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Technical Report for the Interagency Ecological Program (IEP) Pelagic Organism Decline (POD) Workgroup:

Tier 1 Risk Assessment of California Department of Boating and Waterways Aquatic Herbicide Use in the Sacramento-San Joaquin River Delta

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This report is a deliverable of Task 3 of the Technical Report for the Interagency Ecological Program (IEP) Pelagic Organism Decline (POD) Workgroup. Although Task 3 was initially supposed to be the conversion of DBW hardcopy monitoring data to electronic format, the data was already in electronic format. However, additional analysis of this data was necessary and a Tier 1 risk assessment was felt to be the best method.

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Executive Summary

Since 2001, the California Department of Boating and Waterways (DBW) has conducted an extensive water quality monitoring program in conjunction with its aquatic herbicide applications. In this report, the risk quotient calculation method utilized by the Aquatic Pesticide Monitoring Program (a USEPA Tier 1 risk assessment) was used to determine if there are patterns of Level of Concern exceedances that indicate the possibility of adverse impacts on the Delta aquatic ecosystem due to DBW aquatic herbicide applications. Level of Concern exceedances are indicative only of the need for further investigation of an application scenario and do not, in and of themselves, indicate adverse impacts. This type of risk analysis cannot quantify the potential additive or synergistic effects of all pelagic organism stressors (one of which would be aquatic herbicides) within the Delta.

This risk assessment indicates that, with the exception of diquat dibromide applications, DBW herbicide applications are unlikely to have the potential to cause Delta ecosystem water quality impacts. While there were a number of Level of Concern exceedances for diquat, DBW and all regulatory agencies involved were aware of this potential prior to application. NOAA Fisheries requested that, when possible, diquat used adjacent to salmon migratory routes should be reduced or avoided when that species is likely to be present. USFWS determined that diquat impact to aquatic invertebrates is minimal, temporary, and not likely to jeopardize Delta smelt but has required avoidance in areas where and when the smelt are known to be present. For 2006, NOAA has allowed DBW to treat sites in April and May with fluridone, which has allowed the use of diquat to be discontinued.

Introduction

Since 2001, the California Department of Boating and Waterways (DBW) has conducted an extensive water quality monitoring program in conjunction with its aquatic herbicide applications. These monitoring programs were developed in consultation with United States Department of Agriculture- Agricultural Research Service (USDA-ARS) staff, follow rigorous QA/QC procedures, and utilize experienced California Department of Fish and Game (CDFG) testing laboratories. Because of the scale of DBW's weed control efforts, its dataset is the only one in the state of sufficient scientific rigor to contain information on a range of aquatic herbicides and a full suite of ancillary water quality measurements and toxicity test data.

Although DBW has distributed annual monitoring reports to local regulators and other interested parties since 2001, these reports (per permit requirements) provide little additional data analysis beyond reporting and explanation of any permit violations. This report will use the risk quotient calculation method utilized by the Aquatic Pesticide Monitoring Program (Siemering 2004) to provide additional analysis of the DBW dataset. The purpose of this analysis is to determine if there are patterns of risk quotient Level of Concern (LOC) exceedances that indicate the possibility of adverse impacts on the Delta aquatic ecosystem due to DBW aquatic herbicide applications.

Background

DBW has collected water samples in conjunction with its aquatic herbicide applications since 1985. From 1985 to 1999 only rudimentary sampling was conducted. From 2001 hence, the DBW monitoring program has been extensive and well documented.

From 1985 to 1999, a limited number of water samples were collected in association with DBW 2,4-D applications to control water hyacinth. The decision to sample was made by the original Task Force of state and federal agency representatives assembled to assist DBW in developing its weed control programs. The State Water Resource Control Board (SWRCB) recommended that DBW conduct the monitoring to document the actual extent of the breakdown of 2,4-D in Delta waters. This sampling was not conducted under NPDES permit requirements, but rather the Department of Pesticide Regulations and County Agricultural Commissioners. Only 2,4-D sample concentrations were determined. No water quality parameters were measured and no toxicity tests performed.

In 2000, due to legal uncertainties from the *Talent* decision fallout, no herbicide applications were made and therefore no monitoring was conducted. Applications resumed with the 2001 aquatic weed control season (generally April to September). In

2001, DBW began working closely with the USDA-ARS to develop rigorous monitoring plans for the DBW water hyacinth and *Egeria densa* control programs.

The water hyacinth program uses Weedar 64 (2,4-D dimethylamine based) and Aquamaster (glyphosate based) herbicides. 2,4-D is the primary herbicide with glyphosate being used when crops near the application areas require it. These herbicides are tank mixed with a surfactant prior to application to increase herbicide efficacy. From 2001-2003 the surfactant used was R-11, a nonylphenol polyethoxylate (NPE) based product. NPE products have been shown to contribute to endocrine disruption in rainbow trout (Xie et al. 2005). Starting in 2004, DBW has used the surfactant Agridex that is a paraffin based petroleum oil and polyoxyethylate polyol fatty acid ester. Agridex has been determined to pose no threat of toxicity even at high application rates (WSDE, 2003)

The *Egeria densa* program uses Reward (diquat dibromide based) and liquid and pelleted Sonar (fluridone based) herbicides. Early in the *Egeria* control program Reward was primarily used, but in recent years Sonar has been the primary herbicide. No surfactant is tank mixed with these herbicides.

Post-*Talent*, NPDES permits have been required for all aquatic pesticide applications in California. In 2001, most applicators opted to follow the emergency general NPDES permit issued by the SWRCB. Because of continuing legal uncertainty with the general permit, DBW filed for and received an individual NPDES permit that required monitoring far in excess of that required in the general permit. Had the SWRCB-issued general permit been invalidated, this individual permit would have allowed DBW to continue herbicide applications. In addition, a U.S. Fish and Wildlife Service (USFWS) Biological Opinion and National Oceanic and Atmospheric Administration National Marine Fisheries Service (NOAA Fisheries) Biological Opinion placed additional requirements on DBW's aquatic herbicide application programs. Prior to 2001, NMFS and NOAA requirements did not apply to DBW aquatic herbicide applications.

While under the requirements of its individual permit, DBW was required to conduct sampling, chemical analysis, and toxicity testing at two sites per chemical, per water body type where treatments occur (three) and per season (three-spring, summer, fall). A total of 36 sites in a treatment year, approximately 20 % of all treated sites, were sampled. In addition, DBW funded research to determine toxicity endpoints for Delta Smelt and Sacramento Splittail fish. The CDFG Water Pollution Control Lab conducted the sample analysis. The CDFG Aquatic Toxicology Laboratory performed the toxicity testing. DBW scientific staff collected the samples. This level of monitoring was far in excess of that required under the statewide emergency permit drafted by the SWRCB.

The DBW *Egeria* control program followed the terms of its individual NPDES permit through 2004, when it began following the requirements of the general NPDES permit promulgated in 2004. This program continued to conduct water toxicity testing in 2005, although it was not a requirement of the permit.

The water hyacinth control program operated under its individual permit until 2005. Beginning in 2006, this program will follow the terms of the general NPDES permit.

State of DBW Monitoring Data

Due to the changing focus of the monitoring as well as programmatic development, the DBW monitoring data is of varying quality and varying states of accessibility. The limited data gathered from 1985 through 1999 is presently in hardcopy form only. Given the lack of associated water quality data and limited scope of this monitoring, this data is of no scientific value. DBW has the hardcopy reports, but is not expending any resources to enter the data into a database.

The data collected since 2001 is all currently in electronic format as well as hardcopy. The data collected in 2001 and 2002 is in multiple electronic formats, but not in a single unified database. The data collected in 2003, 2004, and 2005 is currently in an Arcview database maintained by DBW GIS/ IT staff.

In 2003, the monitoring site naming conventions were changed due to a programmatic reorganization. This shift has complicated efforts to integrate the 2001 and 2002 data with later data collections. Integrating the 2001 and 2002 data with the later data involves a large scale ‘translation’ of site identification codes and reorganization of disparate data files. This is labor intensive and requires in-depth knowledge of the monitoring programs as well as easy access to the hardcopy lab reports. While it is of interest to DBW to integrate this earlier data into a database, it is, understandably, a low staff priority.

Data Analysis Methods

The annual control program reports produced by DBW, while thorough in presentation of collected data and graphical displays of sampling locations, do not conduct analysis of the data gathered beyond that required by the NPDES permit. This is appropriate given that the reports are produced for permit compliance by an herbicide applicator and not a scientific organization conducting research.

In order to provide a risk-potential framework for the herbicide concentration results, risk quotients (RQ) were calculated according to USEPA methods (USEPA, 1998) from the DBW monitoring data collected in 2003, 2004 and 2005. All data collected by DBW, including water toxicity tests, herbicide concentrations and water quality measurements, were reviewed to determine whether there were trends that may indicate environmental impacts from the aquatic herbicide applications. 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 identify areas in which additional monitoring and risk characterization may be needed to fully explore potential impacts of aquatic herbicides. Risk quotients do not themselves indicate impacts.

Risk quotients were calculated by dividing water chemical concentrations by an acute or chronic toxicity reference value (TRV):

$$RQ = \frac{Exposure}{Toxicity}$$

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).

Risk quotients were calculated for each herbicide and surfactant measurement in the DBW dataset. USEPA Tier 1 risk characterizations are meant to be protective, not predictive, and are based on conservative (i.e., worst-case) assumptions about potential exposure and effects. This has the effect of highlighting outliers within the dataset and does not address the potential effect of all applications taken as a whole. According to the ECOFRAM methodology, 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. A Tier 1 analysis is also not capable of quantifying possible additive or synergistic effects from all stressors within an environment. This type of analysis would require far more extensive monitoring and research.

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 1. Levels of Concern 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. The LOC regulatory limits are not related to herbicide concentrations allowed by NPDES permits, the Central Valley Basin Plan or other state numerical limits.

Table 1. 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.

TRVs 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 was used. The TRVs used in this analysis were derived from peer-reviewed academic literature, FIFRA registration documents, CDFG-ATL laboratory reports, and other government reports.

In this analysis, it was assumed that LOC exceedances would be identified for some samples. It can readily be agreed that additional in-depth study of specific herbicide applications would be useful, however the extreme variability of application site conditions within the Delta make such individual studies of limited use. Not only would such in-depth data be of little to no use at other application sites, but temporal variation in site conditions (i.e. seasonal fluctuations, water management impacts, and rapid plant growth) make such studies of limited use at the initial point of concern as well. This data analysis will look for patterns of LOC exceedances. If patterns are observed, the additional lines of data available will be utilized for further data analysis.

Toxicity Reference Values for Risk Quotient Calculations

The TRVs used for the risk quotient calculations are listed in Table 2. The test species selected were either one of the three standard water toxicity test species or fish or plant species found in the Delta. One LC50 and one LOEC for each test species was sought. Where multiple reference values were available the most conservative (i.e. the lowest) reference value was used. For 2,4-D and glyphosate, care was taken to use reference data for the same chemical form of the herbicide as that used by DBW. Whenever possible TRVs for the exact herbicide formulations used by DBW were utilized. The toxicity between herbicide formulations can vary substantially. For RQ calculation purposes, Delta smelt and Sacramento Splittail fish are considered endangered species.

Table 2. Toxicity Reference Values

Herbicide	**Test Species**	**Test Endpoint**	**Value**	**Units**	**Source**
Sonar	*D. magna*	LC50	3600	µg/l	Hamelink, 1986
	D. magna	NOEC	200	µg/l	Hamelink, 1986
	P. promelas	LC50	6200	µg/l	CDFG-ATL, 2002
	P. promelas	NOEC	1880	µg/l	CDFG-ATL, 2002
	Delta smelt	LC50	6100	µg/l	CDFG-ATL, 2002
	Delta smelt	NOEC	1280	µg/l	CDFG-ATL, 2002
	Stonewort	E C50	20	µg/l	Burkhart and Stross, 1990
2,4-D	*D. magna*	LC50	176	mg/l	WSDE, 2001
	D. magna	NOEC	27.5	mg/l	WSDE, 2001
	P. promelas	LC50	285	mg/l	Mayer and Ellersieck, 1986
	P. promelas	NOEC	17.1	mg/l	WSDE, 2001
	Rainbow trout	LC50	100	mg/l	Mayer and Ellersieck, 1986
	Delta smelt	LC50	149.4	mg/l	CDFG-ATL, 2002
	Delta smelt	NOEC	128	mg/l	CDFG-ATL, 2002
Diquat Dibromide	*S. capricornutum*	EC50	19	µg/l	Fairchild et al. 1997
	S. capricornutum	NOEC	44	µg/l	Fairchild et al. 1997
	D. magna	LC50	3000	µg/l	Bishop and Perry, 1981
	P. promelas	LC50	1.4	mg/l	CDFG-ATL, 2002
	P. promelas	NOEC	1.1	mg/l	CDFG-ATL, 2002
	Duckweed	LOEC	11	µg/l	Fairchild et al. 1997

	Duckweed	EC50	18	µg/l	Fairchild et al. 1997
	Delta smelt	LC50	1.1	mg/l	CDFG-ATL, 2002
	Delta smelt	NOEC	0.82	mg/l	CDFG-ATL, 2002
Glyphosate	*P. promelas*	LC50	97	mg/l	Folmar et al ,1979
	Delta smelt	LC50	5.5	mg/l	CDFG-ATL, 2002
	Delta smelt	NOEC	3.8	mg/l	CDFG-ATL, 2002
	Sacramento splittail	LC50	3900	µg/l	CDFG-ATL, 2002
	Sacramento splittail	NOEC	1900	µg/l	CDFG-ATL, 2002
R-11	P. promelas	LC50	3.9	mg/l	CDFG-ATL, 2002
	P. promelas	NOEC	2.5	mg/l	CDFG-ATL, 2002
	Delta smelt	LC50	2.2	mg/l	CDFG-ATL, 2002
	Delta smelt	NOEC	1.7	mg/l	CDFG-ATL, 2002
Agridex	Rainbow trout	LC50	>1000	mg/l	WSDA, 2004
	D. magna	LC50	>1000	mg/l	WSDA, 2004

Data Analysis by Pesticide

2,4-D

Table 3 shows the number of risk quotients calculated for each sampling year and the percentage of those risk quotients that exceeded an LOC. DBW's 2,4-D monitoring data generated no LOC exceedances.

Table 3. 2,4-D Risk Quotient Summary Table

	# Calculated Quotients	# LOC Exceedances	% LOC Exceedances
2003	784	0	0
2004	427	0	0
2005	588	0	0

Diquat

Table 4 shows the number of risk quotients calculated for each sampling year and the percentage of those risk quotients that exceeded an LOC.

Table 4. Diquat Risk Quotient Summary Table

	# Calculated Quotients	# LOC Exceedances	% LOC Exceedances
2003	378	23	6.1
2004	108	21	19.4
2005	108	12	11.1

From the three years of data analyzed, a sizeable number of samples generated LOC exceedances. The majority of these exceedances were for duckweed and *Selenastrum*, but some Delta smelt, Daphnia magna and fathead minnow LOCs were also exceeded. All exceedances were generated from samples collected post-application.

Prior to application, DBW, the Central Valley Regional Water Quality Control Board (CVRWQCB), USFWS and NOAA Fisheries were aware of the potential for problems associated with diquat applications. The EPA diquat label also has a warning about the potential impact to aquatic invertebrates. NOAA Fisheries has requested that whenever possible the amount of diquat used adjacent to salmon migratory routes be reduced or avoided when that species is likely to be present (DBW, 2005) The USFWS has determined that diquat impact to aquatic invertebrates is minimal, temporary, and not likely to jeopardize Delta smelt but has required that avoidance continue in areas where and when the smelt are known to be present (DBW, 2005).

It is also important to note that diquat dibromide is used heavily in terrestrial applications in areas adjacent to DBW treatment areas. It is likely that waterways are receiving diquat inputs from these terrestrial applications (Siemering, 2004).

For 2006, NOAA Fisheries has allowed DBW to treat *Egeria* sites in April and May with fluridone. This earlier start date for fluridone usage has allowed DBW to discontinue the use of diquat dibromide for 2006. It may be used in the future as conditions dictate.

Fluridone

Table 5 shows the number of risk quotients calculated for each sampling year and the percentage of those risk quotients that exceeded an LOC. Risk quotients were calculated for applications of liquid Sonar only. The Ecofram Tier 1 risk assessment methodology is not applicable to pelleted herbicide applications. Most DBW fluridone applications are with pelleted fluridone.

Table 5. Fluridone Risk Quotient Summary Table

	# Calculated Quotients	# LOC Exceedances	% LOC Exceedances
2003	70	3	4.3
2004	70	5	7.1
2005	49	3	6.1

While some LOC exceedances occurred following Sonar applications, all the exceedances were for the Stonewort EC50. Given that Sonar is an herbicide that is effective on a wide range of plants, these exceedances are hardly surprising. This finding is similar to that found by the APMP in its study of pelleted fluridone on typha germination and growth (Siemering, 2005). These exceedances indicate that nontarget plants may be affected by Sonar applications and that care should be taken to prevent this wherever possible. The areas where DBW is applying Sonar tend to be virtual monocultures of invasive plant species targeted for removal. DBW applications are unlikely to cause appreciable nontarget plant impacts.

Glyphosate

Table 6 shows the number of risk quotients calculated for each sampling year and the percentage of those risk quotients that exceeded an LOC. There were only a small number of exceedances calculated for Delta smelt (1) and Sacramento splittail (3) fish. This small number could be the result of overapplication, poor mixing and dispersion within the water column, or additional input from terrestrial sources. Given the multitude of inputs to the Delta and challenges associated with conducting sampling there, having only four exceedances in three years indicates that DBW glyphosate applications are not likely to pose a risk to the aquatic environment.

Table 6. Glyphosate Risk Quotient Summary Table

	# Calculated Quotients	# LOC Exceedances	% LOC Exceedances
2003	195	0	0
2004	280	0	0
2005	360	4	1.1

R-11

Table 7 shows the number of risk quotients calculated for each sampling year and the percentage of those risk quotients that exceeded an LOC. No samples collected in 2003 yielded detectable concentrations of R-11. In 2004 DBW switched to Agridex which is much less toxic than R-11 and also does not contain known endocrine disrupting compounds.

Table 7. R-11 Risk Quotient Summary Table

	# Calculated Quotients	# LOC Exceedances	% LOC Exceedances
2003	560	0	0
2004	NA	NA	NA
2005	NA	NA	NA

Agridex

Table 8 shows the number of risk quotients calculated for each sampling year and the percentage of those risk quotients that exceeded an LOC. DBW sample data generated no LOC exceedances.

Table 8. Agridex Risk Quotient Summary Table

	# Calculated Quotients	# LOC Exceedances	% LOC Exceedances
2003	NA	NA	NA
2004	160	0	0
2005	312	0	0

Conclusions

With the exception of diquat dibromide, the RQ values calculated here indicate that DBW's herbicide applications are unlikely to be causing toxicity to nontarget aquatic organisms. The potential risk with diquat has been acknowledged by DBW. The appropriate regulatory entities (NOAA Fisheries, CVRWQCB, and USFWS) have studied the problem, issued mitigating guidelines, and determined the risk to be minimal.

As stated previously, the RQ methodology applied in a Tier 1 assessment is structured to be a conservative test that can only be used to rebut the presumption of a risk of adverse effects due to herbicide applications (Giesy et al, 2000). If the RQs exceed the various LOCs, the potential for toxicity is indicated but not demonstrated. If the RQ value is greater than 100 or 1000, the margins of safety inherent in the conservative assumptions used to derive the RQ values are likely to be exceeded and potential risk to the organism and the ecosystem is indicated (Giesy et al, 2000). No RQ values calculated in this study approach this safety threshold.

If such thresholds were exceed greater in-depth monitoring at application sites would be warranted. This Tier 2 risk assessment would have to address the multitude of confounding factors inherent in any water quality monitoring conducted in the Delta.

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