Assessment of Potential Aquatic Herbicide Impacts to California Aquatic Ecosystems

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Abstract A series of legal decisions culminated in 2002 with the California State Water Resources Control Board funding the San Francisco Estuary Institute to develop and implement a 3-year monitoring program to determine the potential environmental impacts of aquatic herbicide applications. The monitoring program was intended to investigate the behavior of all aquatic pesticides in use in California, to determine potential impacts in a wide range of water-body types receiving applications, and to help regulators determine where to direct future resources. A tiered monitoring approach was developed to achieve a balance between program goals and what was practically achievable within the project time and budget constraints. Water, sediment, and biota were collected under "worst-case" scenarios in close association with herbicide applications. Applications of acrolein, copper sulfate, chelated copper, diquat dibromide, glyphosate, fluridone, triclopyr, and 2,4-D were monitored. A range of chemical analyses, toxicity tests, and bioassessments were conducted. At each site, risk quotients were calculated to determine potential impacts. For sediment-partitioning herbicides, sediment quality triad analysis was performed. Worst-case scenario monitoring and special studies showed limited short-term and no long-term toxicity directly attributable to aquatic herbicide applications. Risk quotient calculations called for additional risk characterizations; these included limited assessments for glyphosate and fluridone and more extensive risk assessments for diquat dibromide, chelated copper products, and copper sulfate. Use of surfactants in conjunction with aquatic herbicides was positively associated with greater ecosystem impacts. Results therefore warrant full risk characterization for all adjuvant compounds.

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Introduction

Many organic chemicals and copper-based products have been registered as aquatic herbicides to control nuisance weeds and algal blooms by the US Environmental Protection Agency (US EPA) and the California Department of Pesticide Regulation (DPR) (Table 1). The active ingredients found in many aquatic herbicides are the same as those commonly used in terrestrial herbicides. However, the exact formulations (*i.e.*, the active ingredient and any adjuvants) usually differ. For example, a terrestrial-use form of glyphosate, known as Roundup, contains nonylphenol ethoxylate (NPE) surfactants that are toxic to aquatic organisms, whereas an aquatic-use form, AquaMaster, does not include surfactants. The exact formulation used for aquatic applications must be considered when evaluating their potential impacts. Several aquatic herbicides are produced in multiple forms (Table 1), which might have very different toxicological profiles. It has been difficult to assess potential impacts of these herbicides on aquatic ecosystems because of a lack of chemical, toxicological, and bioassessment data collected at application sites.

In the past few years, the use of aquatic herbicides in California has been affected by legal and regulatory issues.

Table 1 California registered aquatic herbicides and algaecides

Herbicide form with aquatic use label	Trade Name(s)[a]	Registrant
Acrolein	Magnacide H	Baker Petrolite
Copper sulfate	Multiple	Multiple
Copper ethanolamine	Cutrine-Plus, K-Tea	Applied Biochemists, Griffin
Copper ethylenediamine	Komeen	Griffin
Copper carbonate	Nautique, Captain	SePRO
Diquat dibromide	Reward	Syngenta
Dipotassium salt of endothall	Aquathol	Cerexagri
Fluridone	Sonar	SePRO
Glyphosate isopropyl amine	Aquamaster, Rodeo	Monsanto, Dow
Imazapyr	Habitat	BASF
Triclopyr triethylamine (TEA)	Renovate	SePRO
2,4-D dimethyl acetate (DMA)	Weedar 64	Multiple
2,4-D butoxyethyl ester (BEE)	Aquakleen	Cerexagri

Note: In California, herbicides applied to flooded rice fields are considered terrestrial rather than aquatic applications

[a] Trade name listing is not exhaustive

In 2001, the US Ninth Circuit Court of Appeals ruled in *Headwaters, Inc. v. Talent Irrigation District* (US Ninth Circuit Court of Appeals 2001) that registration and labeling of aquatic pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) did not preclude the requirement to obtain a permit under the National Pollutant Discharge Elimination System (NPDES) to discharge pesticides into waters of the United States. The California State Water Resource Control Board (SWRCB) issued an emergency NPDES permit in July 2001 (California State Water Resource Control Board 2001), which was challenged in court as insufficiently protective (Waterkeepers 2001). Consequently, there were no legal applications of aquatic herbicides in the 2001 application season (April–September).

The legal challenge to the SWRCB permit was settled with the SWRCB agreeing to fund a 3-year (2002–2004) aquatic pesticide research and monitoring program (APMP), from which an acceptable general NPDES permit would be developed. The San Francisco Estuary Institute (SFEI), a nonprofit research organization with a Board of Directors including scientists, environmental advocates, regulators, and dischargers to San Francisco Bay, was designated to implement the APMP. The APMP also evaluated case studies of nonchemical alternatives to pesticides, identifying some economically viable mechanical and biological alternatives (David et al. 2006; Greenfield et al. 2006), but found production of viable plant fragments to be a major concern (David et al. 2006; Spencer et al. 2006). The APMP chemical monitoring results were used to develop a statewide general NPDES permit issued in the spring of 2004 for the discharge of aquatic pesticides for aquatic weed control (California State Water Resource Control Board 2004). This permit requires individual permit holders to conduct chemical characterizations and monitoring of aquatic-use-labeled herbicides and tank-mixed surfactants containing NPE before and after application.

In 2006, the US EPA codified that a permit was not needed for aquatic herbicide applications. The basis for this decision is that a pesticide applied in compliance with FIFRA is not a "pollutant" under the language of the Clean Water Act at the time of application (Lauffer 2007). Due to potential future legal challenges, the SWRCB has not rescinded the current NPDES permit but does allow dischargers to terminate permit coverage.

The SWRCB required the APMP to direct its research and monitoring efforts to the following:

1. Determine fate and transport of applied chemicals
2. Conduct toxicity testing to evaluate the acute and chronic sublethal and lethal effects of applied pesticides on nontarget aquatic organisms
3. Determine the effect of repeated pesticide exposure on phytoplankton, macrophyte, benthic macroinvertebrate, and epiphytic macroinvertebrate community structure

The purpose of these efforts was to evaluate, under worst-case scenarios, the potential impacts that the major use aquatic herbicides might have on California's waterways. The goal was to help the SWRCB determine when monitoring by applicators might be required and where to direct future resources.

Tiered Risk Assessment

The monitoring program was intended to investigate the behavior of all pesticides currently in use in California and determine potential impacts in a wide range of water-body types receiving applications. A tiered approach was developed to achieve a balance between program goals and

what was practically achievable. In addition, ranking schemes and selection criteria were developed to guide site selection, pesticide priority, and monitoring methods. The tiers developed were defined as follows:

Tier 1. Information-based research. Conduct a literature review to identify likely pesticide/environmental couplings where accumulation is likely or unlikely, determine annual usage from the California Department of Pesticide Regulation Pesticide Use Report (PUR) database, and develop a permit holder database to identify best possible candidate monitoring sites. Develop a ranking scheme to identify the level of efforts required for each pesticide.

Tier 2. Field monitoring. Conduct sampling to confirm the presence or absence of pesticides in aquatic ecosystems, potential water and sediment toxicity, and impacts to nontarget invertebrate populations.

Tier 3. Special studies. Conduct special projects to address technical sampling issues or more fully characterize specific aquatic pesticide environmental impacts.

The results from each tier guided the implementation of studies in subsequent tiers. Thus, it was not necessary to conduct Tier 2 and 3 studies for all aquatic herbicides. The Tier 3 special studies are discussed in detail in separate publications:

1. The evaluation of estrogenic activities of some herbicides and surfactants using a rainbow trout vitellogenin assay (Xie et al. 2005)
2. Determination of long-term nontarget plant toxicity of pelleted fluridone (Siemering 2005)
3. Development of diagnostic tests of indicators of acrolein ecosystem impacts (Siemering 2005)
4. Evaluation and case study demonstration of pesticide fate and transport models (Wadley et al. 2003)
5. Evaluation of nonchemical alternatives to aquatic pesticides (David et al. 2006; Greenfield et al. 2006, 2007; Spencer et al. 2006)

Methods

Tier 1. Information-Based Research

To identify the level of effort required for each herbicide, each was ranked by several criteria: aquatic uses, amount used, common usage, toxicity/risk, public concern, reliable analytical methods, and regulatory significance. Information for these rankings was collected through a literature review (Siemering et al. 2005) and from the CDPR PUR. The final rankings were determined in consultation with the professional opinions of a committee of state and federal regulators, academic researchers, and industry scientists.

The APMP then conducted Tier 2 field monitoring of all but one reviewed herbicide.

Tier 2. Field Monitoring

Target aquatic herbicides identified in Tier 1 were monitored at 16 diverse water bodies throughout California (Fig. 1, Table 2) using a triad approach of concurrent chemical, biological, and physical assessments (Barbour et al. 1996). Two surfactants, R-11 and Target Prospreader Activator (TPA), were used and monitored at select sites (Table 2). Monitoring took place during the herbicide application seasons (roughly May through September) of 2002–2004. Individual monitoring plans were developed based on site characteristics and application specifics. These plans are detailed in the APMP annual reports (Siemering 2004, 2005; Siemering et al. 2003). All sites were monitored prior to, immediately following, and two weeks after herbicide application. This "worst-case scenario" design evaluated the fate of pesticides applied at normal field concentrations and yielded data on both acute and, for an herbicide subset, longer-term pesticide impacts.

For three herbicides—copper sulfate, fluridone, and glyphosate—additional monitoring was conducted over a longer time period (up to 3–4 months after application) at a minimum of three locations that had received repeated applications of one herbicide during the 2003 application season. This sampling frequency was deemed appropriate to detect potential biotic community response. During individual sampling events, the order of sampling collection at a site was as follows: (1) physical habitat assessment, (2) water quality parameters, (3) macrophyte surveys, (4) sediment parameters, and (5) bioassessments.

At each location where monitoring took place, a reference site was also monitored (Table 2). The reference sites selected were as similar as possible to the treated sites minus the application of pesticide. In flowing water bodies, this was often immediately upstream of a treatment area. In lentic systems, an untreated portion of the water body or an adjacent similar water body was selected.

Field and Laboratory Methods

Laboratory analytical methods were selected to have sufficiently sensitive method detection limits (MDLs) to allow comparison to published effects thresholds (Table 3). Because of the high volatility of acrolein, the program also developed an in-field derivitization method for acrolein sampling (Siemering 2005). Organic chemical herbicides are typically collected in glass and metals-based herbicides are collected in polyethylene bottles. However, a literature review and consultation with the manufacturers indicated

Fig. 1 Sampling locations
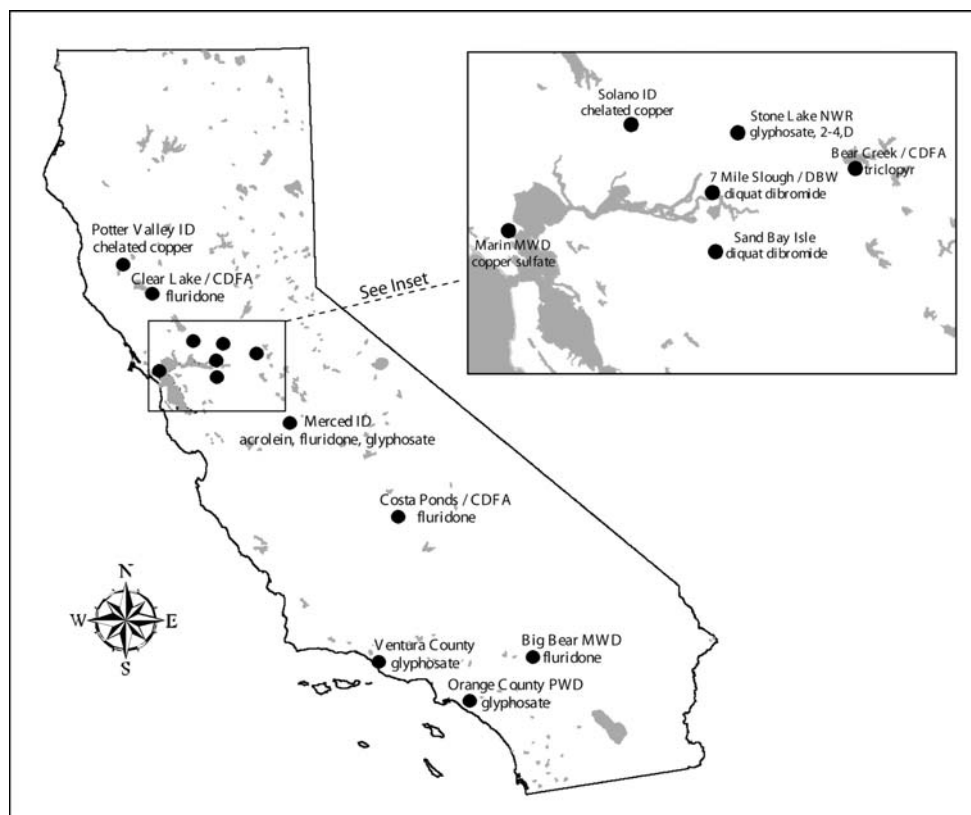
that for several organic herbicides, because of their sorption characteristics, samples were more appropriately collected in polyethylene bottles (Table 4). Samples were stored on ice immediately upon collection and delivered to the analytical laboratories within 24 h for processing. All pesticide analyses were performed by the California Department of Fish and Game (CDFG) Water Pollution Control Laboratory (Rancho Cordova, CA).

Water toxicity was determined using the three standard US EPA species (*Selenastrum capricornutum*, *Ceriodaphnia dubia*, and *Pimephales promelas*), including both the acute and chronic *Ceriodaphnia* and *Pimephales* tests. Testing protocols followed US EPA (1994) recommendations for ambient toxicity testing and were consistent with existing California SWRCB monitoring and assessment programs. For copper assessment, the *Selenastrum* test was not performed (because the copper herbicides are listed as algaecides) and a juvenile rainbow trout (*Onchorhynchus mykiss*) test was used rather than the *Pimephales* test. For sediment particle-bound pesticides that might pose a risk to benthic species, the US EPA *Hyallela azteca* test was used (US EPA 1998). For pelleted fluridone, a common cattail (*Typha latifolia*) test was utilized (Muller et al. 2001).

Bioassessment monitoring was performed to determine the cumulative impact of aquatic pesticides on nontarget communities by assessing organism diversity and biotic integrity. To accomplish this goal, the study employed a rapid bioassessment protocol (Harrington and Born 1999; Hayworth and Melwani 2005; USEPA 2003). Bioassessment data were collected from benthic and epiphytic macroinvertebrates, zooplankton, and phytoplankton. In addition, preliminary information was accrued on macroinvertebrate species assemblages for select types of lentic and lotic systems around California (Hayworth and Melwani 2005).

Data Interpretation

Risk quotients (RQs) were calculated following US EPA (1998) by dividing water chemical concentrations (C) by a toxicity reference value (T): RQ = C/T. The toxicity reference values were accepted toxicity measurements [50% lethal concentration (LC_{50}), median effective concentration (EC_{50}), lowest observed effect concentration (LOEC), no observed effect concentration (NOEC), or maximum acceptable toxicant concentration (MATC)]. Calculated RQs identified areas in which additional monitoring and risk characterization might be needed to fully explore potential impacts of aquatic herbicides. The RQs were calculated for all herbicide concentration data collected by the APMP. These calculations are appropriate for initial, US EPA Tier 1 risk characterizations, which are meant to be protective, not predictive, and are therefore based on conservative (*i.e.*, worst case) assumptions about potential exposure and effects (US EPA 1999).

Table 2 Sampling locations and permit holders for each pesticide application evaluated in this study

Pesticide	NPDES permit holder[a]	Treated site	Control site	Target weed	Method of application	Surfactant applied
Acrolein	Merced Irrigation District	LeGrande and Planada canals	Untreated canal section	Macrophyte control	Injection below canal weir	No
Copper sulfate	Marin Municipal Water District	Bon Tempe and Nicasio reservoirs[b]	Lake Lagunitas	Bon Tempe for benthic algae; Nicasio for floating algae	Boat-mounted hopper for benthic, dissolved for floating	No
Copper ethanolamine	Solano Irrigation District	Byrnes Canal	Untreated canal section	Macrophytes and filamentous algae	Injection above canal weir	No
Copper ethanolamine (emulsified)	Potter Valley Irrigation District	Treated canal	Untreated canal section	Macrophytes and filamentous algae	Injection above canal weir	No
Diquat dibromide	Dept. of Boating and Waterways	7-Mile Slough	Untreated slough area	Egeria densa and Myriophyllum aquaticum (parrot feather)	Spray from boat	No
Diquat dibromide	Sand Bay Isles Homeowners Assoc.	Sand Bay Isle Pond	Untreated Sand Bay Isle Pond	Potamogeton pectinatus (sago pondweed)	Spray from boat	No
Glyphosate	US Fish and Wildlife Service and Calif. Dept. of Boating and Waterways	Lower Stone Lake[b]	Upper Stone Lake	Eichhornia crassipes (water hyacinth)	Spray from boat	Yes
Glyphosate	Merced Irrigation District	Atwater Canal	Untreated canal section	Emergent macrophytes	Spray from truck-mounted boom	Yes
Glyphosate	Ventura County Flood Control District	Doris Drain stormwater canal	Untreated canal section	Emergent macrophytes	Spray from truck-mounted boom	Yes
Glyphosate	Orange County Public Works Dept.	Bolsa Chica Canal	Untreated canal section	Emergent macrophytes	Spray from truck-mounted boom	Yes
Fluridone (liquid)	Calif. Dept. of Food and Agriculture	Costa ponds[b]	Untreated pond	Hydrilla verticillata and macrophytes	Spray from boat	No
Fluridone (liquid)	Merced Irrigation District	Main Canal	Untreated canal section	Macrophyte control	Drip injection below canal weir	No
Fluridone (pellet)	Big Bear Municipal Water District	Big Bear Lake treated area	Untreated lake area	Myriophyllum spicatum (Eurasian water milfoil)	Pellets spread by boat	No
Fluridone (pellet)	Calif. Dept. of Food and Agriculture	Clear Lake	Untreated lake area	Hydrilla verticillata	Pellets spread by boat	No
Triclopyr	Calif. Dept. of Food and Agriculture	Bear Creek	Untreated creek section	Emergent macrophytes	Hand spray	Yes
2,4-D	US Fish and Wildlife Service and Dept. of Boating and Waterways	Treated Stone Lake slough	Untreated slough	Eichhornia crassipes	Spray from boat	Yes

a Corresponds to locations identified in Figure 1

b Long-term study sites

Table 3 Herbicide analytical methods and MDLs

Medium	Compound	Method	Target MDL
Water	Acrolein	LC-MS[a]	0.005 μg/L
	Copper	Electrothermal AAS[b]	1.0 μg/L
	2,4-D	HPLC-MS[c]	0.01 μg/L
	Diquat dibromide	HPLC-DAD[d]	0.50 μg/L
	Fluridone	ELISA[e]	0.5 μg/L
		HPLC-MS	0.001 μg/L
		HPLC/DAD	0.001 μg/L
	Glyphosate	HPLC/DAD	5.00 μg/L
	Surfactants	HPLC/DAD	0.20 μg/L
	Triclopyr	LC-MS	0.002 μg/L
Sediment	Copper	Electrothermal AAS	20 μg/kg
		Flame AAS	100 μg/kg
	2,4-D	HPLC-MS	0.1 μg/kg
	Fluridone	HPLC-MS	2.00 μg/kg
		HPLC/DAD	2.00 μg/kg
	Triclopyr	LC-MS	0.20 μg/kg
Tissue	Copper	Electrothermal AAS	20 μg/kg
		Flame AAS	100 μg/kg
	2,4-D	LC-MS	0.1 μg/kg
	Fluridone	HPLC-MS	2.00 μg/kg
		LC-MS	0.20 μg/kg

[a] Liquid chromatography–mass spectrometry

[b] Atomic absorption spectrometry

[c] High-performance liquid chromatography–mass spectrometry

[d] High-performance liquid chromatography/diode array detector

[e] Enzyme-linked immunosorbent assay

Risk quotients were compared to levels of concern (LOCs), which are determined by the US EPA Office of Pesticide Programs (OPP) (US EPA 2006). LOCs are unitless values that allow for simple determination of possible exceedances of regulatory limits (Table 5). If an RQ exceeds an LOC value, further investigation of an application scenario is indicated.

The US EPA interprets exceedances of LOCs as follows:

Acute high risk: high potential for acute risk; regulatory action might be warranted in addition to restricted-use classification.

Acute restricted use: high potential for acute risk; might be mitigated through restricted-use classification.

Acute endangered species: high potential for acute risk to endangered species; might be mitigated through restricted-use classification.

Chronic risk: high potential for chronic risk; regulatory action might be warranted.

For toxicity reference values (TRVs) in the risk quotient calculations, one LC_{50} and one NOEC were sought for each test species (Table 6). Where multiple reference values were available, the most conservative (*i.e.*, the lowest) reference value was used. Care was taken to use reference data for the same herbicide chemical form as that used at the monitoring locations. TRVs used to calculate RQs come from standard toxicity test species, any federally listed or California-listed species, or plants or fish native to California. TRV sources included the US EPA Acquire database, CDFG reports, peer-reviewed academic literature, and other government reports (Table 6).

In addition to RQ calculations, chemical characterization, toxicity tests, and benthic bioassessment data were combined to produce sediment quality triad data summary tables for the pesticides where sediment accumulation was a potential concern (Barbour et al. 1996).

Results and Discussion

Tier 1 Screening

Tier 1 literature review results are summarized in Table 7 and detailed in Siemering et al. (2005). The Tier 1 evaluation ranked acrolein and copper sulfate as the highest priority chemicals for Tier 2 analysis, due to high toxicity, mobility, and public concern (Table 8). Although

Table 4 Bottle types for trace elements and organic chemicals measured

Applied pesticides	Sample bottle type	Reference
Acrolein	Glass	Nordone et al. (1996a, 1996b)
Copper (copper sulfate and chelated copper)	Polyethylene	Diamond et al. (1997); Finlayson (1980)
2,4-D	Glass	Waite et al. (2002); Muir and Grift (1987)
Diquat dibromide	Polyethylene	Poovey et al. (2002); Randall et al. (2003)
Fluridone	Polyethylene	Netherland et al. (2002); Fox et al. (1994)
Glyphosate	Polyethylene	Gardner and Grue (1996); Paveglio et al. (1996); Oppenhuizen and Cowell (1991)
Surfactants	Glass	Loyo-Rosales (2003)
Triclopyr	Glass	Gardner and Grue (1996); Getsinger et al. (2003)

Table 5 Aquatic animal and plant levels of concern

Risk category	Risk quotient	Level of concern
Aquatic animals		
Acute risk	$C/(LC_{50}$ or $EC_{50})$	0.5
Acute restricted use	$C/(LC_{50}$ or $EC_{50})$	0.1
Acute endangered species	$C/(LC_{50}$ or $EC_{50})$	0.05
Chronic risk	$C/(MATC, NOEC,$ or $LOEC)$	1
Aquatic plants		
Acute risk	$C/(LC_{50}$ or $EC_{50})$	1
Acute endangered species	$C/(LC_{50}$ or $NOEC)$	1

glyphosate was ranked the lowest due to chemical characteristics and low toxicity (Table 8), it was among the compounds selected for Tier 2 monitoring because of its heavy use and perceived public concern in California. No Tier 2 monitoring was conducted on imazapyr due to its limited use in California during the study period (CDPR 2003).

Tier 2 Field Monitoring

2,4-D

One application of 2,4-D [in the 2,4-D dimethylamine (DMA) salt formulation] with added surfactant was monitored at Stone Lake National Wildlife Refuge. During this single application, RQs did not indicate the need for further information, nor was toxicity observed (Table 9). Sediment quality triad results also indicated no evidence of pesticide-induced environmental degradation. Bioassessment indicated no significant difference in benthic macroinvertebrate communities before versus two weeks after treatment of a slough (Hayworth and Melwani 2005). Field studies by both Parsons et al. (2001) and the Washington State Department of Ecology (2001) also found that 2,4-D (DMA) applications are unlikely to cause environmental impacts. However, vitellogenin-induction laboratory experiments indicate that 2,4-D might cause endocrine disruption at legal application rates (Xie et al. 2005).

Acrolein

Because acrolein undergoes both rapid volatilization and hydrolysis, standard methods were inadequate for sampling waters to which acrolein had been applied. Sampling in 2002 with standard sample collection procedures yielded measurable results within hours after application (4600 µg/L; Table 9) but not 72 h after application despite measurable results with an in-field colorimetry method. Consequently,

a field sampling method was developed to accurately determine concentrations of acrolein and its derivatives in water, particularly at low concentrations. Two methods were combined to sample at low acrolein water concentrations: (1) addition of 2,4-dinitrophenylhydrazine (DNPH) as a stabilizing agent immediately following sample collection and (2) elimination of all bottle headspace (Siemering 2005).

In 2003, field samples were obtained from the Merced Irrigation District LeGrand and Planada canals 24 h after an acrolein application at the LeGrand Canal headgates. Four samples were collected from each downstream site and one untreated site above the headgates. Three samples from each site were treated with DNPH. All were collected with no bottle headspace and analyzed with liquid chromatography (mass spectrometry (LC-MS) for acrolein and its primary breakdown product 3-hydroxypropanal (3-HPA). The DNPH-treated samples from the LeGrand Canal site had 0.05 µg/L (SD = 0.003) acrolein and 46 µg/L (SD = 4) 3-HPA compared to <0.02 µg/L acrolein and 14 µg/L 3-HPA in the untreated sample (Table 9). The Planada Canal samples had 0.08 µg/L (SD = 0.01) acrolein and 413 µg/L (SD = 15) 3-HPA for DNPH-treated samples compared to <0.02 µg/L acrolein and 42 µg/L 3-HPA for the untreated sample (Table 9). All detected acrolein values were two orders of magnitude below the lowest LC_{50} values (Table 6).

Rapid volatilization precluded standard water toxicity testing of acrolein-treated water samples. However, extremely low acrolein LOEC values suggest that any detectable pesticide presence would cause high mortality to test species. Because of the biocidal nature of acrolein, the development of low-cost phytomonitoring diagnostic response tests (*e.g.*, algal growth on suspended substrate) to detect the presence of acrolein outside of designated treatment areas was attempted, but results were inconclusive (Siemering 2005). Bioassessment results indicated no discernable differences between an acrolein-treated portion of an irrigation canal and a reference station (Hayworth and Melwani 2005).

Although acrolein is highly toxic to target and nontarget plants and animals within the treatment zone, it is not persistent in the environment and had no discernable impact on benthic communities or areas outside but immediately adjacent to the treatment zone. These findings are similar to those of Nordone et al. (1996a, 1998), who found that acrolein and 3-HPA did not persist in irrigation canals and that acrolein was metabolized so rapidly by fish and shellfish that neither it nor its major oxidative and reductive metabolites could be detected in tissue 24 h after a nonlethal exposure.

Copper Sulfate and Chelated Copper Compounds

Copper sulfate applications were monitored in two reservoirs of the Marin Municipal Water District. In the

Table 6 Toxicity reference values used for risk quotient calculations

Herbicide	Test species	LC$_{50}$	NOEC	Units	Source
Acrolein	D. magna	20		μg/L	Macek et al. (1976)
	P. promelas	24	14	μg/L	Spehar (1989)
	Rainbow trout	14		μg/L	Holcombe et al. (1987)
Copper sulfate	C. dubia	60	25	μg/L	Murray-Gulde et al. (2002)
	P. promelas	675.2	125	μg/L	Murray-Gulde et al. (2002)
Copper ethanolamine	C. dubia	91.7	50	μg/L	Murray-Gulde et al. (2002)
	P. promelas	1114.6	375	μg/L	Murray-Gulde et al. (2002)
Copper ethanolamine (emulsified)	C. dubia	56.3	25	μg/L	Murray-Gulde et al. (2002)
	P. promelas	480.8	200	μg/L	Murray-Gulde et al. (2002)
Fluridone	D. magna	3600	200	μg/L	Hamelink (1986)
	P. promelas	6200	1880	μg/L	CDFG (2002)
	Delta smelt	6100	1280	μg/L	CDFG (2002)
	Stonewort	20[a]		μg/L	Burkhart and Stross (1990)
2,4-D (DMA)	D. magna	176	27.5	mg/L	Ward and Boeri (1991)
	P. promelas	285		mg/L	Mayer and Ellersieck (1986)
	P. promelas		17.1	mg/L	Dill et al. (1990) in JMPR (1997)
	Rainbow trout	100		mg/L	Mayer and Ellersieck (1986)
	Delta smelt	149.4	128	mg/L	CDFG (2002)
Diquat dibromide	S. capricornutum	19[a]	44	μg/L	Fairchild et al. (1997)
	D. magna	3000		μg/L	Bishop and Perry (1981)
	P. promelas	1.4	1.1	mg/L	CDFG (2002)
	Duckweed	18[a]	11[b]	μg/L	Fairchild et al. (1997)
	Delta smelt	1.1	0.82	mg/L	CDFG (2002)
Glyphosate	P. promelas	97		mg/L	Folmar et al. (1979)
	Delta smelt	5.5	3.8	mg/L	CDFG (2002)
	Sacramento splittail	3900	1900	μg/L	CDFG (2002)
Triclopyr	S. capricornutum	4.3		mg/L	USEPA (2000)
	D. magna	950		mg/L	Gersich et al. (1984)
	P. promelas	88.5	72.5	mg/L	Mayes et al. (1984)
Surfactant (R-11)[c]	C. dubia	5.7	0.42/0.91[d]	mg/L	CDBW (2003)
	P. promelas	1.1	0.34/0.67[d]	mg/L	CDBW (2003)
	Delta smelt	0.7	0.1/0.19[d]	mg/L	CDBW (2003)
	Sacramento Splittail	3.9	1.9/3.14[d]	mg/L	CDBW (2003)
Surfactant (TPA)	C. dubia	5.5	0.43/0.95[d]	mg/L	CDFG (2004)
	P. promelas	3.0	0.43/0.43[d]	mg/L	CDFG (2004)

[a] EC$_{50}$ value shown

[b] LOEC value shown

[c] R-11 and TPA were found to have similar chemical characteristics (Xie et al. 2005)

[d] 7-day NOEC/7-day LOEC values

reservoir treated with dissolved copper sulfate, a peak Cu concentration of 38.1 μg/L occurred at 24 h postapplication, exceeding both the acute (0.5 × 60 = 30 μg/L) and chronic (1.0 × 25 = 25 μg/L) LOC (Tables 5, 6, and 9). The peak Cu concentration was 7.6 μg/L (Table 9) at one week post application, exceeding the acute restricted use LOC for *Ceriodaphnia* (0.1 × 60 = 6 μg/L). Toxicity to juvenile trout and *Ceriodaphnia* was detected immediately after and up to a week following application.

Sampling in the Bon Tempe Reservoir following treatment with granular copper sulfate for benthic algae control showed dissolved Cu sediment concentrations (0.0016–2.37 mg/L) exceeded a published LC$_{50}$ value (0.042 mg/L)

for *Hyallela* (Mastin and Rodgers 2000). Total Cu sediment concentrations (338–1880 mg/kg) exceeded the National Oceanographic and Atmospheric Administration copper Effects Ratio Low value of 34 mg/kg (NOAA 1999). Significant mortality in *Ceriodaphnia* and juvenile trout was observed immediately after application. Mortality and growth inhibition were also observed in some of the sediment toxicity tests. Finally, sediment quality triad data indicated Cu-induced ecosystem degradation in half of the samples (Table 10). Benthic invertebrate bioassessments indicated lower diversity and abundance and a greater percentage of oligochaete abundance in a Cu-treated reservoir (Bon Tempe) than a nontreated lake (Lagunitas),

Table 7 Tier 1 literature review results summary

Herbicide	Primary use	Mechanism of toxicity	Solubility	Fate	Confounding factors	Data gaps
Acrolein	Nonselective contact aquatic herbicide. Used for submerged macrophytes and algae in habitats with rapid flow, such as irrigation canals and drainage ditches.	Reacts with the sulfhydryl component of enzymes. Breaks down cell walls and disrupts cell ability to inactivate toxins.	208,000 ppm at 20°C	Highly reactive and volatile. Significant microbial degradation typically causes half-life of <1 day to several days. Not retained in sediment. Does not bioaccumulate due to very low K_{ow} (~1).	None identified	Toxicity tests with repeated concentration measurements to account for volatilization. Chronic effects measurements in zooplankton, amphipods, or insects.
Copper sulfate	Nonselective aquatic herbicide/algaecide. Used extensively in drinking water reservoirs.	Photosynthesis and cell growth inhibitor. Cu^{2+} is primary toxic form.	230,550 ppm at 25°C	Highly water soluble with no degradation. Strong particle and dissolved organic carbon (DOC) affinity causes rapid sediment deposition. Transport occurs between water and sediment (advection/flux)	Toxicity is temperature, pH, and hardness dependent, with greater toxicity in softer waters. Bioavailability is influenced by sorption to DOC and particles.	Toxic effects on amphibian embryos and larvae, and chronic effects to benthic invertebrates.
Diquat dibromide	Nonselective contact herbicide for emergent and submerged aquatic plants. Surfactant use recommended for emergent vegetation.	Causes superoxide to be generated during photosynthesis, which damages cell membranes and cytoplasm. Leads to desiccation.	700,000 ppm at 20°C	Water column concentrations typically drop below detection within days to weeks after application. This results from binding to particles and sediment and retention in plant tissue. Biodegradation and photolysis might be minor loss pathways. Low K_{ow} suggests low bioaccumulation potential.	Greater toxicity to fish in soft waters and at low pH. Binds to organic matter (total suspended solids; plant biomass).	Chronic effects on invertebrates (e.g., Hyallela azteca)
Endothall	The potassium and amine salts are selective contact herbicides to control a range of algae, submerged and emergent vegetaion.	Inhibition of messenger RNA activity. Decreasing rate of respiration and lipid metabolism, inhibiting protein synthesis and interfering with normal cell division.	100 g/L at 20°C	Rapidly degrades in water. Half-life is 4–7 days for dipotassium endothall and 7 days for technical endothall in surface water. Biodegrades more slowly in anoxic conditions.	Dimethylalkylamine salt of endothall is more toxic than the dipotassium salt to fish and other nontarget organisms. Increasing water temperature causes a slight increase in toxicity of this formulation.	California resident species. Chronic effects on invertebrates (e.g., Hyallela azteca and Ceriodaphnia dubia)

Table 7 continued

Herbicide	Primary use	Mechanism of toxicity	Solubility	Fate	Confounding factors	Data gaps
Fluridone	Selective aquatic herbicide for submersed and emergent vascular plants in bodies of water with little water movement. Recommended application is 0.1 mg/L. Multiple applications necessary to maintain a concentration between 5 and 20 ppb	Systemic: inhibits production of carotene, which enhances degradation of chlorophyll and inhibits photosynthesis.	12 mg/L at 25°C	Stable to hydrolysis, but photodegrades. Sunlight intensity and penetration are main factors in half-life. Degrades more slowly under anaerobic and low dissolved oxygen (DO) conditions. Low K_{ow} and experiments indicated low potential to bioaccumulate to biomagnify. Half-life in water is 20 days under anaerobic aquatic conditions and up to 9 months.	Not hardness, temperature, pH, or salinity dependent. Binds to organic matter.	Amphibians and macroinvertebrate toxicity test data.
Glyphosate	Systemic herbicide for floating and emergent macrophytes. Surfactant recommended for emergent vegetation	Inhibits a key enzyme (5-enolpyruvylshikimate-3-phosphate (EPSP) synthase) used to make amino acids. Interruption of phenylalinine biosynthesis; inhibition of elongation; photosynthetic disruption.	11.6 g/L at 25°C.	Once glyphosate enters the water column, it is quickly adsorbed to soil particles. Microbial degradation begins immediately and glyphosate is broken down to its metabolite amniomethylphosphonic acid (AMPA) and CO_2. Not expected to bioconcentrate.	Bioavailability influenced by sorption to colloids, DOC, and larger particles.	Resident amphibian embryos and larvae. Toxicity with and without surfactant.
2,4-D	Postemergent systemic herbicide. Often used with a polymer thickener. Surfactant recommended for emergent vegetation control.	Hormone that stimulates stem elongation and nucleic acid/protein synthesis, stimulating uncontrolled growth until death. Affects enzyme activity/respiration/cell division.	571,333 mg/L at 25°C. Precipitates in hard water as Ca/Mg salts.	Rapid hydrolysis to 2,4-D acid, then binds to sediments. Bioaccumulation not expected.	Persistent at temperatures below 7°C	Resident species, aquatic insects.

Table 8 Aquatic herbicide categorical ranking, from 1 (lowest risk) to 5 (highest risk)

Chemical	Selectivity	Toxicity				Chemical characteristics			Public concern	Sum of criteria scores	Final rank
		Indirect	Ecosystem	Terrestrial	Human	Half-life	K_{ow}	Mobility			
Acrolein	5	4	5	2	4	1	1	5	5	32	5
Copper sulfate	2	4	4–5	1–2	1	2[a]	2	2–3	5	26	4
Diquat dibromide	3	4	2–3	1	1	1	1	1	3	18	1
Endothall	2	4	2	1	1	2	3	3	2	19	2
Fluridone	3	2	1	1	1	3	2–3	3	1–2	19	2
Glyphosate	5	1	1	1	1	1	1	1	4	16	1
Triclopyr	1	4	2	1	1	2	3	3	3–4	19	2
2,4-D (salt)	1	3	2–3	1–2	1	2	3	2	3–4	20	3

[a] Bioavailable form

Table 9 Results of Tier 2 chemistry and toxicity monitoring

Compound (N stations)	Concentration range (µg/L)				Toxicity (A = acute, C = chronic 0 = none, — = test not performed)				
	Control[a]	Hours post application	Days post application	Weeks post application	*Selenastrum*[b]	*C. dubia*	*H. azteca*	Fish[c]	*Typha*
2, 4-D (4)	0.14	20	—	ND	0	0	A	A	—
Acrolein (4)	ND	**4600**	0.05–0.08	—	—	—	—	—	—
3-Hydroxypropanol (4)	ND	ND	ND–430	—	—	—	—	—	—
Copper sulfate (22)	**ND–7.9**	**ND–126**	**8–38.1**	**ND–7.6**	—	A, C	A, C	A	—
Chelated copper (16)	ND	**4.2–1430**	ND–2.4	—	—	A, C[d]	A, C[d]	A, C[d]	—
Diquat dibromide (5)	0.79–13.8	**180–400**	**4.33–4.5**	—	A	A, C	C	0	—
Fluridone (12)	ND–0.05	1.34–7.2	—	**0.17–102**	A	0	0	A	A
Glyphosate (4)	ND–13.6	**36.9–820**			A	0	—	0	—
Triclopyr (4)	ND	6.65–250	12		0	0	—	0	—
TPA (22)	**ND–570**	ND–188	ND–2390		—[e]	—[e]	—[e]	—	—
R-11 (10)	ND–25.4	ND–22.6	ND–69.7		—[e]	—[e]	—[e]	—	—

Note: Chemical concentration ranges are presented, with values exceeding 0.5 of acute LC_{50}s (0.1 for endangered species) or 1.0 of chronic LOELs presented in **boldface**. ND = below MDLs (Table 3). Toxicity results indicate whether there was significant difference from negative controls for acute (A) or chronic (C) toxicity. 0 = no significant difference from controls

[a] Either pretreatment or upstream of treatment section

[b] *Selenastrum capricornutum*. For pelleted fluridone, *Typha latifolia* was used

[c] *Pimephales promelas*. For copper herbicides, juvenile *Onchorhynchus mykiss* was used

[d] Toxicity also detected prior to application

[e] Toxicity tests for surfactants not conducted

suggesting a possible adverse impact of Cu treatment on the benthic community (Hayworth and Melwani 2005).

The peak concentration of Cu for the Bon Tempe Reservoir immediately following application was 126 µg/L (Table 9), which exceeded acute and chronic LOCs for *Ceriodaphnia* (30 and 25 µg/L) and the chronic LOC for fathead minnow (125 µg/L; Table 6). The peak concentration 24 h postapplication (8.4 µg/L) exceeded the *Ceriodaphnia* acute restricted use LOC (6 µg/L).

Chelated Cu formulations are likely to have distinct behavior from copper sulfate in aquatic environments, depending on the chelating agent and other adjuvants. Chelated Cu herbicides were therefore monitored during applications in two irrigation canal systems. Solano Irrigation District Byrnes Canal was treated with a product of mixed copper ethanolamines and a Potter Valley Irrigation District canal used the same product of mixed copper ethanolamines in an emulsified formulation. In both systems monitored, the water samples were almost uniformly toxic before and after the applications. This high baseline toxicity precluded definitive conclusions about mixed copper ethanolamines from the toxicity tests.

Table 10 Summary of sediment quality triad data for copper sulfate in Bon Tempe Reservoir or fluridone in Clear Lake

Chemistry	Toxicity	Benthos	Cu (2003)	Cu (2004)	Fluridone	Interpretation
+	+	+	3	5	4	Evidence of pesticide-induced degradation.
−	−	−	0	3	0	No evidence of pesticide-induced degradation.
+	−	−	1	0	2	Pesticide is not bioavailable.
−	+	−	0	1	2	Other pollutants or conditions exist with potential to cause degradation.
−	−	+	0	0	0	Benthic response not due to pesticide.
+	+	−	1	0	0	Pesticide might be stressing the ecosystem.
−	+	+	0	0	0	Other pollutants or conditions are causing degradation.
+	−	+	1	1	1	Pesticide is not bioavailable or benthic response is not due to chemistry.
Total No. of stations	6	10	9			

Note: Numbers indicate total number of sampling stations in each combination. A plus (+) for chemistry indicates a concentration exceeding a Sediment Quality Guideline Effects Range Low for Cu (Suedel et al. 1996) or a Stonewort pore water EC_{50} for fluridone (Burkhart and Stross 1990). A plus (+) for toxicity indicates a significant decrease relative to control in amphipod growth or percent survival (for Cu) or in *Typha* growth or percent germination (for fluridone). A plus (+) for benthos indicates that either chironomid genera richness or total species richness was significantly different from reference stations

In the Byrnes Canal system, chelated Cu herbicide was injected as water flowed through a weir and mixing was achieved rapidly. Monitoring was conducted immediately downstream of the mixing zone and then at points further downstream. Immediately downstream of the mixing zone, treated water concentrations were high enough to exceed acute and chronic LOCs for all test species (Tables 5 and 6) from the time the application began until cessation, with a peak Cu concentration of 1430 µg/L (Table 9). At a point several miles downstream, only acute restricted use LOC exceedances were observed for *Ceriodaphnia*, indicating dilution of the herbicide. In the Potter Valley Irrigation District canal treated with emulsified mixed copper ethanolamines, monitoring was conducted at only one station several kilometers downstream of the application point, and no risk quotient LOC exceedance was observed.

Monitoring of Cu-based herbicide applications (chelated and nonchelated) indicated the need for additional monitoring due to RQ exceedances, water toxicity, accumulation in sediment, and possible benthic community degradation. However, depending on the characteristics of the treated water body, most of the applied copper will likely rapidly become sequestered. Haughey et al. (2000) and Gallagher et al. (2005) found that Cu accumulated in reservoir sediment was not bioavailable under normal conditions. Hullebusch et al. (2002) found that Cu content in the water column only returned to its background level two months after Cu addition, but they speculated that this Cu was not truly dissolved Cu due to the high level of natural organic matter in the water. An anodic stripping voltammetry method described by Deaver and Rodgers (1996) would likely provide better data on the amount of "available" Cu present following a Cu-based herbicide treatment, but it is beyond the technical capabilities of most organizations conducting monitoring.

Diquat Dibromide

Diquat dibromide was sampled at two locations: a small pond (Sand Bay Isle) and a slough in the Sacramento-San Joaquin River Delta (7-Mile Slough/DBW). RQ calculations of preapplication samples from the slough showed acute *Selenastrum* exceedances and acute and chronic duckweed exceedances (Table 9). This slough receives inputs from surrounding agricultural lands that are commonly treated with terrestrial-use labeled forms of diquat.

At one hour after application, diquat RQs exceeded acute and chronic LOCs for *Selenastrum* and duckweed (peak RQ of 36.36) and acute restricted use LOCs for fathead minnow and Delta smelt (RQ of 0.36) in both locations. Diquat levels at 7-Mile Slough also exceeded *Selenastrum* acute restricted-use LOCs 24 h after application. Water toxicity tests indicated toxicity in the samples taken from 7-Mile Slough after application but not in water samples from Sand Bay Isle Pond.

Based on a number of LOC exceedances as well as some toxicity, additional risk characterization of diquat dibromide applications are warranted. However, other studies have found that diquat is not persistent in water (Grzenda et al. 1966; Langeland and Warner 1986; Langeland et al. 1994) and is rapidly removed from water by plants and sediment (Coats et al. 1964; Simsiman 1976). The results from the monitoring of 7-Mile Slough might have been compromised by terrestrial inputs of diquat dibromide, as

this herbicide is in widespread use in the surrounding farmland.

Fluridone

Liquid fluridone concentrations at Merced Irrigation District's Main Canal increased progressively over three sampling periods from below detection (preapplication) to 37 µg/L (during application) to 102 µg/L (4 weeks after application) (Table 9). Liquid fluridone concentrations at the Costa Ponds/CDFA site ranged from 0.05 µg/L (pre-application) to 7.2 µg/L (1 h postapplication). At Big Bear Lake (Big Bear MWD), pelleted fluridone applications resulted in sediment fluridone concentrations ranging from 5.88 to 300 µg/kg. Sediment toxicity at Big Bear Lake could not clearly be attributed to fluridone. A long-term study of pelleted fluridone at Clear Lake (Clear Lake/CDFA) found sublethal toxicity (decreased shoot and root length) to *Typha*, indicating a potential for impacts to nontarget plants (Siemering 2005). Sediment quality triad data also indicated the potential for nontarget impacts (Table 10). Also, the peak concentration risk quotient (5.10) for stonewort growth (EC_{50} of 20 µg/L) did exceed the acute LOC (0.5; Table 5). Fluridone (applied in pellet or liquid form) at either location was not found to be definitively toxic to or have LOC exceedances for *C. dubia*, *P. promelas*, Delta smelt, or sediment amphipods.

Toxicity to *Typha* at the Clear Lake site indicates the potential for nontarget plant impacts. Fluridone in sediment can remain toxic to plants up to 70 weeks after treatment (Muir et al. 1980) and its dissipation is variable (West et al. 1983). Fluridone was persistent in Clear Lake sediments up to 3 years after treatment (406 ppb), although redistribution within the lake cannot be ruled out. This persistence might interfere with recolonization by native plants following application, although Madsen et al. (2002) found that long-term application of fluridone did not significantly impact the native plant species' diversity. Fluridone has been the predominant Clear Lake *Hydrilla* control agent for 10 years. Its primacy is cause for concern, as this treatment regime is similar to that which led to the development of herbicide-resistant *Hydrilla* in Florida (Arias et al. 2004; Koschnick et al. 2006).

Glyphosate

At the Orange County Public Works Department Doris Drain and Ventura County Bolsa Chica Canal, Delta smelt and Sacramento splittail acute restricted-use and acute endangered-species LOCs were exceeded within 1 h of glyphosate spray application (peak concentration of 1800 µg/L; Table 9). No LOC exceedance was observed 24 h after treatment at either site. Both of these canals were very small, with little possibility of dilution. At two sites where larger channels were treated (Merced Irrigation District Atwater Canal and Stone Lake National Wildlife Refuge Lower Stone Lake), there were no LOC exceedance. However, glyphosate is often applied with a surfactant that might have much higher toxicity than the active ingredient. Although surfactants were used with all four monitored applications, no toxicity was found (Table 9). Other field studies of glyphosate and glyphosate + surfactant applications have reported similar results (Gardner and Grue 1996; Henry et al. 1994; Linz et al. 1999; Simenstad et al. 1996).

Based solely on toxicity data, no further risk characterization associated with glyphosate applications alone is warranted. The RQ calculations indicate the potential need for further characterization only if sensitive species are present and the volume of water treated is small.

Triclopyr

Triclopyr was monitored during one application to a stream (Bear Creek/CDFA). Triclopyr peak concentration RQs resulted in no LOC exceedance. The peak triclopyr concentration (250 µg/L; Table 9) was well below the LC_{50} of the most sensitive test organism (4300 µg/L for *S. capricornutum*). Petty et al. (2003) found that results from laboratory and field studies indicated that dissipation rates of the parent triclopyr and its metabolites are similar and relatively rapid. The Washington State Department of Ecology (2004) determined that there is little chance of impacts to aquatic animals and manageable potential impacts to nontarget plants. Data from our single monitoring site showed similar results.

Nonionic Surfactants

When treating floating or emergent vegetation, surfactants are generally necessary and suggested by the registration label to increase herbicide effectiveness. Surfactants are tank-mixed with herbicides immediately prior to application. This practice is of concern because surfactants can be orders of magnitude more toxic to aquatic organisms than the herbicide (Giesy et al. 2000 and references therein), there is typically little available toxicological information about them, and each might have a different toxicological profile (Haller and Stocker 2003). Because surfactants do not directly cause plant mortality, they do not undergo the scrutiny that active ingredients do under FIFRA regulations.

Six APMP sites used one of two NPE-based surfactants: TPA and R-11. Due to the lack of published toxicological data on these compounds, the CDFG Aquatic Toxicology Laboratory determined 7-day LC_{50}, NOEC, and LOEC values for both (Table 6) and they are similar to those determined by Smith et al. (2004). R-11 was used at the Stone Lake National Wildlife Refuge with 2,4-D and glyphosate to control water hyacinth. TPA was used with glyphosate by the Orange County Public Works Department, Ventura County Flood Control District, and Merced Irrigation District and with triclopyr by the California Department of Food and Agriculture.

At the triclopyr/TPA application site (Bear Creek), acute restricted-use and chronic risk LOCs were exceeded for *C. dubia* and *P. promelas* preapplication (570 µg/L; Table 9) and 24 h after application (2390 µg/L; Table 9). These two NPE concentrations are likely due to discharge of waste upstream of the application point. NPEs are found in many commonly used industrial and household cleaners (Dow Chemical 2006). Surfactant concentrations were also found at the CDBW diquat dibromide application site (where no surfactant was used for the application) and registered an acute restricted-use LOC exceedance for Delta smelt (69.7 µg/L), again showing the ubiquity of this chemical. Although only limited LOC exceedances were found, vitellogenin-induction experiments in rainbow trout indicate that these surfactants can be endocrine disruptors at typical application rates (Xie et al. 2005), suggesting a need for research and monitoring beyond that typical of permit-compliance monitoring.

At the conclusion of the APMP, it was recommended to the SWRCB that full risk characterizations be performed for all surfactants used in California. In the 2004 permit revision, the SWRCB required chemical monitoring of any NPE containing surfactants that effectively stopped their use while monitoring was required. However, users simply switched to an alternative surfactant about which little is known.

Conclusions and Information Needs

Worst-case scenario monitoring and studies conducted over 3 years showed limited indication of short-term and no long-term toxicity definitively due to aquatic herbicide applications (Table 9). RQ calculations showed the need for limited additional risk characterizations for glyphosate and fluridone and more extensive risk characterizations for diquat dibromide, chelated Cu products, and copper sulfate. Triclopyr RQ calculations suggested no further need for risk characterizations, although only a single station was monitored.

Surfactants and other adjuvants applied with aquatic herbicides are more likely to cause ecosystem impacts. Few chemical monitoring or toxicity data are available for the vast majority of the adjuvant chemicals in use and full risk characterizations are warranted for all adjuvant compounds. In one Tier 3 study from this monitoring program, NPE surfactants and 2,4-D DMA were shown to cause vitellogenin induction in rainbow trout (Xie et al. 2005). However, NPEs are ubiquitous in industrial, household, and agricultural chemicals, and the relative amount contributed by aquatic herbicide applications might be comparatively small. Similarly, terrestrial applications of 2,4-D DMA far exceed the amounts used in aquatic applications. The effects of terrestrially applied herbicides, through runoff and drift, on the aquatic system were not studied.

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