San Francisco Estuary Invasive *Spartina* Project

2004 Water Quality Monitoring Report

Prepared for

San Francisco Estuary Invasive Spartina Project
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Submitted to

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Summary

Spartina alterniflora or Atlantic smooth cordgrass is an invasive plant species that rapidly spreads throughout the tidal mudflats and salt marshes of the San Francisco Estuary. To prevent the extinction of native cordgrass and to preserve and restore the integrity of this ecosystem, partners of the Invasive *Spartina* Project conducted Aquamaster® (glyphosate) and Habitat® (imazapyr) applications as part of a control effort where non-native forms of *Spartina* were identified. Under current state regulations (State Water Quality Control Board Water Quality Order No. 2004-0009-DWQ), coverage under the Statewide General NPDES Permit is required for all aquatic pesticide applications, and the regulated entities must prepare and implement an Aquatic Pesticide Application Plan (APAP; Attachment 1), including a water quality monitoring program. The water quality monitoring described in this report was conducted by the San Francisco Estuary Institute to satisfy NPDES permit compliance monitoring requirements.

The results for water quality showed no significant changes throughout the monitoring period of seven to eight days. Slight variations in water quality concentrations did not exhibit a consistent pattern at the four sampling sites and were most likely not associated with the pesticide treatments.

Measured herbicide concentrations were below the analytical method detection limit for glyphosate (< 10 μg/L) and distinctively lower than any published acute or chronic effect concentrations for aquatic organisms for imazapyr. Impacts from theses pesticide applications on the nearby ecosystem are therefore unlikely.

Introduction

Site Description

Forty-two sites throughout the San Francisco Bay region were treated during September and October of 2004 (Figure 1). The ISP categorized each of the sites receiving applications as on or more of four distinct types (listed below). According to current permit requirements, four sites of the 42 must be monitored, and at least one sample must be taken from each type of site. The sites selected for monitoring represented the most likely 'worst-case' scenarios for potential retention of herbicide within the aquatic environment. The sites monitored were all from Type I, II, and III environments. There were only two Type IV sites and these sites were subject to a high degree of constant flushing and therefore were measurable concentrations of herbicide in the water column were highly unlikely.

Site Types:

I. Tidal/Microtidal Marsh, Former Diked Bayland, Backbarrier Marsh
II. Fringing Tidal Marsh, Mudflats, and Estuarine Beaches
III. Major Tidal Slough, Creek or Flood Control Channel
IV. Urbanized rock, rip-rap, docks, ramps, etc.

Three of the monitored sites were located on the Bair-Greco Island Complex, along the west side of the San Francisco Bay, immediately north of the Dumbarton Bridge, in San Mateo County (Figures 1 & 2). Type I, II and III sites were present in this area. The fourth monitoring site was in the Old Alameda Creek Channel in Alameda County, on the east side of the San Fran-

cisco Bay (Figure 3), draining the largest watershed in the southern San Francisco Bay region. This was a type I site.

Aquatic Pesticides Applied

Habitat® (with the active ingredient imazapyr) was applied at the Old Alameda Creek Channel on September 15, 2004. The non-ionic spray adjuvant Agri-Dex® was used in the pesticide mixture as a surfactant. Habitat® is manufactured by BASF Corporation, Research Triangle Park, North Carolina and Agri-Dex® is manufactured by Helena Chemical Company, Collierville, Tennessee. Agri-Dex® is comprised of petroleum oil, fatty acid esters, and ethoxylated derivatives. Since it does not contain nonylphenol ethoxylate, chemical concentration analysis was not required. Imazapyr applications were conducted under a Department of Pesticide Regulation experimental use permit (Attachment 2).

Aquamaster® (with the active ingredient glyphosate) was applied at three selected monitoring sites on the Bair Greco Island on September 21 and September 28, 2004. Aquamaster® is manufactured by Monsanto Company in St. Louis, Missouri. LI 700® was mixed with glyphosate as a surfactant and drift control agent. LI 700® is manufactured by Loveland Industries Inc., Greeley, Colorado, and is comprised of phosphatidyl choline, methylacetic acid, and alkyl polyoxyethelene ether. Since it does not contain nonylphenol ethoxylate, chemical characterization of LI 700® was not required. The pesticide mixture also contained Blazon® as a blue spray pattern indicator, which is manufactured by Milliken Chemical in Inman, South Carolina.

Sampling Events

The monitoring events were tailored to characterize the potential risk involved with glyphosate and imazapyr applications. According to permit requirements, the monitoring conducted included background monitoring that happened up to 24 hours prior to the application, application event monitoring, and post-application event monitoring. The application event samples were collected immediately adjacent to the treatment area after sufficient time had elapsed such that treated water would have had entered the adjacent area (Figures 1 & 2). The post-application event samples were taken from the downstream edge of the treatment area one week after application. Herbicide applications occurred at low tide and sampling occurred during the slack tide after low tide. Field blank and sample duplicates were collected from each sampling event (Table 1).

Sampling Procedures

Samples were collected using sampling procedures developed for the State Water Resources Control Board (SWRCB) Aquatic Pesticide Monitoring Program (APMP). The San Francisco Estuary Institute (SFEI) conducted this work for the SWRCB. All procedures are outlined in the APMP Quality Assurance Program Plan (2004). The QA plan can be found at www.sfei.org.

Field Equipment

Water samples were collected using a portable peristaltic pump, and samples were then stored in pre-cleaned High Density Polyethylene (HDPE) bottles. Temperature, electrical conductivity, salinity, pH, and dissolved oxygen were measured with a portable multimeter Multi 340i Sensor (Wissenschaftliche-Technische Werkstaetten GmbH & Co. KG, in Germany). Turbidity was measured with a field turbidimeter (Hach, Model 2100P).

Sampling Analysis

Following collection, water samples were stored on ice and shipped to California Department of Fish and Game, Water Pollution Control Laboratory on the same day for overnight delivery. The samples were analyzed for imazapyr concentration and hardness within the appropriate holding times. The analytical method used for imazapyr was Liquid Chromatograph/Mass Spectrometer –

Atmospheric Pressure Ionization-ElectroSpray, for the analysis of hardness method SM 2340C was used.

Glyphosate samples were analyzed by Sequoia Analytical Laboratories using EPA Method 547 and hardness samples were analyzed using EPA Method 200.7. The analytical laboratories adhered to all QA requirements outlined in the APMP QA plan.

Application Rates and Surface Area

At the Old Alameda Creek Channel, a total of 60 acres were treated with imazapyr. Ten gallons of a pesticide-surfactant mixture were applied per acre. The contents of the mixture were 6 pints of Habitat®, 2 pints of Agri-Dex®, and water to total 10 gallons.

Glyphosate treatments at the Bair-Greco Island complex covered a total area of approximately 98 acres. For 2.5 acres 256 ounces of glyphosate (5 % solution) were mixed with 4 to 8 ounces of LI 700® (surfactant), 32 ounces of Blazon® (blue dye), and water to total 10 gallons.

Monitoring Results

No adverse effects on water quality were observed from either the application of imazapyr or glyphosate.

Imazapyr

Habitat® (or imazapyr) was used in conjunction with the non-ionic surfactant Agri-Dex®. Measured imazapyr concentrations were 7.2 μg/L and 8.2 μg/L (duplicate) directly after the pesticide application. Concentrations decreased within six days to 0.45 μg/L and 0.46 μg/L (duplicate) at the treated site (Table 2). LC 50s for imazapyr in fish were reported at 3,300 μg/L for the Japanese eel (*Anguilla japonica*) (Yokoyama et al. 1988) and at 6,700 μg/L for rainbow trout (*Oncorhynchus mykiss*) (US EPA 2000). Immobility was observed for the water flea *Daphia magna* at a concentration of 6,600 μg/L (US EPA 2000). This indicates that the imazapyr concentration found at the treated site probably had no adverse effects on the aquatic community, since the measurements were about three orders of magnitude lower than any observed effect or lethal concentrations for aquatic organisms.

Glyphosate

Aquamaster® (or glyphosate) was used with the non-ionic surfactant LI 700® and the blue spray pattern indicator Blazon®. Measured concentrations were all below the detection limit of 10 μg/L (Sequoia Analytical Laboratory) (Table 1). Glyphosate was determined to be moderately toxic for aquatic organisms by the Pesticide Action Network North America with LC50s ranging between 1,000 and 10,000 μg/L. A study conducted by Mayer and Ellensieck (1986) determined the LC 50 for crayfish *Orconectes nais* at 7,000 μg/L.

Conventional Water Quality Parameters

Conventional water quality parameters (Table 2) showed that the Old Alameda Creek Channel was more fresh water influenced than the Bair-Greco Island sites. Lower dissolved oxygen concentrations, as well as lower hardness and electrical conductivity measurements indicated a greater distance of the Alameda site from the San Francisco Estuary. However, hardness values are still above 3,000 $CaCO_3$ mg/L at this location, which suggests that calcium can cause a noticeable antagonism to glyphosate. According to a research study, water with greater than 150 $CaCO_3$ mg/L will form glyphosate-salt complexes that are not easily absorbed by leaves and have to be out-competed by different salts added to the water column while spraying (Boerboom 2001). On the other hand, these complexes make the excess pesticide less bioavailable for non-target aquatic organisms as well. Occasionally observed increases in turbidity before and during

the application time could have also caused the pesticides to bind rapidly to particles, thus decreasing its bioavailability for aquatic organisms.

Dissolved Oxygen

All monitored sites exhibited low levels of dissolved oxygen, including the background samples. Concentrations varied from 3.2 mg/L at B2 North Quadrant to 7.4 mg/L at Bay Slough, both measured at the one week post-sampling event. Within this range, concentration fluctuated without exhibiting any significant patterns at the four sites. A change in dissolved oxygen concentrations due to the herbicide applications is therefore unlikely (Figure 3).

Electrical Conductivity (EC)

The EC varied from 27.3 µS at the Alameda site to 74.2 µS at the Bay Slough site (Figure 4). Measurements throughout the sampling period were fairly consistent and did not exhibit any significant changes associated with the chemical treatment.

Turbidity

Turbidity values varied widely from 13 NTU at Steinberger Slough to over 1,000 NTU at the Old Alameda and the Bay Slough site. Figure 5 displays this fluctuation graphically and shows no consistent change in turbidity after the treatment period.

Hardness

Hardness is a measurement of the concentration of divalent metal ions. In this study, hardness was measured as a concentration of calcium salt (CaCO3) and expressed in mg/L water. Concentrations ranged from 3,540 mg/L at the Alameda site to 5,900 mg/L at the Steinberger Slough site (Figure 6). Water is considered very hard with calcium carbonate concentrations over 300 mg/L.

Recommendations for Improvements to the APAP

Due to the formation of unfavorable glyphosate-calcium complexes in hard water that are not easily absorbed by the plant leaves, the addition of ammonium sulfate to spray water would most likely increase the ammonium salt concentration that could out-compete the glyphosate-calcium complex. The glyphosate-ammonium complex is more readily absorbed by the plants (Boerboom 2001).

References

Boerboom, C. 2001 Ammonium Sulfate Requirements with Glyphosate. Weed Science, University of Wisconsin.

Mayer, F.L.J., and M.R. Ellersieck. 1986. Manual of Acute Toxicity: Interpretation and Data Base for 410 Chemicals and 66 Species of Freshwater Animals. Resource Publication No. 160, US Department of the Interior, Fish and Wildlife Services, Washington, DC, pp. 505.

Pesticide Action Network North America. Pesticide Database. http://www.pesticideinfo.org/Index.html

US Environmental Protection Agency. Office of Pesticide Programs. 2000. Pesticide Ecotoxicity Database. Environmental Fate and Effects Division, US EPA, Washington, DC.

Yokoyama, T., H. Saka, S. Fujita, and Y. Nishiuchi. 1988. Sensitivity of Japanese Eel, *Anguilla japonica*, to 68 Kinds of Agricultural Chemicals. Bulletin for Agricultural Chemistry Inspection Station, Vol. 28, pp. 26-33.

Attachments

1. Aquatic Pesticide Application Plan
2. State Department of Pesticide Regulation Research Authorization

Figures

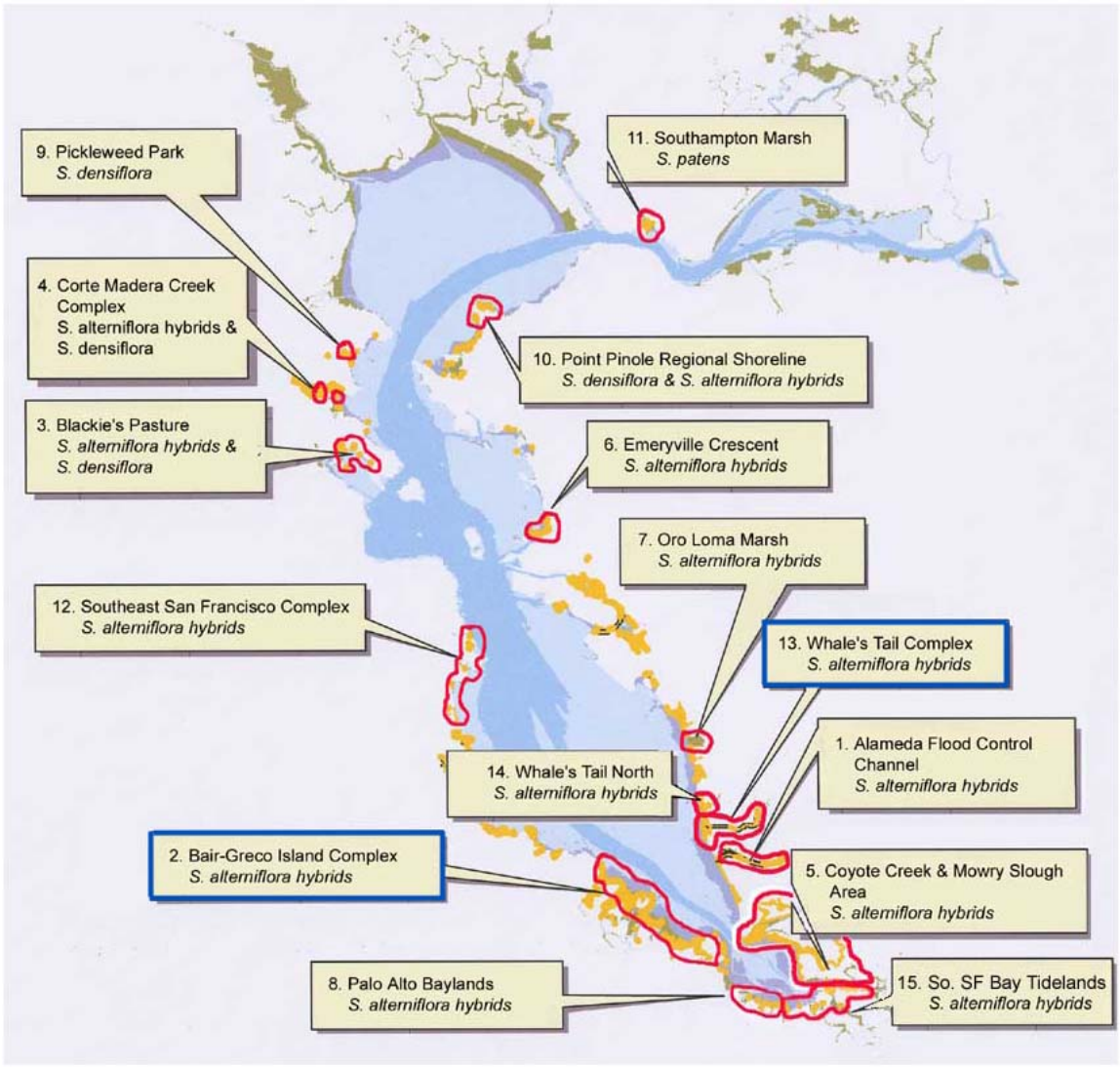

Figure 1. Water Quality Sampling Locations, San Francisco Estuary, 2004 Spartina Control Program

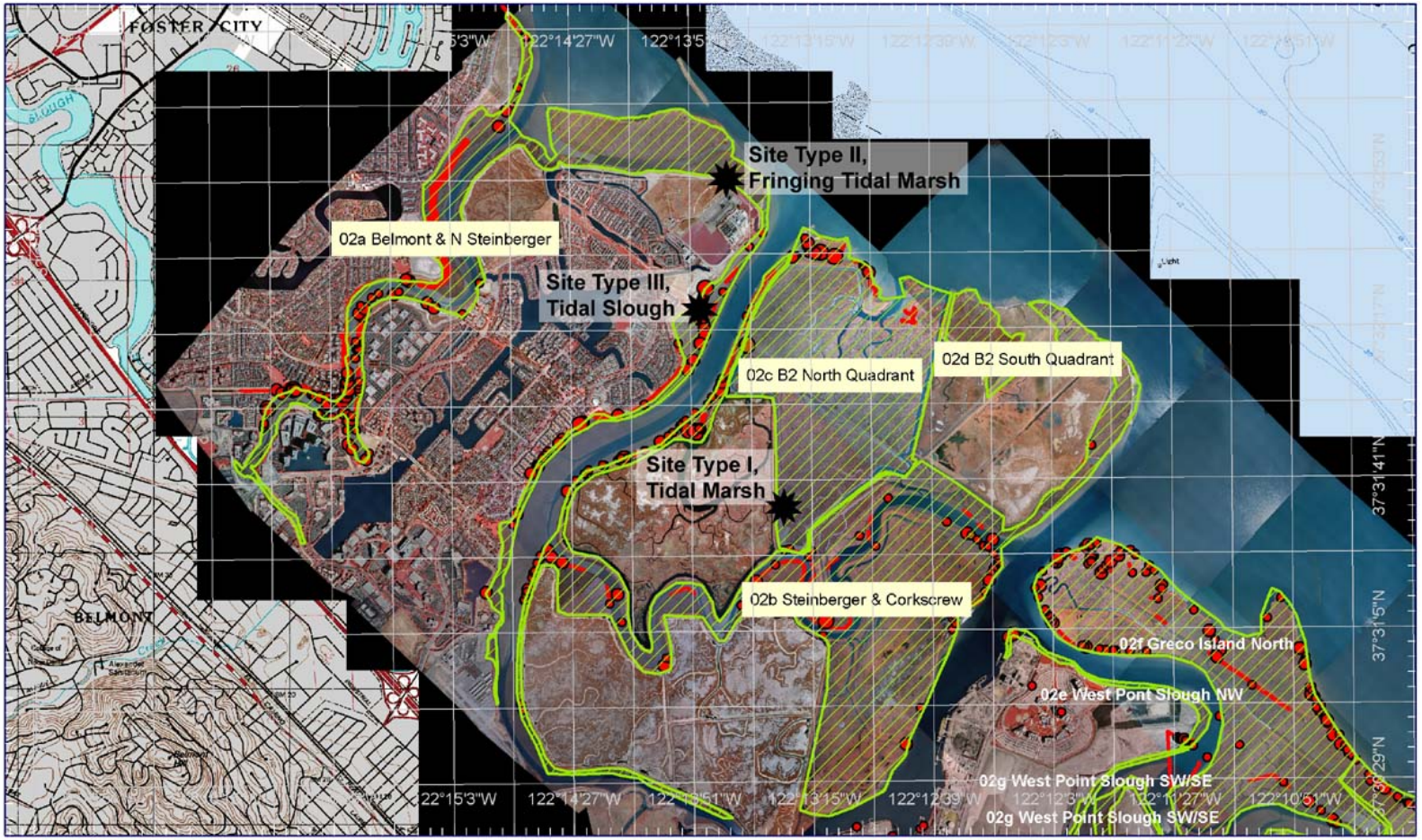

Figure 2.
West San Francisco Bay Water Quality Sampling Locations, 2004 Spartina Control Program

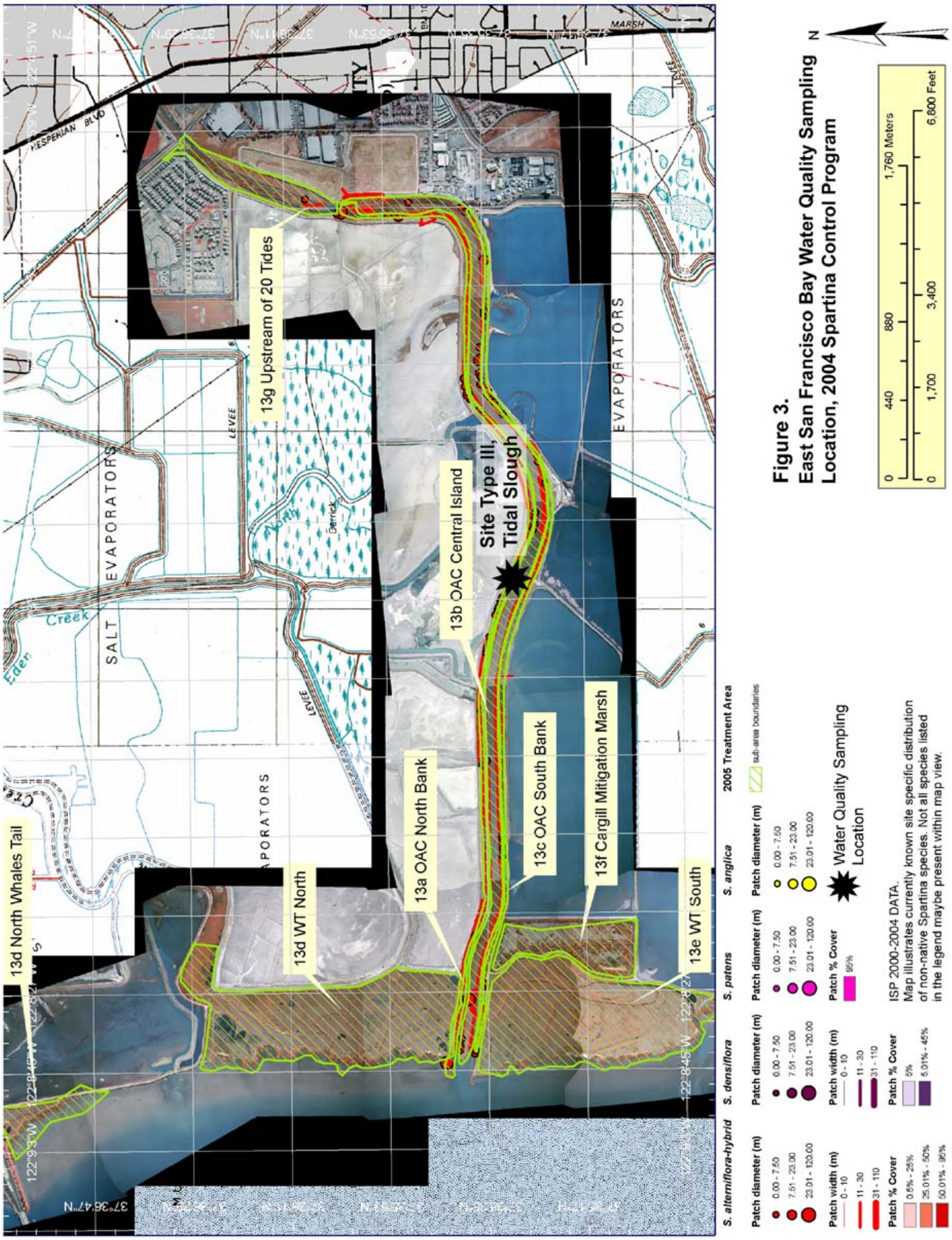

Figure 3.
East San Francisco Bay Water Quality Sampling Location, 2004 Spartina Control Program

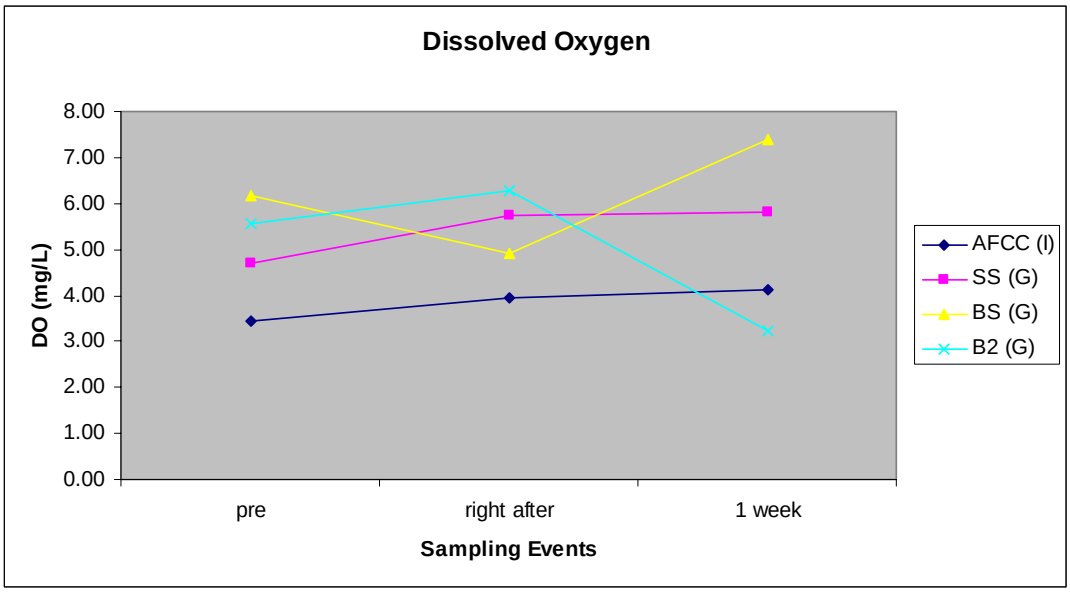

Figure 4. Dissolved oxygen concentrations.

AFCC = Old Alameda Creek Channel, SS = Steinberger Slough, BS = Bay Slough, B2 = B2 North Quadrant. (I) = Imazapyr application site, (G) = Glyphosate application site.

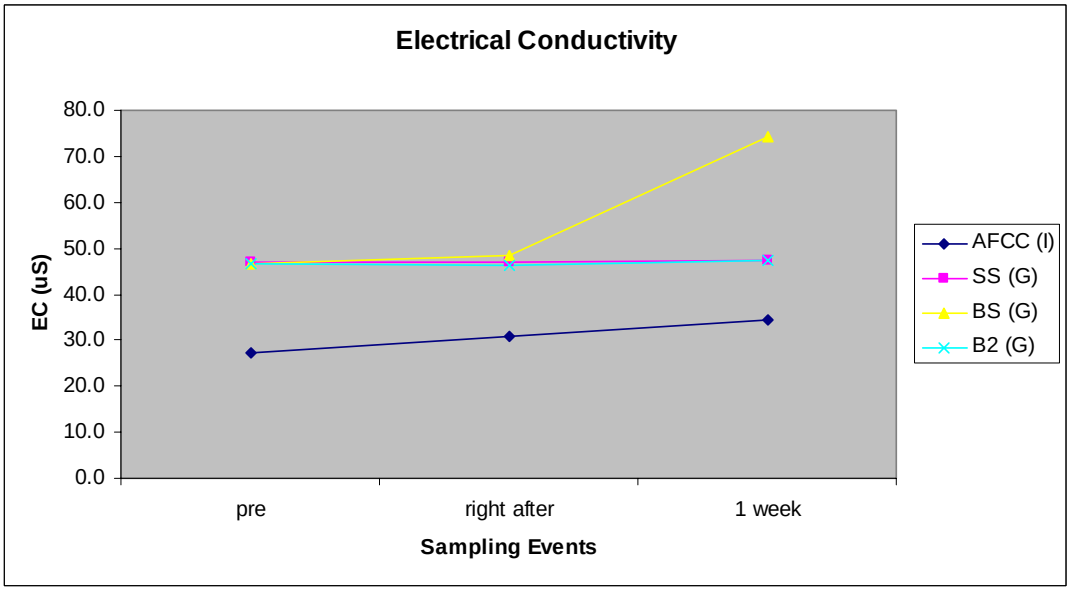

Figure 5. Electrical conductivity measurements.

AFCC = Old Alameda Creek Channel, SS = Steinberger Slough, BS = Bay Slough, B2 = B2 North Quadrant. (I) = Imazapyr application site, (G) = Glyphosate application site.

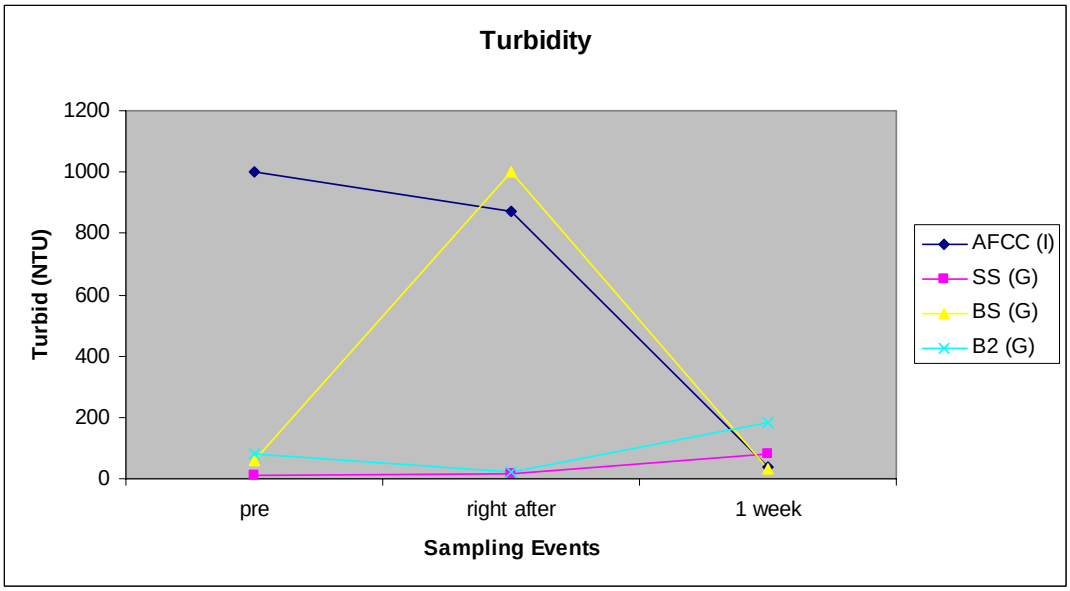

Figure 6. Turbidity measurements.

AFCC = Old Alameda Creek Channel, SS = Steinberger Slough, BS = Bay Slough, B2 = B2 North Quadrant. (I) = Imazapyr application site, (G) = Glyphosate application site.

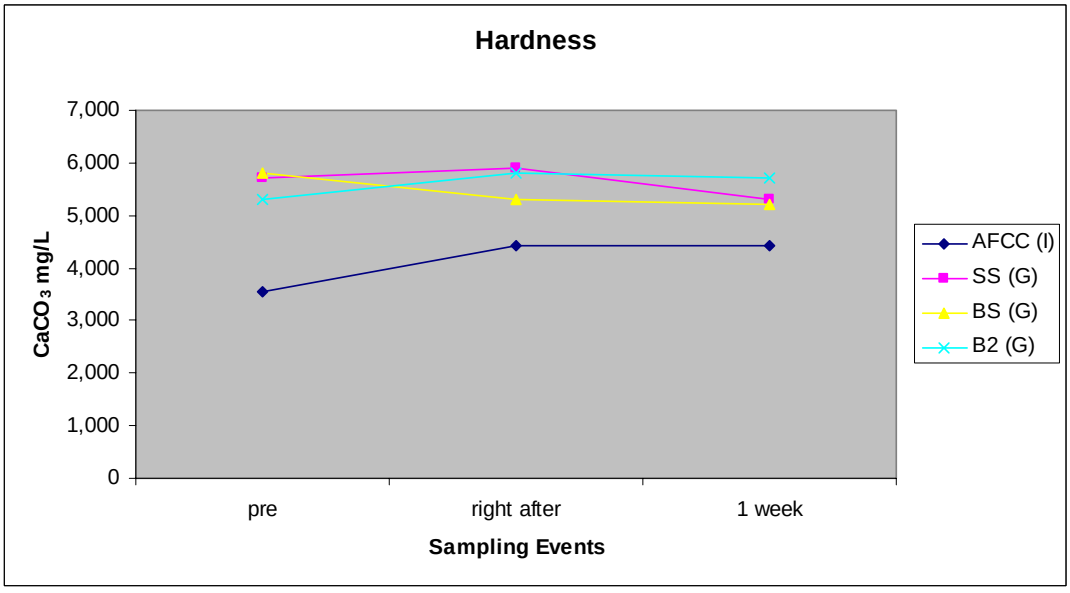

Figure 7. Hardness Concentrations.

AFCC = Old Alameda Creek Channel, SS = Steinberger Slough, BS = Bay Slough, B2 = B2 North Quadrant. (I) = Imazapyr application site, (G) = Glyphosate application site.

Tables

Table I: Summary of water quality sampling program for the Invasive *Spartina* Project 2004

Sites	Type	Sampling Events	QA	Pesticide	Surfactant
B2 North Quadrant	I	Pre, immediately after, 1 week post	1 blank and 1 duplicate sample per event	Glyphosate	LI 700
Steinberger Slough & Mouth North	II	Pre, immediately after, 1 week post	1 blank and 1 duplicate sample per event	Glyphosate	LI 700
Bay Slough	III	Pre, immediately after, 1 week post	1 blank and 1 duplicate sample per event	Glyphosate	LI 700
Oro Loma Marsh	I	Pre, immediately after, 1 week post	1 blank and 1 duplicate sample per event	Imazapyr	Agri-Dex

Table 2. Water quality analysis results for three sampling events at four sampling sites.

Invasive Spartina Project Results

Sample ID	Location	Date	Air Temp	Time	Imazapyr	Glyphosate	Hardness ($CaCO_3$ mg/L)	DO	Temp	pH	Temp	EC	Temp	Sal	Turbidity
			C	24 hour clock	µg/L	µg/L	CaCO3 mg/L	mg/L	C		C	µS	C	ppt	NTU
Ala 0	Alameda Flood Control Channels	9/15/2004	13	7:10	ND		3,540	3.45	19.1	7.88	19.2	27.3	19.2	29.7	>1000
Ala 1	Alameda Flood Control Channels	9/15/2004	20	10:40	7.20		3,540	3.94	20.6	7.90	21.1	30.8	20.7	29.8	870
Ala 1 Dup	Alameda Flood Control Channels	9/15/2004	20	10:40	8.20		3,510	3.94	20.6	7.90	21.1	30.8	20.7	29.8	870
Ala 1 Bla	Alameda Flood Control Channels	9/15/2004	20	10:40	0.43		< 1.0	3.94	20.6	7.90	21.1	30.8	20.7	29.8	870
Ala 2	Alameda Flood Control Channels	9/21/2004	29	14:20	0.45		4,440	4.12	19.3	7.79	20.2	34.5	19.6	21.6	35.3
Ala 2 Dup	Alameda Flood Control Channels	9/21/2004	29	14:20	0.46		4,440	4.12	19.3	7.79	20.2	34.5	19.6	21.6	35.3
Ala 2 Bla	Alameda Flood Control Channels	9/21/2004	29	14:20	ND		ND	4.12	19.3	7.79	20.2	34.5	19.6	21.6	35.3
S 0	Steinberger Slough	9/21/2004	17	8:44		ND	5,700	4.71	17.6	7.94	17.0	47.1	17.5	30.1	12.5
S 0 Dup	Steinberger Slough	9/21/2004	17	8:44		ND	5,600	4.71	17.6	7.94	17.0	47.1	17.5	30.1	12.5
S 0 Bla	Steinberger Slough	9/21/2004	17	8:44		ND	ND	4.71	17.6	7.94	17.0	47.1	17.5	30.1	12.5
S 1	Steinberger Slough	9/21/2004	27	11:40		ND	5,900	5.73	19.6	7.92	20.1	46.9	19.6	30.3	14.5
S 2	Steinberger Slough	9/27/2004	19	12:10		ND	5,300	5.82	18.3	8.06	18.6	47.3	18.4	30.2	81.5
S 2 Dup	Steinberger Slough	9/27/2004	19	12:10		ND	4,800	5.82	18.3	8.06	18.6	47.3	18.4	30.2	81.5
S 2 Bla	Steinberger Slough	9/27/2004	19	12:10		ND	ND	5.82	18.3	8.06	18.6	47.3	18.4	30.2	81.5
F 0	Bay Slough	9/21/2004	18	9:20		ND	5,800	6.17	16.6	8.14	16.7	46.8	16.7	30.0	61.4
F 1	Bay Slough	9/21/2004	30	13:20		ND	5,300	4.92	29.5	7.89	29.6	48.4	29.4	31.9	>1000
F 2	Bay Slough	9/27/2004	19	13:30		ND	5,200	7.40	20.1	8.11	20.4	74.2	19.9	30.4	30.6
T 0	B2 South Quadrant	9/27/2004	19	12:30		ND	5,300	5.56	19.5	7.98	19.8	46.8	19.8	30.0	79.4
T 1	B2 South Quadrant	9/28/2004	23	13:00		ND	5,800	6.29	20.4	8.03	20.7	46.4	20.6	29.9	24.1
T 1 Dup	B2 South Quadrant	9/28/2004	23	13:00		ND	5,500	6.29	20.4	8.03	20.7	46.4	20.6	29.9	24.1
T 1 Bla	B2 South Quadrant	9/28/2004	23	13:00		ND	ND	6.29	20.4	8.03	20.7	46.4	20.6	29.9	24.1
T 2	B2 South Quadrant	10/4/2004	18	12:20		ND	5,700	3.22	18.6	7.66	19.0	47.2	18.7	30.4	183.0
T 2 Dup	B2 South Quadrant	10/4/2004	18	12:20		ND	5,600	3.22	18.6	7.66	19.0	47.2	18.7	30.4	183.0
T 2 Bla	B2 South Quadrant	10/4/2004	18	12:40		ND	ND	3.22	18.6	7.66	19.0	47.2	18.7	30.4	183.0