

For DFG use only	
Proposal No.	Region

Section 1: Summary Information

1. Project title:	Fungicides in Water and Sediment in the Sacramento-San Joaquin Delta
2. Applicant name:	California Department of Fish and Game
3. Contact person:	Stella McMillin
4. Address:	1701 Nimbus Rd. Suite F
5. City, State, Zip:	Rancho Cordova, CA 95670
6. Telephone #:	916-358-2954
7. Fax #:	916-358-2953
8. Email address:	smcmillin@ospr.dfg.ca.gov
9. Agency Type:	Federal Agency <input type="checkbox"/> State Agency <input checked="" type="checkbox"/> Local Agency <input type="checkbox"/> Nonprofit Organization <input type="checkbox"/> University (CSU/UC) <input type="checkbox"/> Native American Indian Tribe <input type="checkbox"/>
10. Certified nonprofit Organization:	Yes <input type="checkbox"/> No <input checked="" type="checkbox"/> If yes, specify the nonprofit organization registration number: See www.pd.dgs.ca.gov/smbus/nonprofit
11. New grantee:	Yes <input checked="" type="checkbox"/> No <input type="checkbox"/>
12. Amount requested:	\$488,050
13. Total project cost:	\$488,050
14. Topic Area(s):	Primary: Ecosystem Water and Sediment Quality Secondary: Estuary Foodweb Productivity
15. ERP Project type:	Primary: Research Secondary: Monitoring
16. Ecosystem Element:	Primary: Contaminants Secondary: Bay-Delta Aquatic Foodweb
17. Water Quality Constituent:	Pesticides
18. At-Risk species benefited:	Delta smelt, Central Valley steelhead ESU, Central Valley spring-run chinook salmon ESU, Sacramento splittail, Sacramento River winter-run chinook salmon ESU
19. Project objectives:	This project is designed to determine whether water and sediment in areas receiving agricultural inputs in the Sacramento-San Joaquin Delta contain fungicides, and to determine whether any occurring fungicides are toxic to aquatic and sediment invertebrates.
20. Time frame:	3 years

Section 2: Location Information

1. Township, Range, Section: and the 7.5 USGS Quad map name.	
2. Latitude, Longitude (in decimal degrees, Geographic, NAD83):	Surface water sampling sites: Napa River 38-05'-51"N, 122-15-43.9"W Carquinez Strait 38-02'-22.9"N, 122-09-01.8"W Suisun Bay 38-02'-43.8"N, 122-55-07.7" Grizzly Bay 38'06'-50.4"N, 122-01-46.3"W Sacramento River 38-10'-43.7"N, 121-39-55.1"W Sacramento River 38-16'-26.5"N, 121-39-13.6"W Hood 38-22'-03.6"N, 121-31-13.6"W Cache Slough 38-17'-02.7"N, 121-43-04.3"W Old River 38-01'-09.1"N, 121-34-55.9"W Rough and Ready Island 37-57'-45.4"N, 121-21-55.9"W
3. Location description:	Surface water and sediment will be sampled from 10 sites listed above.
4. County(ies):	Solano, Contra Costa, Sacramento, San Joaquin
5. Directions:	
6. Ecological Management Region:	
7. Ecological Management Zone(s):	Sacramento-San Joaquin Delta Suisun Marsh/North San Francisco Bay
8. Ecological Management Unit(s):	North Delta East Delta Central and West Delta Suisun Bay and Marsh Napa River
9. Watershed Plan(s):	
10. Project area:	This project includes only monitoring.
11. Land use statement:	All sites are aquatic.
12. Project area ownership:	% Private _____ % State _____ % Federal _____ <i>Enter ownership percentages by type of ownership.</i>
13. Project area with landowners support of proposal:	No private land will be used.

Section 3: Landowners, Access and Permits

1. Landowners Granting Access for Project: (Please attach provisional access agreement[s])	No private land will be used.
2. Owner Interest:	
3. Permits:	
4. Lead CEQA agency:	
5. Required mitigation:	Yes <input type="checkbox"/> No <input checked="" type="checkbox"/>

Section 4: Project Objectives Outline:

1. List task information:

This project will help accomplish the task specified in Goal 6, Water and Sediment Quality, Objective1: Reduce loadings and concentration of toxic contaminants in all aquatic environments in the Bay Delta estuary to levels that do not adversely impact aquatic organisms, wildlife, and human health. High fungicide use in the estuary watershed may be impacting aquatic invertebrates and adversely impacting the food chain. It is necessary to monitor for fungicides in order to determine, and if necessary reduce, their impact.

2. Additional objectives:

3. Source(s) of above information:

Section 5: Conflict of Interest

To assist ERP staff in managing potential conflicts of interest as part of the review and selection process, we are requesting applicants to provide information on who will directly benefit if your proposal is funded. Please provide the names of individuals who fall in the following categories:

- Persons listed in the proposal, who wrote the proposal, will be performing the tasks listed in the proposal, or who will benefit financially if the proposal is funded; and/or
- Subcontractors listed in the proposal, who will perform tasks listed in the proposal, or will benefit financially if the proposal is funded.

Primary Contact for Proposal:

Primary Investigator:

Co-Primary Investigator:

Supporting Staff:

Subcontractor:

Provide the list of names and organizations of all individuals not listed in the proposal who helped with proposal development along with any comments.

Last Name	First Name	Organization	Role
McMillin	Stella	CDFG	Primary Contact
Goh	Kean	DPR	Co-Primary Investigator
Crane	Dave	CDFG	Co-Primary Investigator
Waligora	Dan	CDFG	Supporting Staff

Section 6: Project Tasks and Results Outline

1. Detailed Project Description

The Pelagic Organism Decline (POD) in the Sacramento-San Joaquin Delta has been well documented and several hypotheses given for its cause. One of the hypotheses is that the decline of indicator fish species is due to disruption of the food chain because of pollutants. Liver glycogen depletion studies support the food limitation explanation for the POD (IEP 2005). Much of the research on food limitation has focused on primary productivity. However, phytoplankton biomass trends for the last decade have been positive in the Delta and neutral in Suisun Bay (Jassby 2008). An alternate hypothesis is that the availability of zooplankton is impacting sensitive fish species. There is evidence of a decline in copepod species in the estuary (Sommer et al. 2007). A cause of this decline may be contaminants.

There is much data from the last two decades on the presence and toxicity of such pollutants as organophosphate pesticides, carbamate pesticides, and organochlorine pesticides. More recently, pyrethroid pesticides have been monitored in water and sediment in the watershed. However, it is estimated that current monitoring data is lacking for about half of the pesticides applied in the watershed (Kuivila and Hladik 2008). This includes the fungicides, with monitoring data for only two of the 33 fungicides applied in the estuary (Kuivila and Hladik 2008). Five of the twenty pesticides applied in the greatest amounts in the estuary watershed are fungicides. Toxicity values for these materials to aquatic invertebrates range from 9.1 to 330 $\mu\text{g/L}$ (Siepmann and Bruhn 1999, Table 1). Crops of high fungicide use include almonds, lettuce, strawberries, walnuts, peaches, grapes, onions, tomatoes and landscape. Fungicides tend to be used during times of heavy irrigation or wetter months (Figure 1). With the exception of chlorothalonil, none of these materials have been monitored in the watershed.

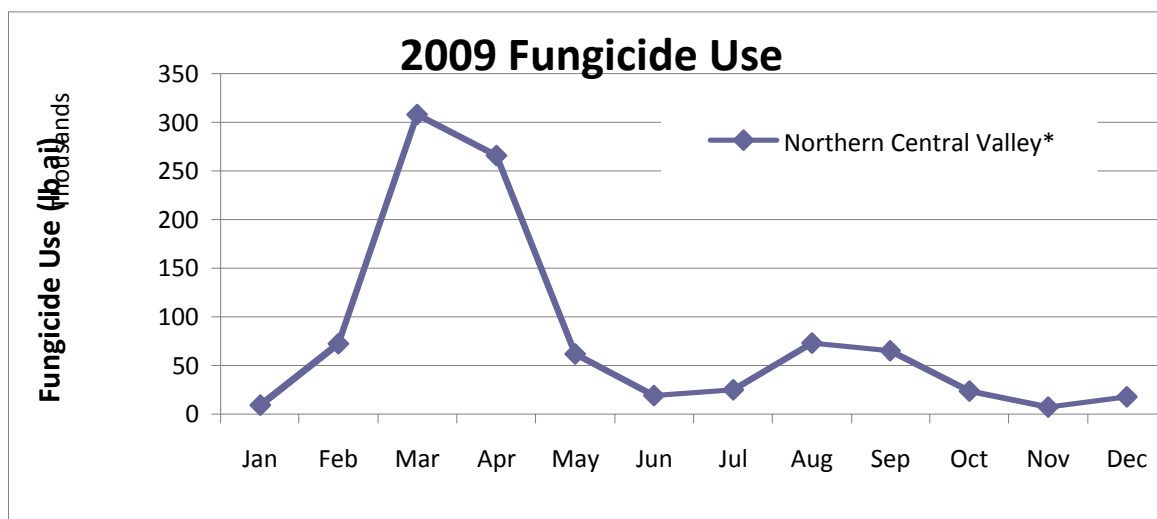
Besides being moderately to very highly toxic to aquatic organisms, commonly used fungicides possess chemical characteristics likely to cause sediment toxicity. They tend to have high adsorption coefficients (K_{oc} values) and be persistent in sediment (Table 1). When pesticides were evaluated for their potential to cause sediment toxicity using the criteria of adsorption to sediment, persistence in aquatic environments, and invertebrate toxicity values, several categories of fungicides were ranked as requiring sediment toxicity testing (Maund et al. 1997). These fungicides included benomyl, chlorothalonil, propiconazole and maneb. Ziram was highly toxic and persistent but had too low of a K_{oc} value, indicating that it might be more likely to remain in water than move to sediment.

In monitoring of stream and pond sediments in Sweden, the two of the three most frequently detected pesticides were the fungicides fenpropimorph and propiconazole (Kreuger et al. 1999). Propiconazole was found in 40% of samples taken from effluent, streams and a river downstream of banana plantations in Costa Rica. Chlorothalonil, which is less widely used, was also found (Castillo et al. 2000). The limited monitoring data available for these materials indicates that these materials have the potential to persist in water and sediment.

Because of this lack of monitoring data on potentially toxic materials, the USGS has recommended that fungicides be represented in monitoring programs. They also recommended that monitoring programs pay more attention to sediment-associated pesticides. It is essential that we fill in this data gap to evaluate if these materials are impacting sensitive aquatic populations.

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Figure 1. Fungicide Use in 2009 in the Northern Central Valley (fungicides include captan, chlorothalonil, maneb, mancozeb, and ziram).



*Removed the following Central Valley Counties: Fresno, Tulare, Kern, Kings

Table 1. Fungicide use (in San Francisco Estuary watershed), environmental fate, and toxicity.

Fungicide	Amount applied (1000s of kg)	Lowest invert LC ₅₀ (□g/L)	Lowest fish LC ₅₀ (□g/L)	K _{oc}	Sediment half life
Ziram	286	5	9.7	400	months
Maneb	199	60	148	>2,000	12-36 days
Chlorothalonil	154	3.6	16	1,380	1-3 months
Mancozeb	100	16	400	>2,000	1-7 days
Captan	88	360	46	200	1-10 days

2. Background and Conceptual Models

The bottom-up hypothesis of POD focuses on the decline in food available to sensitive fish species. Evidence supporting the influence of food limitation on the POD includes histological analyses of fish collected from the Delta. There is evidence of a decline in copepod and mysid species in the estuary (reference). These invertebrates are very sensitive to fungicides widely used in agriculture around the estuary. These fungicides are used extensively during the wet season and may be running off into water. Their high affinities for sediment and long half-lives in sediment mean that they may be present for several months following their introduction.

4. Approach and Scope of Work

Task 1. Project management and administration

The Department of Fish and Game will provide project management and administrative support for the project throughout the two-year duration. Cost for this function is included in 22% overhead for each individual task.

Task 2. Identify and selecting sampling locations.

The California Department of Pesticide Regulation (CDPR) will select sampling sites. Sites that receive runoffs from agricultural and urban areas and that are near sensitive habitats (nursery areas used by sensitive fish species) will be selected. Ten proposed sites below will be visited for final inclusion (Table 2; Figure 2). These sites are historical monitoring sites selected for their relevance as pelagic fish spawning grounds and high potential for pesticide runoff (Werner 2010). Surface

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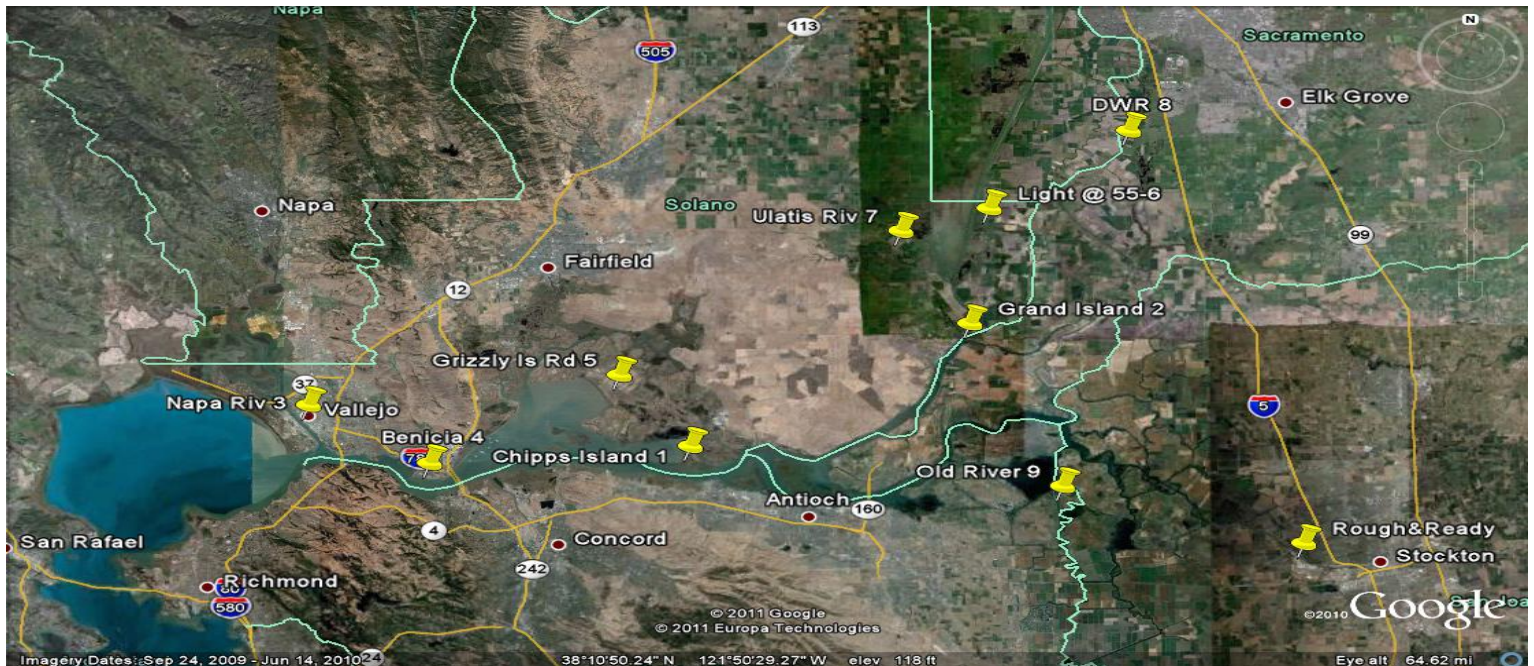
water and sediment will be collected during first storm runoff, and twice in the spring and twice in summer to coincide with the peak spawning periods. Grab samples or depth integrated samples will be taken according to DPR Standard Operating Procedures and QA/QC (DPR 2011).

Table 2. Proposed fungicide monitoring sites.

Site	Location	Latitude	Longitude
340	Napa River, at the seawall	38-05'-51"N	122-15-43.9"W
405	Carquinez Straight, just west of Benicia army dock	38-02'-22.9"N	122-09-01.8"W
508	Suisun Bay, off Chipps Island, opposite Sac. North Ferry Slip	38-03'-34.58"N	121-55-3.89"W
602	Grizzly Bay, northeast of Suisun Slough at Dolphin	38-06'-50.4"N	122-02-46.3"W
711	Sacramento River at the tip of Grand Island	38-10'-43.7"N	121-39-55.1"W
Light 55	Sacramento River Deep Water Channel at Light 55	38-16'-26.5"N	121-39-13.6"W
Hood	DWR water quality monitoring station	38-22'-03.6"N	121-31-13.6"W
Cache-Ulatis	Upper Cache Slough, mouth of Ulatis Creek	38-17'-02.7"N	121-43-04.3"W
902	Old River at mouth of Holland Cut	38-01'-09.1"N	121-34-55.9"W
Rough&Ready	San Joaquin, Rough & Ready Island	37-57'-45.4"N	121-21-55.9"W

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Figure 2. Map of Sampling Sites



Task 3. Implement sampling program.

CDPR will collect water and sediment samples at ten sites three times during the wet season and twice during the dry season. Sufficient volume will be taken for chemical analysis and toxicity testing. In addition, water temperature, pH, salinity, conductivity, and dissolved oxygen readings will be collected in situ.

Fungicides that will be analyzed include captan, chlorothalonil, maneb, mancozeb, and ziram.

Sediment toxicity tests will be performed using amphipod *Hyallorella azteca*. Acute aquatic toxicity tests will be performed using cladoceran *Ceriodaphnia dubia*.

Task 3 will take place during Fiscal Year 2.

Task 4. Analyze data and evaluate hypothesis.

Results from chemical analysis and toxicity tests will be compiled and analyzed to answer scientific questions and refine model. Known toxicity values for amphipod *Hyallorella azteca* and cladoceran *Ceriodaphnia dubia* will be used to calculate number of toxic units for each sample that shows toxicity. Amphipods and cladocerans have similar sensitivity to fungicides as do copepods. For example, EC50 values for maneb are 60 – 100 µg/L for cladocerans, 100 µg/L for amphipods, and 110 µg/L for copepods (USEPA ECOTOX database). Task 4 is dependent upon data gathered in Task 3. It will occur during Fiscal Years 2 and 3.

4. Deliverables.

- Semi-annual reports: delivered by June 1 and December 1 of each project year.
- Final report: delivered by completion of project.
- Project summary for public audience at beginning of project.
- Project summary for public audience at project completion.
- Project closure summary report
- Presentations at CALFED Science Conferences, Interagency Ecological Program meetings, State of the Estuary meetings, and other relevant meetings and workshops.
- Periodic updates at POD Water Quality Group meetings.
- Presentations upon request of CALFED Science Program staff.
- Copy of all published material resulting from grant.

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5. Feasibility

Each component of our study team has decades of experience in performing successful projects similar to the one we are proposing. Sufficient time and money have been allocated to successfully execute the proposed tasks. Relevant studies indicate that the research is likely to yield results that will result in increased understanding of the Bay-Delta. No environmental permits or compliances are required. Final authority for project management decisions will belong to the principal investigators.

6. Relevance to the CALFED ERP

This proposal responds to Objective 1 of Goal 6. It will allow us to determine the extent of fungicide contamination in the estuary and allow us to estimate the impact on aquatic organisms.

One of the key objectives of CalFed is Ecosystem Restoration. It is recognized that the sensitive estuarine ecosystem is impacted by agricultural and urban land use. It is likely that these effects include exposure to fungicides. In order to mitigate these impacts, the first step is to monitor fungicides in the estuary and determine their sources.

7. Expected quantitative result (project summary):

This project will result in a better understanding of the impacts of urban and agricultural fungicide use on aquatic organisms. If impacts are found, mitigation can be developed to lessen these effects. Results of this study would have implications very important to this watershed but not limited to the watershed. Fungicides are used worldwide and it is important to determine if their use impacts aquatic environments.

8. Other products and results:

9. Qualifications

Department of Fish and Game Pesticide Investigations Unit: Study design and data analysis. Ms. McMillin has 12 years of experience evaluating pesticide impacts on fish and wildlife in California. She is an environmental scientist with the Department of Fish and Game's Pesticide Investigations Unit and serves as the Pesticide Effects Coordinator for the state.

Department of Pesticide Regulation Environmental Monitoring Program: Sampling protocol, site selection and execution. Dr. Goh is an Environmental Program Manager for the California Department of Pesticide Regulation. He has more than 30 years of experience designing, coordinating, and supervising complex research in pesticides environmental fate and contamination.

Department of Fish and Game Water Pollution Control Laboratory: Chemical analysis. Mr. Crane is an Environmental Program Manager for the Department of Fish and Game. He has supervised DFG's Water Pollution Control Laboratory for 13 years. The Water Pollution Control Laboratory has extensive experience analyzing pesticides in water, sediment, and tissue in California.

Department of Fish and Game Aquatic Toxicology Laboratory: Sediment and aquatic toxicity tests. The Aquatic Toxicology Laboratory is supervised by Mr. Dan Waligora. The ATL has been performing toxicity tests since the 1980s and has extensive experience with sediment and aquatic toxicity.

10. Literature Cited

Castillo, L.E, C. Ruepert, and E. Solis. 2000. Pesticide residues in the aquatic environment of banana plantation areas in the north Atlantic zone of Costa Rica. *Environmental Toxicology and Chemistry* 19(8): 1942-1950.

DPR 2011. California Department of Pesticide Regulation. Standard Operating Procedures. <http://www.cdpr.ca.gov/docs/emon/pubs/sop.htm>

Interagency Ecological Program. 2008. Pelagic organism decline progress report: 2007 synthesis of results. 52 pages.

Jassby, A. 2008. Phytoplankton in the upper San Francisco estuary: recent biomass trends, their causes and their trophic significance. *San Francisco Estuary and Watershed Science*. 24 pages.

Kreuger, J., M. Peterson, and E. Lundgren. 1999. Agricultural inputs of pesticide residues to stream and pond sediments in a

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small catchment in southern Sweden. *Bulletin of Environmental Contamination and Toxicology* 62:55-62.

Kuivila, K.M. and M.L. Hladik. 2008. Understanding the occurrence and transport of current-use pesticides in the San Francisco estuary watershed. *San Francisco Estuary and Watershed Science*. 19 pages.

Maud, S., I. Barber, J. Dulka, J.Gonzalez-Valero, M. Hamer, F. Heimbach, M. Marshall, P. McCahon, H. Staudenmaier, and D. Wustner. 1997. Development and evaluation of triggers for sediment toxicity testing of pesticides with benthic macroinvertebrates. *Environmental Toxicology and Chemistry* 16(12):2590-2596.

Siepmann, S. and L. Bruhn. 1999. Hazard Assessment of the Fungicides Benomyl, Captan, Chlorothalonil, Maneb, and Ziram to Aquatic Organisms. California Department of Fish and Game Office of Spill Prevention and Response Administrative Report 99-1. Sacramento, California. 53 pages.

Sommer, T., C. Armor, and R. Baxter. 2007. The collapse of pelagic fishes in the upper San Francisco Estuary. *Fisheries* 32:270-277.

Werner et al. (2010). Pelagic Organism Decline: Acute and Chronic Invertebrate and Fish Toxicity Testing in the Sacramento-San Joaquin Delta. Final Report submitted to the California Department of Water Resources.
http://www.science.calwater.ca.gov/pdf/workshops/POD/Werner%20et%20al_2010_POD2008-2010_Final%20Report.pdf

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Section 7: Project Budget

1. Detailed Project Budget (Excel spreadsheets can be used)

Personal Services	Hourly Rate/ Unit Cost	Quantity Year 1	Cost Year 1	Quantity Year 2	Cost Year 2	Quantity Year 3	Cost Year 3	Cost All years
DFG Environmental Scientist Range C	32.45			528	17133.6	528	17133.6	34267
DPR Environmental Scientist Range C	32.45	352	11422.4	1670	54191.5			65614
Total: Personal Services								
Operating Expenses								
Travel/per diem: DPR			1400		6400			
Sampling materials:					5150			
Aquatic toxicity test	600			50				30000
Sediment toxicity test	1200			50				60000
Chemical analysis: water	620			50				31000
Chemical analysis: sediment	620			50				31000
Total: Operating Expenses								
			1400		11550		0	152000
Equipment								
Subtotal								
			14222.4		94425.1		17133.6	403881
Overhead: 20.84%								
								84169
Total project cost								
								488050

2. Budget justification

3. Administrative overhead:

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The California Department of Fish and Game charges 20.84% overhead.