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AQUATIC PESTICDES MONITORING PROGRAM

Aquatics Herbicides: Overview of Usage, Fate and Transport, Potential Environmental Risk, and Future Recommendations for the Sacramento-San Joaquin Delta and Central Valley

DRAFT

A White Paper Submitted to the Interagency Ecological Program Contaminants Work Group

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1. Introduction

1.1. Aim

This document summarizes the current knowledge of the potential role of aquatic herbicides in the decline of pelagic organisms in the upper San Francisco estuary, including Suisun Bay and the Sacramento-San Joaquin River Delta. Most of the information was gathered by the Aquatic Pesticide Monitoring Program (APMP), funded by the California State Water Resources Control Board, and through collaborations with aquatic herbicide applicators throughout the state. The APMP conducted research on aquatic pesticides, including insecticides and herbicides. Only the results pertaining to the aquatic herbicides (including algaecides) are presented in this paper.

The remainder of this introduction presents the reasons for the study, a brief introduction to the aquatic herbicides used in California, recent regulatory issues, and current herbicide use in response to those issues. Section 2 presents more information about the individual herbicides, their transport, and environmental fates. Section 3 describes the design of and presents results from the APMP. Two issues of special concern— (1) the use of unregulated adjuvants and (2) adjuvant and herbicide induced endocrine disruption—are discussed in Section 4. Section 5 briefly reviews issues concerning analytical methods. Sections 6 and 7 present conclusions, information needs, and recommendations for further study.

1.2. The Problem—Pelagic Organism Decline in the Delta

Fish populations in the Sacramento-San Joaquin River Delta have declined dramatically over recent years. The reasons for the declines are not yet known but probably result from several factors. The California Department of Water Resources (DWR) Interagency Ecological Program (IEP) is currently considering three broad areas of concern: effects of water projects, invasive species, and toxins. Water projects in the Delta may have altered nursery grounds for young fishes, and invasive phytoplankton, zooplankton, and larger consumers, such has clams and jellies, may have affected food webs. Studies of toxins are focusing on recent increases in blooms of toxin-producing blue-green algae, increased use of pyrethroid pesticides, and herbicides.

The use of organic and copper-based herbicides to control aquatic plants and algal blooms has been identified in the IEP Pelagic Organism Decline (POD) workplan as a possible cause of aquatic-biota toxicity in the Delta. In addition to registered aquatic herbicides, non-registered tank-mixed adjuvants (compounds added to herbicide formulations to facilitate their effectiveness or application) may also be a significant stressor on pelagic organisms of the food webs in the Delta. These adjuvants vary widely in toxicity, modes of action, and chemical class. Some adjuvants are known to have endocrine-disrupting properties, and there is little to no toxicity data for most of them.

1.3. Aquatic Herbicides

Aquatic herbicides include a variety of organic chemicals and copper-based products that have been registered for aquatic use by the U.S. Environmental Protection Agency (USEPA) and the California Department of Pesticide Regulation (DPR) and that are applied directly to waterbodies to control nuisance weeds and algal blooms. Registered aquatic herbicides in California include acrolein, copper sulfate, chelated copper, diquat dibromide, endothall, fluridone, imazapyr, and 2,4-D, marketed under a variety of trade names (Table 1).

Aquatic herbicides can be effective tools to control unwanted vegetation, but no significant detrimental impacts to public health or the environment should result from their use. It has been difficult to assess the effects of aquatic herbicides on the environments to which they are applied because of a lack of field-collected data on the environmental and toxicological effects on organisms other than surrogate laboratory species and a lack of data on confounding interactions with environmental factors.

Table 1. California Registered Aquatic Herbicides and Algaecides

Active Ingredient	Trade Name(s)[1]	Registrant
Acrolein	Magnacide H	Baker Petrolite
Copper sulfate	Multiple	Multiple
Chelated Copper	Cutrine, Clearigate	Multiple
Diquat Dibromide	Reward	Syngenta
Endothall	Aquatthol	Cerexagri
Fluridone	Sonar	SePRO
Glyphosate	Aquamaster, Rodeo	Monsanto, Dow
Imazapyr	Habitat	BASF
Triclopyr	Renovate	SePRO
2,4-D DMA	Weedar 64	Multiple

[1]Trade name listing is not exhaustive

The active ingredients found in many aquatic herbicides are the same as those commonly used in terrestrial herbicides, however, the exact formulations (that is, the active ingredient and any adjuvants) usually differ. For example, the terrestrial-use form of glyphosate, known as Roundup, contains nonlyphenol ethoxylate (NPE) surfactants that are toxic to aquatic organisms, while the aquatic-use form, AquaMaster, does not include surfactants. The exact formulation used for aquatic applications must be considered when evaluating their potential impacts. (Note that herbicides applied to flooded rice fields are considered terrestrial rather than aquatic applications.)

Several of the chemicals listed in Table 1 are produced in multiple forms, which may have very different toxicological profiles and of which only one or possibly two will have the aquatic-use label. The aquatic-use forms of compounds with multiple herbicide registrations are shown in Table 2.

Table 2. Specific Herbicide Compounds with Aquatic Use Label

General Herbicide Name	Herbicide Form with Aquatic Use Label
2,4-D	2,4-D dimethyl acetate (DMA)
	2,4-D butoxyethyl ester (BEE)
Triclopyr	Triclopyr triethylamine (TEA)
Chelated Copper	Copper ethanolamine
	Copper carbonate
Glyphosate	Glyphosate isopropyl amine
Endothall	Dipotassium salt of endothall

1.4. Recent Regulatory Issues and Aquatic Pesticide Monitoring

Recent use of aquatic herbicides in the Delta has been affected by legal and regulatory issues. In 2001, the U.S. Ninth Circuit Court of Appeals ruled in *Headwaters, Inc. v. Talent Irrigation District* 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 State Water Board issued an emergency NPDES permit in July 2001, but that that action was also challenged in court (*Waterkeepers of Northern California v. State Water Resources Control Board*, Alameda County Superior Court No. 2001-022050). Consequently, there were no legal applications of aquatic herbicides in the 2001 application season (generally April-September).

The legal challenge was settled with an agreement that the State Water Board would fund the APMP, an aquatic pesticide research and monitoring program, from which an acceptable general NPDES permit would be developed. The San Francisco Estuary Institute (SFEI), a non-profit research organization with a Board of Directors including scientists, environmentalists, regulators, and dischargers to San Francisco Bay, was designated to implement the APMP. The settlement mandated the expenditure of $1,950,000 for monitoring and research and $600,000 on the analysis and development of alternatives to the use of chemical aquatic pesticides.

SFEI conducted the following studies of registered aquatic pesticides throughout California over a period of three consecutive years:

1) Assessment of fate and transport of applied materials and breakdown products, including residence times in the environment, mass loading, and bioaccumulation.

2) Assessment of impacts to beneficial uses, including assessments of potential routes of exposure, effects monitoring on a range of species, and biochemical and/or physiological testing of sublethal effects such as reproduction and growth.

3) Characterization of sediments in areas suspected of potential sediment accumulation.

4) Characterization of accumulation in organisms where potential persistence or bioaccumulation is suspected.

5) Monitoring of community parameters, such as organism diversity and health, including evaluations of nontarget plants and animals.

These studies were used to develop a statewide general NPDES permit for the discharge of aquatic pesticides for aquatic weed control, which was issued in the spring of 2004. The permit requires individual permittees to conduct chemical characterizations and monitoring of aquatic-use-labeled herbicides and tank-mixed surfactants containing NPE before and after application. To ease the burden on individual herbicide applicators and to answer continued, more general concerns, the State Water Board directed staff to develop a joint or regional monitoring option for permittees. However, no timeline for

development of such an option has been specified and it has not been a State Water Baord priority.

1.5. Recent Aquatic Herbicide Use in the Delta

During the 2001 application season, when the legal use of aquatic herbicides was not possible, aquatic weeds that had been close to being controlled spread extensively throughout the upper regions of the Delta. Consequently, the acreage requiring and receiving treatment by the California Department of Boating and Waterways (DBW) increased when applications were again permitted, although in many cases, DBW has not yet achieved control of nuisance plants.

Anecdotally, the aquatic plant control community has suggested that the total number of applications decreased following the recent legal rulings, in response to the substantial permitting and permit-required monitoring. Prior to 2001, small landowners might have treated limited areas once or twice a summer, for a total cost of a few hundred dollars for the chemical purchase and an applicator. Currently, procuring an NPDES permit costs $1000, and the associated monitoring for a single application costs approximately $1500. To mitigate these cost increases, some applicators have joined together under large application plans, others have turned to nonchemical methods of weed control, and some landowners no longer attempt to control aquatic weeds.

While direct aquatic applications may have declined, the Delta continues to receive inputs of herbicides from terrestrial weed-control applications, through spray drift and runoff. Most of the active chemicals used in aquatic formulations are also used for terrestrial applications, and quantities used for terrestrial weed control are far greater. For example, the California Department of Pesticide Regulation's Pesticide Use Report (PUR) data show that in 2003, about 200,000 pounds of copper sulfate pentahydrate, the primary algaecide used by drinking water utilities, was used for "water area" while about 3,000,000 pounds were used on "rice" (CDPR 2003).

The multiple sources of and the complexity of the other stressors found in the Delta confounded APMP monitoring efforts to determine impacts of aquatic herbicide applications within the Delta on declines of pelagic organisms. Therefore, the APMP

focused efforts on areas where confounding factors were not present or could be accounted for.

1.6. A Note on Use of the DPR PUR Database

When a pesticide is used, the applicator is required to submit detailed information concerning the application to the DPR PUR database. Unfortunately, the PUR does not differentiate between aquatic and terrestrial applications. Therefore, the applicator is left to determine the best use category under which to classify a particular application. Some categories are obviously aquatic, while others are not. Several defined uses may include aquatic applications, for example, Water Area, Rights of Way, Regulatory Pest Control, Public Health, Ditch Bank, Un-Cultivated Non-Ag, and Landscape Maintenance. Table 3 below lists the amounts likely used for aquatic applications along with the total statewide usage for each herbicide studied.

For example, fluridone is registered for aquatic weed control only. However, in the 2003 PUR Summary Report usage is reported in the categories of Landscape Maintenance, Regulatory Pest Control, Rights of Way, Unknown, and Water Area. For herbicides with terrestrial and aquatic labels it is impossible to say with certainty how much is being used for aquatic applications.

Table 3. Aquatic Herbicide Poundage Applied 2001-2003

Active Ingredient	2001[1] (total applied)	2002[1] (total applied)	2003[1] (total applied)
Acrolein	233,199 (233,928)	283,192 (283,540)	272,732 (272,732)
Copper sulfate	158,811 (4,054,735)	119,584 (3,793,198)	231,729 (5,090,597)
Chelated Copper	4,354 (21,592)	6,511 (52,599)	2,305 (23,371)
Diquat Dibromide	3,538 (63,896)	4,655 (62,657)	1,791 (66,154)
Endothall	466 (1,755)	1,438 (4,124)	402 (3,166)
Fluridone	3,937 (3,937)	4,183 (4,549)	2,686 (3,012)
Glyphosate	4,333 (4,406,667)	9,922 (5,625,731)	7,734 (5,630,143)
Imazapyr	0 (15,758)	0.5161 (15,475)	0.4379 (11,975)
Triclopyr	0 (75,329)	1.59 (73,935)	9.4 (60,697)
2,4-D DMA	126 (398,568)	239 (452,154)	355 (512,827)

[1]The aquatic herbicide poundage listed is determined by the authors best estimates based on professional experience. PUR reporting procedures make it impossible to determine exact amounts for many chemicals.

2. Environmental Transport and Fate

Because individual aquatic herbicides differ considerably in their chemical compositions, their transport and fates in the environment also differ considerably. This section summarizes information about the individual herbicides, their modes of action, use patterns, and on the physical and chemical properties that influence their transport

and fate. All the information included in this section is excerpted from the APMP literature review. This review may be found in its entirety at www.sfei.org. Summary tables for each herbicide identify data gaps that may require further study before complete assessments can be made.

2.1. Acrolein

Acrolein is a nonselective algaecide and aquatic herbicide that reacts with various vital proteins and breaks down cell walls. When used as an aquatic herbicide, acrolein controls submersed and floating vegetation in irrigation canals and drainage ditches. It is extremely water soluble; application is made by injecting the chemical into flowing water at a point of good mixing, such as downstream of a weir or siphon. The dead plant tissues gradually disintegrate and float downstream, with the disintegration taking from three days to two weeks. Acrolein has also been used in the manufacture of colloidal forms of metals; making plastics, perfumes, and other chemicals; as a warning agent in methyl chloride refrigerant; and in military poison-gas mixtures. Usage, key physical characteristics, and data gaps for acrolein are summarized in Table 4.

Studies under natural and sterile water/sediment conditions have indicated that microbial degradation plays a significant role in the transformation of acrolein in aquatic systems, with a reduction in half-life being associated with the presence of viable microbial populations (Smith et al. 1995). In a California field-dissipation study, the half-life of acrolein was 7.5 hours in a canal without weeds and 10 hours in a weeded canal (Baker Petrolite Corporation 1990).

In the Baker studies, both sterile and non-sterile systems resulted in the production of the primary hydrolytic degradation product, 3-hydroxypropanal. Several metabolic products that were ephemeral in nature were also found, including acrylic acid, allyl alcohol, propionic acid, propanol, and 3-hydroxypropionic acid. The terminal metabolites were oxalic acid and carbon dioxide. Acrolein is metabolized easily in soil and is mineralized to CO_2. In field-dissipation studies, a DT_{50} of 7.5-10.2 hours was detected. Metabolic pathways involving oxidation, reduction, and hydration have been proposed (Tomlin 2000).

Table 4. Acrolein Summary Table

Primary use	Nonselective contact aquatic herbicide. Used for submerged macrophytes and algae in habitats with rapid flow, such as irrigation canals and drainage ditches.
Mechanism of Toxicity	Reacts with the sulfhydryl component of enzymes. Breaks down cell walls and disrupts cell's ability to inactivate toxins.
Solubility	208,000 ppm at 20° C
Fate	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 log K_{ow} (~1.0).
Confounding Factors	None identified
Data Gaps	Toxicity tests with repeated concentration measurements to account for volatilization. Chronic effects measurements in zooplankton, amphipods, or insects.

2.2. Copper Sulfate and Chelated Copper Forms

Copper sulfate is a naturally occurring inorganic salt. In addition to its use as a herbicide, copper is an essential trace element for plant and animal nutrition. Copper sulfate is used as an aquatic herbicide in both the copper sulfate and copper sulfate pentahydrate forms. Chelated copper herbicides are typically copper ethanolamine complexes or copper carbonate. Their formulations are designed keep the active copper in solution as long as possible. The toxicologies of the chelated copper forms are distinct from copper sulfate and from each other. Usage, key physical characteristics, and data gaps for copper are summarized in Table 5.

Copper sulfate is used as a fungicide, algaecide, and molluscicide. As a fungicide, it is used to control bacterial and fungal diseases of fruit, vegetable, nut, and field crops, including mildew, leaf spots, blights, and apple scab. Copper sulfate is used as an algaecide in irrigation and municipal water-treatment systems. Chelated copper herbicides are used for macrophyte control and as algaecides. Because high concentrations are necessary to kill macrophytes, chelated copper treatments are typically only carried out in irrigation-district feed-water canals with minimal chance of discharge to natural waterbodies.

Three processes control the fate of copper in the environment: transport to lower soil levels by groundwater percolation; binding to soil components; and breakdown into metabolites (Hartley 1983). Copper is considered to be among the more mobile of the heavy metals in surface environments. Copper is bound, or adsorbed, to organic

materials, and to clay and mineral surfaces, depending on the level of acidity or alkalinity of the soil. The distance that copper travels in soil is limited by its strong adsorption to many types of surfaces. Although copper sulfate is highly water soluble, the copper ions are strongly adsorbed or precipitated to soil particles (EXTOXNET 1996), and the leaching potential is low in all but sandy soils.

Table 5. Copper Summary Table

Primary use	Aquatic herbicide – algaecide. Used extensively in drinking water reservoirs.
Mechanism of Toxicity	Photosynthesis and cell growth inhibitor. Cu^{2+} is primary toxic form.
Solubility	230,550 ppm at 25° C (anhydrous)
Fate	Highly water soluble with no degradation. Strong particle and DOC affinity causes rapid sediment deposition. Transport occurs between water and sediment (advection/flux).
Confounding Factors	Toxicity is temperature, pH, and hardness dependent, with greater toxicity in softer waters. Bioavailability is influenced by sorption to DOC and particles.
Data Gaps	Toxic effects on amphibian embryos and larvae, and chronic effects to benthic invertebrates.

2.3. Diquat Dibromide

Diquat dibromide is a quick-acting contact herbicide and plant growth regulator causing injury only to the parts of the plant to which it is applied. It causes superoxide production during photosynthesis, which damages cell membranes and cytoplasm. As a nonselective desiccant, it dries all vegetative material it contacts. Usage, key physical characteristics, and data gaps for diquat dibromide are summarized in Table 6.

Studies suggest that diquat dibromide is not persistent in water, its environmental fate being governed primarily by its adsorption to soil and plant matter, evidenced by its high organic carbon coefficients (Ferguson et al. 1994). In the presence of soil and sediment particles, it is rapidly biologically inactivated through its strong binding to the clay minerals. Uptake of diquat dibromide into aquatic macrophytes has been observed (Newman and Way 1966, Cavell and McIntosh 1976, Austin and Calderbank 1964); however, the simultaneous high adsorption to sediments and the lack of measurable residues in the dissolved phase make adsorption coefficients difficult to determine. Adsorption to minerals is rapid and complete with only trace amounts (less than 0.01%) remaining in solution. Once adsorbed and no longer available to target organisms, diquat

can remain in the soil environment for an extended period of time. Diquat has been found in the pools and pond sediment four years after application (Gangstad 1986).

Diquat dibromide remaining in the water column is degraded by microorganisms (Summers 1980) with a half-life of less than 48 hours in water (EXTOXNET 1996). In addition to microbial degradation, photochemical degradation is important and can be rapid in aqueous solutions or on plant surfaces and depends on the characteristics of the aqueous system and the presence of plants (Tegala and Skidmore, 1987, WHO 1984). Processes such as hydrolysis, volatilization, and oxidation are relatively insignificant.

Table 6. Diquat Dibromide Summary Table

Primary use	Non-selective contact herbicide for emergent and submerged aquatic plants. Surfactant use is recommended for applications to emergent plants.
Mechanism of Toxicity	Causes superoxide to be generated during photosynthesis, which damages cell membranes and cytoplasm. Leads to desiccation.
Solubility	700,000 ppm at 20 ° C
Fate	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 may be minor loss pathways. Low K_{ow} suggests low bioaccumulation potential.
Confounding Factors	Greater toxicity to fish in soft waters and at low pH. Binds to organic matter (TSS; plant biomass).
Data Gaps	Chronic effects on invertebrates (e.g. *Hyallela azteca*)

2.4. Endothall

Endothall is a selective contact herbicide and a member of the dicarboxylic acid chemical class (Thomson 1993, Bohmont 1981). The potassium and amine salts of endothall are used to control a variety of plants, including plankton, pondweed, niad, coontail, milfoil, elodea, and algae in waterbodies and rice fields. Endothall is also used to control annual grass and broadleaf weeds in sugar beets, spinach, and turf fields. Usage, key physical characteristics, and data gaps for endothall are summarized in Table 7.

Endothall is highly mobile in soil; however, rapid degradation limits the extent to which it is leached. Endothall disappears from soils in 7 to 21 days (Kidd and James

1991). Half-lives have been measured as 4 to 5 days in clay soils and 9 days in soils with high organic content (Howard 1991).

Endothall is rapidly degraded in water (Kidd and James 1991, USEPA 1994). The half-lives in surface waters have been measured as 4 to 7 days for dipotassium endothall and about 7 days for technical endothall (Reinert 1987). Biodegradation occurs more slowly in the absence of air (Howard 1991).

Table 7. Endothall Summary Table

Primary use	The potassium and amine salts of endothall are used as selective, contact aquatic herbicides to control a variety of plants including plankton, pondweed, niad, coontail, milfoil, elodea, and algae in water bodies and rice fields at 2-6kg active ingredient /ha.
Mechanism of Toxicity	Inhibition of messenger RNA activity. Decreasing rate of respiration and lipid metabolism, inhibiting protein synthesis and interfering with normal cell division.
Solubility	100 g/L at 20°C
Fate	Endothall is rapidly degraded in water. Its half-life is 4 to 7 days for dipotassium endothall and about 7 days for technical endothall in surface water. It biodegrades more slowly in anoxic conditions.
Confounding Factors	Dimethylalkylamine salt of endothall is more toxic than the dipotassium salt to fish and other non-target organisms. Increasing water temperature causes a slight increase in toxicity of this formulation.
Data Gaps	Resident species. Chronic effects on invertebrates (e.g. *Hyallela azteca* and *Ceriodaphnia*).

2.5. Fluridone

Fluridone is a selective systemic herbicide used to control submerged and emergent aquatic plants. Fluridone reduces carotenoid biosynthesis by inhibition of phytoene desaturase, which causes chlorophyll depletion and subsequent inhibition of photosynthesis. Fluridone takes 30 to 90 days to kill target plants and should be applied before or just after plants start their seasonal growth (WSDE 2001). Usage, key physical characteristics, and data gaps for fluridone are summarized in Table 8.

Fluridone is most strongly sorbed to hydrosoils of high organic matter and silt content. Muir et al. (1980) found that more than 50% of the herbicide applied to ponds could not be accounted for ten days after application. Microorganisms have been found to be major factors in degradation of fluridone in terrestrial soils (PMEP 1986). In another field study, extensive photodegradation resulted in no major degradation products of fluridone being identified (Muir and Grift 1982b).

Table 8. Fluridone Summary Table

Primary use	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 5-20 ppb.
Mechanism of Toxicity	Systemic - inhibits production of carotene, which enhances degradation of chlorophyll and inhibits photosynthesis.
Solubility	12 mg/L at 25° C
Fate	Stable to hydrolysis, but photodegrades; sunlight intensity/penetration are main factors in half-life. Degrades more slowly under anaerobic and low DO conditions. Low K_{OW} and experiments indicated low potential to bioaccumulate or biomagnify. Half-life in water is 20 days under anaerobic aquatic condition up to 9 months.
Confounding Factors	Not hardness, temperature, pH or salinity dependent. Binds to organic matter.
Data Gaps	Amphibians and macroinvertebrates.

2.6. Glyphosate

Glyphosate is a nonselective, post-emergent, and systemic herbicide used on agricultural and nonagricultural areas around the world (WHO 1994). It works by inhibiting the synthesis of the enzyme 5-enolpyruvylshikimic acid-3-phosphate synthase (EPSP), which is needed for production of aromatic amino acids: tyrosine, tryptophan, and phenylalanine. These amino acids aid in synthesis of proteins that link primary and secondary metabolism (Tu et al. 2001). Glyphosate is not effective on submerged or mostly submerged foliage and therefore is only applied to control emergent foliage (WSDE 2001). Glyphosate is commonly sold as Rodeo or AquaMaster in the formulation of isopropylammonium. Glyphosate is relatively nontoxic to animals because it acts on plant enzymes that are not present in animals (Tu et al. 2001). Usage, key physical characteristics, and data gaps for glyphosate are summarized in Table 9.

Glyphosate adsorbs strongly to soil particles once it has enters the water, and this strong adsorption prevents excessive movement in the environment (Schuette 1998). Strong adsorption slows microbial degradation leading to possible persistence of one year (Tu et al. 2001). Glyphosate is readily degraded to aminomethylphosphonic acid (AMPA) by soil microbes, and AMPA is then degraded to carbon dioxide (Gardner and Grue 1996, USEPA 1993). The primary metabolite of glyphosate, AMPA is nontoxic and degrades microbially more slowly than its parent compound (Tu et al. 2001).

Glyphosate is highly water-soluble at 11,600 ppm at 25°C (Schuette 1998, Tu et al. 2001). The half-life of glyphosate in water ranges from 35 to 63 days (Glyphosate Herbicide Fact Sheet). Degradation of glyphosate in water is generally slow, because there are usually fewer microorganisms than in soil (Schuette 1998). Photodegradation may also aid in breakdown. The half-life of glyphosate in deionized water under ultraviolet light was reported by Lund-Hoie and Friestad (1986) to be four days, degrading into AMPA (Tu et al. 2001, Gardner and Grue 1996). Hydrolysis and oxidation do not readily occur in the field (Tu et al. 2001). Glyphosate has a hydrolysis half-life of more than 35 days with little propensity toward hydrolytic decomposition (Schuette 1998).

Table 9. Glyphosate Summary Table

Primary use	Systemic herbicide for floating and emergent plants (duckweed, loosestrife, cattails, etc.). Surfactant use is recommended for emergent plant applications.
Mechanism of Toxicity	Inhibits a key enzyme that plants and bacteria use to make amino acids called EPSP synthase. Structurally, glyphosate resembles the chemical structure of the amino acid glycine. Because of its structural similarity to glycine, glyphosate binds the active site of the EPSP synthase enzyme that is critical for the production of aromatic amino acids. Interruption of biosynthesis of phenylalinine; inhibition of elongation; photosynthetic disruption.
Solubility	11.6 g/L at 25°C
Fate	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.
Confounding Factors	Bioavailability influenced by sorption to colloids, DOC, and larger particles.
Data Gaps	Resident amphibian embryos and larvae. Toxicity with and without surfactant.

2.7. Triclopyr

Triclopyr is a selective systematic herbicide that has traditionally been used to control woody and herbaceous broadleaf plants (Hofstra and Clayton 2001). More recently, in its triethalymine salt (TEA) formulation, it has been used to control aquatic plant species, such as *Myriophyllum spicatum* L. (Getsinger et al. 1997, Sprecher et al. 1998), *Myriophyllum aquaticum* (Compliance Services International 2001), *Lythrum salicaria, Eichhornia crassipes* and *Alternanthera philoxeroides* (SePRO 2003). Triclopyr functions as an auxin mimic or synthetic auxin, killing the target weed by

causing uncontrolled and disorganized plant growth (Tu et al. 2001). Usage, key physical characteristics, and data gaps for triclopyr are summarized in Table 10.

In water, hydrolysis of the amine salt formulation occurs rapidly, resulting in the formation of triclopyr acid. Half-lives in water are 2.8 to 14.1 hours, depending on season and water depth. In water, photolysis is the main breakdown process for triclopyr (EXTOXNET 1996).

In soil and groundwater environments, the salt formulation quickly converts to triclopyr acid, which in turn is rapidly degraded to a relatively nontoxic salt (EXTOXNET 1996). The resulting salt is moderately persistent in soil environments but further degraded by microorganisms. The half-life of triclopyr compounds in soil range from 30 to 90 days depending on soil environment conditions, with an average of 46 days (EXTOXNET 1996). In a study of 15 soil types (U.S. Forest Service 1984), the half-life of one of the breakdown products (trichloropyridinol) ranged from 8 to 279 days, with 12 of the soil types having half-lives of less than 90 days. Longer half-lives may be a result of colder and/or more arid conditions (EXTOXNET 1996).

Table 10. Triclopyr Summary Table

Primary Use	Selective systematic herbicide in Tea form
Mechanism of Toxicity	Mimics the plant growth hormone auxin (indole acetic acid), causes uncontrolled and disorganized plant growth that leads to plant death
Solubility	acetone = 581; acetonitrile = 92.1; hexane = 0.09; ethyl acetate = 271
Fate	Hydrolysis occurs rapidly with half-lives in water of 2.8-14.1 hours. Photolysis is the primary breakdown process in water. Microbial degradation occurs in soil with a soil half-life of 30-90 days. Bioconcentration is not likely.
Confounding Factors	Much longer half-life of triclopyr in soil than in water. Herbicide break-down is significantly slower in anaerobic environments.
Data Gaps	Amphibian data is not available for the TEA formulation of triclopyr. NOEC and LOEC data is also sparse.

2.8. 2,4-D

There are many forms of 2,4-D, including acid, salt (mostly amine), and ester formulations. Ester formulations are particularly toxic to fish and other aquatic life. 2,4-D is a selective herbicide that kills dicots by mimicking the growth hormone auxin, causing uncontrolled growth and eventual death (Tu et al. 2001). It is used for cultivated agriculture, pasture, rangeland, forest, home, and garden applications and to control

aquatic vegetation (EXTOXNET 1996). Usage, key physical characteristics, and data gaps for 2,4-D are summarized in Table 11.

2,4-D has low persistence in soil, with a half-life in soil is less than seven days (Wauchope 1992), primarily due to degradation by soil microbes (Howard 1991). Microorganisms also readily degrade 2,4-D In aquatic environments. Rates of breakdown increase with increased nutrients, sediment load, and dissolved organic carbon. Under oxygenated conditions, the half-life is one to several weeks (Howard 1991).

Despite its short half-life in soil and in aquatic environments, 2,4-D has been detected in groundwater supplies in at least five States and in Canada (Howard 1991). Very low concentrations have also been detected in surface waters throughout the U.S. (USEPA 1992).

Table 11. 2,4 D DMA Summary Table

Primary use	Post emergent systemic herbicide –used for hyacinth, milfoil (liquid). Often used with polymeric thickener.
Mechanism of Toxicity	Hormone that stimulates stem elongation & nucleic acid/protein synthesis, stimulating uncontrolled growth until death. Affects enzyme activity/respiration/cell division.
Solubility	Relatively soluble. Precipitates in hard water as Ca/Mg salts
Fate	Rapid hydrolysis to 2,4 D acid then bound to sediments. 2,4 D DMA < 2,4 D BEE in sediments. Bioaccumulation not expected.
Confounding Factors	Persistent at temperatures <7 C
Data Gaps	Resident Species, aquatic insects

3. APMP Monitoring Results

3.1. Tiered Risk Assessment Approach for Aquatic Pesticides

The APMP used a tiered monitoring approach to gather the data necessary to draft the statewide NPDES permit for aquatic herbicides:

Tier 1. Literature review of pesticide/environmental couplings to identify situations in which accumulation and persistence of aquatic herbicides are likely or unlikely. From this review a priority ranking of the target herbicides was completed.

Tier 2. Sampling and analysis program to confirm presence or absence of pesticides in the aquatic environment. Monitoring consisted of water, sediment, and tissue analyses for pesticide concentrations. Standard toxicity tests were also used to evaluate the potential for effects of contaminated water or sediments on aquatic biota.

Tier 3. Special studies, including bioassessments, California-listed-species studies, and/or sublethal effects studies, to more fully characterize environmental impacts of aquatic herbicides for which the literature or monitoring suggested that effects were likely. These techniques were also used to bridge data gaps in concerning existing knowledge about the target aquatic pesticides.

The results of studies from each tier guided the implementation of studies from subsequent tiers. Thus, it was not necessary to conduct the entire suite of studies for all aquatic herbicides based. A the end of the project in early 2005, SFEI staff, collaborating scientists, and State Water Board staff agreed that this approach had been a cost-effective and scientifically defensible means for gathering the data needed to draft the NPDES permit and for identifying future information needs.

3.1.1. Tier 1 Herbicide Ranking

To identify the level of effort required, each herbicide 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 the Tier 1 literature review, conducted by SFEI, and from the CDPR

PUR. The final rankings were determined in consultation with the professional opinions of a committee of regulators, researchers, and industry scientists (Table 12). The APMP then conducted Tier 2 monitoring of the ranked herbicides. Two herbicides, imazapyr and endothall, were not included in Tier 2: imazapyr had not yet received its aquatic-use designation, and endothall has very limited use in California. Higher-ranked herbicides were addressed first to allow time for the possible implementation of more complex Tier 3 special studies before the project end.

Table 12. Aquatic Herbicide Ranking Table

Chemical	**Selec-tivity**	**Toxicology**				**Chemical Characteristics**			**Public Concern**	**Sum of Criteria Scores**	**Final Rank**
1 – low risk **5 – high risk**		Indirect	Eco-system	Terrestrial	Human	Half-life	Kow	Mobility			
Acrolein	5	4	5	2	4	1	1	5	5	32	**1**
Copper Sulfate	2	4	4 - 5	1 – 2	1	2[1]	2	2 – 3	5	26	**2**
Diquat dibromide	3	4	2 - 3	1	1	1	1	1	3	18	**5**
Endothal	2	4	2	1	1	2	3	3	2	19	**4**
Fluridone	3	2	1	1	1	3	2-3	3	1 – 2	19	**4**
Glyphosate	5	1	1	1	1	1	1	1	4	16	**6**
Triclopyr	1	4	2	1	1	2	3	3	3 – 4	19	**4**
2,4-D (salt)	1	3	2 - 3	1 – 2	1	2	3	2	3 – 4	20	**3**

[1]Bioavailable form

3.1.2. Tier 2 Sampling Strategy

APMP monitoring sampled target aquatic herbicides from a diverse range of waterbody types located in various regions throughout California. The frequency and level of sampling varied because of individual herbicide and site-specific issues (e.g., presence of other potential contaminants, availability of reference sites). The program focused on short-term rather than long-term effects and coordinated with aquatic herbicide users, sampling during and following herbicide applications. Closely tying the monitoring efforts to herbicide applications allowed assessment of 'worst-case' scenarios. Using the triad approach, the target aquatic herbicides were monitored at 18 sites throughout the state. Most herbicides were monitored for no more than two weeks after direct application, with the extent and level of bioassessment sampling conducted as time and budget allowed. For three herbicides—copper sulfate, fluridone, and glyphosate—monitoring was conducted over a longer time period (up to three to four months after application) at a minimum of three locations that had received repeated applications of one herbicide during the 2003 application season.

3.1.3. Tier 3 Special Studies

Special studies, designed and conducted to attain greater in-depth knowledge of target herbicides, were generally conducted when a specific risk was identified that may not have been captured using standard toxicity testing and chemical characterization or when a more sensitive monitoring technique was needed. The following special studies were conducted during the course of the APMP:

1) The evaluation of estrogenic activities of some herbicides and surfactants using a rainbow trout vitellogenin assay.
2) Determination of long-term nontarget plan toxicity of pelleted fluridone
3) Development of diagnostic tests of indicators of acrolein ecosystem impacts.
4) Methods development for in-field derivitization of acrolein treated water samples.
5) Evaluation and case study demonstration of pesticide fate and transport models.
6) Application of *in situ* toxicity tests for study of aquatic insecticide impacts.

3.2. Data Interpretation—Use of Risk Assessment Methods to Assess Monitoring Data

All data from the APMP, including water and sediment toxicity tests, bioassessments, and chemical characterizations, were reviewed to determine whether there were trends that may have indicated environmental effects of the aquatic herbicide applications. Additionally, to provide a risk-potential framework for the herbicide concentration results, risk quotients were calculated according to USEPA methods (USEPA, 1998). These risk quotients are part of the first step of a four-part risk-characterization process outlined in the ECOFRAM draft Aquatic Report (USEPA 1999):

> "The purpose of the tiered process is to provide a logical progression of tests and risk assessment approaches to address the potential risks of toxicants to aquatic systems. The common feature of all tiered regulatory processes is a progression beginning with conservative assumptions and moving toward more realistic estimates. Tiered processes tend to be cost effective in that they ensure that resources are expended on herbicide product/issues meriting attention. … The tiers are differentiated primarily by the data available at that state in the risk

assessment process and the relative cost of achieving risk refinement appropriate for that tier of analysis."

Calculated risk quotients identified areas in which additional monitoring and risk characterization may be needed to fully explore potential impacts of aquatic herbicides. Risk quotients to not themselves indicate impacts.

Risk quotients (RQ) were calculated by dividing water chemical concentrations by an acute or chronic ecotoxicity value:

$$RQ = {}^{Exposure}\!/_{Toxicity}$$

Exposure = an estimated environmental water concentration or actual water concentration field data.

Toxicity = an accepted toxicity measurement (i.e., LC50, LD50, EC50, EC25, NOEC, LOEC, or MATC).

The risk quotients calculated for the APMP used the highest herbicide concentrations measured during monitoring of each herbicide. The use of these peak values is appropriate for initial, USEPA 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. If possible risk is identified in a USEPA Tier 1 analysis, then a USEPA Tier 2 analysis (addressing the probability and magnitude of effects on sensitive species using conservative exposure scenarios) is indicated. USEPA Tier 2 analyses were not undertaken during the APMP.

Risk quotients are compared to Levels of Concern (LOC), which are determined by the USEPA Office of Pesticide Programs (OPP). LOCs for aquatic animals and plants are shown in Table 13. LOCs are unitless values that allow for simple determination of possible exceedances of regulatory limits. An LOC exceedance is indicative only of the need for further investigation of an application scenario.

Table 13. Aquatic Animal and Plant Levels of Concern

Risk Presumption	RQ	LOC
Acute Risk	EC/LC50 or EC50	0.5
Acute Restricted Use	EC/LC50 or EC50	0.1
Acute Endangered Species	EC/LC50 or EC50	0.05
Chronic Risk	EC/ MATC or NOEC	1

The USEPA interprets exceedances of LOCs as follows:

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

Acute restricted use: the potential for acute risk is high but may be mitigated through restricted-use classification.

Acute endangered species: the potential for acute risk to endangered species is high but may be mitigated through restricted-use classification.

Chronic risk: the potential for chronic risk is high; regulatory action may be warranted.

Toxicity test values used to calculate risk quotients may come from standard toxicity test species or any federally or California-listed species study. When there are multiple toxicity values for the same test species, the lowest value is used. The toxicity measurements used by the APMP were derived from peer-reviewed academic literature, FIFRA registration documents, and other government reports. Risk quotients were also calculated for sediment herbicide concentrations where toxicity values were available. However, the USEPA LOCs are not applicable to herbicide concentrations in sediments, and there are no comparable regulatory values for sediment.

In addition, chemical characterization, toxicity tests, and benthos bioassessment data were combined to produce sediment quality trend data summary tables for the pesticides where sediment accumulation was a potential, using methodology adapted from the USEPA triad approach (Barbour et al 1996). This risk assessment approach could be used effectively with monitoring data already collected by the California Department of Boating and Waterways (DBW) and the Invasive Spartina Project (ISP). Given their large number of data points it may be possible to conduct statistical analysis of any LOC exceedances.

3.3. Data Results

The three years of monitoring and special studies conducted during the course of the APMP are summarized by individual herbicide. Additional detail can be found in the APMP Phase 2, Phase 3, and bioassessment reports, which are available on the SFEI website (www.sfei.org).

3.3.1 2,4-D

Only one application of 2,4-D (in the 2,4-D dimethylamine salt formulation) with added surfactant was monitored. During this single application, no toxicity was observed, nor did risk quotients indicate the need for further information (Tables 14 and 15). However, vitellogenin-induction laboratory experiments indicate that 2,4-D may cause endocrine disruption at legal application rates. The vitellogenin-induction studies indicate a need for further study of the aquatic 2,4-D formulations and their primary breakdown products, a level of research that extends beyond that typical of permit-compliance monitoring.

Table 14. Peak Concentration Risk Quotient Calculations for 2,4-D Application

Experimental Concentration Range	Toxicity Value	Toxicity measurement, regulatory tolerance, action or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)
27.5 µg/l	315 µg/l	Chinook salmon LC50	0.087
	7.2 mg/l	*D. magna* LC50	0.0038
	100 mg/l	*P. promelas* LC50	0.000275
	128 mg/l	Delta smelt NOEC	0.000215

Table 15. Summary of 2, 4-D (DMA) Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	# 2003 Sampling Stations (Total #)	Possible Conclusion
+	+	+		Evidence of pesticide-induced degradation
–	–	–	2 (2)	No evidence of pesticide induced degradation
+	–	–		Pesticides are not bioavailable
–	+	–		Chemicals other than pesticide or conditions exist with potential to cause degradation
–	–	+		Benthic response not due to pesticide
+	+	–		Pesticide may be stressing the system
–	+	+		Chemicals other than pesticide or conditions are causing degradation
+	-	+		Pesticide is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a concentration that exceeded the porewater LC50 reported for Chironomus plumosus
A plus(+) for toxicity indicates a significant decrease relative to control in either amphipod growth or percent survival
A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the reference stations

3.3.2 Acrolein

Because of acrolein rapidly volatilizes, standard environmental sampling methods were inadequate for sampling waters to which acrolein had been applied. Consequently, the APMP first focused on development of a field-sampling method that would allow for accurate determination of the herbicide in water. Refinement of the sampling methodology began in 2003, and results indicated that the method worked well at low acrolein water concentrations, making it possible to measure acrolein residues.

Rapid volatilization also precluded conduct of standard water toxicity tests of acrolein. However, extremely low lowest-observable-effects-concentration (LOEC) values suggest that any detectable presence of acrolein would cause high mortality to test species.

The APMP explored development of novel diagnostic response tests (e.g., phytomonitoring, sentinel bivalves, and fish studies), and additional work is warranted. Such tests have the potential to provide low-cost, low-tech methods of detecting acrolein outside of designated treatment areas.

3.3.3. Copper Sulfate

Copper sulfate applications were monitored in three reservoirs. In one reservoir treated with dissolved copper sulfate, toxicity to juvenile trout and *Ceriodaphnia* was detected immediately after and up to a week following application. Peak concentration risk quotients showed acute and chronic LOC exceedances (Table 16). At 24 hours after application, the risk quotients continued to show acute and chronic LOC exceedances, and at one week post-application, the risk quotients showed acute LOC exceedances.

In water-toxicity tests of water from a reservoir treated with granular copper sulfate, significant mortality immediately after application was observed in *Ceriodaphnia* and juvenile trout. Mortality and growth inhibition were also observed in some of the sediment samples. Sediment copper concentrations at many sites exceeded a published LC50 value for *Hyallela*. However, the level of toxicity observed in the sediments indicated that most of the copper was not bioavailable (Table 17).

These findings indicate a need for further risk characterization associated with copper sulfate applications.

Table 16. Water Risk Quotient Calculations for Copper Sulfate Applications (Reservoir System)

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		Peak Concentration: 0.0653 mg/l	t+24 hour conc.: 0.0381 mg/l	t+1 week conc.: 0.0076 mg/l
0.068 mg/l	*C. dubia* EC50	**<u>0.96</u>**	**<u>0.56</u>**	**<u>0.11</u>**
0.03 mg/l	Daphnid NOEC	**<u>2.18</u>**	**<u>1.27</u>**	0.25
0.8 mg/l	Rainbow Trout 48hr LC50	0.08	0.048	0.0095
2300 mg/l	Duckweed EC50	.00003	1.6E-5	3.3E-6

Table 17. Summary of Copper Sulfate Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	# 2003 Sampling Stations (Total)	# 2004 Sampling Stations (Total)	Possible Conclusion
+	+	+	3(6)	5(10)	Evidence of copper-induced degradation
–	–	–		3(10)	No evidence of copper induced degradation
+	–	–	1(6)		Copper is not bioavailable
–	+	–		1(10)	Chemicals other than copper or conditions exist with potential to cause degradation
–	–	+			Benthic response not due to copper
+	+	–	1(6)		Metals may be stressing the system
–	+	+			Chemicals other than copper or conditions are causing degradation
+	–	+	1(6)	1(10)	Copper is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a concentration of Cu that exceeded either the Sediment Quality Guideline ERL for Cu or porewater reported in Suedel et al. 1996.
A plus(+) for toxicity indicates a significant decrease relative to control in either amphipod growth or percent survival.
A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the Lagunitas reference stations.

3.3.4 Chelated Copper

Chelated copper herbicides were monitored during applications in two irrigation canal systems. One system used a product of mixed copper ethanolamines, and the other used the same product of mixed copper ethanolamines in an emulsified formulation. Chelated copper formulations are likely to have distinct behavior from copper sulfate and each other in aquatic environments, depending on the chelating agent and other adjuvants. Copper carbonate is the active ingredient in other chelated copper products; no monitoring of copper carbonate-based herbicides was conducted.

In both systems monitored, the water samples were almost uniformly toxic before and after the applications (Table 18). Therefore, no definitive conclusions could be

drawn about the toxicity of mixed copper ethanolamines. The sediment-quality-triad calculations indicated the possibility of effects of copper on the systems (Table 19).

Further risk characterization associated with chelated copper applications is warranted.

Table 18. Water Risk Quotient Calculations for Chelated Copper Applications (Irrigation Canal Systems)

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		Peak Concentration: 1.43 mg/l	t+4 hour conc.: 0.0988 mg/l	t+11 hour conc: 0.0988 mg/l
9.9 mg/l	Water flea *Alonella* LC50	**0.144**	0.01	0.002
0.0023mg/l	Fathead Minnow larvae 48hr LC50	**621**	**43**	**7.39**

Table 19. Summary of Chelated Copper Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	# 2003 Sampling Stations (Total)	Possible Conclusion
+	+	+	1(2)	Evidence of copper-induced degradation
–	–	–		No evidence of copper induced degradation
+	–	–		Copper is not bioavailable
–	+	–	1(2)	Chemicals other than copper or conditions exist with potential to cause degradation
–	–	+		Benthic response not due to copper
+	+	–		Metals may be stressing the system
–	+	+		Chemicals other than copper or conditions are causing degradation
+	–	+		Copper is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a Cu concentration that exceeded either the Sediment Quality Guideline ERL or porewater LC50 reported for Hyalella azteca
A plus(+) for toxicity indicates a significant decrease relative to control in either amphipod growth or percent survival
A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the reference stations

3.3.5 Diquat Dibromide

Diquat dibromide was sampled at two locations, a small pond and a delta slough. Diquat risk quotients almost uniformly exceeded LOCs for all sampling periods in the Delta slough (including preapplication) and at one hour after application in the pond (Table 20). Diquat may be applied with a surfactant, which may have much higher toxicity than the active ingredient, and its inclusion could affect the results. Sediment

concentrations were not considered, as diquat, when irreversibly adsorbed to sediments, is not bioavailable.

Toxicity test and risk quotient results indicate the need for further risk characterization.

Table 20. Water Risk Quotient Calculations for Diquat Dibromide Applications

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		preapplication conc.: 7-Mile: 13.8 µg/l Sand Bay: 0.79 µg/l	t+1 hour conc.: 7-Mile: 180 µg/l Sand Bay: 400 µg/l	t+24 hours conc.: 7-Mile: 4.5 µg/l
19 µg/l	*S. capricornutum*. EC50 (growth)	**$RQ_{7\text{-}Mile}$=0.73** $RQ_{Sand\ Bay}$=0.04	**$RQ_{7\text{-}Mile}$=9** **$RQ_{Sand\ Bay}$=21**	**$RQ_{7\text{-}Mile}$=0.24**
44 µg/l	Algae NOEC (biomass growth)	$RQ_{7\text{-}Mile}$=0.31 $RQ_{Sand\ Bay}$=0.02	**$RQ_{7\text{-}Mile}$=4** **$RQ_{Sand\ Bay}$=9**	$RQ_{7\text{-}Mile}$=0.1
32 µg/l	D. magna LC50	**$RQ_{7\text{-}Mile}$=0.43** $RQ_{Sand\ Bay}$=0.025	$RQ_{7\text{-}Mile}$=**5.6** $RQ_{Sand\ Bay}$=**13**	**$RQ_{7\text{-}Mile}$=0.14**
36 µg/l	Daphnid NOEC	$RQ_{7\text{-}Mile}$=0.38 $RQ_{Sand\ Bay}$=0.02	**$RQ_{7\text{-}Mile}$=5** **$RQ_{Sand\ Bay}$=11**	$RQ_{7\text{-}Mile}$=0.125
120 µg/l	Minnow NOEC	$RQ_{7\text{-}Mile}$=0.115 $RQ_{Sand\ Bay}$=6E-3	**$RQ_{7\text{-}Mile}$=1.5** **$RQ_{Sand\ Bay}$=3.3**	$RQ_{7\text{-}Mile}$=0.038
7600 µg/l	P. promelas LC50	$RQ_{7\text{-}Mile}$=0.0018 $RQ_{Sand\ Bay}$=1E-4	$RQ_{7\text{-}Mile}$=0.02 $RQ_{Sand\ Bay}$=0.05	$RQ_{7\text{-}Mile}$=6E-4
11 µg/l	Duckweed LOEC	**$RQ_{7\text{-}Mile}$=1.25** $RQ_{Sand\ Bay}$=0.72	**$RQ_{7\text{-}Mile}$=16** **$RQ_{Sand\ Bay}$=36**	$RQ_{7\text{-}Mile}$=0.4
18 µg/l	Duckweed EC50	**$RQ_{7\text{-}Mile}$=0.76** $RQ_{Sand\ Bay}$=0.044	**$RQ_{7\text{-}Mile}$=10** **$RQ_{Sand\ Bay}$=22**	**$RQ_{7\text{-}Mile}$=0.25**

3.3.6 Fluridone

Fluridone (applied in pellet or liquid form) was not found to be definitively toxic to or have LOC exceedances for three species water organisms or sediment amphipods (Tables 21 and 22). The peak concentration risk quotient for stonewort did exceed an acute LOC. Fluridone was found to cause sublethal toxicity (decreased shoot and root length) to *Typha*, indicating a potential for impacts to nontarget plants.

Further risk characterization of fluridone impacts on nontarget plants is warranted. Further, there is cause for concern about the development of genetic resistance to fluridone in plant populations in Florida (Rodgers 2004).

Table 21. Peak Risk Quotient Calculations for Liquid Fluridone Application

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		Preapplication concentration: Non Detect	Mid Application: 37 µg/l	Post Application: 102 µg/l
2.1 mg/l	*D. magna* LC50	0	0.018	0.048
200 µg/l	*D. magna* NOEC	0	0.185	0.51
6.2 mg/l	*P. promelas* LC50	0	0.006	0.016
1.88 mg/l	*P. promelas* NOEC	0	0.02	0.054
1.28 mg/l	Delta smelt NOEC	0	0.029	0.08

Table 22. Summary of Fluridone Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	# 2003 Sampling Stations (Total)	Possible Conclusion
+	+	+	4(9)	Evidence of pesticide-induced degradation
–	–	–		No evidence of pesticide induced degradation
+	–	–	2(9)	Pesticides are not bioavailable
–	+	–	2(9)	Chemicals other than pesticide or conditions exist with potential to cause degradation
–	–	+		Benthic response not due to pesticide
+	+	–		Pesticide may be stressing the system
–	+	+		Chemicals other than pesticide or conditions are causing degradation
+	–	+	1(9)	Pesticide is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a concentration that exceeded the porewater EC50 reported for Stonewort
A plus(+) for toxicity indicates a significant decrease relative to control in either plant growth or percent germination
A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the reference stations

3.3.7. Glyphosate

Glyphosate was monitored at several stream locations throughout the state. No toxicity was found to be associated with glyphosate applications and no LOC exceedances were calculated. However, glyphosate is often applied with a surfactant that may have much higher toxicity than the active ingredient.

Based on risk quotients and toxicity data, no further risk characterization associated with glyphosate applications alone is warranted. Risk characterizations are warranted when a surfactant is used.

3.3.8. Triclopyr

Triclopyr was monitored during at one application. Triclopyr peak concentration risk quotients resulted in no LOC exceedances. Triclopyr is often applied with a surfactant which may have much higher toxicity than the active ingredient.

Limited further triclopyr risk characterization is warranted. Risk characterizations of triclopyr with a surfactant are warranted.

3.3.9. Nonionic surfactants

The most commonly used surfactants at APMP monitoring sites were NPE-based surfactants, including Target Prospreader Activator and R-11. Peak concentration risk quotients in these applications indicated exceedances of LOCs for a wide range of animal species including Delta smelt and Sacramento splittail, which are among the pelagic fishes of concern in the Delta (Tables 23-25). Vitellogenin-induction experiments in rainbow trout indicate that these surfactants can be endocrine disruptors at typical application rates. There is a wide range of adjuvant surfactants available, each one having a different toxicological profile. Risk characterizations are warranted on all surfactants.

Table 23. Peak Concentration Risk Quotient Calculations for Surfactant (R-11) during 2,4-D Application

Experimental Concentration Range	Toxicity Value	Toxicity measurement, regulatory tolerance, action or guidance value	Risk Quotient (Risk quotients in bold and underlined indicate an LOC exceedance)
22.6 µg/l	5700 µg/l	*C. dubia* LC50	0.004
	420 µg/l	*C. dubia* NOEC	0.05
	1100 µg/l	*P. promelas* LC50	0.02
	340 µg/l	*P. promelas* NOEC	0.06
	700 µg/l	Delta smelt LC50	0.03
	100 µg/l	Delta smelt NOEC	**0.2**
	3900 µg/l	Sacramento splittail LC50	0.006
	1900 µg/l	Sacramento splittail NOEC	0.01

Table 24. Risk Quotient Calculations for Surfactant (R-11) during Glyphosate Application in Stormwater Control Channel

Toxicity value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		preapplication conc.: <RL µg/l	t+0 hour conc.: 120 µg/l	t+3 hour conc.: 19.6 µg/l
5700 µg/l	*C. dubia* LC50	0	0.021	0.003
420 µg/l	*C. dubia* NOEC	0	0.29	0.047
1100 µg/l	*P. promelas* LC50	0	**0.11**	0.018
340 µg/l	*P. promelas* NOEC	0	0.35	0.058
700 µg/l	Delta smelt LC50	0	**0.17**	0.028
100 µg/l	Delta smelt NOEC	0	**1.2**	0.196
3900 µg/l	Sacramento splittail LC50	0	0.031	0.005
1900 µg/l	Sacramento splittail NOEC	0	0.063	0.01

Table 25. Risk Quotient Calculations for Surfactant during Triclopyr Application

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)			
		preapplication conc.: 570 µg/l	t+0 hour conc.: Non Detect	t+2 hours conc.: 185 µg/l	t+24 hours conc.: 2390 µg/l
5700 µg/l	*C. dubia* LC50	**0.1**	0	0.032	**0.42**
420 µg/l	*C. dubia* NOEC	**1.36**	0	0.44	**5.7**
1100 µg/l	*P. promelas* LC50	**0.52**	0	**0.17**	**2.17**
340 µg/l	*P. promelas* NOEC	**1.68**	0	0.54	**7.03**
700 µg/l	Delta smelt LC50[a]	**0.81**	0	**0.26**	**3.41**
100 µg/l	Delta smelt NOEC [a]	**5.7**	0	**1.85**	**23.9**
3900 µg/l	Sacramento splittail LC50 [a]	**0.15**	0	0.047	**0.61**
1900 µg/l	Sacramento splittail NOEC [a]	0.30	0	0.097	**1.26**

[a.] Delta smelt and Sacramento splittail toxicity data for R-11. TPA and R-11 have very similar chemical and toxicity characteristics.

4. Aquatic Herbicide Issues of Special Concern

4.1. Tank-Mixing of Adjuvants

One application practice common to aquatic herbicide users that gives cause for concern is "tank-mixing" by the applicator of adjuvants, primarily surfactants, to the active ingredient herbicide immediately prior to application. Surfactants increase the effectiveness of herbicides, such as glyphosate, triclopyr, 2,4-D, and diquat dibromide, for applications to floating or emergent vegetation. The practice is a special concern because there is typically little toxicological information about these adjuvants, and some are known to be highly toxic to aquatic life. Under FIFRA regulations, herbicide formulations undergo extensive testing prior to receiving approval for application. When a herbicide is registered, the FIFRA label delineates the appropriate uses, dosages, and hazards associated with the product. For terrestrial applications, herbicide formulations typically contain the active ingredient and a wide range of adjuvants. Selling the herbicide as a formulation allows the manufacturer to provide the best product for the appropriate application. It is not unusual for these formulations to be too toxic to aquatic life to be approved for use as aquatic herbicides.

For aquatic applications, formulations normally contain only the active ingredient without adjuvants. However, when herbicides are used to treat floating or emergent vegetation, surfactants are generally necessary and suggested by the registration label.

To not use a surfactant would require use of a much greater amount of the relatively expensive active ingredient. A loophole in the FIFRA registration process allows applicators to mix lightly regulated adjuvants with highly regulated aquatic-use-labeled herbicides after separate purchase of the materials. This process allows applicators to, in effect, recreate a form of the terrestrial-use herbicide, which would not have, had it been sold as the mixture, been approved for aquatic use. The California general NPDES permit begins to address this issue by requiring additional monitoring if NPE surfactants, found by the APMP to be highly toxic and potential endocrine disruptors, are used. However, there remains concern that the requirement encourages users to shift to other adjuvants, about which little may be known.

4.2. Aquatic Herbicide and Surfactant Induced Endocrine Disruption

Few studies have addressed the estrogenic effects of combined exposure of herbicides and surfactants. In one APMP special study, researchers from the University of California Riverside used an *in vivo* rainbow trout vitellogenin assay to evaluate the estrogenic potencies of four herbicides (2,4-D, triclopyr, diquat dibromide, and glyphosate), two alkylphenol ethoxylate-containing surfactants (R-11 and Target Prospreader Activator (TPA)), and the binary mixtures of surfactants with the herbicides. A degradation product of 2,4-D, 2,4-dichlorophenol, is known to be estrogenic (Jobling et al 1995). Triclopyr has a similar chemical structure to 2,4-D and its degradation product trichloropyridinol is also the main metabolite of chlorpyrifos which is weakly estrogenic (Andersen et al 2002). One study has shown that diquat does not appear to be estrogenic (Kojima et al 2004). Degradation products of alkylphenolic polyethoxylates, such as NPE and octylphenol ethoxylates (OPE), bind estrogen receptors (Routledge and Sumpter 1996) and cause estrogenic effects in fish (Routledge et al 1998: Jobling and Sumpter 1993).

To evaluate the effects of combined surfactant/herbicide exposure in a field setting, water was collected from Anderson Pond south of Redding California near the Sacramento River at the northern end of the Sacramento Valley. Anderson Pond is under surveillance and treatment by the California Department of Food and Agriculture for control of *Hydrilla*.

The study found that 2,4-D and the two APE-containing surfactants were estrogenic to rainbow trout at environmentally relevant concentrations. Greater than additive responses were observed in the laboratory when 2,4-D or triclopyr were combined with one surfactant TPA. Response curves differed between the herbicides, with the 2,4-D-and-TPA mixture displaying a U-shaped dose response. The estrogenic response of triclopyr with TPA was greater than additivity at mid-range concentrations and diminished at the highest concentration. Estrogenic activity was observed in pond water treated with triclopyr and TPA at levels similar to laboratory values with the combined compounds. These data suggest caution should be utilized when using NOEC and LOEC values to assess estrogenic activity for individual compounds, and that utilization of additive responses are likely inappropriate for endocrine-mediated endpoints.

5. Analytical Methods for Aquatic Herbicides

At the beginning of the APMP, there was considerable discussion concerning the potential need for analytical methods development. As methods development is very costly, a screening process was used to determine whether current methods could provide ecologically relevant chemical concentrations data. Because the NPDES permit holders are required to conduct monitoring, only those methods that could be performed by contract and state analytical laboratories were reviewed. More sensitive methods may require rare equipment or be highly labor intensive. It was decided that if the minimum detection level of a current analytical method was one order of magnitude more sensitive than the lowest LC50 or NOEC for any species listed in the EPA Acquire database for a particular herbicide, then no additional methods development was necessary.

The screening process indicated that current methods for water and sediment analyses of the aquatic herbicides are sufficiently sensitive, and no further method development was required. Method detection limits (MDLs) are shown in Table 27, and threshold toxicology data are shown in Table 28. Because of high volatility of acrolein, the APMP did develop an in-field-derivitization method for sampling of that herbicide (Siemering 2005).

Table 27. Herbicide Analytical Methods, and Method MDLs

Medium	Compound	Method	Target MDL
Water	Acrolein	LC-MS	0.005 µg/L
	Copper		1.0 µg/L
	2,4-D	HPLC-MS	0.005 µg/L
	Diquat dibromide	HPLC, LC-MS	0.50 µg/L
	Fluridone	SePRO method ELISA	0.5 µg/L
		HPLC-MS	0.001 µg/L
		HPLC-Fluorescence	0.05 µg/L
	Glyphosate	HPLC-Fluorescence	5.00 µg/L
	Surfactants	HPLC-MS	2.0 µg/L
	Triclopyr	HPLC-MS	0.020 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- Fluorescence	25.00 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

Table 28. Herbicide minimum effect concentrations (test & non-target species)

Herbicide	Water
2,4-D	8.3 µg/L (NOEC Grass shrimp)
	0.3 mg/L (4-day LC_{50} Chinook salmon)
Acrolein	0.04 µg/L (5-day LOEC *Skeletonema costatum*)
Copper (copper sulfate, chelated copper)	0.04 mg/L (4-day LOEC *Ceriodaphnia dubia*)
	0.03 mg/L (4-day NOEC *Ceriodaphnia dubia*)
Diquat dibromide	5.4 µg/L (32-day LOEC *Fundulus heteroclitus*)
Fluridone	0.8 mg/L (4-day NOEC Walleye)
	200 µg/L (Coho salmon alevin)
Glyphosate	42 mg/L glyphosate (NOEC fathead minnow)
	1.0 mg/L surfactant (4-day LC_{50} fathead minnow)
Triclopyr	260 µg/L (Coho Salmon Alevin LC50)

ELISA tests are currently available only for fluridone and triclopyr analysis in water. While these tests are considerably less expensive than other analytical methods, they were considered unacceptable by the State Water Board and their use not allowed for the permit-mandated water quality monitoring.

The evaluation of methods also found that correct sample bottle type is highly dependent on individual herbicide chemical characteristics. Standard environmental sampling practice indicates that organic chemical herbicides are collected in glass bottles. However, a review of the literature and consultation with the manufacturers indicated that

for several herbicides, because of their sorption characteristics, some samples were more appropriately collected in polyethylene bottles (Table 29).

Table 29. Aquatic Herbicide Bottle Types for Trace Elements and Organic Chemicals Measured in the APMP

Applied Pesticides	Sample Bottle Type
Acrolein	Glass
Copper (copper sulfate and chelated copper)	Polyethylene
2,4-D	Glass
Diquat dibromide	Polyethylene
Fluridone	Polyethylene
Glyphosate	Polyethylene
Surfactants	Glass
Triclopyr	Glass

6. Conclusions and Information Needs

The APMP evaluations suggested that potential impacts of aquatic herbicides on pelagic organisms in the Delta are not likely to be significant for most herbicides in use. Worst-case-scenario monitoring and studies conducted over three years showed little indication of short-term and no long-term toxicity of herbicide applications. Risk quotient calculations showed few LOC exceedances.

Surfactants and other adjuvants applied with aquatic herbicides are more likely to contribute to pelagic organism declines in the Delta. The risk quotient calculations resulted in several LOC exceedances for NPE surfactants. Few chemical monitoring or toxicity data are available for the vast majority of the adjuvant chemicals in use.

NPE surfactants and 2,4-D DMA were shown to cause vitellogenin induction in rainbow trout and hence could contribute to pelagic organism declines. However, it is important to note that NPEs are ubiquitous in industrial, household and agricultural chemicals, and the relative amount contributed by aquatic herbicide applications is comparatively small. Similarly, terrestrial applications of 2,4-D DMA dwarf the amounts used in aquatic applications. The effects of terrestrially applied herbicides, through runoff and drift, on the aquatic system have not been studied.

While the APMP monitored aquatic herbicide applications at a number of sites for three years, the total amount of data gathered was small, and indicated that additional monitoring is necessary. The current NPDES permit-required monitoring has limited

value for addressing continued scientific questions. Monitoring data collected by large application programs (e.g., DBW, ISP, and the California Department of Food and Agriculture (CDFA)) may prove useful after additional data analysis.

The risk quotient calculations revealed gaps in toxicity data. For example, there is additional need for toxicity data pertaining to endangered fish from the upper Delta. Sublethal endpoint data were sparse for all herbicides.

In conclusion, while there is no compelling linkage between what we know about the pelagic organism decline and aquatic herbicide use, there are several outstanding questions that merit further evaluation. These issue are itemized in Section 7.

7. Recommendations

1. Use existing datasets from large monitoring programs to conduct additional risk-quotient calculations. These calculations would provide greater clarification of the additional information needed to make a complete risk assessment of aquatic herbicides. In particular, the Boating and Waterways aquatic herbicide use data should be combined with some screening fate and transport modeling to determine if the risk quotient levels are sufficient to warrant further sampling.
2. Conduct additional endocrine-disruption research on active ingredient herbicides and adjuvant chemicals.
3. Conduct toxicity testing of adjuvant chemicals.
4. Consider the combined impacts of aquatic and terrestrial applications of target herbicides. Frequently, the same herbicide is applied in far greater quantities for terrestrial applications, and it is likely that both applications are impacting upper Delta water quality.
5. Conduct risk assessments of new herbicides (e.g., imazapyr) as they receive their aquatic- use labels .
6. Advocate for PUR data submission procedures that clearly identify aquatic applications and differentiates them from terrestrial applications.

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