticide product. Pesticides may not legally be applied to non-registered sites of use.

7.1 Data Sources

DPR maintains a database that includes the sites of use for all California-registered pesticide products (DPR, 2002). This database was used to identify the urban sites of use for products containing study list pesticides. The urban sites were then reviewed to identify the uses of greatest interest from the water quality perspective.

7.2 Approach to Sites of Use Review

The sites of use review used methodology previously developed in a review of diazinon and chlorpyrifos products (TDC Environmental, 2001). The methodology involves the following steps:

1. Obtain DPR listing of sites of use for all products containing each study list pesticide.
2. Remove from the sites of use list all agricultural crops and other non-urban sites of use.[23]
3. Correct the list based on a quality assurance review of labels for products listed for applications to water or to the sewer system.[24]

In general, the approach to developing the urban sites of use lists was inclusive, rather than exclusive. In other words, sites like drinking water reservoirs that might not be strictly urban were included in an effort to avoid excluding activities that are not strictly urban but that commonly are associated with—or occur in—urban areas. This approach ensures that urban sites of use lists are comprehensive.

7.3 Urban Sites of Use of Study List Pesticides

Not surprisingly, all the study list pesticides have many urban use sites, as shown in Table 7-1 (on the next page). Cypermethrin had the shortest list of urban sites of use (64), while permethrin, piperonyl butoxide, and pyrethrins are all registered for more than 300 urban sites of use. Lists of urban sites of use for the study list pesticides are in Appendix D.

7.4 Water Quality Evaluation of Sites of Use

The sites of use of water quality interest were identified with a two-step process. First, each of the study list pesticides was reviewed to determine if it may be applied on any of

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[23] In general, sites with DPR site codes between 100 and 31000 are agricultural or other non-urban sites (*e.g.*, forests) and thus can quickly be omitted from consideration. Also removed from the list of urban sites of use were pesticide repackaging/formulation sites (99000 series), uncultivated agricultural area sites (66000 series) and farm animals, mushroom houses, and barns (61000 series).

[24] This step is necessary because the list of sites of use in the DPR Product/Label database was previously found to contain many data entry errors for these use sites (TDC Environmental, 2001). Within the project budget, it was impossible to obtain and review all product labels. Labels were obtained from the U.S. EPA product label database, which contains electronic images of product labels (U.S. EPA, 2002). While California may have its own labels for pesticide products, California labels cannot include any uses that are not included on Federal labels—and thus, labels from the U.S. EPA database are adequate for determining if a use is not allowed.

Table 7-1. Summary of Study List Pesticide Urban Sites of Use

Name	Urban Sites of Use	Outdoors and indoors at residential, institutional, and commercial buildings	Large outdoor areas[a]	Ornamental plants	Lawns	Golf courses	Wood structures	Water sites[b]	Sewer Sites[c]	Pets	Other Sites of Interest
Bifenthrin	98	X	X	X	X	X	X			X	
Carbaryl	80	X	X	X	X	X		X		X	
Cyfluthrin	108	X	X	X	X	X	X			X	Floor drains
Cypermethrin	64	X	X	X	X		X			X	Bathrooms, human face gear and footwear
Deltamethrin	133	X	X	X	X	X	X		X	X	Floor drains, human sites, human bedding
Esfenvalerate	84	X	X	X	X	X	X			X	Floor drains
Imidacloprid	81	X	X	X	X	X	X			X	
Malathion	90	X	X	X	X	X		X		X	Human sites, catch basins, tidal areas
Permethrin	316	X	X	X	X	X	X		X	X	Textiles, human bedding, human body, human clothing, laundry, fabric treatments
Piperonyl Butoxide	348	X	X	X	X	X	X	X	X	X	Human drinking water systems, tidal areas, human bedding, human body, human clothing, laundry, diapers
Pyrethrins	363	X	X	X	X	X	X	X	X	X	Textiles, fabrics, and fibers; human drinking water systems; tidal areas; human bedding, human body, human clothing, laundry, diapers

[a] Includes broadly defined sites like urban areas, rights of way, and mosquito abatement.

[b] Includes one or more of the following uses (DPR site codes between 65000 and 65999): drainage ditches, irrigation ditches, swimming pools, aquatic areas (general), human drinking water systems, ponds, lakes, marshes, catch basins.

[c] Includes DPR site code 65026—Sewage Systems (Septic Tanks, Sewers, Etc.), and/or DPR site code 67008—Sewage Disposal Areas (Municipal And Other)

Source: DPR Pesticide Product/Label Database (DPR, 2002); entries for water and sewer sites verified with product labels by TDC Environmental (see text).

the sites of use where diazinon and chlorpyrifos applications were found to be of concern for water quality (TDC Environmental, 2001). That evaluation of urban diazinon and chlorpyrifos uses found the following:

- Applications to outdoor impervious surfaces had the greatest potential to release the applied pesticides to surface water.
- Two other uses also had a high potential for surface water releases of the applied pesticide: applications resulting in discharges to the sewer system and applications to outdoor plants and soil (including ornamental landscaping, lawns, and golf courses).
- Applications directly to surface waters (including applications via storm drains) were found to have a potentially high potential for surface water releases, but these were fairly uncommon uses of diazinon and chlorpyrifos.
- A common chlorpyrifos use—underground injection to control pests in wood structures was also found to have relatively high potential for surface water releases, if conditions existed to facilitate transport of the otherwise relatively immobile pesticide (*e.g.*, subsurface water flows).

On the basis of the above, the following sites of use were identified as being of interest to water quality:

- Outdoors at residential, institutional, and commercial buildings, and other large outdoor area application sites
- Sewer sites (sites where application results in sewer discharge of the pesticide)
- Ornamental plants, lawns, nurseries, and golf courses
- Water sites (sites where application results in release of the pesticide to surface water)
- Wood structures

The second step in the assessment was to review remaining urban sites of use to identify any other sites that have previously been connected to incidents of surface water toxicity. This review identified one additional site of use of interest—applications to pets. Pet applications of pesticides have previously been associated with toxicity in wastewater treatment plant effluent (U.S. EPA, August 1999).[25]

Table 7-1 summarizes the 9 types of study list pesticide product sites of use that are of water quality interest. This analysis shows that most of the study list pesticides may be applied on most of the urban sites of use of water quality interest.

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[25] This use was not considered in the diazinon and chlorpyrifos product screening for water quality implications because pet application uses had been terminated by U.S. EPA and pesticide manufacturers prior to that evaluation (TDC Environmental, 2001).

8.0 SALES AND USE OF STUDY LIST PESTICIDES

8.1 Data Sources

Sales and use information were taken from California Department of Pesticide Regulation (DPR) annual summaries of pesticide sales and pesticide use (DPR, 1999, 2000, 2001; and DPR, October 2001). The most recent pesticides sales and reported use data (at the time this analysis was completed) were for the year 2000, which means that market changes due to the reduction of diazinon and chlorpyrifos uses may not be evident. Additionally, it is important to recognize that sales data may not be reflective of actual pesticide use, as sales data are based on a tax paid by the pesticide manufacturer when products are shipped, which (due to shipment scheduling practices) may not be directly related to retail sales of pesticides or to applications by commercial and residential users in the same time period.

8.2 Sales of Study List Pesticides

Table 8-1 gives total sales of each pesticide for 1998, 1999, and 2000 (the most recent data available when this analysis was completed), based on taxes paid by product manufacturers to DPR.

Table 8-1. Product Sales
(Data in Pounds of Active Ingredient)

Name	Number of Registrants[a]	Sales		
		2000	1999	1998
Bifenthrin	<4	NR[b]	NR[b]	NR[b]
Carbaryl	43	563,605	639,593	506,802
Cyfluthrin	9	39,126	30,579	62,181
Cypermethrin	9	50,573	43,845	72,052
Deltamethrin	8	8,323	2,103	NR
Esfenvalerate	35	42,878	41,163	41,384
Imidacloprid	12	95,908	106,710	77,054
Malathion	30	1,047,077	1,494,142	925,264
Permethrin	159	437,037	289,841	308,533
Piperonyl Butoxide	211	149,763	173,956	131,493
Pyrethrins	207	35,203	41,500	47,412

[a] In the year 2000.
[b] Not reported (fewer than four registrants).
Source: DPR Pesticides Sold reports (DPR, 1999, 2000, and 2001).

8.3 Urban Use of Study List Pesticides

Table 8-2 (on page 46) contains information about use of the study list pesticides in the year 2000, including total reported use in California and an estimate of California urban use. The estimate of urban use was made from reported use data and sales data. Reports of pesticide use were sorted to select urban pesticide applications. In California, pesticide uses for the production of any agricultural commodity, except livestock; for the treatment of post-harvest agricultural commodities; for landscape maintenance in parks, golf courses, and cemeteries; for roadside and railroad rights-of-way; for poultry and fish production; any application of a restricted material; any application of a pesticide designated by DPR has having the potential to pollute ground water[26] when used outdoors in industrial and institutional settings; and any application by a licensed pest control operator must be reported the County Agricultural Commissioner, who, in turn, reports the data to DPR. DPR prepares annual summary reports on the basis of this data. While the summary reports lack the detail necessary to allow a detailed tally of reported urban pesticide applications, they are sufficiently detailed to allow selection of “urban” categories (like structural pest control and landscape maintenance) to create an estimate of the urban portion of the reported pesticide use.[27]

The primary exceptions to the use reporting requirements are home and garden use and most industrial, commercial, and institutional pesticide applications not made by professional applicators.[28] Because these activities occur primarily in urban areas, it is reasonable to assume that essentially all unreported uses of the study list pesticides are urban. This assumption allows a rough estimate of unreported pesticide use to be made by subtracting reported use from sales data for the same time period. The total estimated urban use of each pesticide shown in Table 8-2 is a summary of the urban portion of the reported use data and estimated unreported use.

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[26] Carbaryl, diazinon, and malathion are on this list. It should be noted such reporting is probably incomplete because of the ready availability of these products to persons other than licensed pest control applicators.

[27] For purposes of this analysis, the following categories of use from DPR’s annual compilation reports were defined as urban uses: landscape maintenance, public health, regulatory pest control, rights of way, structural pest control, vertebrate control, regulatory pest control, uncultivated non-agricultural sites, airports, buildings/non-agricultural outdoor, food processing plants, and industrial sites. Most of the reported urban uses fell into a few categories (structural pest control, landscape maintenance, public health, and regulatory pest control). Many other categories may also include some applications in urban areas (*e.g.*, nurseries, greenhouses, sod/turf), so this "urban" estimate is likely to understate actual urban use.

[28] Pesticides used in consumer products are often unreported, or reported as applied at the product-manufacturing site rather than at the site where the products are used.

Table 8-2. Product Sales and Use Analysis for Calendar Year 2000 (Data in Pounds of Active Ingredient)

Name	Sales	Reported Use (Agricultural & Urban)	Urban Reported Use		Unreported Use[a]		Estimated Total Urban Use[b]
			Quantity	Fraction of Reported Use (%)	Quantity	Fraction of Product Sales (%)	
Bifenthrin	NR[c]	31,047	12,045	39%	Unknown[c]	Unknown	Unknown
Carbaryl	563,605	364,966	13,317	4%	198,639	35%	211,956
Cyfluthrin	39,126	27,083	15,320	57%	12,043	31%	27,363
Cypermethrin	50,573	136,285	126,974	93%	--[d]	--[d]	126,974
Deltamethrin	8,323	10,911	10,806	99%	--[d]	--[d]	10,806
Esfenvalerate	42,878	32,022	479	1%	10,856	25%	11,335
Imidacloprid	95,908	101,410	35,789	35%	--[d]	--[d]	35,789
Malathion	1,047,077	489,650	69,250	14%	557,427	53%	626,677
Permethrin	437,037	385,581	246,350	64%	51,456	12%	297,806
Piperonyl Butoxide	149,763	24,967	18,160	73%	124,796	83%	142,956
Pyrethrins	35,203	4,357	3,536	81%	30,846	88%	34,382

[a] Sales minus reported use. This generally consists of urban uses, such as household uses and non-reported uses at commercial, industrial, and institutional facilities.
[b] Urban reported use plus unreported use (which was assumed to be zero if sales were less than total reported use).
[c] Sales data are not public (see Table 8-1).
[d] Sales are less than reported use. Imidacloprid and deltamethrin are within typical year-to-year sales/use data variations for products where almost all use is reported (Singhasemanon, 2003). There is no apparent reason for the cypermethrin discrepancy—DPR data showed no apparent gross error in use reporting (Singhasemanon, 2003) and sales data are consistent with data for 1999 and 2001 (DPR, 2000; DPR 2002).
Note: the following categories in the use report were defined as "urban" for purpose of this analysis: landscape maintenance, public health, regulatory pest control, rights of way, structural pest control, vertebrate control, regulatory pest control, uncultivated non-ag, airport, buildings/non-ag outdoor, food processing plant, industrial site.
Source: DPR Summary of Pesticide Use Report for 2000 (preliminary data) (DPR, 2001) and DPR pesticide sales data for the year 2000 (DPR, 2001).

9.0 AQUATIC TOXICITY

The primary reason for concern about pesticides in surface water is their toxicity to aquatic species. This section includes an overview of aquatic toxicity data for study list pesticides to provide context—and comparison values—for the analysis in this report. This section is by no means comprehensive—there are thousands of toxicity data points for study list pesticides. Instead, the focus of this section is on the lowest toxicity values, since protecting sensitive classes of species is a goal of water quality protection programs.

This section also reviews toxicity testing methods to evaluate the ability of existing methods to assess environmental effects of study list pesticides. While standard aquatic toxicity testing methods are available, these methods generally rely on the assumption that the concentration of the pesticide will remain relatively constant in the test container—not always the case for the study list pesticides. When incidents of aquatic toxicity are identified, toxicity identification evaluation procedures can be employed—but can only produce useful results if methods for identifying potential toxicants exist. For many of the pesticides on the study list, standard toxicity testing procedures may miss incidents of aquatic toxicity.

9.1 Data Sources

Information about toxicity testing was obtained from the scientific literature and from interviews with scientists familiar with toxicity testing and toxicity identification evaluations for San Francisco Bay area surface water samples (Miller, 2002; Ogle, 2002; Denton, 2003). Aquatic toxicity data were obtained from the U.S. EPA Ecotox database (formerly Acquire) (U.S. EPA, 2002) and the DPR Ecotox database (DPR 2002). Information in these databases is subject to scientific review prior to data entry and must meet the quality assurance standards of the agencies managing the databases.[29]

Data reported in this section are subject to the following uncertainties:

- Testing methods may have presented erroneous results (*e.g.,* high or low values). Toxicity data sets for study list pesticides include multiple data points for the same test with the same species, with results occasionally spanning more than an order of magnitude. In order to ensure a conservative approach to the analysis, the lowest values are compiled in this report. It is possible that the true toxic concentration may be higher than the lowest reported values.
- Testing methods may not have accounted for losses of pesticides in toxicity testing containers—in other words, organisms may have been exposed to pesticide concentrations considerably lower than the nominal concentrations in the toxicity testing. This is particularly a problem with pyrethroid toxicity tests and is likely to lead to reports of no effect at concentrations that may actually harm the test organism.
- Almost all reported results are based on “nominal” concentrations[30] rather than a measurement of the actual concentration in the testing container.[31] Often the pesticide concentration that causes toxicity is below the detection limit of standard chemical analytical methods (see Section 12).

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[29] This report relies on the database quality assurance procedures; the original data sources for the aquatic toxicity data compiled in this report were not re-reviewed.

[30] Concentration calculated from the amount of pesticide used to mix the testing solution.

[31] Data from U.S. EPA Office of Pesticide Programs FIFRA-required testing is a notable exception. All FIFRA required tests must report measured concentrations.

- Differences in toxicity testing methods may affect the test results. Data in this section may be from tests conducted in accordance with standard U.S. EPA Office of Water methods, U.S. EPA Office of Pesticide Programs (FIFRA) methods, or other standard methods applicable at the time of the testing.
- For most of the study list pesticides, there are many data gaps in the toxicity testing data sets. Toxicity to many common aquatic toxicity test species has not been assessed.
- While aquatic test organisms are selected to be representative of more sensitive species in various phyla, the species are typically not the most sensitive species in aquatic ecosystems, as more sensitive organisms are not amenable to laboratory settings (nor is it appropriate to test threatened and endangered species).
- Although toxicity testing is a standard approach to understanding the potential for a pollutant to impact an aquatic ecosystem,[32] test methods do not address many factors that affect an organism's response to a pollutant (like real-world exposure regime, responses to multiple stressors, and seasonality).

Few measurements of endpoints other than the concentration lethal to 50% of test organisms (LC50) were identified. Sub-lethal effects, which necessarily occur at concentrations below the concentration that kills aquatic organisms, can have important impacts on aquatic ecosystems.

These factors indicate that the data in this section may not fully represent the potential for study list pesticides to affect surface water habitats. While it is possible concentrations discussed in this section are higher than concentrations that are environmentally relevant, the types of testing errors and data gaps make it likely that concentrations below those described here may have meaningful effects on aquatic ecosystems.

9.2 Aquatic Toxicity Data for Study List Pesticides

The aquatic toxicity test species evaluated for biological effects in this report are listed in Table 9-1 (on the next page). These were selected to include the following species:

- Standard toxicity test species (such as *Daphnia magna*, *Oncorhynchus mykiss*, and *Lepomis macrochirus*) required by U.S. EPA under FIFRA as part of evaluating a pesticide for registration;
- Standard toxicity test species (such as *Ceriodaphnia dubia* and *Pimephales promelas*) required under the Clean Water Act (40 CFR Part 136) to assess the potential for toxicity in effluents, ambient surface waters, and/or storm waters; and
- Standard toxicity test species that must be evaluated to derive acute and chronic water quality criteria (guidelines require a minimum of at least eight different families in order to develop water quality criteria) (U.S. EPA 1984).

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[32] Laboratory single species toxicity test results have been found to be reliable qualitative predictors of aquatic ecosystem community impacts (U.S. EPA 1999).

Table 9-1. Species Selected for Aquatic Toxicity Data Review

Species Name	Common Name
Invertebrates	
Ceriodaphnia dubia	Water flea
Daphnia magna	Water flea
Daphnia pulex	Water flea
Hyalella azteca	Scud
Gammarus lacustris	Scud
Gammarus fasciatus	Scud
*Americamysis bahia**	Opossum shrimp
Penaeus sp.	Shrimp
Crassostrea virginica	American oyster
Crassostrea gigas	Pacific oyster
Vertebrates	
Pimephales promelas	Fathead minnow
Oncorhynchus mykiss	Rainbow trout
Salvelinus fontinalis	Brook trout
Lepomis macrochirus	Bluegill
Cyprinodon variegatus	Sheepshead minnow
Menidia beryllina	Inland silverside
Plants	
Selenastrum capricornutum	Green algae
Skeletonema costatum	Diatom

*Formerly known as *Mysidopsis bahia*
Salt water species are in the shaded areas of the table.
Sources: See text.

Table 9-2 (on the next page) summarizes the lowest toxicity data identified for study list pesticides. Table 9-3 (on pages 51 through 54) contains the lowest toxicity test values for each pesticide for all of the toxicity test species evaluated for this report. The notable elements of this data set are summarized below:

- Carbaryl is very highly toxic to aquatic crustaceans, with most LC50s below 50 ppb. Fish are somewhat less sensitive to carbaryl; however, many fish LC50s are below 1,000 parts per billion (ppb).
- Malathion (like organophosphorous pesticides diazinon and chlorpyrifos) is acutely toxic to aquatic crustaceans, with some LC50s below 1 ppb. Although fish LC50s are generally greater than 1 ppb, malathion is also very highly toxic to certain fish, notably *Menidia beryllina*, which has a 96-hour LC 50 of 0.03 ppb.
- Imidacloprid, a newer pesticide, does not have extensive reported toxicity testing. Available data, though limited, suggest that imidacloprid can be very highly toxic to aquatic crustaceans, but generally not acutely toxic to fish. The 96-hour LC50 value for *Americamysis bahia* (34 ppb) is markedly lower than other toxicity data for this pesticide.
- The pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, permethrin) are very acutely toxic to aquatic insects and crustaceans, with most LC50s well below 1 ppb. In contrast to diazinon and chlorpyrifos, pyrethroids are also very highly toxic to fish. They have negative temperature coefficients of toxicity, which means that their toxicity increases in colder water (Miller and Adams, 1982).

- Piperonyl Butoxide (PBO) can be very highly toxic to aquatic crustaceans and fish. Its role as a synergist could, however, be far more environmentally meaningful than its inherent toxicity. Because PBO inhibits the detoxification enzyme for pyrethroids, it enhances or prolongs the toxic response in an organism (Zimmerman *et al.*, 2001). The enhancement depends on the specific pyrethroid and ranges from 10 times to 150 times (Miller, 2002). Carbamate pesticide toxicity can also be enhanced by PBO; for example, carbaryl toxicity enhancement by a factor of 70 has been reported (Jones, 1998).

Table 9-2. Summary of Lowest Aquatic Toxicity Data for Study List Pesticides

Pesticide	**Lowest Toxicity Data Identified**	
	Fresh Water	**Salt Water**
Bifenthrin	0.07 ppb *Ceriodaphnia dubia*, 48-H LC50	0.00397 ppb *Americamysis bahia*, 96-H LC50
Carbaryl	1.1 ppb *Daphnia magna*, 24-H LC50 0.0115 ppb *Daphnia pulex*, 48-H EC50	5.7 ppb *Americamysis bahia*, 96-H LC50 5.5 ppb *Penaeus sp.* 24-H EC50
Cyfluthrin	0.14 ppb *Ceriodaphnia dubia*, 48-H LC50 0.025 ppb *Daphnia magna*, 48-H EC50	0.00242 ppb *Americamysis bahia*, 96-H LC50
Cypermethrin	0.36 ppb *Daphnia magna*, 48-H LC50 0.5 ppb *Oncorhynchus mykiss*, 96-H LC50	0.005 ppb *Americamysis bahia*, 96-H LC50
Deltamethrin	0.01 ppb *Daphnia magna*, 96-H LC50 0.003 *Daphnia magna*, 96-H EC50	0.017 ppb *Americamysis bahia*, 96-H LC50
Esfenvalerate	0.07 ppb *Oncorhynchus mykiss*, 96-H LC50	0.038 ppb *Americamysis bahia*, 96-H LC50
Imidacloprid	10,440 ppb *Daphnia magna*, 48-H LC50	34 ppb *Americamysis bahia*, 96-H LC50
Malathion	0.27 ppb *Daphnia magna*, 24-H LC50 0.098 ppb *Daphnia magna*, 24-H EC50	0.03 ppb *Menidia beryllina*, 96-H LC50
Permethrin	0.075 ppb *Daphnia magna*, 48-H LC50	0.046 ppb *Americamysis bahia*, 96-H LC50
Piperonyl Butoxide	2.4 ppb *Oncorhynchus mykiss*, 96-H LC50	1.25 ppb *Penaeus duorarum*, 96-H LC 50 8.8 ppb *Cyprinodon variegatus*, 96-H LC50
Pyrethrins	5.2 ppb *Oncorhynchus mykiss,* 96-H LC50	1.4 ppb *Americamysis bahia*, 96-H LC50

Source: U.S. EPA Ecotox (Acquire) database (U.S. EPA, 2002) and DPR Ecotox database (DPR, 2002).

Table 9-3. Summary of Aquatic Toxicity Data for Study List Pesticides (Lowest Values)

Test Species	Bifenthrin		Carbaryl		Chlorpyrifos		Cyfluthrin		Cypermethrin		Deltamethrin		Diazinon	
	Test	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**
Invertebrates														
Ceriodaphnia dubia	48-h LC50	0.07	48-h LC50 48-h EC50	11.6 3.06	96-h LC50	0.053	48-h LC50	0.14					48-h LC50 96-h LC50	0.25 0.32
Daphnia magna	48-h LC50 48-h EC50	0.32 1.6	24-h LC50 48-h LC50 24-h EC50 48-h EC50	1.1 7.2 0.66 2.77	96-h LC50	0.4	48-h LC50 48-h EC50	0.17 0.025	24-h LC50 48-h LC50 24-h EC50 48-h EC50	0.53 0.36 2 1	24-h LC50 48-h LC50 96-h LC50 24-h EC50 48-h EC50 96-h EC50	0.11 0.037 0.01 0.113 0.029 0.003	96-h LC50	0.21
Daphnia pulex			48-h LC50 48-h EC50	6.4 0.0115	72-h LC50	0.12							48-h LC50	0.65
*Americamysis bahia**	96-h LC50	0.004	96-h LC50	5.7	96-h LC50	0.035	96-h LC50	0.00242	96-h LC50	0.005	96-h LC50	0.0017	96-h LC50	4.2
Hyalella azteca					96-h LC50	0.04							96-h LC50	6.51
Gammarus lacustris			24-h LC50 48-h LC50 96-h LC50	40 22 16	96-h LC50	0.11							96-h LC50	170
Gammarus fasciatus			24-h LC50 96-h LC50	50 26	96-h LC50	0.32							96-h LC50	0.2
Penaeus sp.			24-h EC50 48-h EC50	5.5 2.5					96-h LC50	0.036			24-h LC50	8.5
Crassostrea virginica	48-h EC50	285	14-d LC50 48-h EC50 24-h LOEC	3,000 2,100 1,000	96-h EC50	34	96-h EC50	2.69	96-h EC50	370	96-h EC50	8.2	96-h EC50	880
Crassostrea gigas									48-h LC50	2,270				

Table 9-3. Summary of Aquatic Toxicity Data for Study List Pesticides (Lowest Values) (Continued)

Test Species	Bifenthrin		Carbaryl		Chlorpyrifos		Cyfluthrin		Cypermethrin		Deltamethrin		Diazinon	
	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)
Vertebrates														
Pimephales promelas	96-h LC50*	0.26	24-h LC50 96-h LC50 LOEC MATC NOEC	5,940 5,010 200 250 250	96-h LC50	120	96-h LC50*	2.49					96-h LC50	3700
Oncorhynchus mykiss	96-h LC50	0.15	24-h LC50 48-h LC50 96-h LC50	860 860 320	96-h LC50	7.1	48-h LC50 96-h LC50	0.57 0.3	12-h LC50 24-h LC50 48-h LC50 96-h LC50	2.5 5 5 0.5	24-h LC50 48-h LC50 96-h LC50	0.7 0.5 0.25	96-h LC50	20
Salvelinus fontinalis			24-h LC50 96-h LC50	770 680									96-h LC50	450
Cyprinodon variegatus			96-h LC50	1,200	96-h LC50	136	96-h LC50	4.05	96-h LC50	0.73	96-h LC50	0.36	96-h LC50	1470
Menidia beryllina					96-h LC50	4.2								
Lepomis macrochirus	96-h LC50	0.35	24-h LC50 48-h LC50 96-h LC50	3,400 2,500 760	96-h LC50	1.3	96-h LC50	0.87	96-h LC50	1.78	96-h LC50	0.36	96-h LC50	22
Plants														
Selenastrum capricornutum			4-d EC20 5-d EC50	1,040 1,100									7-d EC50	6400
Skeletonema costatum			96-h EC50 12-d EC50	900 1,600	96-h EC50	255								

Table 9-3. Aquatic Toxicity Data for Study List Pesticides (Lowest Values) (Continued)

Test Species	Esfenvalerate		Imidacloprid		Malathion		Permethrin		Piperonyl Butoxide		Pyrethrins	
	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)
Invertebrates												
Ceriodaphnia dubia					24-h LC50 48-h LC50	3.18 1.14	48-h LC50	0.55	48-h LC50	330		
Daphnia magna	48-h LC50* 48-h LC50 48-h EC50	0.24 0.27 0.15	48-h LC50 48-h EC50	10,440 85,200	24-h LC50 48-h LC50 24-h EC50 21-d EC50	0.27 1.6 0.098 0.34	48-h LC50* 72-h LC50 96-h LC50 48-h EC50 96-h EC50	0.075 6.8 0.3 0.112 0.039	48-h LC50 48-h EC50	2,830 100	48-h LC50	11
Daphnia pulex					48-h EC50	1.8	3-h LC50 48-h LC50 72-h LC50	9,200 2.75 0.08	48-h LC50	1,620		
*Americamysis bahia**	96-h LC50*	0.038	96-h LC50*	34	96-h LC50	2.2	96-h LC50	0.046	96-h LC50*	320	96-h LC50*	1.4
Hyalella azteca	42-D LOEC	0.05							96-h LC50	530		
Gammarus lacustris					24-h LC50 48-h LC50 96-h LC50	3.8 1.8 1.62						
Gammarus fasciatus					24-h LC50 48-h LC50 96-h LC50 5-d LC50	1.2 0.5 0.5 0.48						
Penaeus sp.					24-h LC50 48-h LC50 96-h LC50	3.55 2.25 12	96-h LC50	0.17	96-h LC50	1.25		
Crassostrea virginica			96-h LC50*	>145,000	14-d LC50 48-h EC50 96-h EC50	2660 9,070 2,900	48-h EC50 96-h EC50	1000 40.7	48-h EC50 96-h EC50	4,100 230	96-h LC50*	87
Crassostrea gigas							48-h EC50	1,050				

Table 9-3. Aquatic Toxicity Data for Study List Pesticides (Lowest Values) (Continued)

Test Species	Esfenvalerate		Imidacloprid		Malathion		Permethrin		Piperonyl Butoxide		Pyrethrins	
	Test	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**	**Test**	**Result (ppb)**
Vertebrates												
Pimephales promelas	24-h LC50 48-h LC50 96-h LC50	0.24 0.24 0.22			24-h LC50 96-h LC50	12,400 8,650	24-h LC50 48-h LC50 96-h LC50*	5.4 32.1 2				
Oncorhynchus mykiss	96-h LC50* 96-h LC50	0.26 0.07	96-h LC50	83,000	24-h LC50 48-h LC50 96-h LC50	5 4.6 2.8	24-h LC50 48-h LC50 96-h LC50	4.3 6 0.62	24-h LC50 48-h LC50 96-h LC50	4,000 15,300 2.4	96-h LC50*	5.2
Salvelinus fontinalis					72-h LC50 96-h LC50	150 120	24-h LC50 96-h LC50	4 2.3				
Cyprinodon variegatus	96-h LC50*	430	96-h LC50*	161,000	96-h LC50	33	96-h LC50	7.8	96-h LC50	8.8	96-h LC50*	16
Menidia beryllina					96-h LC50	0.03	96-h LC50	27.5				
Lepomis macrochirus	96-h LC50*	0.26	96-h LC50	105,000	24-h LC50 96-h LC50 48-h EC50	70 20 86	24-h LC50 96-h LC50	6.6 0.79	24-h LC50 96-h LC50	8,200 4.2	96-h LC50*	10
Plants												
Selenastrum capricornutum												
Skeletonema costatum												

Source: All values from U.S. EPA Ecotox (Acquire) database (U.S. EPA, 2002), except values marked with an *, which are from the DPR Ecotox database (DPR, 2002).

There are quite a few gaps in the toxicity testing data for many of the study list pesticides. Table 9-4 indicates the species for which there are not aquatic toxicity test data in the U.S. EPA and DPR databases.

Table 9-4. Aquatic Toxicity Data Gaps
(X = Data Gap)

	Invertebrates										***Vertebrates***						***Plants***	
Pesticide	*Ceriodaphnia dubia*	*Daphnia magna*	*Daphnia pulex*	*Hyalella azteca*	*Gammarus lacustris*	*Gammarus fasciatus*	*Americamysis bahia*	*Penaeus sp.*	*Crassostrea virginica*	*Crassostrea gigas*	*Pimephales promelas*	*Oncorhynchus mykiss*	*Salvelinus fontinalis*	*Lepomis macrochirus*	*Cyprinodon variegatus*	*Menidia beryllina*	*Selenastrum capricornutum*	*Skeletonema costatum*
Bifenthrin			X	X	X	X		X		X			X		X	X	X	X
Carbaryl				X						X						X		
Cyfluthrin			X	X	X	X		X		X			X			X	X	X
Cypermethrin	X		X	X	X	X					X		X			X	X	X
Deltamethrin	X		X	X	X	X		X		X	X		X			X	X	X
Esfenvalerate	X		X		X	X		X	X	X			X			X	X	X
Imidacloprid	X		X	X	X	X		X		X	X		X			X	X	X
Malathion				X						X							X	X
Permethrin				X	X	X											X	X
Piperonyl Butoxide					X	X				X	X		X			X	X	X
Pyrethrins	X		X	X	X	X		X		X	X		X			X	X	X

Salt water species are in the shaded areas of the table.
Source: Gaps in Table 9-3.

Sediment toxicity is likely to be quite important, particularly for pyrethroids, which are likely to accumulate in sediments (see Section 13); however, sediment toxicity data are not readily available. The only pyrethroid sediment toxicity values identified were for cypermethrin. Toxicity of cypermethrin-containing sediments depended on sediment organic carbon content (more carbon, less toxic), with 10-day LC50s as low as 3.6 ppm for *Hyalella azteca* and 13 ppm for *Chironomus tentans* (Maund *et al.*, 2002).

Non-lethal endpoints may also be very important environmentally. Unfortunately determination of such endpoints is much less standardized than LC50 measurements—and the environmental meaning of such endpoints is generally not well understood. For example,

- Many pyrethroids have deleterious effects at sub-lethal concentrations. Examples of such deleterious effects in fish include behavioral changes like rapid gill movement, erratic swimming, altered schooling activity, and swimming at the water surface (Denton, 2001). In daphnids, concentrations of pyrethroids as low as 0.01 ppb reduced reproduction and lowered rates of filtration of food (Day, 1989).

- Exposure to cypermethrin at concentrations less than 0.004 ppb significantly impaired salmonids olfactory responses. This impairment could disrupt reproductive functions (Moore and Waring, 2001).
- Frogs exposed to malathion and esfenvalerate exhibited immune system effects at concentrations as low as 180 ppb (esfenvalerate) and 2,000 ppb (malathion) (Kiesecker, 2002).
- Several pyrethroids and their products of metabolism and/or environmental decomposition were found to have endocrine activity (Tyler *et al.*, 2000).

Cumulative toxicity among study list pesticides is likely. Cumulative toxicity may include cumulative effects of substances with identical or similar mechanisms of toxicity (*e.g.*, pyrethroids as a group, malathion with other organophosphorous pesticides), combined effects of two or more common pesticides (*e.g.*, enhanced esfenvalerate toxicity in the presence of diazinon; Denton *et al.*, 2003); or combinations of stressors (Relyea and Mills, 2001).[33]

9.3 Toxicity Testing of Surface Water Samples

Laboratories use standardized toxicity tests to determine whether surface water samples may be toxic to aquatic species. On the basis of previous testing and pesticide chemical properties, standardized toxicity test methods are expected to be able to detect surface water toxicity due to carbaryl, malathion, imidacloprid, and PBO. For pyrethroids, pesticide partitioning onto toxicity testing container surfaces has been shown to interfere with toxicity testing (Miller *et al.*, 2002), thus throwing into doubt the ability of standard toxicity test methods to measure pyrethroids and pyrethrin-caused toxicity in surface waters. While the environmental meaning of these testing problems is currently under investigation, it is very likely that these losses cause negative (“not toxic”) test results for surface water samples that initially contained toxic concentrations of pyrethroids or pyrethrins.

9.4 Toxicity Identification Evaluation for Surface Water Samples

If a surface water sample is found to be toxic to laboratory test organisms, scientists can use toxicity identification evaluation (TIE) procedures to attempt to identify the cause of the toxicity (U.S. EPA, 1998). TIEs involve fractionation of samples to separate chemical contaminants in the water sample, followed by toxicity testing of each component and detailed chemical analysis of the toxic fraction. Ideally, the toxic component can be separated out from the surface water sample (thus eliminating toxicity) and then added back into the sample (thus proving that it was indeed the critical toxicant). While debate exists about the need for formal TIE procedures for each substance, the existence of a publication demonstrating the ability to identify a substance as a toxicant using the TIE approach provides assurance that laboratories will be able to link observed toxicity to its cause.

Of the pesticides on the study list, a TIE procedure has only been published for carbaryl (Bailey *et al.*, 1997). Given the chemical similarity of malathion to other organophosphorous pesticides for which TIE procedures are well documented (*i.e.*, diazinon and chlorpyrifos), it is fairly certain that malathion-caused toxicity can be

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[33] In conjunction with predator-induced stress, exposure to carbaryl concentrations well below the LC50 (3-4% of the LC50) created high mortality rates in tree frog tadpoles.

identified (Ogle, 2002; Miller, 2002). U.C. Davis and the private laboratory AQUA-Science are currently developing TIE procedures for certain pyrethroids; however, the development process is far from complete (Miller, 2002). This review did not identify any publications documenting TIEs finding any other study list pesticide as the toxicity source.[34]

For each of the remaining study list pesticides, more investigation into TIE procedures is needed, as summarized in Table 9-5. When toxicity is caused by these pesticides, scientists can use existing TIE procedures to identify these pesticides as a possible cause of the toxicity and to rule out other toxicity sources, and then use chemical analysis measurements[35] to establish the probable cause of the toxicity (Ogle, 2002; Miller, 2002).

Table 9-5. Toxicity Testing Methods for Study List Pesticides in Water

Pesticide	Will current toxicity testing procedures work?	Are TIE procedures available?
Pyrethroids (Bifenthrin, Cyfluthrin, Cypermethrin, Deltamethrin, Esfenvalerate, Permethrin) and Pyrethrins	Losses on walls of toxicity testing containers are likely to underestimate the magnitude of the toxicity*	Identifying pyrethroids or pyrethrins as the cause of toxicity using a TIE approach is generally considered possible but has not yet been performed. Material losses on equipment are likely to make TIEs difficult. Formal methods are in development for some pyrethroids.*
Malathion	Yes	Yes
Carbaryl	Yes	Yes
Imidacloprid	Yes	Will be possible to isolate toxicity in water-soluble fraction, but may be difficult to link toxicity specifically to imidacloprid.
Piperonyl Butoxide	Probably	Probably

*Research on these problems by U.C. Davis and AQUA-Science is currently in progress.
Sources: Ogle, 2002 and Miller, 2002.

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[34] Several publications used the correlation methods described in the next paragraph to attribute toxicity to other study list pesticides.

[35] Should methods with environmentally relevant detection limits become available. Since such methods are currently not available for most pyrethroids or for pyrethrins, laboratories have used addition of PBO (which will enhance pyrethroid- and pyrethrin-caused toxicity) as a “quick and dirty” screening method.

10.0 REGULATORY STANDARDS

10.1 Data Sources

Most of the information in this section was obtained directly from the relevant regulatory agencies from reports, regulations, or summaries. Information was obtained from U.S. Environmental Protection Agency (U.S. EPA), California Department of Fish and Game (DFG), California Department of Pesticide Regulation (DPR), the California Department of Food and Agriculture (CDFA), the National Oceanic and Atmospheric Administration (NOAA), the National Academy of Sciences, California Air Resources Board (CARB), and California Office of Environmental Health Hazard Assessment (OEHHA) and the compilation of water quality goals prepared by the Central Valley Regional Water Quality Control Board (Marshack, 2000). Canadian water quality guidelines were obtained from the Canadian Council of Ministers of the Environment (CCME).

10.2 Water Quality Criteria

There are no adopted water quality objectives for California surface waters for any of the study list pesticides (U.S. EPA, 2000).[36] For some study list pesticides, DFG has followed the standard water quality criteria guidelines (U.S. EPA, 1985) to develop criteria. A search for water quality criteria from other entities was conducted to identify other possible reference values. Only two additional values were identified during this search. Table 10-1 lists the water quality criteria identified for study list pesticides. All values in Table 10-1 are based on protection of aquatic life.

Table 10-1. Surface Water Quality Criteria for Study List Pesticides

Pesticide	**Fresh Water**		**Salt Water**	
	Value	**Source**	**Value**	**Source**
Bifenthrin	--		--	
Carbaryl	2.53 ppb*	DFG	0.81 ppb*	DFG
Cyfluthrin	--		--	
Cypermethrin	0.002 ppb	DFG	--	
Deltamethrin	0.0004 ppb	Canadian Water Quality Guideline	--	
Esfenvalerate	--		--	
Imidacloprid	--		--	
Malathion	0.43 ppb	DFG	0.34 ppb	DFG
Permethrin	0.03 ppb	DFG	0.001 ppb	DFG
Piperonyl Butoxide	--		--	
Pyrethrins	0.01 ppb	National Academy of Sciences	--	

Note: All values are maximum concentrations (for DFG values "criterion maximum concentration") unless marked with a "*" indicating that the value is also the criterion continuous concentration.
Sources: DFG, 1998a; DFG, 1998b; DFG, 2000; Pawlisz *et al.*, 1998; CCME, 2002; NAS/NAE, 1973.

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[36] Almost all adopted water quality criteria are for the priority pollutants listed in the Clean Water Act. Few currently used insecticides (*e.g.*, none of the pyrethroids) are on the priority pollutants list.

Only one sediment quality guideline was identified for any of the study list pesticides—U.S. EPA developed a draft sediment quality advisory level for malathion of 0.067 microgram per gram organic carbon in sediments (U.S. EPA, 1997).

10.3 U.S. EPA Regulatory Status

As explained in Section 2.4, U.S. EPA is currently conducting two types of regulatory reviews of most registered pesticides:

- U.S. EPA must re-register any pesticide initially registered prior to November 1, 1984 (unless the pesticide was re-registered prior to August 3, 1996). This involves a complete review of the pesticide's human health and ecological effects, which is documented in a Registration Eligibility Documents (REDs). For pesticides that are part of a group with a common mode of action, an "Interim RED" (IRED) is generated until the results of a cumulative risk assessment for the group are available to be incorporated into a final RED.
- U.S. EPA must review all food-related pesticide exposures to comply with new standards under the Food Quality Protection Act (FQPA) by August 2006. For pesticides registered prior to November 1, 1984, U.S. EPA is integrating the FQPA review into the re-registration process. For newer pesticides, U.S. EPA is only conducting "tolerance reassessments" (determination of the pesticide residue limits in food), which do not include consideration of ecological risks.

Table 10-2 (on the next page) provides the status (as of January 2003) of insecticides on the study list in U.S. EPA's reregistration and FQPA review processes. To set scheduling priorities, U.S. EPA divided pesticides into three groups, with the intent of completing the top priority reviews first. While the prioritization has not been followed perfectly, it is reasonable to assume that pesticides in higher priority groups will be reviewed prior to pesticides in lower priority groups. Table 10-2 notes the priority grouping for pesticides for which reviews have not been scheduled.

10.4 DPR Regulatory Status

California's Department of Pesticide Regulation registers each pesticide product each year. The California re-registration process differs greatly from U.S. EPA's—the process, as implemented by DPR, provides for an essentially automatic renewal for all pesticide registrations. Should the state learn that a pesticide might be causing an adverse effect on humans or on California's environment, the law calls for DPR to place the pesticide in "re-evaluation," a process by which the state can require or conduct additional studies to determine whether the pesticide should continue to be used in California. While a pesticide is in re-evaluation (a process that may take many years), it continues to maintain its registration for use in the state. One of the study list pesticides—cyfluthrin—is currently in re-evaluation due to pesticide illness reports associated with its use.

Under California law (Food and Agricultural Code sections 13121-13130), DPR must regularly review the toxicology database of all registered pesticide active ingredients. If DPR identifies possible adverse human health effects, then it places a pesticide on a list of substances for which it plans to evaluate by conducting a risk assessment. (Normally these risk assessments do not include ecological assessments or risks to aquatic species.) If DPR decides on the basis of the risk assessment that the use of a pesticide results in a significant adverse human health effect, the law requires DPR to suspend or cancel the pesticide.

Table 10-2. U.S. EPA Registration Status for Study List Pesticides

Pesticide	U.S. EPA Registration Status	Schedule
Bifenthrin	Future food tolerance review only	Anticipated by August 2006 (middle priority group)
Carbaryl	Currently in re-registration review. A cumulative risk assessment for carbamate pesticides is planned but has not been initiated.	Preliminary risk assessment completed in 2002 IRED due by June 30, 2003 RED date uncertain (depends on completion of cumulative risk assessment)
Cyfluthrin	Future food tolerance review only	Anticipated by August 2006 (middle priority group)
Cypermethrin	Future reregistration*	Anticipated by August 2006 (top priority group)
Deltamethrin	Future food tolerance review only	Anticipated by August 2006 (middle priority group)
Esfenvalerate	Future food tolerance review only	Planned during 2003
Imidacloprid	Future food tolerance review only	Anticipated by August 2006 (lowest priority group)
Malathion	Currently in re-registration. A cumulative risk assessment for organophosphorous pesticides is nearly complete.	Revised risk assessment completed 2000 IRED anticipated in 2003 RED date uncertain (depends on completion of cumulative risk assessment)
Permethrin	Future reregistration*	Planned during 2003
Piperonyl Butoxide	Future reregistration	Anticipated by August 2006 (middle priority group)
Pyrethrins	Future reregistration*	Anticipated by August 2006 (middle priority group)

*Pyrethroids that are candidates for reregistration are likely to be evaluated cumulatively as well as individually. U.S. EPA has not announced a timeline for pyrethroid reregistrations.
Source: U.S. EPA registration status information (U.S. EPA, April 2002 and January 2003).

Because DPR identifies more pesticides requiring evaluation than it can evaluate, it sets priorities for conducting risk assessments. Through this process, DPR has initiated risk assessments for deltamethrin, carbaryl, imidacloprid, and cyfluthrin. DPR has designated the following priorities for risk assessments for other study list pesticides:

- Esfenvalerate - High Priority
- Cypermethrin - Moderate Priority
- Permethrin - Moderate Priority
- Pyrethrins - Moderate Priority
- Piperonyl butoxide - Low Priority

In 1987, DPR completed a risk assessment for malathion. Between 1991 and 1997, DPR completed five smaller risk assessments on individual products or uses of bifenthrin.

10.5 Other Regulatory Agency Activities Related to Study List Pesticides

Pesticides may appear on a variety of regulatory lists that may trigger regulatory actions that affect use of a pesticide. The following lists were reviewed to determine the status of study list pesticides:

- Proposition 65 (Prop. 65)—List of chemicals known to the state of California to cause cancer or reproductive toxicity.
- Air Toxics "Hot Spots" Information and Assessment Act List (AB 2588 Toxic Air Pollutant List)—Implementation of this act required the state to develop a list of chemical substances that may pose a threat to public health when present in the ambient air.
- Toxic Air Contaminant Identification List—Under California's Toxic Air Contaminant Identification and Control Act (AB 1807), the state uses a risk assessment process to identify substances as toxic air contaminants.
- Office of Pesticide Programs (OPP) List of Chemicals Evaluated for Carcinogenic Potential—U.S. EPA reviews data relating to pesticide toxicity to determine potential for carcinogenicity and classifies pesticides accordingly.
- Birth Defects Prevention Act List—California's Birth Defects Prevention Act (SB 950) required DPR to develop a list of the top 200 pesticides that DPR determined to have the most significant data gaps, widespread use, and which were suspected to be hazardous to people.[37] The Act required DPR to call in missing data on these 200 pesticides. All required data has been submitted for all currently registered pesticides.
- DPR Groundwater Protection List—DPR must create a list of pesticides having the potential to pollute ground water.[38]

Table 10-3 (on the next page) summarizes the status of study list pesticide in regard to the above lists.

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[37] California Code of Regulations, Division 6. Pesticides and Pest Control Operations, Chapter 2. Pesticides, Subchapter 1. Pesticide Registration, Article 3. Supplemental Data Requirements, Section 6198.5. List of Active Ingredients Identified Pursuant to Section 13127.

[38] California Code of Regulations, Division 6. Pesticides and Pest Control Operations, Chapter 4. Environmental Protection, Subchapter 1. Groundwater Article 1. Pesticide Contamination Prevention, Section 6800. Groundwater Protection List.

Table 10-3. Regulatory Status of Study List Pesticides

Pesticide	Prop. 65	Birth Defects Prevention Act List	DPR Groundwater Protection list	AB 2588 Toxic Air Pollutant	Toxic Air Contaminant	U.S. EPA OPP Carcinogen Evaluation
Bifenthrin	—	—	—	—	—	Possible Human Carcinogen (Group C)[a]
Carbaryl	—	X	X	List A-I	Listed	Possible Human Carcinogen (Group C)
Cyfluthrin	—	—	—	—	—	Not likely to be carcinogenic to humans
Cypermethrin	—	—	—	—	—	Possible Human Carcinogen (Group C)
Deltamethrin	—	—	—	—	—	Not evaluated
Esfenvalerate	—	—	—	—	—	Evidence of non-carcinogenicity for humans (Group E)
Imidacloprid	—	—	X	—	—	Evidence of non-carcinogenicity for humans (Group E)
Malathion	—	X	—	—	Candidate[b]	Suggestive evidence of carcinogenicity but not sufficient to assess human carcinogenic potential
Permethrin	—	X	—	—	Candidate[b]	Possible Human Carcinogen (Group C)
Piperonyl Butoxide	—	X	—	—	Candidate[b]	Possible Human Carcinogen (Group C)
Pyrethrins	—	X	—	—	Candidate[b]	Likely to be carcinogenic to humans

"—" means that the substance is not listed. "X" means that it is listed.

[a] U.S. EPA OPP formerly assigned group designations to various carcinogenicity designations. Recent classifications use descriptive terminology instead of the group classification.

[b] All pesticides on SB 950 list were automatically placed on the AB 1807 list for future evaluation.

Source: Compiled from regulatory agency sources listed in text.

11.0 ENVIRONMENTALLY RELEVANT CONCENTRATIONS

To evaluate the importance of the presence of a pesticide in surface water, a comparison threshold is needed. Since the purpose of this analysis is predictive (evaluation of what effects may occur in the future) rather than retrospective, it will not be possible to rely simply on environmental monitoring data to estimate potential risks associated with use of the study list pesticides. Instead, the analysis will need to rely, in part, on comparison of estimates to a threshold concentration value. Given the limitations of available data (for example, the lack of water quality criteria for most study list pesticides), this report uses an "environmentally relevant concentration" as the comparison value. The "environmentally relevant concentration" is intended to be a concentration above which adverse effects to aquatic ecosystems may occur—and below which aquatic ecosystems should be minimally impacted. This section describes the selection of the environmentally relevant concentrations for each study list pesticide.

11.1 Data Sources

This section uses the aquatic toxicity data in Section 9 and the water quality criteria in Section 10. The two referenced sections describe the limitations of the available data and note data gaps.

11.2 Approach to Selecting Environmentally Relevant Concentrations

Water quality professionals typically rely on water quality criteria to determine the environmental relevance of the presence of a chemical in a discharge or a surface water body. The U.S. Environmental Protection Agency (U.S. EPA) has developed numerous water quality criteria.[39] States may also develop their own water quality criteria, which is particularly desirable when special situations in a water body modify the environmental effects of a pollutant. Since adopted criteria—or in their absence, criteria developed for non-regulatory purposes using U.S. EPA's standard methods—are the preferred reference values, these are considered preferred values for purposes of this report. While Section 10 notes water quality criteria from Canada and from the National Academy of Sciences, these criteria were developed by very different methods—and for this reason, are not considered "preferred values."

In the absence of water quality criteria, it is necessary to look to the aquatic toxicity data on which water quality criteria would be based. The first step in developing water quality criteria (U.S. EPA, 1985) is to evaluate the distribution of acute and chronic toxicity data like concentrations lethal to 50% of test organisms (LC50s), lowest observed effect concentrations (LOECs), and no observed effect concentrations (NOECs). Development of water quality criteria entails an initial calculation based on LC50s for several of the most sensitive species.[40] For acute water quality criteria ("criterion maximum concentrations") the result is ultimately divided by a factor of two,[41] since 50% mortality is not considered appropriate for water quality protection. Calculation of chronic water quality criteria ("criterion continuous concentrations") involves division of the result by an "acute-chronic ratio," which is estimated on the basis of several sets of same-species

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[39] Most U.S. EPA water quality criteria are for the priority pollutants listed in the Clean Water Act. Few currently used insecticides (*e.g.*, none of the pyrethroids) are on the priority pollutants list.

[40] The process requires evaluation of data from a minimum of 8 different families of aquatic species. Values from four of the most sensitive families are used in the calculation (if data from a very large number of families are available, the method may not include values from one or more of the most sensitive families).

[41] To determine a concentration that will not cause severe adverse effects on too many organisms (water quality criteria are generally designed to protect 95 percent of all fish and aquatic invertebrates).

acute and chronic toxicity data.[42] Since relatively few chronic toxicity data are available for study list pesticides, this analysis relies on acute toxicity data. Although it uses data from several species (rather than from the single most sensitive species), the water quality criteria development process almost always winds up developing criteria that are somewhat lower than the acute toxicity value for the most sensitive species. Therefore, it is a reasonable approach to select the lowest LC50 values as the environmentally relevant concentration in the absence of a water quality criterion. Given the many aquatic toxicity data gaps (see Table 9-4 [on page 55]) and the fact that chronic toxicity is ignored, this approach is likely to select concentrations that are somewhat higher—and potentially significantly higher—than water quality criteria (when and if they are developed).

11.3 Selected Environmentally Relevant Concentrations

Using the approach described above, the concentration values in Table 11-1 were selected as the environmentally relevant concentrations for purposes of this analysis. Given the extensive data gaps in aquatic toxicity testing, it is entirely possible that concentrations below these values have environmental effects. Values like these, because they are based only on the effects of individual chemicals, ignore potential additive and synergistic effects. Nevertheless, the weight of the current evidence suggests that these values are a reasonable starting point for a qualitative evaluation of the potential for aquatic risk from urban use of study list pesticides.

Table 11-1. Environmentally Relevant Concentrations for Study List Pesticides*

Pesticide	Fresh Water		Salt Water	
	Concentration (ppb)	Source	Concentration (ppb)	Source
Bifenthrin	0.07	*Ceriodaphnia dubia* 48-H LC50	0.00397	*Americamysis bahia* 96-H LC50
Carbaryl	2.53	DFG	0.81	DFG
Cyfluthrin	0.14	*Ceriodaphnia dubia* 48-H LC50	0.00242	*Americamysis bahia* 96-H LC50
Cypermethrin	0.002	DFG	0.005	*Americamysis bahia* 96-H LC50
Deltamethrin	0.01	*Daphnia magna* 96-H LC50	0.017	*Americamysis bahia* 96-H LC50
Esfenvalerate	0.07	*Oncorhynchus mykiss* 96-H LC50	0.038	*Americamysis bahia* 96-H LC50
Imidacloprid	10,440	*Daphnia magna* 48-H LC50	34	*Americamysis bahia* 96-H LC50
Malathion	0.43	DFG	0.34	DFG
Permethrin	0.03	DFG	0.001	DFG
Piperonyl Butoxide	2.4	*Oncorhynchus mykiss* 96-H LC50	1.25	*Penaeus duorarum* 96-H LC 50
Pyrethrins	5.2	*Oncorhynchus mykiss* 96-H LC50	1.4	*Americamysis bahia* 96-H LC50

*It is not appropriate to compare values based on different types of sources to evaluate the relative toxicity of study list pesticides.

Source: Water quality criteria (if available) from Section 10 or lowest toxicity value from Section 9; see text description of selection process.

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[42] This is almost always a value greater than 2.

Some of the analysis in this report includes comparison to diazinon and chlorpyrifos. For chlorpyrifos the environmentally relevant concentrations were based on the adopted U.S. EPA water quality criteria. For diazinon, since there are no adopted U.S. EPA criteria, the DFG water quality criterion was used for fresh water (DFG, 2000), and since there is no DFG salt water value, the salt water value was based on the draft U.S. EPA salt water quality criterion (U.S. EPA, 1998). The "criterion maximum concentration"[43] values were used for consistency with the water quality criteria values used for the study list pesticides. These values are listed in Table 11-2.

Table 11-2. Environmentally Relevant Concentrations for Diazinon and Chlorpyrifos

Pesticide	Fresh Water		Salt Water	
	Concentration (ppb)	**Source**	**Concentration (ppb)**	**Source**
Chlorpyrifos	0.083	U.S. EPA	0.011	U.S. EPA
Diazinon	0.08	DFG	0.82	U.S. EPA

Source: Water quality criteria (see text).

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[43] Short-term (1-hour) exposure criteria.

12.0 CHEMICAL ANALYSIS

To determine the presence of a pesticide in surface water, a chemical analysis method must be available. For a chemical analysis method to be generally useful to water quality professionals, it should be designed such that a competent analytical laboratory can readily conduct precise and accurate measurements of the substance in environmental water samples with detection limits that are well below environmentally relevant levels. As explained below, for most of the pesticides on the study list, there is no analytical method currently available that meets these criteria.

12.1 Data Sources

Five regulatory agency chemical analytical methods sources were consulted for this review:

- U.S. EPA Approved Analytical Methods for Water and Wastewater. The primary source for water quality chemical test methods is the U.S. EPA, which has approved laboratory methods for the analysis of surface water and wastewater samples. U.S. EPA publishes almost all of these methods as regulations.[44] Competent analytical laboratories rely on these methods, which are generally considered the primary method for analysis of water pollutants.
- Pesticide Registrant Methods. Under FIFRA, pesticide registrants are required to submit to U.S. EPA an analytical method for measuring each registered pesticide in foods and water samples. Hard copies of these methods are available from the U.S. EPA Pesticide Program Environmental Chemistry Laboratory. Because only about 25% of these methods have been evaluated by U.S. EPA's laboratory,[45] it is uncertain whether a competent analytical laboratory can produce satisfactory analytical results with one of these methods.
- California Department of Food and Agriculture (CDFA). CDFA's laboratory supports the California Department of Pesticide Regulation water quality monitoring programs.
- California Department of Fish and Game (DFG). The DFG laboratory supports a variety of California water quality monitoring programs.
- U. S. Geological Survey (USGS). To support its extensive surface water quality monitoring programs, USGS develops and publishes its own analytical methods for pollutants in surface water.

In addition, commercial immunoassay product information was reviewed to identify immunoassay methods applicable to surface water samples containing study list pesticides.

12.2 Existing Analytical Methods for Study List Pesticides in Water

Table 12-1 (on the next page) summarizes the U.S. EPA approved surface water analytical methods and the lowest detection limit analytical methods identified for study list pesticides.[46] Currently, U.S. EPA (whose methods are generally relied on for water quality regulatory actions) does not have any approved method for measuring bifenthrin,

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[44] See the U.S. EPA Internet site for details: http://www.epa.gov/waterscience/methods/

[45] U.S. EPA's description of the methods notes that some methods have deficiencies and that the Environmental Chemistry Laboratory makes no claim of method validity (Flynt, June 5, 2002.)

[46] Table 12-1 is not intended be comprehensive inventory of all available methods.

Table 12-1. Chemical Analysis Methods for Study List Pesticides in Water[a]

Pesticide	U.S. EPA Approved Method		Other Methods	
	Method Number	Method Detection Limit (ppb)	Analytical Technique	Method Detection Limit (ppb)[b]
Bifenthrin	--	--	CDFA Method	0.05
			DFG Method	0.01
			USGS is developing a method[c]	
Carbaryl	632	0.02	Immunoassay reported in literature	0.01
Cyfluthrin	1660	2	Registrant method	0.01
			CDFA method	0.05
			DFG method	0.01
			USGS and DFG are developing methods[c]	
Cypermethrin	--	--	DFG method	0.05
			USGS and DFG are developing methods[c]	
Deltamethrin	--	--	DFG method	0.05
Esfenvalerate	1660	2	Registrant method	0.05
			CDFA method	0.05
			DFG method	0.01
			USGS and DFG are developing methods[c]	--
			Immunoassay reported in literature	0.1
Imidacloprid	--	--	Registrant method	0.05
			CDFA method	0.05
			EnviroLogix immunoassay kit[d]	0.2
			Immunoassay reported in literature	0.5-1
Malathion	1657	0.011	USGS published method	0.0059
Permethrin	508.1	0.007-0.008	USGS and DFG are developing methods[c]	--
			CDFA method	0.05
			DFG method	0.02
			Immunoassay reported in literature	0.002
Piperonyl Butoxide	--	--	USGS published method	0.0059
Pyrethrins	1660	1	Registrant method	0.01 to 0.06

[a] Where multiple methods exist from the same source, the method with the lowest detection limit is described.

[b] Most of these are not a true method detection limit. Methods described this value in a variety of ways, such as “selected as the quantitation limit,” “minimum detectable concentration,” “routine limit of determination,” “reporting limit,” and “limit of quantitation.”

[c] Lower detection limit methods for bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, esfenvalerate, and permethrin are in development according to Kuivila *et al.*, 2001. DFG (in partnership with USGS) is developing lower detection limit methods for cyfluthrin, cypermethrin, esfenvalerate, fenvalerate, permethrin and resmethrin (Crane, 2003).

[d] Actual laboratory performance may differ from the vendor claims, and kit design may affect practical usability of these methods for water samples (Miller, 2002).

Sources: U.S. EPA, *Methods and Guidance for the Analysis of Water, Version 2*, May 1999 (confirmed that these are most current methods); pesticide registrant methods obtained from the U.S. EPA Pesticide Program Environmental Chemistry Laboratory (Flynt, 2002); CDFA, 1999; Gana, 2003; Crane, 2003, Zimmerman *et al.*, 2001; Shan *et al.*, 2000; Shan, *et al.*, 1999; Lee, *et al.*, 2001; Abad and Montoya, 1997.

cypermethrin, deltamethrin, imidacloprid, or piperonyl butoxide. When no U.S. EPA-approved method exists, scientists may seek to obtain a copy of the method required to be provided to U.S. EPA by the pesticide registrant. However, U.S. EPA records of pesticide registrant-supplied methods do not include methods for three of the five pesticides without U.S. EPA-approved methods (bifenthrin, deltamethrin, or piperonyl butoxide).[47]

The methods identified in Table 12-1 involve rather time-consuming laboratory work by skilled chemists, which means that these methods are relatively expensive. Use of such methods for screening large volume samples to obtain low detection limits (*e.g.*, parts per trillion) is difficult (Shan *et al*., 2000). Cost saving opportunities are few for this group of insecticides. For example, although pyrethroids are a family of chemically related substances, methods for most pyrethroids differ—no single method exists to conduct a “scan” for this family of chemically related substances.

Immunoassays show great promise for analysis of pesticides, as immunoassay methods have great specificity for the substance being measured, are often relatively inexpensive and easy to use, and have the potential to offer relatively low detection limits (on the part per trillion level). For example, San Francisco Bay Area water quality programs found immunoassay methods highly valuable for rapid, low-cost analysis of urban runoff and surface water for diazinon and chlorpyrifos. To date, two immunoassays have been developed and commercialized by a private vendor (EnviroLogix, Inc.) for study list pesticides (for imidacloprid and for certain pyrethroids as a group).[48]

12.3 Chemical Analysis Methods in Development

Due to the limitations of available methods, research is currently underway to develop better chemical analysis methods for some study list pesticides, as noted in Table 12-1. Some examples of such research include:

- USGS and DFG Method Development. The U.S. Geological Survey (USGS) and the California Department of Fish and Game (DFG) have been developing low detection limit methods for the analysis of pesticides in water.
- Immunoassay Method Development. While few enzyme-linked immunosorbent assays (ELISAs) have been commercialized, development of immunoassay methods for study list pesticides is a research focus for scientists like Professor Bruce Hammock and colleagues at U.C. Davis (Shan *et al.*, 2000; Shan *et al.*, 1999; Lee *et al.*, 2001.; Li and Li, 2000; Abad and Montoya, 1997).

Despite the lack of methods from an agency source for deltamethrin and cypermethrin, it is very likely that research-level methods exist for the analysis of these pesticides, as manufacturers and research scientists need them for their work.

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[47] Due to record keeping problems at U.S. EPA, it is not clear if these methods were ever submitted to OPP (Flynt, June 5 and June 10, 2002.)

[48] The vendor states that the Imidacloprid Microwell Plate Assay is intended for analysis of imidacloprid in ground and surface water samples at concentrations of 0.2 to 6 ppb. The assay does not claim to provide exceptionally precise analytical results, with the coefficient of variation of measured sample concentrations claimed to be from about 2 to 7%. The Synthetic Pyrethroids Microwell Place Assay was intended for analysis of certain pyrethroids (cyfluthrin, deltamethrin, cypermethrin, and lambda-cyhalothrin) in methanol extracts (*e.g.*, extracts of surface water samples). It was designed to measure cyfluthrin concentrations of 20 to 80 ppb; other pyrethroid concentrations are approximated with the cyfluthrin calibration. The assay was not designed to distinguish among detected pyrethroids. The assay experiences interferences from other pyrethroids.

12.4 Sample Handling Procedures

When collecting and handling water samples for pesticide analysis, container selection and sample management are always issues. While analytical chemists have developed standard sample collection and handling methods to avoid sample contamination or analyte losses, researchers have identified special problems with handling of pyrethroid-containing samples (Kuivila *et al.*, 2001; Miller, *et al.*, 2002; Lee *et al.*, 2002). The primary issue is that because pyrethroids interact with sampling equipment and sample containers, the measured concentration in the sample can be significantly lower than the environmental concentration of the pesticide. To address this, it will be necessary to develop appropriate sampling and storage procedures for environmental samples that may contain pyrethroids.

12.5 Practical Data Quality Issues

Comparing the available chemical analysis methods to the environmentally relevant concentrations identified in Section 11 reveals that current methods do not provide the ability to detect environmentally relevant concentrations of many study list pesticides in surface waters (see Table 12-2). Adequate methods do not exist for bifenthrin, cyfluthrin, cypermethrin, deltamethrin, imidacloprid, and permethrin. Fortunately, USGS and DFG have funding to develop lower detection limit methods for most of these pesticides. No organization was identified with firm plans for developing low detection limit methods for deltamethrin or imidacloprid.

Table 12-2. Comparison of Environmentally Relevant Concentrations for Study List Pesticides to Lowest Chemical Analytical Method Detection Limit

Pesticide	Lowest Environmentally Relevant Concentration (ppb)[a]	Lowest U.S. EPA, USGS, or CDFA-Approved Chemical Analytical Method Detection Limit (ppb)	Adequate Method Exists for Surface Water Quality Analysis[b]	Method Development in Progress[c]
Bifenthrin	0.00397	0.01	No	Yes
Carbaryl	0.81	0.02	Yes	--
Cyfluthrin	0.00242	2	No	Yes
Cypermethrin	0.002	0.05	No	Yes
Deltamethrin	**0.01**	**0.05**	**No**	**--**
Esfenvalerate	0.038	0.01	Yes	Yes
Imidacloprid	**34**	**No approved method**	**No**	**--**
Malathion	0.34	0.0059	Yes	--
Permethrin	0.001	0.007-0.008	No	Yes
Piperonyl Butoxide	1.25	0.0059	Yes	--
Pyrethrins	1.4	1	Yes	--

[a] Lowest water quality standard or lowest LC50 value from Ecotox (Acquire) database.

[b] Agency-approved methods have detection limits lower than environmentally relevant concentration (based on lowest water quality standard or LC50 value). Ideally, analytical methods should have detection limits at least ten times lower than the environmentally relevant concentration.

[c] Lower detection limit methods for bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, esfenvalerate, and permethrin are in development according to Kuivila, K. K., Pedersen, T. L., Houston, J. R., von Phul, P. D., and L. A. LeBlanc, "Pyrethroid Insecticides in the San Francisco Estuary: II. Sampling and Analytical Challenges," *San Francisco Estuary, Achievements, Trends, and the Future, abstracts from the 5th Biennial State of the Estuary Conference*, October 9-11, 2001. DFG is developing lower detection limit methods for cyfluthrin, cypermethrin, esfenvalerate, fenvalerate, permethrin and resmethrin (Crane, 2003).

Sources: Tables 11-1, 12-1, and references cited above.

The practical application of the methods described in this section may not achieve the detection limits listed in Table 12-1. Environmental samples are substantially different than the pure laboratory samples used to develop chemical analysis and toxicity testing methods. Detection limits in environmental samples are likely to be higher than the values listed in this section, primarily because substances other than the analyte can interfere with the ability to conduct chemical analysis of water samples. Such interferences are particularly common in wastewater samples, but may also occur in surface water and runoff samples. While chromatographic methods (most of the chemical analysis methods described in this section) are particularly subject to interferences, immunoassay methods can also experience interferences from other elements in environmental samples—for example, oil and grease in first flush storm water runoff samples have proven problematic (Miller, 2002).

Only field validation of the methods can determine the ability of these methods to provide desired information in environmental samples. For example, field validation is essential to determine the practical quantification limits for pesticides in surface water and wastewater samples. Some of the methods discussed in this section have been validated with surface water samples—but most have not.

Different analytical methods can provide different pieces of information about environmental samples. Depending on the purpose of the testing, method-specific differences can be either useful or misleading. For example, immunoassays are often not specific to one analyte—this can preclude identifying which of a group of chemically similar substances was measured—but occasionally allows measurement of degradates that have similar toxicity. Immunoassays typically measure only dissolved substances in a sample—special sample preparation (*e.g.*, solvent extraction) must be conducted for measurement of particle-bound substances.

Due to the shortcomings of sample handling methods and chemical analysis methods for pyrethrins and pyrethroids, literature reporting of surface water concentration measurements and toxicity testing should be reviewed carefully and treated cautiously:

- Losses in containers may cause scientists to report artificially low concentrations.
- Given that detection limits are generally somewhat higher than environmentally relevant concentrations, “non-detect” results do not necessarily mean that environmentally relevant concentrations of the pesticide are not present.

13.0 EVALUATION OF POTENTIAL WATER QUALITY IMPLICATIONS

The approach to this analysis is to assess the potential for urban use of study list pesticides to cause surface waters receiving urban runoff to exceed the "environmentally relevant concentration" identified in Section 11. Although this is a qualitative evaluation, it proceeds through each of the same steps that a quantitative environmental risk assessment would consider:

- What are the pesticide application rates?
- What fraction of the pesticide may decompose at typical urban application sites?
- What is the potential for the pesticide to be washed from urban application locations into surface water?
- What is the fate of the pesticide once it reaches surface water?

The final step is to use the qualitative analysis—together with available aquatic toxicity and surface water data—to assess the weight of the evidence as to the potential for the pesticide to exceed the environmentally relevant concentration for an environmentally relevant time period.[49] If so, it is likely that adverse effects to aquatic ecosystems receiving urban runoff will occur.

13.1 Data Sources

This section relies on the pesticide use and chemical property data presented in earlier sections of this report. Most of the other information in this section was obtained from the scientific literature, primarily from technical journals. Surface water quality and toxicity data came from the U.S. Geological Survey National Water Quality Assessment (USGS NAWQA), the California Department of Pesticide Regulation (DPR) and published papers in scientific journals.

Environmental fate information was obtained from basic reference books on pyrethroids, pyrethrins, and piperonyl butoxide (Leahey, 1985; Jones, 1998; Casida and Quistad, 1995), DPR environmental fate reviews (Fecko, 1999; Casjens, 2002; Bacey, 2000; Xu, 2000; Goh, 1990; Jones, 1999), and journal articles considering environmental fate of deltamethrin and esfenvalerate (Pawlisz et al, 1998; Samsoe-Petersen et al., 2001). A few U.S. Environmental Protection Agency (U.S. EPA) studies specific to study list chemicals were also consulted (U.S. EPA, undated; U.S. EPA, 2000; U.S. EPA, 2002).

13.2 Available Ambient Aquatic Toxicity and Surface Water Quality Data

The scientific literature was reviewed to identify examples of surface water quality monitoring and aquatic toxicity testing of environmental samples containing study list pesticides. While rather extensive monitoring data for carbaryl and malathion exists, it appears that relatively little monitoring has considered other study list pesticides. The lack of convenient chemical analysis methods at environmentally relevant concentrations, as well as the relative recent entry of most other study list pesticides in widespread use probably contribute to the lack of information. Table 13-1 (on the next page) summarizes the findings of the literature review.

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[49] This analysis considers both individual effects and cumulative effects among pesticides with similar modes of toxicity.

Table 13-1. Summary of Surface Water Concentration and Toxicity Data for Study List Pesticides

Pesticide	Findings
Carbaryl	In the USGS NAWQA studies, carbaryl was found in about 40% of urban stream samples and exceeded a North American aquatic life criterion in 10% of samples from 8 urban streams (Gilliom *et al.*, 1999; Hoffman *et al.*, 2000).
Imidacloprid	Imidacloprid runoff from turf plots had concentrations as high as 490 ppb (Ambrust and Peeler, 2002).
Malathion	In the USGS NAWQA studies, malathion was found in more than 20% of urban surface water samples; more than 50% of sampled urban streams had at least one sample exceeding a North American aquatic life criterion (Gilliom *et al.*, 1999; Hoffman *et al.*, 2000). Malathion was detected in many Southern California surface water and storm water runoff samples. Its presence in runoff from Southern California urban and integrated (combined urban and agricultural) sites and in surface waters receiving nursery runoff was linked to surface water runoff toxicity (Kim *et al.*, 2001). A survey of pesticides in Brazilian surface waters detected malathion in about a quarter of rivers samples taken in the northeastern Pantanal Basin (Laabs *et al.*, 2002).
Pyrethroids (Bifenthrin, Cyfluthrin, Cypermethrin, Deltamethrin, Esfenvalerate, Permethrin)	Bifenthrin was detected in many Southern California surface water and storm water runoff samples. In surface waters receiving runoff from Southern California nurseries, bifenthrin has been linked to surface water runoff toxicity (Kim *et al.*, 2001). Storm water runoff from an orchard treated with esfenvalerate was highly toxic to *Pimephales promelas* (fathead minnow) and *Ceriodaphnia dubia* (water flea) (Werner *et al.*, 2002). In river draining a South African region with intensive agriculture, deltamethrin was detected at a level of 1.4 ppb during a rainstorm. Cypermethrin, fenvalerate, and cyfluthrin were not detected (Dabrowski *et al.*, 2002). A survey of pesticides in Brazilian surface waters (northeastern Pantanal Basin) did not detect cyfluthrin, deltamethrin, or permethrin, but cypermethrin and permethrin were found in rainwater (Laabs *et al.*, 2002). Early NAWQA investigations did not detect permethrin (Hoffman *et al.*, 2000); however, recent data only available on the Internet shows it was detected in four urban watersheds at concentrations up to 0.011 µg/l (USGS, 2002).[50] Permethrin runoff from an agricultural field in a low rainfall year had concentrations from 0.023 to 0.2 ppb. In a high rainfall year, concentrations were generally much higher, with measurements as high as 4.4 ppb (Carroll *et al.*, 1981).

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[50] Testing was only for the cis isomer, which is the more stable isomer.

Table 13-1. Summary of Surface Water Concentration and Toxicity Data for Study List Pesticides (Continued)

Pesticide	Findings
Pyrethroids (continued)	Investigations currently in progress at the U.C. Davis Aquatic Toxicology Group Granite Canyon Laboratory have found that sediment samples from California's Central Valley, Salinas River, and Santa Maria areas were toxic to *Hyalella azteca*. Preliminary TIEs attribute the toxicity to pyrethroids (Anderson, 2003). An investigation currently being conducted by the Department of Integrative Biology at U.C. Berkeley has detected pyrethroids in most sediment samples collected from Central Valley surface waters and found one instance of sediment toxicity to *Hyalella azteca* that is attributed to pyrethroids (Weston, 2003).
Pyrethrins	Runoff from agricultural test plots contained 0.020 to 0.036 ppb of pyrethrins in runoff from storms up to 45 days after application (Antonious *et al.*, 1997).
Piperonyl Butoxide	An environmental risk assessment prepared by PBO manufacturers estimated that surface water PBO concentrations could reach 5.77 ppb for 96 hours (Jones, 1998). An investigation of runoff from agricultural test plots did not detect PBO (detection limit 0.075 ppb) (Antonious *et al.*, 1997).

Source: TDC Environmental literature review; individual data sources cited in table.

13.3 Application Rates

Since the purpose of this investigation is to explore the consequences of potential increased use of study list pesticides as substitutes for urban uses of diazinon and chlorpyrifos, current pesticide use data (see Section 8) are only somewhat relevant. To explore the question of whether future use has the potential to release environmentally meaningful quantities of a study list pesticide in an urban watershed, application quantities and environmentally meaningful concentrations were compared with an "application rate index" developed for purposes of this report. The application rate index provides a convenient benchmark for comparing study list pesticides to other pesticides known to be applied in environmentally relevant quantities (*e.g.,* diazinon and chlorpyrifos).

The application rate index was created as follows:

1. Calculate the application quantity for 1,000 square feet. On the basis of typical label instructions, the amount of active ingredient applied per 1,000 square feet was determined.[51] When application rates instructions differed by application location, the rate for application types similar to those found most likely to contribute to urban runoff of diazinon and chlorpyrifos (applications to impervious surfaces, such as applications around buildings to control ants) was selected.

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[51] 1,000 square feet is on the order of a typical urban residential application surface area and is somewhat smaller than a typical industrial, commercial, or institutional application (*e.g.*, a band around a building to control ants or a full lawn treatment for grubs).

2. Calculate the quantity of pesticide active ingredient in 1,000,000 gallons of water at the environmentally relevant concentration.[52]
3. Calculate the application rate index by dividing #1 by #2.

The application rate index is the amount of water, in millions of gallons, that could reach the environmentally relevant concentration if the pesticide applied to one 1,000 square foot area were instead diluted with water. The index can theoretically have any value, with higher values indicating relatively more "potential aquatic toxicity" in a typical application of the product. Table 13-2 shows the calculated application rate indexes for study list pesticides, as well as for diazinon and chlorpyrifos.

Table 13-2. Application Rate Indexes for Study List Pesticides

Pesticide	Fresh Water	Salt Water
Bifenthrin	10-20	175-350
Carbaryl	3-22	4-30
Chlorpyrifos	*35-200*	*270-1,500*
Cyfluthrin	0.3-3	15-190
Cypermethrin	1,500-3,000	600-1,200
Deltamethrin	300-460	7-11
Diazinon	*170*	*16*
Esfenvalerate	1.2-10	2.2-18
Imidacloprid	0.0001	0.03
Malathion	71-90	640-810
Permethrin	48-800	1,440-24,000
Piperonyl Butoxide	0.07	0.14
Pyrethrins	2-14	0.01-0.1

Source: TDC Environmental calculation (see text).

Since spills could contribute to environmental releases of study list pesticides, a similar benchmark calculation was conducted to compare the quantity of active ingredient in one quart of a typical study list pesticide product (typically a concentrate) to the quantity of pesticide active ingredient in 1,000,000 gallons of water at the environmentally relevant concentration. This "container quantity index" is the amount of water, in millions of gallons, that could reach the environmentally relevant concentration if one typical one-quart container were diluted with water. The index can theoretically have any value, with higher values indicating relatively more "potential aquatic toxicity" in a typical container of the product. Table 13-3 (on the next page) shows the calculated container quantity indexes for study list pesticides, as well as for diazinon and chlorpyrifos.

Tables 13-2 and 13-3 show that a single typical urban residential application of a study list pesticide—as well as a single typical residential product container—contains environmentally meaningful quantities of most study list pesticides. Comparing the values in Table 13-2 to each other, it is clear that most study list pesticides are applied at relative rates that are similar to pesticides that have previously been found in urban surface waters at environmentally relevant concentrations (diazinon, chlorpyrifos, carbaryl, and malathion). Excluding the synergist PBO (which cannot be directly

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[52] While this calculation is not intended to simulate pesticide wash-off and runoff to creeks, creek flow rate information provides context for the selection of 1 million gallons as the water quantity. San Francisco Bay area urban creek flows depend on many factors including watershed size and rain volumes. Most creek flows are in the range of a less than one to a few million gallons per day (dry weather) to more than 50 or 100 million gallons per day (significant rain event) (USGS, 2003).

compared to the insecticides), only imidacloprid, which is less toxic to aquatic species, is sold and applied in relatively small quantities.

Table 13-3. Container Quantity Indexes for Study List Pesticides

Pesticide	Fresh Water	Salt Water
Bifenthrin	340	6,000
Carbaryl	59	81
Chlorpyrifos	*530*	*4,000*
Cyfluthrin	460	26,000
Cypermethrin	56,000	22,000
Deltamethrin	16,000	384
Diazinon	*780*	*76*
Esfenvalerate	19	35
Imidacloprid	0.01	2
Malathion	570	5,100
Permethrin	2,600	77,000
Piperonyl Butoxide	9	17
Pyrethrins	1,000	8

Source: TDC Environmental calculation (see text).

13.4 Environmental Fate on Outdoor Urban Application Locations

In the urban environment, a pesticide may break down into other chemicals due to the effects of environmental elements like light, water, and microbial activity. A pesticide may dissolve in water that flows over it. A pesticide may bind to environmental materials like soil or stream sediments. These changes reduce the amount of the pesticide that may eventually be washed to surface waters.

In this report, a qualitative overview of the fate of the study list pesticides in the most environmentally relevant urban settings is provided in three parts, all of which rely on chemical property and environmental fate data presented in Section 4. This subsection looks at the fate of the pesticide on outdoor urban surfaces—particularly impervious surfaces. Outdoor applications on impervious surfaces were previously found to be the likely source of most of the diazinon and chlorpyrifos in urban runoff (TDC Environmental, 2001). The tendency of a pesticide to wash off from surfaces is discussed in Section 13.5. Section 13.6 reviews the fate of study list pesticides once they reach urban surface waters.

Carbaryl and Malathion. Microbial activity plays a major role in the decomposition of both carbaryl and malathion on outdoor surfaces. On impervious surfaces (where little microbial activity occurs), both carbaryl and malathion would be expected to decompose sufficiently slowly that a meaningful fraction would remain long enough to be washed off by rain or other flows. In landscaping, however, both pesticides should decompose more quickly (particularly on soil), suggesting that releases from landscaping would be relatively less.

Pyrethroids. Pyrethroids are somewhat stable after application to outdoor surfaces. Microbial activity appears to play a significant role in decomposition, as decomposition rates on aerobic soils are higher than those in anaerobic or sterile conditions. This suggests that on impervious surfaces, a meaningful fraction of applied pyrethroids would likely remain long enough to be washed off by rain or other flows. Even in landscaping, decomposition rates are likely to be slow enough that a significant fraction of applied pyrethroids may remain when rain or other water flows from landscaping may occur.

Pyrethrins and Piperonyl Butoxide. In sunlight, pyrethrins and PBO both decompose relatively quickly, suggesting that they may decompose prior to wash-off unless they are applied immediately prior to rain or other water flows (*e.g.*, by irrigation runoff) (Casida and Quistad, 1995; Jones, 1998). The rapid photodecomposition of pyrethrins quickly eliminates the "residual" often desired for long-term insect control around structures and is a primary reason that pest control companies promote photostable synthetic pyrethroids. In landscaping, where pyrethrins and PBO are present on surfaces not fully exposed to sunlight, both decompose with half-lives of a few weeks, suggesting that a fraction of the applied material will be available to wash off.

Imidacloprid. After application, imidacloprid should be sufficiently stable on both impervious surfaces and landscaping that a large fraction the pesticide will remain long enough to be washed off by rain or other water flows.

13.5 Transport from Outdoor Application Locations to Surface Water

Impervious Surfaces

Only two studies quantifying pesticide wash-off from outdoor impervious surfaces were identified, neither of which evaluated study list pesticides:

- Alameda County found that 11% of diazinon active ingredient washed off paved test plots in a series of model rainstorms (total 2.6 inches of rain) (Feng and Scanlin, 2001).[53]
- A British university measured herbicide wash-off from impervious surfaces next to roads (Ramwell *et al.*, 2002). Wash-off fraction from a total of 25 mm rainfall (several storms) were as follows: Atrazine—20% and 73% (two tests with different rainfall patterns); Diuron—66%, Glyphosate—35%, Oryzalin—4%, Oxadiazon—6%.

Several studies measured pesticide-wash-off from surfaces somewhat analogous to urban impervious surfaces. Three such studies are relevant to this analysis—two of study list pesticide wash-off from plant leaves, and for comparison, a study of diazinon wash-off from glass plate surfaces intended to simulate plant leaves:

- Most (60 to 78%) bifenthrin was washed off of cotton plant leaves by 13 mm of simulated rainfall 0.25 to 4 hours after application (Mulrooney and Elmore, 2000).
- In a study of permethrin wash-off from the surfaces of cotton plants, about 35% of the permethrin was washed off by a simulated 25 mm rainstorm 2 hours after application. An additional 76 mm of simulated rain removed another 11% of the pesticide (Willis *et al.*, 1986).
- In a study of pesticide wash-off from coated glass plates a simulated 25 mm rainstorm removed essentially all of the applied diazinon (Cohen, 1986).

While these studies suggest that pesticide runoff from urban impervious surfaces may be significantly greater than runoff from agricultural fields, they do not provide the basis for quantitative wash-off estimates. The studies suggest that wash-off of environmentally meaningful fractions of study list pesticides is possible and that diazinon's wash-off behavior may not be particularly unusual.

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[53] Wash-off studies use a variety of methodologies (including natural rainfall and simulated rain events of various intensities), so wash-off values are not directly comparable. All percentages reported for wash-off are based on the amount of pesticide active ingredient applied.

Turf and Agricultural Sites

A review of pesticide wash-off data from agricultural sites concluded that wash-off fractions for most pesticides are below 2% except in unusual circumstances. The review estimated that about 1% of applied water insoluble pesticide quantity runs off an agricultural field (Wauchope, 1978). More recent evaluations of pesticide wash-off from agricultural sites suggest that runoff fractions can differ significantly among pesticides and experimental conditions:

- In an investigation of permethrin runoff from an agricultural field, <0.01% of the applied permethrin ran off in a low-rainfall year, but in a high rainfall year more than 0.5% ran off (Carroll *et al.*, 1981).
- In two separate locations, 0.21 to 0.3% of cyfluthrin applied to cotton fields was washed off in one to four rain events (Casjens, 2002).
- About 1% of diazinon applied to turf has been found to run off (Sudo, 1992 and Evans, 1998).
- A review of pesticide wash-off from turf plots (Haith, 2001) showed the following mean pesticide runoff fraction for multiple tests: 2,4-D—4.34%, chlorpyrifos—0.53%, diazinon—0.68%, dicamba—3.64%, dithiopyr—0.32%, mecoprop—3.72%.
- Wash-off from pre-saturated turf test plots in what the investigators called "severe case" experiments generated an average annual runoff loss of 9% of applied 2,4-D, 15% of dicamba, and 11% of mecoprop; most (about 2/3rds) of the losses were in the first post-treatment rain events. Similar tests of only the first post-application runoff events yielded much lower losses for chlorpyrifos (0.00019%) and chlorothalonil (0.17%) (Ma *et al.*, 1999).

Despite the variation in the wash-off data, the limited available data suggest that there is no reason to assume that wash-off behavior for pyrethroids will differ significantly from the wash-off of diazinon and chlorpyrifos.

Surface Water Mobility Index

Researchers from pesticide manufacturer Syngenta recently derived a "surface water mobility index" (SWMI) on the basis of the analysis of pesticide runoff data from several U.S. watersheds (Chen *et al.*, 2002). The relatively straightforward index is based on two environmental fate parameters—soil aerobic degradation half-life (T_h) and organic carbon-normalized soil/water sorption coefficient (K_{oc}).

$$\mathrm{SWMI} = \frac{e^{-3.466/T_h}}{(1+0.00348K_{oc})}\,(1+0.00026K_{oc})$$

The unitless index can theoretically have values between zero and one, with the value of zero being the least mobile and one the most mobile (most likely to be transported to surface water). Chen *et al*. found that the SWMI correlated well with both peak and mean surface water monitoring data from three agricultural watersheds. A review of pesticide wash-off from turf plots also linked the differences in runoff fraction to pesticide K_{oc} values and the soil aerobic decomposition half life (Haith, 2001). The SWMI is a tool intended to allow evaluation of the relative runoff and erosion potential for different pesticides and to provide a quick estimate of relative potential concentration levels in watersheds.

Table 13-4 shows the SWMI for the study list pesticides, diazinon, and chlorpyrifos. Interestingly, the SWMI for chlorpyrifos, which is among the insecticides most frequently detected in urban surface waters, is not substantially higher than SWMIs for pyrethrins and pyrethroids. Substances with the lowest SWMIs in Table 13-4 have been detected in surface waters, suggesting that all of the SWMIs in the table are sufficiently large to mean that wash-off of environmentally meaningful fractions is possible.

Table 13-4. Surface Water Mobility Indexes (SWMI) for Study List Pesticides

Pesticide	**Soil Aerobic Half Life (days)**	**K_{oc}**	**SWMI**
Bifenthrin	97 to 156	240,000	0.0738
Carbaryl	46	288	0.4979
Chlorpyrifos[a]	*39 to 51*	*9,930*	*0.0933*
Cyfluthrin	34	31,000	0.0751
Cypermethrin	14 to 60	61,000	0.0720
Deltamethrin	34	46,000 to 1,630,000[b]	0.0678
Diazinon	*17*	*1,520*	*0.1809*
Esfenvalerate	77	5,273	0.1171
Imidacloprid	27	132 to 310[b]	0.5257
Malathion	Not available	1,200	--
Permethrin	108	39,300	0.0789
Piperonyl Butoxide	927	1,810	0.2007
Pyrethrins I	14 to 60	39,000	0.0742
Pyrethrins II	14 to 60	5,200	0.1122

[a] Chlorpyrifos value differs from source's calculation because different (preferred) half life and K_{oc} values were used. Calculations were checked with values in source paper.

[b] When aerobic soil half life or K_{oc} was reported as a range, used the median in the calculation.

Source: Calculated using the method of (Chen *et al*., 2002).

These results should be viewed with caution. The SWMI is a new method that has not been extensively tested. It may not be applicable to urban watersheds nor to impervious surface applications. The SWMI calculation relies on somewhat uncertain input data (see Section 4.1).

Watershed Scale Studies of Pesticide Runoff

A USGS team explored the relationship between the amount of various insecticides applied in agricultural watersheds across the U.S. to the amount measured in streams draining those watersheds, expressing the result as an “annual load as a percent of use” (LAPU) (Capel *et al.*, 2001). In general, LAPU values for pesticides are relatively low. Table 13-5 (on the next page) gives the measured LAPUs relevant to this report.

The primary difference between the watershed LAPU values and studies of pesticide wash-off from individual fields is that the watershed-level measurements account for processes that occur in the watershed, like pesticide decomposition and partitioning into stream sediments. Partitioning into sediments (a process considered in the next subsection) is a possible explanation for the relatively low LAPU for permethrin (the only pyrethroid in the study) as compared to malathion, carbaryl, diazinon, and chlorpyrifos.[54]

Table 13-5. Annual Load as a Percent of Use (LAPU) for Selected Pesticides

Pesticide	**LAPU**
Carbaryl	0.033
Chlorpyrifos	*0.032*
Diazinon	*0.085**
Malathion	0.045
Permethrin	0.0005
Average of 14 Insecticides	0.078

*Artificially high value due to non-agricultural uses in the study watershed that could not be quantified.
Source: Capel *et al.*, 2001.

13.6 Environmental Fate in Surface Waters

This subsection looks at the fate of study list pesticides in the primary types of surface waters that receive urban runoff in the San Francisco Bay area, which are small creeks and the San Francisco Bay estuary. Like Section 13.4, this section relies on chemical property and environmental fate data presented in Section 4. The focus of this portion of the environmental fate review is on information that is relevant to the question of whether any of the study list pesticides may be present in urban surface waters at or above the environmentally relevant concentration for environmentally relevant time periods.

This subsection mentions two partition coefficients that are commonly used as indicators of the likelihood that a substance will sorb onto (bind to) sediments and soils. These partition coefficients are:

- K_{ow}—octanol/water partition coefficient, a laboratory measurement of the fraction of the substance that is dissolved in octanol (a non-polar organic solvent) in a container that holds both octanol and water.
- K_{oc}—organic carbon normalized partition coefficient, a measurement of the fraction of a substance that sorbs to natural organic matter in soils/sediments (useful because most pesticides are non-polar organic molecules for which the tendency to sorb to soils and sediments correlates with organic content).

These two partition coefficients are likely to be related to each other, but the relationship depends on an individual pesticide's chemistry.

Standard studies to evaluate the fate of pesticides in aquatic ecosystems involve test conditions (*i.e.*, farm ponds) relatively high in organic carbon in comparison to the natural state of Bay Area or other urban creeks, which—without human impacts—would generally be relatively low in carbon-laden materials. Standard sediment partitioning measurements involve highly mixed solutions of sediment and water, which do not resemble sediment quantity, mixing, or characteristics that should normally be found in Bay Area creeks. Such test conditions dramatically enhance both the rate and the total amount of pesticide partitioning into sediments. Even San Francisco Bay, which is relatively rich in organic carbon, generally exhibits conditions very different from these test conditions.

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[54] Another possibility is that the analytical detection limit for the water quality monitoring that forms the basis for these calculations may have precluded measurement of environmentally significant quantities of permethrin.

Carbaryl and Malathion. Relative to other study list pesticides (except imidacloprid), both carbaryl and malathion are more soluble in water and have relatively lower tendencies to bind to soils and sediments. Their environmental properties suggest that once these two pesticides enter surface waters they will occur in the water column and will—to some degree—bind to sediments. Both will most likely decompose by hydrolysis, since Bay area surface waters typically have pHs above 7. Insufficient information is available about likely accumulation and decomposition rates to predict whether carbaryl and malathion will accumulate to meaningful concentrations in sediments.

Imidacloprid. With its high water solubility and low K_{ow}, a significant fraction of imidacloprid should remain in the water column once it enters surface waters. Imidacloprid degrades relatively quickly in water by photolysis, which is likely to be the primary decomposition pathway in surface waters. Unfortunately, such decomposition can only occur at the surface of well-sunlit waters, which will limit the rate at which imidacloprid will decompose in environmental surface waters (note that healthy creeks have vegetative canopies that limit penetration of light to the creek surface and sunlight penetrates only the top few feet of Bay waters). While imidacloprid may partition into sediments, it is likely to biodegrade sufficiently quickly and/or to partition back into the water column at a rate sufficient to avoid accumulation in sediments.

Pyrethroids. With their high K_{ow} and K_{oc} values, pyrethroids will tend to move into the sediment phase after entering the water column. The rate of this partitioning (which may occur over a few hours to a few weeks) may be quite important to their potential for adverse effects on aquatic ecosystems, but cannot be estimated for typical San Francisco Bay area surface waters on the basis of available data, which do not reflect creek sediment characteristics nor anticipated mixing conditions.[55] Esfenvalerate, with its substantially lower K_{ow} and K_{oc}, is likely to partition into sediments more slowly and to a lesser degree than other pyrethroids. Once in sediments, pyrethroids should decompose slowly, but may persist long enough to accumulate to meaningful concentrations. Sediment accumulation is particularly likely for bifenthrin (Fecko, 1999) and permethrin, which decompose slowly under anaerobic conditions. Pyrethroids remaining in the water column may eventually decompose by photolysis (decomposition rates vary), assuming sufficient sunlight penetrates receiving waters.

Pyrethrins. In surface waters, the fate of pyrethrins should be similar to that of pyrethroids, with the substantial difference that pyrethrins are likely to decompose much more quickly. Near the water surface in sunlit waters, pyrethrins will decompose very quickly. In sediments, where the majority of pyrethrins are likely to partition, pyrethrins should decompose sufficiently rapidly to prevent accumulation of high concentrations.

Piperonyl butoxide (PBO). Due to its moderate solubility and moderately high K_{ow} value, PBO is expected to partition primarily into sediments after it flows into surface waters (Jones, 1998). As with pyrethroids, the rate of this partitioning may be environmentally important in San Francisco Bay area surface waters, but cannot be estimated with available information. Since PBO is relatively stable in the absence of sunlight and microbial activity, it is likely that it will accumulate in sediments. PBO remaining in the water column should decompose by photolysis, assuming sufficient sunlight penetrates receiving waters.

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[55] Laboratory studies showing partitioning to sediment phases within a few hours involve unrealistic sediment/water mixing conditions (Maund *et al*. 2002). While most pyrethroids partition in to sediments in farm test ponds within 24 hours (Leahey, 1985), this rapid partitioning may be facilitated by the relatively large amount of organic matter in such systems. In contrast, modeling of typical stream mixing anticipates that partitioning will occur over a period of more than 2 weeks (Capel, 2001).

Many of the study list pesticides are relatively insoluble in water—but all are sufficiently soluble to cause surface waters to exceed environmentally relevant concentrations. This relationship can quickly be shown with a simple calculation, dividing a pesticide's solubility in water by its environmentally relevant concentration (values above one indicate solubility greater than the environmentally relevant concentration). The resulting "solubility indexes" are compiled in Table 13-6.

Table 13-6. Solubility Indexes for Study List Pesticides

Pesticide	Fresh Water	Salt Water
Bifenthrin	1,400	25,000
Carbaryl	43,000	140,000
Chlorpyrifos	*14,000*	*110,000*
Cyfluthrin	140	8,300
Cypermethrin	2,000	800
Deltamethrin	200	120
Diazinon	*750,000*	*73,000*
Esfenvalerate	3*	5*
Imidacloprid	49	15,000
Malathion	300,000	380,000
Permethrin	200	6,000
Piperonyl Butoxide	5,800	11,000
Pyrethrins I	38	140
Pyrethrins II	1,700	6,400

*The reported solubility value may be low. See Table 4-2.
Source: TDC Environmental calculation using data in Tables 4-2, 11-1, and 11-2.

13.7 Sewer Discharge Analysis

Since the fate of pesticide discharges to sewer systems is completely different than the fate in outdoor applications, this subsection looks separately at sewer applications.[56] Because almost all California municipalities have sewer systems that are separate from their storm drain systems, this analysis assumes that any discharge to a sewer system would flow to a wastewater treatment plant.[57] Of the study list pesticides, only deltamethrin, permethrin, pyrethrins, and PBO are currently allowed to be applied in sewer systems or used for applications (like pet shampoos) where essentially all applied material is discharged. Since both pyrethrins and PBO decompose quickly in aerobic conditions, this analysis focuses on the pyrethroids, using two deltamethrin products applied to sewer manholes as an example.

Application Rate

Both example products are used in sewer systems primarily to control cockroaches (chlorpyrifos may also be used for this purpose). Application methods are as follows:

- The first product—a dust—is applied by injection into the air in the sewer lines; injection is in one manhole for every 200 feet of sewer line. With this application method, essentially all of the active ingredient eventually enters the sewer discharge flow. The sewer discharge is estimated at 100%.

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[56] This report refers to facilities that treat domestic, commercial, institutional, and industrial wastewater that has been discharged to sewer systems as "wastewater treatment plants." Most of these facilities are owned by public agencies, which is why they are often called "publicly-owned treatment works" or POTWs.

[57] None of the study list pesticides is registered for application to storm drain systems (see Section 7).

- The second product—a liquid—is mixed with paint and applied by spray application inside each manhole. Typically, application involves use of a long wand with a spray head that applies the pesticide-containing paint in a circular pattern inside the manhole. With this application method, much of the active ingredient is incorporated in the paint coating. The primary release pathway would be from "overspray" (droplets carried away by airflow). For flat surfaces under more normal spray paint application conditions, overspray is from 5 to 50% of the total material applied; overspray of 20 to 25% is common with various types of spray equipment (SCAQMD, 2000). Since the overspray quantity is uncertain, sewer discharge estimates will evaluate several overspray fractions. Some material may be washed into the sewer during rainstorms, when water flows into sewer systems (this is termed "inflow"); for purposes of the analysis, such releases are assumed to be negligible.

Table 13-7 provides application quantity estimates for a single manhole application of each of these two products. Applications are assumed to be made at the maximum application rate provided in the label directions.

Table 13-7. Sewer Discharge Estimates for Application of Deltamethrin Products

Product	Quantity Active Ingredient Applied Per Manhole (grams)	Fraction discharged to sewer system	Quantity Active Ingredient Discharged Per Manhole (grams)
Dust	0.0283	100%	0.0283
Liquid, 25% overspray	0.85	25%	0.21
Liquid, 5% overspray	0.85	5%	0.043

Source: TDC Environmental calculations based on label instructions for Delta Dust and Bug Juice.

Fate in Wastewater Treatment Plants

In sewer systems and wastewater treatment plants, wastewater contains significant fractions of solids high in organic content. While wastewater/solids mixing varies in sewer lines themselves, treatment plants all contain process steps that involve substantial mixing of high organic content material with wastewater. This mixing should facilitate relatively rapid partitioning of pyrethroids onto wastewater solids.

While passing through a typical sewer system and while flowing through the process units at a typical wastewater treatment plant, pyrethroids would be unlikely to decompose to any significant extent. The soil aerobic half lives for pyrethroids (see Section 4) suggest that little degradation will occur during wastewater treatment plant processing (typical facilities pass wastewater through in 8 to 24 hours).[58] Given the stability of pyrethroids to hydrolysis, chemical decomposition is unlikely. This means that essentially all of the pyrethroids entering a sewer system would exit either in the sewage sludge or in a wastewater treatment plant's wastewater effluent.

The potential consequences of the presence of pyrethroids in sewage sludge depend on the management of the sludge. Wastewater treatment plants manage sludge by landfilling, incineration, or reuse (typically on agricultural fields). Reuse generally involves application of sludge on agricultural lands, where the incorporated pesticide could potentially be washed off into surface water. Wash-off in such situations would depend on many factors, such as initial concentration, sludge application rate, sludge

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[58] This applies only to standard wastewater treatment plant designs; unusual processes (like treatment wetlands) can involve process times of days or even weeks.

processing and holding time (during which the pyrethroid could decompose significantly), and thus cannot be evaluated in this report.

A small portion of the pyrethroid would be in the wastewater treatment plant's effluent, either in solution or sorbed to solids in the effluent. Wastewater treatment plant removal efficiencies for pesticides depend on a number of plant-specific design elements, as well as on the properties of the pesticide. No removal efficiency data for pyrethroids were identified during the literature review. For other pesticides, real-world removal efficiencies have generally been much lower than might have been expected on the basis of partition coefficients and decomposition rates, for example:

- On the basis of 10 years of data from 5 wastewater treatment plants, Los Angeles County Sanitation Districts found that its treatment processes removed 20% to 43% of lindane from influent wastewater (Heil, 2002).
- A survey of 10 San Francisco Bay area wastewater treatment plants found that 64-98% of diazinon was removed from influent wastewater. The average removal was 85% (Chew *et al.*, 1998).
- The same San Francisco Bay area wastewater treatment plant survey found chlorpyrifos removal ranged from 0% to 89%, with an average removal of 55% (Chew *et al.*, 1998).

These data suggest that while removal efficiencies as high as 99% might be theoretically possible, real-world removal efficiencies may be substantially lower, particularly at the low end of routine variations. To address the uncertainty in removal efficiency, this analysis considers several different removal efficiencies. Table 13-8 shows the quantity of deltamethrin that would not be removed by wastewater treatment and would therefore be discharged into wastewater treatment plant effluent at two theoretical removal efficiencies.

Table 13-8. Wastewater Treatment Plant Discharge Estimates for Application of Deltamethrin Products

Product	**Quantity Active Ingredient Discharged Per Manhole (grams)**	**Quantity in Wastewater Effluent (grams)**	
		80% Removal Efficiency	**99% Removal Efficiency**
Dust	0.0283	0.0057	0.00028
Liquid, 25% overspray	0.21	0.042	0.0021
Liquid, 5% overspray	0.043	0.0086	0.00043

Source: TDC Environmental calculations based on Table 13-7.

Table 13-9 (on the next page) presents the number of manhole treatments that would cause 1,000,000 gallons of wastewater effluent to reach the environmentally relevant concentration in fresh water. Since the environmentally relevant concentration for salt water is somewhat higher, the number of manholes would be larger for salt water discharges.

Since many (about 150) manholes are typically treated by one crew in one day (Gallifant, 2003; Webster, 2003), the information in Table 13-9 suggests that there is the potential for wastewater treatment plant effluent to exceed environmentally relevant concentrations under some conditions.

The estimates in this section are highly uncertain, as they rely on numerous assumptions. Only one type of application is explored—other sources for sewer discharges of study list pesticides exist (*e.g.*, pet treatments and improper cleanup and disposal activities). No clear conclusion can be drawn with regard to the use of pyrethroids for applications involving sewer discharges. Additional investigation is warranted, particularly regarding the removal efficiency in wastewater treatment plants.

Table 13-9. Number of Manhole Treatments Required to Create 1 Million Gallons of Wastewater Effluent at the Environmentally Relevant Concentration

Product	Number of Manholes Treated—Fresh Water		Number of Manholes Treated—Salt Water	
	80% Removal Efficiency	99% Removal Efficiency	80% Removal Efficiency	99% Removal Efficiency
Dust	7	134	11	230
Liquid, 25% overspray	1	18	2	31
Liquid, 5% overspray	4	88	7	150

Source: TDC Environmental calculations based on Tables 13-8 and 11-1.

13.8 Conclusions

The information above suggests that most of the study list pesticides have the potential to exceed the environmentally relevant concentration in surface water for a meaningful time period. Conclusions for each study list pesticide are below.

Carbaryl is one of the most widely used broad-spectrum insecticides. The U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) found it to be the second most commonly detected insecticide in surface water. In the NAWQA data, streams draining urban areas had more frequent detections and higher concentrations of carbaryl than streams draining agricultural or mixed land use areas. Carbaryl has also been found in rain and fog, even in urban areas far from agricultural spraying (U.S. EPA, 2002).

The presence of carbaryl in surface waters has important implications—the U.S. EPA environmental risk assessment for carbaryl found:

- Significant acute risk to freshwater fish and to all aquatic invertebrates,
- Significant chronic risk to freshwater aquatic invertebrates, and
- Exceedances of the endangered species level of concern for freshwater fish and for both freshwater and marine/estuarine aquatic invertebrates.

Since urban watersheds—where concentrations are known to be higher—and certain chronic risks are not evaluated in the U.S. EPA environmental risk assessment, additional significant risks may exist (U.S. EPA, 2002).

Available data show that carbaryl often exceeds the environmentally relevant concentration in surface water and that such exceedances probably occur for a meaningful time period. Use of carbaryl as a substitute for diazinon and chlorpyrifos will only increase the concentration and frequency of carbaryl occurrence in surface waters receiving urban discharges.

Imidacloprid is quite mobile in the environment, but is far less toxic than other study list pesticides. Due to its solubility in water and its environmental stability on application sites, it is very likely to be washed off of outdoor application sites, with its low K_{ow}, high solubility in water, and relatively long soil half-life. When applied to landscaping or in watersheds where storm water runoff is treated by an infiltration method (*e.g.*, basin or swale) or directed to groundwater infiltration basins, rain or irrigation water can move imidacloprid into soil (and potentially to groundwater). On impervious surfaces, rain or other water flows would readily wash imidacloprid off of the application site.

A literature review identified only one article with data on environmental presence of imidacloprid. The lack of data is probably due to the newness of imidacloprid in the marketplace and the lack of a commercially available chemical analysis method.

Although imidacloprid appears to be far less toxic to aquatic species than other study list pesticides, its high water solubility could allow relatively high concentrations to occur in runoff. For example, the one available measurement of imidacloprid runoff had a concentration ten times the LC50 for the mysid *Americamysis bahia*, a standard salt water test organism. Its toxicity could be greater than current data indicate, as it has the highest number of toxicity testing data gaps of any study list pesticide.

The data in this report suggest that there is a potential for use of imidacloprid to cause surface water to exceed the environmentally relevant concentration. Concentrations in surface water will depend to a great degree the locations where imidacloprid is used. Due to the substantial aquatic toxicity data gaps, the environmentally relevant concentration is itself somewhat uncertain.

Malathion, like carbaryl, is one of the most widely used broad-spectrum insecticides. Together with diazinon, chlorpyrifos, and carbaryl, the USGS NAWQA found malathion frequently in surface water, particularly in urban creeks, where the highest concentrations were measured.

Malathion is toxic to aquatic organisms at observed concentrations—many fish kills have been confirmed (U.S. EPA, 2000). According to the U.S. EPA malathion environmental risk assessment, malathion poses significant acute and chronic risks for aquatic invertebrates and some fish. Even at the lowest application rates, the U.S. EPA risk assessment found that levels of concern are exceeded by factors of up to 160 for certain invertebrate groups (U.S. EPA, 2000). Additional significant risks may exist in urban areas (where concentrations are higher)—but urban areas were not evaluated in the U.S. EPA environmental risk assessment.

Available data show that malathion often exceeds the environmentally relevant concentration in surface water and that such exceedances occur for a meaningful time period. Use of malathion as a substitute for diazinon and chlorpyrifos will only exacerbate these problems.

Pyrethroids appear to be increasing in market share rapidly. Since several of these related chemicals appear to be coming into widespread use, the environmental effects of pyrethroid mixtures, rather than individual chemicals, will form the basis of potential environmental effects. Although pyrethroids are generally applied in much smaller quantities than organophosphorous pesticides, these quantities are environmentally meaningful because pyrethroids are very highly toxic to aquatic organisms.

In surface waters, pyrethroids are expected to partition primarily into sediments. The speed of that partitioning, which will depend on flow, mixing, and sediment quality in individual water bodies, will be very relevant for their significance to aquatic ecosystems.[59]

Pyrethroids have been detected in many environmental water samples and have been found to cause toxicity to aquatic species in some environmental water samples (see

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[59] The presence of sediments or particulate matter in the water column has been shown to reduce pyrethroid toxicity to invertebrates and fish (Leahy, 1985).

Table 13-1 [on page 72]). This suggests that the environmental water column concentrations are sufficient (and persist for a sufficiently long time period) to cause toxicity and/or that particulate- or sediment-bound pyrethroids contribute to toxicity. The limited available data do not allow a conclusion as to whether the measurements are anomalies or are indicative that environmentally relevant concentrations may commonly remain in the water column for sufficient time periods to cause aquatic toxicity (Casjens, 2002).

Most pyrethroids have negative insecticidal temperature coefficients, meaning that they are more toxic to target pests at lower temperatures. In some fish, certain pyrethroids exhibited increasing toxicity as temperature decreased (Leahey, 1985).[60] Since California urban streams are generally cooler during runoff events (which occur primarily during the winter months), an increase in toxicity could have environmental importance.

Given their hydrophobicity, pyrethroids are likely to appear in sediments at concentrations several thousand times their water column concentrations. Pyrethroids may decompose slowly enough in sediments for residuals to last for years; if so, sediment concentrations may gradually increase with continued pyrethroid use. In sediments, the accumulated pyrethroids may concentrate sufficiently to cause toxicity to benthic organisms (Maund *et al*, 2002; Weston, 2002).

While currently available data are insufficient for proof of environmental harm, the available information strongly suggest that widespread use of pyrethroids as substitutes for diazinon and chlorpyrifos is likely to cause environmentally relevant concentrations to be exceeded in surface waters, sediments, or both for meaningful time periods. On the basis of available data, it is uncertain whether pyrethroid applications resulting in sewer discharges will have environmental significance.

<u>Pyrethrins</u>, the natural substance that was the inspiration for the more environmentally stable pyrethroids, has the potential to increase use. Pyrethrins products are typically formulated with synergists like piperonyl butoxide, which is a consideration in the evaluation of their potential environmental effects. Available data suggest that pyrethrins are almost 1000 times less toxic than most pyrethroids, but there are many aquatic toxicity data gaps.

Pyrethrins, which are well known for their rapid photodecomposition, are far less stable in the environment than pyrethroids, which is a major reason why pyrethroids were developed (Casida and Quistad, 1995). The shorter environmental lifetime of pyrethrins reduces their potential environmental impacts, if they are applied in locations where decomposition is sufficiently rapid.

The information in this report suggests that should pyrethrins enter widespread use as substitutes for diazinon and chlorpyrifos, there is a potential for use of pyrethrins to cause surface water to exceed the environmentally relevant concentration. Concentrations in surface water will depend to a great degree on the locations where pyrethrins are used. Due to the substantial aquatic toxicity data gaps, the environmentally relevant concentration is itself somewhat uncertain.

<u>Piperonyl Butoxide</u> is the most common synergist in pesticide products. Its ability to enhance pesticide toxicity is not limited to application locations—it may contribute to aquatic toxicity of pyrethrins, pyrethroids, and carbamates in surface waters and sediments.

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[60] For example, permethrin toxicity to rainbow trout increased by an order of magnitude as temperature was decreased from 20°C to 5°C (Kumararaguru, 1982).

Industry water quality modeling data and reported frequent detection in surface water samples indicates that synergism of toxicity from other pesticides in surface waters is possible, as is direct toxicity to sensitive organisms. For synergism to occur, PBO must appear in concentrations sufficiently high to affect the metabolism of the pyrethrin or pyrethroid molecules by target organisms. Available data are insufficient to evaluate whether the concentrations of PBO that may occur in urban surface waters would be sufficient (and persist for a sufficient period of time) to cause this effect.

Like pyrethroids, PBO should partition primarily into sediments after it flows into surface waters (Jones, 1998). In sediments, PBO has the potential to enhance toxicity of other sediment-bound pesticides; however, available data do not allow evaluation as to whether the concentrations likely to be present in sediments would be sufficient to modify metabolism of other pesticides by sediment-dwelling organisms.

14.0 CONCLUSIONS AND RECOMMENDATIONS

14.1 Conclusions

Conclusion 1. Use of bifenthrin, carbaryl, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, malathion, and permethrin as replacements for urban uses of diazinon and chlorpyrifos may cause adverse effects in aquatic ecosystems receiving urban runoff.

- Malathion and carbaryl are among the most frequently detected pesticides in urban surface waters and are commonly detected at concentrations known to cause adverse effects to aquatic ecosystems.
- The pyrethroid pesticides evaluated (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, permethrin) are all extremely toxic to aquatic life (aquatic toxicity occurs at part per trillion concentrations). The limited available data suggests that these pesticides are likely to be washed into urban surface waters where they may cause adverse effects in the water column and/or in sediments. The propensity of pyrethroids to bioconcentrate is of concern—pyrethroids bioconcentrate by factors of hundreds to tens of thousands in fish.
- All of the study list pyrethroids (and lambda cyhalothrin) are entering the urban marketplace, making it very likely that aquatic ecosystems will contain mixtures of these substances. Since pyrethroids have a common mode of toxicity and similar environmental fates cumulative toxic effects are very likely. Cumulative effects may occur among pyrethroids and pyrethrins, between pyrethroids and synergists like PBO, and between pyrethroids and other pesticides in the environment like diazinon (Denton *et al.*, 2003).

Conclusion 2. Depending on application locations, use of imidacloprid and pyrethrins as replacements for urban uses of diazinon and chlorpyrifos may cause adverse effects in aquatic ecosystems receiving urban runoff. Extensive data gaps preclude a more definitive conclusion.

- Imidacloprid appears, on the basis of the limited available data, to be significantly less toxic to aquatic species than any other study list pesticide—but it is also very soluble in water. Its solubility is a significant practical consideration for its use, as it is readily washed away from the application location. Imidacloprid is particularly likely to reach groundwater in locations with shallow groundwater, in regions where storm water runoff is directed to infiltration basins to provide a drinking water supply, and in watersheds where runoff is directed to infiltration-type storm water runoff treatment devices like basins and swales. Because of its potential to cause groundwater contamination, and the major data gaps in toxicity and surface water concentration data, any increased use should be approached with caution at this time.
- Pyrethrins seem to be far less toxic to aquatic species than their pyrethroid cousins—but the available toxicity data set is relatively incomplete. Their rapid photodecomposition on outdoor surfaces makes them attractive from a water quality perspective, as little material should be available to wash off if applications are properly timed. Unfortunately, this rapid photodecomposition has made this natural insecticide less popular in the marketplace than its synthetic cousins. Since pyrethrins products are typically formulated with synergists to increase their effectiveness, the potential environmental effects of synergists need to be considered in evaluating the safety of pyrethrins use.

- Imidacloprid and pyrethrins could be appropriate to recommend in an Integrated Pest Management (IPM) program when lower risk pesticides are unavailable or inappropriate. Prior to encouraging use of these pesticides, identified data gaps should be filled (particularly regarding aquatic toxicity), other "low-risk" alternatives should be evaluated, and an analysis of likely application sites and use rates should be conducted.

Conclusion 3. Use of piperonyl butoxide as a synergist in pesticide products that replace urban uses of diazinon and chlorpyrifos has the potential to contribute to adverse effects caused by other pesticides in aquatic ecosystems receiving urban runoff.

- For piperonyl butoxide, the critical question is whether concentrations sufficient to enhance the toxicity of other pesticides (such as pyrethroids, pyrethrins and carbaryl) may occur in surface water or sediments.
- Other synergists not evaluated in this report, like N-octyl bicycloheptene dicarboximide (commonly known by its brand name MGK® 264), also have the potential to enhance toxic effects from pesticides in surface waters and sediments.

Conclusion 4. While sufficient data were identified to support a weight-of-evidence evaluation, critical data gaps exist for study list pesticides.

- The most important data gaps are in the areas of aquatic toxicity (for pyrethroids, pyrethrins, and imidacloprid) and sediment toxicity (for pyrethroids).
- Almost no surface water or aquatic sediment monitoring has included pyrethroids, pyrethrins, or imidacloprid. The monitoring that has been conducted generally relies on methods that are not capable of measuring environmentally relevant concentrations of these pesticides.

14.2 Recommendations Regarding Data Gaps

Recommendation 1. Fill toxicity testing data gaps.

- Prioritize obtaining both acute and chronic toxicity data for standard fresh water toxicity testing species *Pimephales promelas* (fathead minnow), *Ceriodaphnia dubia* (water flea) and *Selenastrum capriconutum,* green algae.
- Prioritize obtaining toxicity data for imidacloprid and pyrethrins.

Recommendation 2. Evaluate potential for pyrethroid pesticides to accumulate in surface water body sediments at concentrations that may cause toxicity to benthic organisms.

- Obtain benthic organism toxicity data for pyrethroids.
- Estimate potential sediment concentrations of pyrethroids.
- Evaluate potential risks and implement measures to prevent significant risks.

Recommendation 3. Assess water quality implications of the use of synergists other than piperonyl butoxide in products that replace diazinon and chlorpyrifos urban use products.

Recommendation 4. Assess water quality implications of use of the pyrethroid insecticide lambda cyhalothrin as a replacement for urban uses of diazinon and chlorpyrifos. Lambda cyhalothrin has growing agricultural use and began entering the residential retail market as this study neared completion.

Recommendation 5. Make all information necessary to evaluate and prevent surface water quality impacts from pesticides publicly available for every registered pesticide.[61]

- Complete and practical pesticide chemical analysis methods with detection limits no greater than one-tenth of the lowest environmentally relevant concentration (*e.g.*, water quality criterion, LC50, EC50) are needed. Methods should be available for measuring concentrations in water column samples and sediment samples, toxicity testing, sample collection and storage. Methods should be validated for various environmental matrices, including pure water, polluted water (*e.g.*, both urban and agricultural storm water runoff), surface water (both fresh water and salt water), and wastewater treatment plant effluent.
- Measurements of chemical properties related to surface water transport are needed (*e.g.*, formulation-specific wash-off from pervious and impervious surfaces).
- Data sufficient to predict pesticide fate in wastewater treatment plants are needed.
- An evaluation of how the presence of pesticides in sewage sludge might affect crops or surface water runoff at sewage sludge application locations is needed.
- Toxicity test results for all standard water quality test species listed in this report are needed.
- Toxicity test results for sub-lethal effects, like effects on behavior, swimming performance (which affects a fish’s ability to maintain proper position in the water column, avoid predators, and capture food), and reproduction are needed.

14.3 Recommendations Regarding Monitoring

Recommendation 6. Develop practical methods for monitoring urban surface waters and sediments to identify the presence of and to measure possible environmental effects of diazinon and chlorpyrifos replacement pesticides.

- Create standard written procedures for surface water and sediment sample collection, storage, and handling that are appropriate for samples containing pyrethroids, carbamates, and organophosphorous pesticides.
- Identify appropriate methods and test species for surface water and sediment toxicity testing.
- Develop improved Toxicity Identification Evaluation (TIE) procedures to identify potential toxicity due to pyrethroids and imidacloprid.
- Validate sampling procedures and TIE methods with field samples, ideally from sites where diazinon and chlorpyrifos replacements are likely to occur in storm water runoff and/or surface water.

Recommendation 7. Develop methods for chemical analysis of bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, imidacloprid, and permethrin suitable for use by commercial laboratories with detection limits below environmentally relevant concentrations.

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[61] At the Federal level, procedures need to be modified such that data call-ins for all pesticides include the elements listed below. U.S. EPA has not interpreted its guidelines (in 40 CFR Part 158) as requiring these items.

- Prioritize development of methods for chemical analysis of imidacloprid and deltamethrin in water and sediments.
- Support USGS and DFG efforts that are currently in progress to develop low detection limit methods for bifenthrin, cyfluthrin, lambda cyhalothrin, cypermethrin, esfenvalerate, and permethrin.

Recommendation 8. Monitor urban surface waters to identify the presence of and to measure possible environmental effects of diazinon and chlorpyrifos replacement pesticides.

- Monitoring should include samples from urban creeks and from San Francisco Bay. Given the sensitivity of salt water species to many diazinon and chlorpyrifos replacement pesticides, monitoring at creek discharge points ("the Bay margins") is recommended.
- Both the water column and sediments should be monitored.
- Given the number of different pesticides entering the market, the potential for cumulative effects, and the lack of convenient chemical analysis methods, toxicity testing—rather than chemical concentration measurements—will probably be the simplest and most cost-effective primary monitoring strategy. Until ongoing research provides improved methods, toxicity tests may, in some cases, understate toxicity levels in surface water samples and toxicity identification evaluations may, in some cases, only be able to identify a likely class of toxicants, rather than identify the specific chemical causing toxicity.

Recommendation 9. Monitor sales and use of diazinon and chlorpyrifos replacement pesticides in urban areas.

Recommendation 10. Develop specific plans to respond to findings of toxicity in surface waters or sediments.

Recommendation 11. Establish a monitoring network to characterize the presence of pesticides in California surface waters.[62]

- Design the monitoring to measure pesticide occurrence, concentrations, and trends.
- Monitor all types of California surface waters, including urban and rural, saline and fresh, creeks, rivers, bays, and the ocean.
- Monitor during both wet and dry weather.
- Regularly test for all commonly used pesticides, but focus on pesticides known or suspected to occur at environmentally relevant concentrations.
- Select sampling sites to be representative of California watersheds.
- Collect and test both water column and sediment samples.

14.4 Recommendations Regarding Regulatory Activities

Recommendation 12. Maximize the ability of the pesticide registration process to prevent potential water quality problems associated with pesticide use.

- Review surface water impacts for all pesticide registrations.

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[62] Gill, 2002 contains an outline of a possible monitoring program.

- Assess the environmental effects of all proposed sites of use—particularly urban sites of use.
- Address the environmental effects of inert ingredients in individual pesticide products as those products are registered. Consider both direct effects, such as aquatic toxicity, and indirect effects, like facilitation of off-site transport of the active ingredient.
- More thoroughly consider alternatives and other risk mitigation options when registering pesticides (*e.g.*, during environmental review under the California Environmental Quality Act).
- Obtain from pesticide manufacturers chemical analysis methods and data needed to evaluate water quality impacts (see Recommendation 5), including the minimum aquatic toxicity data necessary to develop acute and chronic water quality criteria following U.S. EPA guidelines (U.S. EPA, 1985).

Recommendation 13. Use California and Federal water quality agency expertise during the pesticide registration process to ensure that pesticide applications comply with the Clean Water Act and the Porter-Cologne Water Quality Control Act.

- Use public notices like DPR's weekly notices of materials entering evaluation and Federal Register notices to identify substances entering registration or other regulatory review processes that have the potential to impair water quality.
- Monitor and participate in U.S. EPA pesticide regulatory activities for diazinon and chlorpyrifos replacements to ensure that registration eligibility decisions and other regulatory decisions protect surface water quality (this may involve providing information to assist U.S. EPA in ensuring that environmental risk assessments rely on complete and accurate data, include appropriate environmental concentration estimates, and use methods that fully reflect water quality regulatory program needs).
- Share California monitoring and science data with U.S. EPA and DPR.
- Identify appropriate surface water concentration targets (*e.g.*, U.S. EPA and state water quality criteria) or methods for developing such targets that are consistent with the Clean Water Act and Porter-Cologne Water Quality Control Act to which estimated environmental concentrations can be compared.
- Identify appropriate sewage sludge concentration targets to which estimated sewage sludge concentrations can be compared.
- Identify appropriate sediment concentration targets to which estimated surface water sediment concentrations can be compared.
- Clarify that the risk benefit standards of FIFRA require U.S. EPA to ensure that a pesticide is used in such a manner that mitigation under the Clean Water Act is minimal or unnecessary.

Recommendation 14. Develop a California or Federal "surface water protection list" similar to DPR's ground water protection list.[63]

- Create a formal list of pesticides having the potential to exceed environmentally relevant concentrations in surface water.

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[63] A concept for the application of such a list is in Gill, 2002.

- Implement use restrictions when necessary to prevent surface water quality impacts from pesticides on the surface water protection list.

Recommendation 15. Identify and/or develop methods appropriate for ecological risk assessment of surface water quality impacts of pesticides.

- Define methods for estimating surface water concentrations resulting from outdoor urban pesticide uses.
- Define methods for estimating surface water sediment concentrations resulting from pesticide uses.
- Define methods for estimating wastewater treatment plant influent and effluent concentrations resulting from application and clean-up of pesticides.
- Define methods for determining the potential that a discharged pesticide may interfere with wastewater treatment plant operation.
- Define methods for estimating sewage sludge concentrations resulting from application and clean up of pesticides.

Recommendation 16. Make regulatory changes to facilitate efforts to promote pest management methods that use non-chemical and least-toxic chemical alternatives to pesticides to manage urban pest problems.

- Remove regulatory barriers to education about use of non-toxic or least toxic pest control methods.
- Accelerate registration for least toxic (“reduced risk”) and non-toxic alternative pest control methods.

14.5 Recommendations Regarding Education and Outreach

Recommendation 17. Discourage use of bifenthrin, carbaryl, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, malathion, and permethrin as replacements for urban uses of diazinon and chlorpyrifos.

Recommendation 18. Until further information is available, refrain from recommending imidacloprid and pyrethrins (particularly products with PBO) as substitutes for urban uses of diazinon and chlorpyrifos.

- Widespread use of these pesticides may harm aquatic ecosystems.
- Use of imidacloprid in areas with shallow groundwater, in regions where storm water runoff is directed to infiltration basins to provide a drinking water supply, or in watersheds where runoff is directed to infiltration-type storm water runoff treatment devices like basins and swales (or extensive use of imidacloprid in other regions) may cause groundwater contamination.
- Limited applications of pyrethrins and imidacloprid are less likely to harm aquatic ecosystems than are applications of bifenthrin, carbaryl, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, malathion, or permethrin.
- For impervious surface applications, pyrethrins would have the least potential of any of the study list pesticides to cause harm to aquatic ecosystems. (Treated surfaces should not be subject to rain or irrigation flows for at least several days.)
- For lawn or landscaping applications, imidacloprid or pyrethrins would have the least potential of any of the study list pesticides to cause harm to aquatic ecosystems. (Treated surfaces should not be irrigated to the point of runoff.)

Recommendation 19. Strengthen efforts to promote pest management methods that use non-chemical and least-toxic chemical alternatives to pesticides to manage urban pest problems.

- Insecticide application locations that are the highest priority for IPM implementation are outdoors at residential, institutional, and commercial buildings; any large outdoor area; sewer systems; ornamental plants and lawns; nurseries; golf courses; water; wood structures; and pets.

Recommendation 20. Minimize pesticide wash-off by minimizing use of uncontained chemical pesticides.

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16.0 GLOSSARY AND ABBREVIATIONS

Active ingredient – Pesticide product ingredient registered to control the pest(s) that are the target of the product (*e.g.*, diazinon and chlorpyrifos)

Adjuvants - a class of inert ingredients that increase the effectiveness of the active ingredient and make application easier and/or safer

ARS – Agricultural Research Service, part of the United States Department of Agriculture

Best Management Practices - Feasible actions that, if taken, will minimize pollutant discharges to the sewer and storm drains

CAS# - Chemical Abstracts Service number (unique chemical identifying code)

CCC – Criterion Continuous Concentration (water quality criterion)

CMC – Criterion Maximum Concentration (water quality criterion)

CDFA – California Department of Food and Agriculture

DPR - Department of Pesticide Regulation

EC – Emulsifiable Concentrate

EC50 – Effects concentration that causes the measured effect in 50% of the test organisms during the test time period

ELISA – Enzyme-linked immunosorbent assay

FIFRA - Federal Insecticide, Fungicide, and Rodenticide Act

Formulation – Complete pesticide product, including active ingredient and all other ingredients

FQPA - Food Quality Protection Act

Half Life – Time required for 50% of a quantity of a substance to decompose

HSDB - National Library of Medicine's Toxnet Hazardous Substances Data Bank

Inert ingredient – Pesticide product ingredients other than the active ingredient

IRED – Interim Registration Eligibility Document

K_{oc} – organic carbon normalized partition coefficient

K_{ow} – Octanol/water partition coefficient

LAPU – Annual load as a percent of use

LC50 – Lethal Concentration that kills 50% of test organisms during the test time period

MATC – Maximum Acceptable Toxicant Concentration

MSDS – Material Safety Data Sheet

M.W. – Molecular weight

NAWQA – National Water Quality Assessment, conducted by the United States Geological Survey

Nominal Concentration – Concentration calculated from the amount of material used to mix a solution, rather than measurement of the concentration in the mixed solution

NPDES - National Pollutant Discharge Elimination System

OPP - Office of Pesticide Programs, part of the United States Environmental Protection Agency

PBO – Piperonyl butoxide

PCO - Pest control operator

POTW - Publicly operated treatment works (municipal wastewater treatment plants)

Product Label – The label on a pesticide product offered for retail sale

ppb - Parts per billion (micrograms per liter)

ppm - Parts per million (milligrams per liter)

ppt - Parts per trillion (nanograms per liter)

RED - Registration Eligibility Document

Regional Board - California Regional Water Quality Control Board

Site of use - Location where a pesticide may legally be applied

State Board - State Water Resources Control Board

SWMI - Surface water mobility index

TIE - Toxicity Identification Evaluation

TMDL - Total Maximum Daily Load

Torr - Unit of pressure, approximately 1/760 of an atmosphere

U.S. EPA - United States Environmental Protection Agency

USDA – United States Department of Agriculture

USGS – United States Geological Survey

WP – Wettable powder