Use of Imazapyr Herbicide to Control Invasive Cordgrass (*Spartina spp.)* in the San Francisco Estuary

Water Quality, Biological Resources, and Human Health and Safety

Prepared for

San Francisco Estuary Invasive Spartina Project
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ACRONYMS, ABBREVIATIONS, UNITS, AND SYMBOLS

<	less than
>	greater than
µg/L	microgram per liter
a.e.	acid equivalent
a.i.	active ingredient
AMPA	aminomethylphosphonic acid
atm	atmosphere
b.w.	body weight
BAF	bioaccumulation factor
BCF	bioconcentration factor
Blazon® Blue	Blazon® Spray Pattern Indicator “Blue”
CalEPA	California Environmental Protection Agency
CEQA	California Environmental Quality Act
CO_2	carbon dioxide
Conservancy	California State Coastal Conservancy
DPR	Department of Pesticide Regulation
EC	effect concentration
EC_{25}	concentration causing 25% inhibition of a process
EC_{50}	concentration causing 50% inhibition of a process
EEC	estimated exposure concentration
EIS/EIR	Environmental Impact Statement/Environmental Impact Report
ESA	Endangered Species Act
ESO	esterified seed oil
Estuary	San Francisco Estuary
g/L	gram per liter
gal/acre	gallons per acre
GPS	global positioning system
HDT	highest dose tested
hr	hour
HSDB	Hazardous Substances Database (National Library of Medicine)
ISP	Invasive Spartina Project
juv.	juvenile
K_{oc}	organic carbon partition coefficient
K_{ow}	octanol/water partition coefficient
lb/acre	pounds per acre
LC_{50}	lethal concentration, 50% kill
LD_{50}	lethal dose, 50% kill
LOC	level of concern
LOEC	lowest-observed-effect concentration
LOEL	lowest-observed-effect level

m^3	cubic meter
MATC	maximum allowable toxicant concentration
MBTA	Migratory Bird Treaty Act
mg	milligram
mg/kg	milligram per kilogram
mg/L	milligram per liter
mg/m^3	milligram per cubic meter
mmHg	millimeter mercury
MMRP	Mitigation Monitoring and Reporting Program
MSDS	material safety data sheet
MSO	methylated seed oil
NIS	non-ionic surfactant
NNG	2,4-nitrosoglyphosate
NOEC	no-observed-effect concentration
NOEL	no-observed-effect level
NOS	not otherwise specified
ppm	parts per million
RfD	reference dose
RQ	risk quotient
SBS	silicone-based surfactant
SSPs	Site-specific Plans
T&E	threatened and endangered
$t_{½}$	half-life
USDA	U.S. Department of Agriculture
U.S. EPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service
VOC	vegetable oil concentrate

EXECUTIVE SUMMARY

Under the direction of the California State Coastal Conservancy's ("Conservancy") San Francisco Estuary Invasive Spartina Project ("ISP"), Leson & Associates has prepared this analysis of potential impacts to water quality, biological resources and human health and safety from the use of an imazapyr herbicide for treatment of non-native, invasive salt marsh cordgrasses (genus *Spartina)* in the San Francisco Estuary ("Estuary").

Several non-native *Spartina* species were introduced into the Estuary in recent decades and soon began to spread rapidly. This invasion of non-native *Spartina* species and their hybrids, if left uncontrolled, threatens to displace the native *Spartina* species and cause fundamental changes in the structure, function, and value of the Estuary's tidal lands, and imperil its ecological balance. In 2003, the Conservancy, as the lead agency under the California Environmental Quality Act ("CEQA"), certified the Programmatic Environmental Impact Statement/Environmental Impact Report ("EIS/EIR") for ISP's Spartina Control Program, which aims to eradicate non-native, invasive salt marsh *Spartina* in the Estuary. This program implements a number of treatment techniques, including the application of herbicides. Glyphosate, the herbicide evaluated and approved for use in the Programmatic EIS/EIR, has a number of shortcomings in an estuarine environment. It requires higher application rates than an alternative herbicide, imazapyr, which was recently submitted for registration in California under the brand name Habitat®. Because the use of imazapyr is not specifically addressed and evaluated in the Programmatic EIS/EIR, the Conservancy intends to amend its CEQA analysis of potential environmental impacts to include the use of imazapyr. The Conservancy does not intend to use imazapyr as a replacement of glyphosate but rather as an additional tool to be used by itself or in combination with glyphosate where appropriate. This report evaluates this planned application by analyzing the potential impacts to water quality of the Estuary and potential ecological and human health risks, in support of the Conservancy's planned CEQA amendment. In addition, this report discusses changes in environmental effects compared to the use of glyphosate as discussed in the Programmatic EIS/EIR, identifies approaches to minimize potential increased risks from the use of imazapyr, and discusses the implications of these findings for purposes of CEQA.

Environmental Fate of Imazapyr in Estuarine Environment and Impacts on Water Quality

In water, imazapyr rapidly degrades via photolysis. A number of field studies demonstrated that imazapyr rapidly dissipated from water within several days and no detectable residues of imazapyr were found in either water or sediment within two months. In estuarine systems, dilution of imazapyr with the incoming tides contributes to its rapid dissipation. This suggests that imazapyr is not environmentally persistent in the estuarine environment and does not result in material impacts to water quality.

Ecological Health Risks of Imazapyr Applications

The evaluation presented in this report regarding the potential ecological risks is mainly based on two recent risk assessments: one for imazapyr application for control of non-native, invasive *Spartina* in estuarine habitats in Washington State, and another for forestry application. This report updates and adapts these prior risk assessments for conditions and planned application rates in the Estuary. Risks to wildlife and non-target vegetation are assessed based on more conservative exposure assumptions. In addition, this report evaluates risks based on lower screening levels, including those set forth by the U.S. Environmental Protection Agency for endangered species.

The maximum proposed application rate of imazapyr for control of *Spartina* in the Estuary does not result in aquatic concentrations or terrestrial doses that exceeded screening levels for toxicity to aquatic or terrestrial mammals, birds, invertebrates, or benthos, even under the extremely conservative assumptions and risk scenarios evaluated. A spill scenario is considered highly unlikely because of the best management practices set forth in the Spartina Control Program's Mitigation Monitoring and Reporting Program ("MMRP"). Further, the disturbance created by cleanup efforts would discourage wildlife use of the area. The more stringent screening levels for acute toxicity to endangered fish species are marginally exceeded by the highest measured and modeled imazapyr concentrations in the leading edge of an incoming tide. The conditions and assumptions for these concentrations are extremely conservative and would only be present momentarily and in a small volume of water. The concurrent presence of an endangered fish species is considered highly unlikely and potential impacts are therefore considered insignificant.

Because imazapyr is a highly effective herbicide, non-target plants that are inadvertently directly sprayed are likely to be severely damaged. This risk is particularly acute for vascular plants. Longer-term, enduring adverse effects to non-target vegetation are not expected due to imazapyr's rapid degradation and dissipation.

Human Health and Safety

The evaluation in this report of human health risks is based on a recent risk assessment for the application of imazapyr in forestry applications, which evaluated worst-case scenarios for both workers and members of the general public, *e.g.,* recreational users or residents.

Based on this assessment, typical exposures to imazapyr do not lead to doses that exceed screening levels for either workers or members of the general public. Workers and members of the general public are not expected to experience substantial risk from acute or longer-term exposure to imazapyr. Effects from accidental exposure will be minimized or avoided by compliance with the MMRP.

Relative Ecological and Human Health Effects of Imazapyr versus Glyphosate and Associated Adjuvants

Imazapyr has been demonstrated to be less toxic to aquatic organisms than glyphosate. Combined with the lower application rate for imazapyr, this results in a considerably lower risk to aquatic organisms. The aquatic formulations of both herbicides must be mixed with surfactants for use on post-emergent vegetation such as *Spartina*. The inherent risks of using either herbicide have been shown to increase significantly when mixed with surfactants. However, risks associated with glyphosate/surfactant mixtures are greater than those for imazapyr/surfactant mixtures.

Unlike imazapyr, glyphosate is not photolyzed in water and is readily adsorbed to suspended particles and sediment. Its fate in an estuarine environment is primarily determined by its strong adsorption to sediment particles and the rate of microbial degradation. Residual biomass of treated *Spartina* could also slowly release glyphosate into the environment. Therefore, glyphosate is predicted to be more persistent than imazapyr in an estuarine environment.

Compared to glyphosate, adverse effects of imazapyr to directly-sprayed non-target vegetation would tend to be higher due to it’s higher efficacy. These risks are particularly pronounced for vascular plants. However, this tendency is probably more than offset because of the lower spray volumes used with imazapyr.

Conclusions

The overall weight of evidence from this analysis suggests that imazapyr herbicides can be a safe, highly effective treatment for control and eradication of non-native *Spartina* species in the San Francisco Estuary, offering an improved risk scenario over the existing treatment regime with glyphosate herbicides. From a CEQA perspective, imazapyr’s potential significant impacts to biological resources, and human health and safety, and mitigations required to reduce those impacts to less than significant levels, are encompassed in those impacts and mitigations previously identified for glyphosate. Therefore, no additional mitigation is required for the use of imazapyr.

1. INTRODUCTION

The following sections discuss the purpose of this report, present the sources of information it relied on, and summarize the report's organizational outline.

1.1 Purpose of Report

The purpose of this report is to analyze the potential ecological and human health risks and impacts on water quality associated with using an herbicide containing the active ingredient imazapyr to eradicate non-native, invasive salt marsh cordgrasses (genus "*Spartina")* in the San Francisco Estuary ("Estuary") and to compare these potential risks to those resulting from the use of a glyphosate herbicide. This report builds upon information contained in the Programmatic Environmental Impact Statement/Environmental Impact Report ("EIS/EIR") for the San Francisco Estuary Invasive Spartina Project ("ISP") Spartina Control Program[1,2], which evaluated the use of a glyphosate herbicide for purposes of *Spartina* eradication in the Estuary. The evaluation regarding the potential ecological risks associated with the use of an imazapyr herbicide in addition to and/or in a mixture with glyphosate herbicides in the San Francisco Estuary is mainly based on the findings of a recent standard ecological risk assessment that evaluated the use of an imazapyr herbicide for control of non-native, invasive *Spartina* in estuarine habitats in Washington State ("2003 Entrix report"[3]). The report at hand summarizes relevant information contained in this and other risk assessments, and adapts and interprets them for the San Francisco Estuary.

Specifically, this report

- Updates, adapts, and expands the findings of the 2003 Entrix report regarding the potential ecological risks associated with the use of an imazapyr herbicide in an estuarine environment to incorporate any newer information available and to address San Francisco Estuary conditions and species;

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[1] California State Coastal Conservancy and U.S. Fish and Wildlife Service, Volume I: Final Programmatic Environmental Impact Statement/Environmental Impact Report, San Francisco Estuary Invasive Spartina Project: Spartina Control Program, State Clearinghouse #2001042058, September 2003.

[2] The Final EIS/EIR is a "programmatic" EIS/EIR because it analyzes the potential effects of implementing treatment methods for a regional program rather than the impacts of an individual treatment project. (CEQA Guidelines Section 15168.)

[3] Entrix, Inc., Ecological Risk Assessment of the Proposed Use of the Herbicide Imazapyr to Control Invasive Cordgrass (*Spartina* spp.) in Estuarine Habitat of Washington State, prepared for Washington State Department of Agriculture, October 30, 2003.

- Updates the comparison of relative ecological risks of the use of imazapyr versus glyphosate and associated adjuvants[4] in an estuarine environment from the 2003 Entrix report; and
- Discusses potential changes in impacts to water quality, biological resources, human health (from those identified in the Programmatic EIS/EIR) caused by the use of an imazapyr herbicide on as many as 1,500 acres per year of tidal wetlands for as many as four consecutive years.

1.2 Sources of Information

In addition to the 2003 Entrix report, this report relies on information from a standard human health and ecological risk assessment, published by the U.S. Department of Agriculture ("USDA") Forest Service that evaluated the use of imazapyr for forestry applications ("2004 SERA report"[5]). The report at hand further incorporates unpublished information obtained from the ISP and a number of industry representatives, researchers, and government. In addition, this report includes information from a comprehensive literature search (DIALOG[6], TOXNET[7], and web) and review of publications on ecological impacts, toxicity, and fate and transport of imazapyr and glyphosate herbicides including potential adjuvants, focusing on aquatic, particularly estuarine, environments.[8]

1.3 Organization of Report

This report is organized in six sections including this introduction. The second section presents a brief background of the Invasive Spartina Project and the use of herbicides as a method to control non-native *Spartina*. The second section provides a brief overview of the herbicides imazapyr and glyphosate including their physical/chemical properties and environmental fate and discusses the efficacy and application challenges for control of non-native *Spartina*. The fourth section provides a summary of ecological risk assessment findings from the 2003 Entrix report for imazapyr contrasted with glyphosate. This section summarizes and updates the most important information, highlights its key findings, and adapts the

[4] Adjuvants include surfactants, compatibility agents, drift retardants, suspension aids, and spray buffers.

[5] Syracuse Environmental Research Associates, Inc., Imazapyr - Human Health and Ecological Risk Assessment – Final Report, prepared for USDA, Forest Service, December 18, 2004.

[6] DIALOG offers an online information retrieval system of materially significant databases. As part of the Deep Web, estimated to be 500 times larger than the content accessible via web search engines, DIALOG accesses over 900 databases. Searchable content includes articles and reports from trade publications as well as in-depth repositories of scientific and technical data, government regulations, patents, trademarks and other intellectual property data.

[7] TOXNET, maintained by the U.S. National Library of Medicine, searches a large number of databases on toxicology, hazardous chemicals, and related areas.

[8] The literature search focused on post-2002 publications to identify newer studies that were not incorporated into previous reports such as the 2003 Entrix report, publications by Washington State authorities, or the Programmatic EIS/EIR.

information to San Francisco Estuary conditions. In addition, the section provides information on the ecological risks of glyphosate. The fifth section contains a summary of human health risks from the 2004 SERA report adapted to conditions in the San Francisco Estuary. The report concludes with a summary and conclusions section that summarizes and compares the findings on ecological and human health risks of imazapyr and glyphosate applications, discusses changes in environmental effects and approaches to minimize increased risk, and discusses implications of the findings for purposes of and amendment of the Conservancy's CEQA analysis.

2. BACKGROUND

This background section summarizes the project history of the Spartina Control Program and discusses the use of herbicides for control of non-native invasive *Spartina*.

2.1 Project History

In recent decades, non-native *Spartina* species were introduced into the San Francisco Estuary and soon began to spread rapidly. In 2001 non-native *Spartina* occupied only about 500 acres within 5,000 acres of the Estuary's tidal flats and marshes; by the end of 2004, only three year later, the acreage of non-native *Spartina* had more than doubled and infested about 11,500 acres of tidal marshlands. (Programmatic EIS/EIR, p. 1-17; Olofson 03/05.) This invasion of non-native *Spartina*, if left uncontrolled, threatens to displace the native *Spartina* species, cause fundamental changes in the structure, function, and value of the Estuary's tidal lands, and imperil its ecological balance. One non-native species in particular, Atlantic smooth cordgrass (*S. alterniflora*), and its hybrids with the native Pacific cordgrass (*S. foliosa*) are spreading at an alarming rate and are likely to eventually cause the extinction of native Pacific cordgrass, choke tidal creeks, dominate newly restored salt marshes, and alter or displace thousands of acres of existing shorebird habitat. Potential effects include extensive regional loss of tidal flats; elimination of critical foraging habitat for migratory shorebirds; marginalization of endangered California clapper rail habitat; reduction or elimination of endangered salt marsh harvest mouse habitat; increased need for dredging and flood control; and so forth. (For a detailed discussion, refer to the Programmatic EIS/EIR, Section 1.)

In 2000, the California State Coastal Conservancy ("Conservancy") established the Invasive Spartina Project, a regionally coordinated effort of Federal, State, and local agencies, private landowners, and other interested parties that aims to eradicate non-native, invasive salt marsh *Spartina*. In 2003, the Conservancy, as the lead agency under the California Environmental Quality Act ("CEQA"), certified the Programmatic Environmental Impact Statement/Environmental Impact Report for the San Francisco Estuary Invasive Spartina Project Spartina Control Program. The Spartina Control Program, the "action arm" of the ISP, implements a number of manual, mechanical, and chemical treatment techniques to arrest and reverse the spread of non-native *Spartina* species in the San Francisco Estuary. The Programmatic EIS/EIR addressed the environmental impacts of implementing the Spartina Control Program, identified significant impacts, and summarized the requisite mitigation in a Mitigation Monitoring and Reporting Program ("MMRP"; Programmatic EIS/EIR, Appx. K).

2.2 Use of Herbicides for Control of Spartina

Spartina plants resprout every year from a dense persistent root mass, which spreads as a clone through horizontal underground rhizomes. A rhizome, also called a rootstalk or rootstock, is a fleshy, horizontally creeping underground stem of a plant that often produces new roots and shoots from its nodes that serve to spread the plant by vegetative reproduction. Thus, if a rhizome is cut, it does not die, as would a root, but the cut-off part becomes a separate plant. *Spartina* also has the ability to disperse long distances by way of broken root fragments and floating seeds. *Spartina* often grows in soft sediments. These factors make *Spartina* difficult to eradicate by mechanical means alone.

The use of herbicides in combination with other treatment methods has proven effective for the control of estuarine cordgrass populations elsewhere, *e.g.*, in Washington State, New Zealand, and Northern Ireland, and is a key component of the Spartina Control Program for the San Francisco Estuary. (Patten 2004[9]; ISSG[10]; Hammond & Cooper[11]; Programmatic EIS/EIR, p. 2-23.) For some sites, particularly expansive monoclonal stands of *Spartina* and inaccessible mudflats, herbicide application is the only feasible and time- and cost-effective treatment method that results in a sufficient level of control to facilitate the eradication of non-native *Spartina*. (Patten 03/05[12].)

The Conservancy ultimately approved the Programmatic EIS/EIR's Alternative 1 (Regional Eradication Using All Available Control Methods), which included the use of herbicides in addition to a variety of manual, mechanical and chemical treatment methods and combinations thereof including hand-pulling and manual excavation; mechanical excavation and dredging; mowing, burning, pruning, and flaming; crushing and mechanical smothering; covering/ blanketing; flooding and draining. (Programmatic EIS/EIR, pp. 2-23–2-18.)

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[9] Patten K, Comparison of chemical and mechanical control efforts for invasive Spartina in Willapa Bay, WA, Third International Conference on Invasive Spartina, San Francisco, California, November 8-10, 2004.

[10] Invasive Species Specialist Group, Global Invasive Species Database, Spartina anglica, Management Info and Links; http://www.issg.org/database, accessed April 19, 2005.

[11] Hammond MER, Cooper A, Spartina anglica eradication and inter-tidal recovery in Northern Ireland estuaries; in: Veitch CR, Clout MN (eds.), Turning the Tide: the Eradication of Invasive Species, International Union for the Conservation of Nature, Gland, Switzerland, and Cambridge, United Kingdom, 2002, pp. 124-131.

[12] Personal communication with Kim Patten, Washington State Department of Agriculture, March and April 2005.

At the time the Programmatic EIS/EIR was compiled, the only herbicide registered by the California Environmental Protection Agency ("CalEPA") for use in estuarine habitats was glyphosate (brand names for registered aquatic formulations "Aquamaster®" and "Rodeo®"). Recently, the herbicide imazapyr (brand name "Habitat®"), was submitted to the CalEPA Department of Pesticide Regulation ("DPR") for registration and is expected to be approved for estuarine use in early summer 2005. (Olofson 03/05[13].) The ISP would like to include the use of imazapyr in the Spartina Control Program because under certain estuarine conditions it has several apparent benefits over the use of glyphosate and has been found to have fewer environmental impacts than glyphosate. (*See* Sections 3.2 and 4.) Imazapyr is not intended as a complete replacement of glyphosate but rather as an additional tool to be used by itself or in combination with glyphosate where appropriate. In some situations, the Spartina Control Program will be intentionally using the less effective glyphosate treatment to achieve its control objectives. For example, glyphosate may be used to kill a portion of the vegetation on the site and reduce the site's seed production, at the same time maintaining sufficient cover for the endangered California clapper rail while other areas are naturally revegetating with native plants and not being reinfested by seed from the treated site. As another example, glyphosate might be the herbicide of choice for treatment of sites where there are only few non-native *Spartina* in a matrix of primarily native pickleweed (*Salicornia virginica*). In this case, using the less effective herbicide would be preferable to reduce any potential adverse effects to pickleweed due to overspray. In some instances, imazapyr could be used in a mixture with glyphosate, which could serve as a brown-down[14] indicator. (*See* Section 3.2.) The appropriate treatment method will be determined by site-specific conditions as detailed in the Site-specific Plans ("SSPs"), which are developed annually by the ISP. (Olofson 03/05.)

Because the use of imazapyr was not specifically addressed and evaluated in the Programmatic EIS/EIR, the Conservancy intends to amend its CEQA analysis of potential environmental impacts to include the use of imazapyr.

3. IMAZAPYR AND GLYPHOSATE HERBICIDES FOR CONTROL OF NON-NATIVE SPARTINA

The following sections contain an overview of imazapyr and glyphosate herbicides and their environmental fate followed by a short discussion of the challenges the estuarine

[13] Personal communication with Peggy Olofson, Invasive Spartina Project, Berkeley, CA, March and April 2005.

[14] The term *brown-down*, or burn-down, refers to the visible effect of browning (or yellowing) of leaves or the entire plant after application of an herbicide.

environment poses for their application, and a summary of experiences regarding the efficacy of both herbicides for control of non-native *Spartina*.

3.1 Herbicides Overview

The following sections provide information on the composition of the commercial formulations of imazapyr and glyphosate; describes the mechanisms of action in plants; summarizes application rates and surfactants and colorants proposed for use; and reviews physical and chemical properties, degradation rates, products, and pathways, and general toxicity and bioaccumulation ratings. Attached Table A-1 summarizes key information for both herbicides.

3.1.1 Commercial Formulations

Imazapyr. Imazapyr is the active ingredient ("a.i.") in a number of commercially available formulations for different applications. It was first registered for the control of undesirable vegetation in 1984. In the U.S., it has mainly been used in forestry applications. (Birk 04/05.) In November 2003, imazapyr received Federal registration for use in non-crop aquatic sites under the brand name "Habitat®." (BASF 2004[15].) In February 2005, the manufacturer submitted Habitat® for registration in California to the DPR for the control of aquatic nuisance vegetation, including its use in estuarine environments and registration is expected in June of 2005. (Olofson 03/05.) Imazapyr is typically formulated as either a weak acid or as its isopropylamine salt. Habitat® is a solution of 28.7% isopropylamine salt of imazapyr in water, equivalent to 22.6% imazapyr acid equivalents ("a.e."), and contains a small amount of an acidifier. (BASF 2003[16]; Birk 04/05.) Because Habitat® is purportedly the same formulation as Arsenal® and Arsenal® contains acetic acid, the acidifier in Habitat® is likely also acetic acid. (Birk 04/05; NCAP 2003.) The aquatic formulation Habitat® does not contain any surfactants; however, treatment of postemergent vegetation requires the addition of surfactants to the tank mix. (BASF 2003; Volmer 03/05[17]; *see* Section 3.1.3.)[18] No information has been encountered in the published literature on manufacturing impurities associated with imazapyr. Because virtually no chemical synthesis yields a totally pure product, technical grade imazapyr contains some impurities. However, to some extent, concern for impurities in technical grade imazapyr is reduced by the fact that most existing toxicity studies on imazapyr were conducted with the technical grade product and encompass the toxic potential of the impurities. (SERA 12/04, p. 3-10.) Habitat® may be tank-mixed with other aquatic use herbicides. (BASF 2003.)

[15] BASF Corporation, Habitat® Herbicide for Aquatic and Invasive Vegetation Control, 2004.

[16] BASF Corporation, Habitat® Herbicide, Specimen, EPA Reg. No. 241-426, 2003.

[17] Personal communication, with Joe Volmer, BASF Corporation, March 24, 2005.

[18] Historically, formulations of imazapyr for terrestrial use contained non-ionic surfactants. For reregistration in the U.S., these products were reformulated without surfactants. At present, the only imazapyr formulation for terrestrial use is Arsenal® Railroad. (Volmer 03/05.)

Glyphosate. Glyphosate, first registered in the U.S. in 1986, is among the most widely used pesticides in volume worldwide. (U.S. EPA 09/93[19].) Most commercial formulations of glyphosate are for terrestrial applications and only two formulations, Aquamaster® and Rodeo®, are currently registered for aquatic use. Glyphosate itself is an acid but it is commonly formulated in salt form, most commonly the isopropylamine salt. Aquamaster® and Rodeo® are both aqueous solutions of 53.8% of the isopropylamine salt of glyphosate, equivalent to 48.0% glyphosate a.e. Neither formulation contains inert ingredients other than water or surfactants. (Monsanto 2000[20]; Dow AgroSciences 2001[21].) However, the technical-grade glyphosate used to formulate these products contains a small amount of 2,4-nitrosoglyphosate ("NNG"), an impurity formed during the synthesis of glyphosate. (U.S. EPA 09/93.) All applications of Aquamaster® and Rodeo® require the addition of a non-ionic surfactant to the tank mix for use on aquatic nuisance vegetation. (Monsanto 2000; Dow AgroSciences 2001; *see* Section 3.1.3.)

3.1.2 Mechanism of Action and Effects

The mechanism of action of an herbicide is the biochemical or physical method by which it causes the suppression of growth or death of specific plants. Both imazapyr and glyphosate herbicides are systemic broad-spectrum herbicides[22] that are applied to, and absorbed by, roots and foliage and are rapidly transported via the plant's phloem[23] and xylem[24] to its meristematic tissues[25] or growing regions. (Uptake via roots is irrelevant under estuarine conditions because herbicide applications occur onto shoots and foliage.) Because *Spartina* clones propagate rapidly via rhizomes, the translocation of the herbicide into the rhizomes and their ensuing cell death effectively prevents further spreading of the clone once the aboveground portion of the plant has died. Both herbicides block a specific enzyme in the synthesis of certain amino acids in

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[19] U.S. Environmental Protection Agency, R.E.D. (registration eligibility decision) Facts, Glyphosate, EPA-738-F-93-011.

[20] Monsanto Company, Aquamaster®, Complete Directions for Use in Aquatic and other Noncrop Sites, EPA Reg. No. 524-343, 2000.

[21] Dow AgroSciences LLC, Rodeo®, Specimen Label, EPA Reg. No. 62719-324, revised April 17, 2001.

[22] Broad spectrum (also referred to as non-selective) herbicides are those that are used to control all or most vegetation. Systemic herbicides are absorbed into the living portion of the plant and move within the plant.

[23] In vascular plants, phloem is the tissue that transports organic nutrients, such as sugars, particularly sucrose, amino acids, and certain hormones. The movement in phloem is bidirectional and driven by positive hydrostatic pressures. This process is termed translocation.

[24] In vascular plants, xylem is the tissue that carries water up the root and stem. The xylem sap consists mainly of water and inorganic ions, such as nitrate. The movement of sap in xylem cells is unidirectional and always moves from the roots to the leaves. The most important phenomenon that causes xylem sap to flow is transpirational pull, which is caused by the transpiration of water from leaves. In addition, because the soil solution is more dilute than the cytosol (internal cell fluid) of the root cells, water moves osmotically into the cells, creating so-called root pressure.

[25] Meristematic tissues, or meristems, are undifferentiated (unspecialized) tissues in which cell division occurs.

plants. The ensuing disruption of protein synthesis leads to interference in cell growth resulting in chlorosis[26] and tissue necrosis[27] of new leaves.

Imazapyr. Imazapyr inhibits an enzyme in the biosynthesis of the three branched-chain aliphatic amino acids valine, leucine, and isoleucine. (BASF 2004.) Because animals do not synthesize branched-chained aliphatic amino acids but obtain them from eating plants and other animals, the engineered mechanism for plant toxicity, *i.e.* the interruption of protein synthesis due to a deficiency of the amino acids valine, leucine, and isoleucine, is not generally relevant to birds, mammals, fish or invertebrates. Any toxicity to these receptors occurs through different mechanisms. (Entrix 10/03, p. 24.) Imazapyr is relatively slow acting and it takes several weeks for the plants to show effects. Plants cease to grow initially in the roots and later in the aboveground portions. (Cox 1996 in Entrix 10/03, p. 24.) On *Spartina*, it takes 4-8 weeks after treatment for effects, *i.e.* yellow flagging of the leaf margin, to show and complete plant death can take several months. (Patten 03/04[28]; Patten 03/05.)

Glyphosate. Glyphosate inhibits an enzyme needed to synthesize an intermediate product in the biosynthesis of the aromatic amino acids, essential for protein synthesis and to produce many secondary plant products such as growth promoters, growth inhibitors, phenolics, and lignin. Animals do not synthesize these aromatic amino acids and glyphosate therefore has low toxicity to these receptors. (Schuette 1998[29].) Plants vary in their sensitivity to glyphosate exposure mostly by how readily the herbicide is absorbed and internally transported. (Programmatic EIS/EIR, pp. 3.3-26.) In general, glyphosate herbicides are somewhat faster acting than imazapyr herbicides. Visible effects on most annual weeds occur within two to four days and after 7 days on most perennial weeds. Visible effects are a gradual wilting and yellowing of the plant that advances to complete browning of aboveground growth and deterioration of underground plant parts. (Schuette 1998.) On *Spartina*, complete brown-down occurs within 7 to 21 days. (Patten 03/04.)

3.1.3 Adjuvants

For most foliar applications of herbicide formulations, adjuvants must be added to spray solutions to improve the performance and minimize variation of herbicide efficacy. Examples of adjuvants include surfactants[30] (surface active agents), compatibility agents (used to aid mixing of two or more herbicides in a common spray solution), drift retardants (used to decrease the potential for herbicide drift), suspension aids (used to aid mixing and suspending herbicide

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[26] Chlorosis is a term for the yellowing or whitening of normally green plant tissue because of a decreased amount of chlorophyll.

[27] Necrosis is a term for the death of cells or tissues.

[28] Patten K, Imazapyr for aquatic use, Presentations, March 2004.

[29] Schuette J, California Environmental Protection Agency, Department of Pesticide Regulation, Environmental Fate of Glyphosate, revised November 1998.

[30] Frequently, the term surfactant is used for all types of adjuvants (except colorants).

formulations in solution), spray buffers (used to change the spray solution acidity), and colorants. Surfactants are designed to improve the spreading, dispersing/emulsifying, sticking, absorbing, and/or pest-penetrating properties of the spray mixture. (Tu *et al.* 2001[31].) The pure herbicide formulation mixed with water will stand as a droplet on the waxy leaf surface and the small area of contact therefore provides little potential for uptake of the active ingredient into the foliage. Water droplets containing a surfactant will spread in a thin layer over a waxy leaf surface and improve herbicide uptake by improving herbicide distribution on the leaf surface. As mentioned above, both Habitat® and the glyphosate herbicides Aquamaster® and Rodeo® require the use of surfactants for postemergent applications such as the control of *Spartina*. Without surfactants, the formulation would not sufficiently penetrate the often tough cuticle of postemergent plants. (Volmer 03/05.)

Imazapyr. The Habitat® specimen label recommends a variety of different spray adjuvants for use on postemergent vegetation. For non-ionic surfactants the label recommends a rate of 0.25% v/v[32] or higher, preferably of a surfactant with a hydrophilic to lipophilic ratio between 12 and 17 and with at least 70% surfactant in the formulated product. (This excludes alcohols, fatty acids, oils, ethylene glycol, or diethylene glycol.) Alternately, the label recommends the use of methylated seed oils or vegetable oil concentrates at the rate of 1.5 to 2 pints per acre. For spray volumes greater than 30 gallons per acre, the surfactant should be mixed at a rate of 1%. The label further indicates that these oils may aid in Habitat® deposition and uptake by the plants under moisture or temperature stress. Silicone-based surfactants, which may reduce the surface tension of the spray droplet, allowing greater spreading on the leaf surface as compared to conventional non-ionic surfactants, are also recommended. However, the manufacturer points out that some silicone-based surfactants may dry too quickly, limiting herbicide uptake. (BASF 2004.)

One study from Washington State concluded that the esterified seed oil surfactant tested, Competitor®, performed better than the other surfactants tested, *i.e.* Agri-Dex®, a crop oil-based surfactant, and R-11®, a non-ionic surfactant. This finding is supported by other studies. (Patten 2002[33].) The author recommended using a methylated seed oil surfactant for aerial applications and for unfavorable conditions such as less than 6 hours of drying time or moist leaves. (Patten 03/05.)

Glyphosate. The Aquamaster® and Rodeo® specimen labels recommend the use of a non-ionic surfactant containing at least 50% active ingredient at a rate of 2 or more quarts per 100 gallons of tank mix (0.5% v/v). (Monsanto 2000; Dow AgroSciences 2001.)

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[31] Tu M, Hurd C, Randall JM, Weed Control Methods Handbook: Tools and Techniques for Use in Natural Area, April 2001.

[32] The abbreviation %v/v, percentage volume by volume, describes the concentration of a substance in a mixture or solution. Thus, 0.25% v/v surfactant means that the volume of the surfactant is 0.25% of the total volume of the tank mix.

[33] Patten K, Smooth cordgrass (Spartina alterniflora) control with imazapyr, Weed Technology, vol. 16, pp. 826-832, 2002.

Not all surfactants provide the same effectiveness and surfactant costs vary widely. In general, non-ionic surfactants and crop oil concentrates are the least expensive of the surfactant classes, followed by esterified seed oils and organo-silicates. (Miller & Westra 08/04[34].) The ISP identified a number of potential surfactants for use with Habitat®, Aquamaster®, or Rodeo®. They include the non-ionic surfactants LI-700®, Liberate®, and Cygnet Plus; the crop-oil concentrate Agri-Dex®; the esterified seed oil Competitor®; and the organo-silicones Dyne-Amic® and Kinetic®.[35] Attached Table A-2 summarizes the chemical properties of these surfactants. Based on the anticipated efficacy of the products and their superior relative toxicities, the ISP expects to use Competitor®, Agri-Dex®, LI-700®, and Cygnet Plus, appropriate for addition to the Spartina Control Program. If actual efficacies of these products prove to be inadequate, the ISP will then consider Liberate®, Dyne-Amic®, and Kinetic®. (Olofson 04/05.)

3.1.4 Colorants

A colorant will be added to the herbicide/surfactant solution to enable spray crews to see where they have sprayed after initial evaporation of the solution. Little published information regarding the use of colorants with herbicides exists. Moreover, the manufacturers of the colorants and the suppliers of the herbicides/surfactants do not make recommendations concerning the use of specific colorants. Rather than the manufacturers or suppliers, it is the applicator who usually determines the compatibility of a colorant with an herbicide and the efficacy of the colorant for a particular application. (SERA 12/07, p. 1.)

The ISP has identified Blazon® Spray Pattern Indicator "Blue" ("Blazon® Blue") for use with Aquamaster® or Rodeo® and will likely use the same product for use with Habitat®. (Programmatic EIS/EIR, p. 3.2-13; Olofson 03/05.) Blazon® Blue is a water-soluble non-ionic polymeric colorant. As with most colorant products, the active ingredients are proprietary; the Material Safety Data Sheet ("MSDS") only indicates that it is non-hazardous and non-toxic. The product information sheet reports that the product is non-staining to the skin or clothing. The colorant is typically added at a rate of 3 quarts per 100 gallons of solution, or 16 to 24 ounces per acre sprayed. (*See* Programmatic EIS/EIR, Table 2-2). Product information for Blazon® Blue is provided in Appendix E-2 to the Programmatic EIS/EIR. Table A-2 summarizes the chemical properties of Blazon® Blue.

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[34] Miller P, Westra P, Herbicide Surfactants and Adjuvants, Colorado State University Cooperative Extension, Bulletin no. 0.559, August 23, 2004.

[35] The categorization of surfactant classes is inconsistent and the names of surfactant classes are not necessarily intuitive regarding the content of the surfactant. For example, crop oil concentrates are not made from vegetable oils but from petroleum oils and not all surfactants with mainly non-ionic ingredients, *e.g.,* oils, are classified as non-ionic surfactants. To complicate the fact, surfactant mixtures often contain several ingredients belonging to different surfactant classes. They are typically, but not always, classified based on their main ingredient; for example, the surfactant Agri-Dex® is alternately referred to as crop oil concentrate or as a non-ionic surfactant.

3.1.5 Application Rates

Herbicide mixtures will be sprayed onto target plant surfaces, either manually with backpack sprayers or with spray equipment mounted on trucks, amphibious tracked vehicles, boats, or helicopters (broadcast sprayers or directed spray apparatus). (Programmatic EIS/EIR, p. 2-13; Olofson 03/05.) In certain situations, pastes may be applied to cut stems or solutions wiped or painted on foliage. Application of imazapyr herbicide would follow the same guidelines and precautions set forth in the MMRP for the application of glyphosate herbicides.

Imazapyr. Habitat® tank mixes will be applied with varying concentrations , depending on the application method, of typically at 1 to 1.5 lb a.e. imazapyr/acre. High-volume handheld sprayers will typically use a spray volume of 100 gal/acre. Low-volume directed sprayers will use about 20 gal/acre. The aerial application with helicopters uses a low-volume tank mix of 10 to 30 gal/acre of a 2.5-7.5% solution of Habitat®. The low spray volumes are necessitated by the relatively small helicopter tank volume (~50 gallons), which would otherwise require frequent refilling. Helicopter applications are controlled via global positioning systems ("GPS") and are therefore quite precise. Applications via helicopter result in a uniform, vertical deposition onto the plants. (Patten 03/05.)

Glyphosate. Compared to imazapyr, application of glyphosate requires considerably higher concentrations of the active ingredient to achieve high rates of efficacy. Depending on the application method, the herbicide is applied at a rate up to about 11 lb a.e. glyphosate/acre. Typically, these applications require considerably higher amounts of glyphosate active ingredient per acre than imazapyr.

The exact herbicide solution concentration, the choice of surfactants and colorants, and the determination of application rates will be based on site-specific conditions and are described in the SSPs. Attached Tables A-3a and A-3b provide summaries of potential tank mixtures and application rates for treatment of non-native *Spartina* in San Francisco Estuary with imazapyr and glyphosate herbicides.

Experiences with imazapyr/glyphosate herbicide mixtures are limited and insufficient for tabulation of potential application rates for the various treatment methods of the Spartina Control Program. The most effective application rates will be experimentally determined, following the directions of the more restrictive label.

3.1.6 Chemical/Physical Properties

Imazapyr. Under typical environmental conditions of pH 5-9, imazapyr is ionized and therefore highly soluble in water. The solubility of imazapyr increases with temperature, 9,740 mg/L at 15ºC (59 F), 11,272 mg/L at 25ºC (77 F), and 13,479 mg/L at 35ºC (95 F). Because of its high solubility, imazapyr has an inherently low sorption potential with a low soil organic carbon sorption coefficient[36] ("K_{oc}") of 8.81 (log K_{oc}), suggesting very high mobility in soil and little adsorption to suspended solids and sediment. Its octanol/water partition coefficient[37] ("K_{ow}") has been reported at 0.22[38] (log K_{ow}), reflecting its high solubility in water and low solubility in lipids, and hence low propensity to bioconcentrate. A low bioconcentration factor[39] ("BCF") of 3 was calculated for imazapyr, which suggests a low potential for bioconcentration in aquatic organisms. The vapor pressure[40] of imazapyr, 1.8×10^{-11} mmHg, indicates that imazapyr is not expected to volatilize from dry soil surfaces and its estimated Henry's Law constant[41] of 7.1×10^{-17} atm m^3/mole indicates low volatility of imazapyr from water or moist soil surfaces. (Entrix 10/03, p. 31; HSDB 04/05[42].)

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[36] The soil organic carbon sorption coefficient, or K_{oc}, defines the partitioning of a chemical into the organic fraction of the soil. It is based on the chemical's distribution coefficient K_d, which is the ratio of a chemical's concentration in a solid phase of a solid/water system, normalized to the percent of organic matter contained in the soil.

[37] The octanol/water partition coefficient, or K_{ow}, is the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system. Values of K_{ow} are unitless, and usually measured at room temperature. K_{ow} values range from 10^{-3} to 10^7, (log K_{ow} of -3 to 7). A compound with a high K_{ow} is considered relatively hydrophobic, and tends to have low water solubility, a large soil/sediment adsorption coefficient, a large retardation factor, and a large bioconcentration factor.

[38] The 2003 Entrix report cites a K_{ow} of 1.3 for imazapyr, indicating the same properties. (Entrix 10/03, p. 31.)

[39] Biological tissues may act as an additional reservoir for chemicals applied intentionally or inadvertently to the environment. Bioconcentration refers to the absorption or uptake of a chemical from the media to concentrations in the organism's tissues that are greater than in surrounding environment. The degree to which a contaminant will concentrate in an organism is expressed as the bioconcentration factor, or BCF, which is defined as the concentration of a chemical in an organism's tissues divided by the exposure concentration. Thus, a BCF of 100 means that the organism concentrates that chemical to a concentration 100 times greater than in the surrounding media. The term bioaccumulation refers to the tendency of some chemicals to become increasingly concentrated at successively higher trophic levels of a food chain or food web.

[40] Vapor pressure is a measure of a substance's propensity to evaporate and become a gas. It is measured as the pressure, *i.e.* is force per unit area, exerted by vapor in an equilibrium state, with surroundings at given conditions of temperature and pressure, usually expressed in millimeters of mercury at 68F (20ºC), unless stated otherwise. It increases exponentially with an increase in temperature. The higher the vapor pressure, the greater the tendency of the substance to evaporate.

[41] Henry's law applies to chemicals dissolved in dilute aqueous solutions that have reached equilibrium between the aqueous and adjacent air phase, *i.e.* the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution. At equilibrium for a fixed temperature and chemical the ratio of the chemical concentration in air to the chemical concentration in water is a constant referred to as the Henry's law constant.

[42] National Library of Medicine, Hazardous Substances Database ("HSDB"), queries: imazapyr; glyphosate; glyphosate isopropylamine salt; accessed April 6, 2005.

Glyphosate. Under typical environmental conditions of pH 5-9, glyphosate is ionized. Glyphosate and its salts are readily soluble in water with a solubility of about 12,000 mg/L. Its interactions with soil and sediment are primarily ionic, rather than hydrophobic and pH dependent. Laboratory and field studies indicate that glyphosate is strongly and reversibly adsorbed by soil, sediment, and suspended sediment. Glyphosate is inactivated through soil adsorption. Due to its negligible vapor pressure (7.5×10^{-8} mmHg) and its ionic state in water, glyphosate is not expected to volatilize from water or soil. Its very low Henry's Law constant, less than 1.44×10^{-12} atm-m^3/mole, indicates that it tends to partition in water versus air. Glyphosate's K_{ow} has been reported at 0.00033, indicating its high solubility in water, low solubility in lipids, and thus low potential to bioconcentrate. (HSDB 04/05; Schuette 1998.)

3.1.7 Environmental Fate

The environmental fate of herbicides, adjuvants, or their mixtures is determined by the physical/chemical characteristics described above and the conditions of the environmental compartments, or media, *i.e.* air, water, soils, sediments, and biota.

Imazapyr. The fate of imazapyr after application varies with environmental conditions. Movement through the environment of the weak acid is primarily determined by the pH of the environmental compartments.

Air. Because the vapor pressure and Henry's Law constant for imazapyr are very low, the fate pathway of this herbicide through volatilization is nonexistent.

Soils. Imazapyr is relatively mobile in soils because it adsorbs to soils and sediments only weakly. Adsorption increases with decreasing pH. Above a pH of 5, imazapyr is ionized and does not adsorb to soil. Volatilization of imazapyr from soil is insignificant. Aerobic[43] degradation in soils occurs primarily by very slow microbial metabolism with quinoline as the main metabolite. Anaerobic[44] metabolism in soils appears to be insignificant. (Entrix 10/03, pp. 32-33.)

Sediments. Conditions in sediments differ substantially from those in soils, both in terms of the regular exchange of waters within the sediment pore water and over it, and in the degree of oxygenation in sediments that affect microbial metabolism. Because the pH of sediment surfaces and sediment pore water in intertidal mudflats is above neutral (pH >7), imazapyr will be entirely in its ionized form. Thus, adsorption to sediments is expected to be minimal. (Entrix 10/03, pp. 32-33.) Microbial metabolism in sediments has been determined to be insignificant. One study determined the half-life of imazapyr in the pore water of aerobic sediment at

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[43] Aerobic is a descriptive term for processes or organisms that require the presence of oxygen to occur or to live.

[44] Anaerobic is a descriptive term for a process, such as fermentation or microbial degradation, that can proceed in the absence of oxygen, or organisms that survive in the absence of oxygen.

17 months. Other studies found no degradation in either aerobic or anaerobic sediment. (American Cyanamid 1986b and 1988c in SERA 12/04.)

Water. In aquatic systems, imazapyr is not expected to be biodegraded or adsorbed to sediment particles. Volatilization of imazapyr from water is insignificant. The degradation of imazapyr when applied directly to water largely mimics the pathway by which the herbicide would be mobilized at high tide after application to *Spartina* during low tide. Residual imazapyr on the plants that have not completely dried or did not get absorbed by the plants will be inundated by the incoming tide and presumably solubilized. (Entrix 10/03, pp. 35-38.) Aquatic degradation studies under laboratory conditions demonstrated rapid initial photolysis of imazapyr with reported half-lives ranging from 3 to 5 days. (BASF 2004; American Cyanamid 1986b in SERA 12/04.) The two primary photodegradation products were rapidly degraded with half-lives less than or equal to 3 days and eventual mineralization to carbon dioxide ("CO_2"). (Entrix 10/03, pp. 35-38.)

Degradation rates in turbid and sediment-laden waters, common to estuarine environments, are expected to be lower than those determined under laboratory conditions. In controlled field dissipation[45] studies in two freshwater pond systems with application of 1.5 lb imazapyr a.e./acre, imazapyr rapidly dissipated from the water with first-order half-lives of 1.9 days and 12.8 days. No detectable residues of imazapyr were found in the water and sediment after 14 and 59 days, respectively. (Entrix 10/03, pp. 35–36.) The pond in the study with the longer half-life experienced a turnover[46] during the experiment, which resulted in an increase in suspended particles and decreased clarity. The resulting reduced rate of photolysis explains the differences in the rates of dissipation of imazapyr. (Birk 04/05.)

In estuarine systems, dilution of imazapyr in the incoming tide will contribute to its rapid dissipation and removal from the area where it has been applied. Studies in estuaries in Washington State examined the fate of imazapyr applied at a standard rate of 1.5 lb imazapyr a.e./acre directly to sediment. The study design was conservative because imazapyr was

[45] Unlike laboratory degradation experiments where more variables can be controlled and measured, field experiments are generally termed "dissipation" studies because the multiple variables inherent to such systems limit the range of analyses that can be conducted.

[46] Most lakes in temperate climates experience a turnover of their water bodies in spring and fall. Water is most dense (heaviest) at 39 F (4ºC) and as temperature increases or decreases from 39 F, it becomes increasingly less dense (lighter). In summer, lakes are maintained by climate in what is called a stratified condition. Less dense, warmer water is at the surface and denser, colder water is near the bottom. During late summer and autumn, air temperatures cool the surface water causing its density to increase. The heavier water sinks, forcing the lighter, less dense water to the surface. This continues until the water temperature at all depths reaches approximately 39 F. Because there is very little difference in density at this stage, the waters are easily mixed by the wind. The sinking action and mixing of the water by the wind results in the exchange of surface and bottom waters, which is called "turnover." During spring, the process reverses itself. This time, ice melts, and surface waters warm and sink until the water temperature at all depths reaches approximately 39 F. The sinking of water combined with wind mixing causes spring "turnover."

applied to bare mudflats with no algal or emergent vegetation intercepting the herbicide. The study measured immediate maximum concentrations of imazapyr in intertidal waters and sediment less than 3 hours after application and short-term concentrations between 24 and 72 hours after application. Sediment samples collected 3 hours after application were retrieved immediately after the first tidal wash over the area. Maximum concentrations in water and sediment were detected at 3.4 mg/L and 5.4 mg/kg, respectively. Measurable concentrations of imazapyr declined exponentially in both water and sediment, approaching the zero-asymptote at 40 and 400 hours with half-lives of <0.5 and 1.6 days, respectively. Water collected 20 and 200 feet outside the spray zone with the first incoming tide was 99% lower than the maximum water concentration at the edge of the spray zone. Application of the same amount of herbicide to a stand of 5.5-foot tall *Spartina* resulted in a 75% reduction in concentrations in sediment through interception by the canopy. (Patten 2003[47].) In sum, this research suggests that imazapyr quickly dissipates in estuarine environments. In addition, the same researcher observed that other vegetation immediately colonizes the plots treated with imazapyr after the *Spartina* plants have died, which supports the conclusion of very low persistence of imazapyr in estuarine environments. (Patten 04/05.) A study in Washington State evaluated imazapyr concentrations in water after treatment of non-native *Spartina* directly after and 24 and 48 hours after treatment at the treatment site and directly after treatment away from the treatment site to detect off-site transport. All samples had imazapyr concentrations lower than 0.01 mg/L. The highest concentration was found directly after application at the treatment site at 0.008 mg/L. (Murphy 01/05[48].)

Biological Tissues. As discussed previously in Section 3.1.6, imazapyr has a very low propensity to bioconcentrate or bioaccumulate as indicated by its low log K_{ow} of 0.22 and its calculated BCF of 3. (*See* attached Table A-1.) Several freshwater pond studies with a variety of fish, a crustacean, and a mollusk confirm these theoretical conclusions for aquatic organisms. (Entrix 10/03, p. 39.) In plants, imazapyr residues decline rapidly in the first 24 hours following foliar application with the parent compound remaining as the major residue. (HSDB 04/05.) Half-lives in plants have been determined to vary from 15 to 37 days. (Neary & Michael 1993; Knisel *et al.* 1992; both in SERA 12/04.)

Glyphosate. The fate of glyphosate after application varies with environmental conditions and is largely determined by its adsorption to particles.

Air. Because the vapor pressure and Henry's Law constant for glyphosate are very low, the fate pathway of this herbicide through volatilization is nonexistent.

Soils. In general, glyphosate is moderately persistent in soil. Soil studies have determined glyphosate half-lives ranging from 3 to 130 days. The soil field dissipation half-life averaged 44 to 60 days. In the soil environment, glyphosate is resistant to chemical degradation,

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[47] Patten K, Persistence and non-target impact of imazapyr associated with smooth cordgrass control in an estuary, Journal of Aquatic Plant Management, vol. 41, pp. 1-6, 2003.

[48] Murphy K, 2004 Spartina Eradication Program, Water Quality Monitoring, January 20, 2005.

is stable to sunlight, is relatively non-leachable, and has a low tendency to runoff (except as adsorbed to colloidal matter). It is relatively immobile in most soil environments as a result of its strong adsorption to soil particles. Less than one percent of the glyphosate in the soil is absorbed via the roots. The herbicide is inactivated and biodegraded by soil microorganisms under both aerobic and anaerobic conditions. Rates of decomposition depend on soil and microorganism population types. The primary metabolite of glyphosate is aminomethylphosphonic acid ("AMPA"). Degradation of AMPA is generally slower than that of glyphosate possibly because AMPA may adsorb onto soil particles more strongly than glyphosate and/or because it may be less likely to permeate the cell walls or membranes of soil microorganisms. (HSDB 04/05; Schuette 1998, Programmatic EIS/EIR.)

Sediments. Glyphosate is rapidly and strongly adsorbed to sediment, which appears to be the major sink for glyphosate in aquatic systems. Like in soils, the herbicide is inactivated and biodegraded by microorganisms. (HSDB 04/05; Schuette 1998, Programmatic EIS/EIR.)

Water. Several studies indicate that glyphosate is stable in water at pH ranging from 3 to 6. The photolytic half-life of glyphosate in deionized water exposed outdoors to sunlight was approximately 5 weeks at 100 ppm and 3 weeks at 2000 ppm. Glyphosate shows little propensity toward hydrolytic decomposition. Its hydrolysis half-life is greater than 35 days. It is also stable to photodegradation under visible light but photolyzes when exposed to UV radiation. Glyphosate's loss from water occurs mainly through sediment adsorption and microbial degradation. The rate of microbial degradation in water is generally slower because there are fewer microorganisms in water than in most soils. Studies conducted in a forest ecosystem found that glyphosate dissipated rapidly from surface water ponds high in suspended sediment, with first order half-lives ranging from 1.5 to 11.2 days. In streams, residues were undetectable within 3 to 14 days. Other studies using water from natural sources determined glyphosate's half-life ranging from 35 to 63 days. For all aquatic systems, sediment appears to be the major sink for glyphosate residue. A review of the literature on glyphosate dissipation applied under estuarine conditions suggests that 24 to 48 hours after applications, glyphosate concentrations in water were reduced by more than 60-fold but detected residues were still two orders of magnitude greater than imazapyr residues. (Patten & Stenvall 2002.) A study in Washington State evaluated glyphosate concentrations in water after treatment of non-native *Spartina.* Directly after and 24 and 48 hours after treatment, most samples were lower than 0.1 mg/L. In two samples taken directly after application, glyphosate concentrations of 0.76 and 2.24 mg/L were detected. The latter concentration was collected at the base of a farm dike, possibly indicating runoff from the farm. (Murphy 01/05.)

Biological Tissues. Glyphosate is not expected to bioconcentrate in aquatic organisms. Most studies report minimal retention and rapid elimination in fish, birds, and mammals. (HSDB 04/05.) The highest reported bioaccumulation factor ("BAF") for glyphosate in aquatic freshwater organisms has been determined at 65.5 for tilapia. (Wang *et al.* 1994 in Programmatic EIS/EIR, p. 3.3-26.) Most other studies reported much lower bioaccumulation factors in the range of 0.3 to 1.6 for fish. (Ebasco 1993 in Programmatic EIS/EIR, p. 3.3-26.) In a study of the fate of glyphosate that was applied to two hardwood communities in the Oregon coastal forest, none of the ten Coho salmon fingerlings analyzed had detectable levels of glyphosate or its metabolite AMPA despite glyphosate levels in stream water that were detectable for 3 days and levels in sediment that were detectable throughout the 55 day study period. Levels in herbivores, carnivores, and omnivores were at or below that in ground cover and litter, indicating that glyphosate does not bioaccumulate in higher tropic levels. (Schuette 1998.) According to the U.S. EPA's classification, glyphosate has a low potential to bioaccumulate (BAF <100). (U.S. EPA 09/93.) In one metabolism study with rats, most of the glyphosate administered (97.5 percent) was excreted in urine and feces as the parent compound; less than one percent of the absorbed dose remained in tissues and organs, primarily in bone tissue. Aminomethylphosphonic acid was the only metabolite excreted. A second study using rats showed that very little glyphosate reaches bone marrow, that it is rapidly eliminated from bone marrow, and that it is even more rapidly eliminated from plasma. (U.S. EPA 09/93.)

Studies with a variety of plants indicate that uptake of glyphosate or AMPA from soil is limited but depending upon soil type and conditions, some root uptake may occur. The major pathway for uptake of glyphosate in plants is through the foliage. Surfactants increase the diffusion rate across the plasma membrane, but not the cuticle. Glyphosate is not metabolized by plants. The absorbed compound is readily translocated throughout the plant. (HSDB 04/05; Schuette 1998, Programmatic EIS/EIR; U.S. EPA 09/93.)

Adjuvants. Registration requirements for adjuvants are not as stringent as those for herbicides. The long-term fates of most adjuvants in the environment are largely unknown, partially because of the lack of long-term monitoring data, but also because the ingredients in most adjuvants are not disclosed. Most adjuvant labels or MSDSs include information on the adjuvants' physical properties (boiling and freezing points, specific gravity, evaporation point, etc.), fire and explosion hazard data, reactivity data, and health hazard data. Unlike herbicide labels however, most adjuvant labels or MSDSs do not include information of the compounds' behavior or fates in the environment. Most adjuvant labels and MSDSs also do not describe the adjuvants' mechanisms of action, rates of metabolism within plants, rates of photodegradation or microbial degradation, persistence in the environment, potential for volatilization, or potential mobility in soil or water. It is known that many surfactants adsorb to soil particles. (Tu *et al.* 2001.)

3.2 Efficacy and Application Challenges

Comparison studies of the efficacy of imazapyr relative to glyphosate for the control of non-native *Spartina* have been conducted by a number of researchers. (Patten 2002.) Some studies included a combination of methods such as herbicide/smothering or herbicide/cutting. In most cases, the use of imazapyr was found superior to glyphosate, which exhibited variable control. (Pritchard 1994, Shaw and Gosling 1995, Garnett *et al.* 1992, Kilbride *et al.* 1995, all in Patten 2002; Patten and Stenvall 2002[49]; Patten 2002; Patten 03/05.)

[49] Patten K, Stenvall C, Managing Spartina with glyphosate and imazapyr, Proceedings of the 11th International Conference on Aquatic Invasive Species, Alexandria, VA, February 25-28, 2002.

Imazapyr. Imazapyr has been shown to be effective for control of emerged aquatic nuisance vegetation such common reed (*Phragmites australis*), torpedo grass (*Panicum repens*), giant reed (*Arundo donax*), and others. (Entrix 10/03, pp. 25/26; BASF 2004.) Studies with imazapyr for control of non-native *Spartina* have to date almost exclusively been conducted in Washington State. In an estuarine environment, imazapyr has a number of advantages over the use of glyphosate. First, the quicker drying time (the manufacturer claims rainfastness after 1 hour) of this herbicide facilitates a higher uptake of the active ingredient into the plants before the next tidal inundation washes the formulation off the leaves. Second, unlike glyphosate, imazapyr does not adsorb to particles and therefore remains active until either absorbed by the plant or washed off. Third, according to the manufacturer, the imazapyr formulation can be mixed with brackish or salt water, eliminating the need for access to freshwater. (Birk 04/05.) Fourth, imazapyr herbicide requires considerably lower spray volumes than glyphosate, therefore allowing larger areas to be treated before refilling of tanks becomes necessary. Finally, imazapyr applications in estuarine environments have been demonstrated to be more cost-effective than applications of glyphosate formulations. (Patten 03/05.)

Experiences with Imazapyr from Washington State

Experiences in Washington State regarding the efficacy of imazapyr/surfactant mixtures have been mixed and unpredictable ranging from 100% control to complete failure in a number of experiments conducted during April 1 through October 31. Efficacy did not seem to be correlated to the time of year and failures were most often related to the inherently more uneven hand applications; aerial applications with helicopters were more uniform and typically resulted in better control. In general, efficacy was affected by the time of application, spray volume, the choice of surfactant, and water quality, *i.e.* salinity and suspended sediment. Efficacy was positively correlated with drying time and the quality of the canopy resulting in direct contact with foliage, *i.e.* clean green leaves that are actively photosynthesizing; no sediment/mud on leaves; no epiphytic[50] (algae/eelgrass) or fungi growth on leaves. A low volume application in summer onto *Spartina* infested by fungi showed low efficacy. Further, interference appears to occur with applications onto dense seed heads, requiring higher volume applications for adequate control. Aerial application on 500 to 600 acres in Willapa Bay in late August/early September 2004 (*i.e.* during late anthesis[51]) resulted in 100% control (as observed in spring 2005). (Information regarding application rates, type of surfactant, time of day, and weather conditions were not available.) Application during early morning hours (about 5 a.m.) appeared to be preferable to mid-day applications. An additional benefit of application in the early morning hours is that it is typically not windy that time of day. Further, early morning dew on the *Spartina* canopy slightly prolongs the drying time of Habitat®, which appears to be desirable. (Patten 03/05; Patten 03/04.) Too-quick drying during the heat of the day could result

[50] The term *epiphyte* refers to a plant that grows on another plant; usually restricted to deriving only support and not nutrition.

[51] Anthesis is the period during which a flower is fully open and functional.

in crystallization of the compound, which makes it inaccessible for uptake by plants. (Hammond 2001[52].)

The most recent assessment from Washington State for Willapa Bay regarding control of *Spartina* with Habitat® evaluated varying spray volumes, surfactants, methods of application (aerial and boom spraying). Although a preliminary analysis showed considerable variability between sites, they were still considerably better any previous efforts. (Patten 04/05[53].) Numerous large control sites achieved 90 to 95% control or better. The author concluded that timing of spraying may be significant and suggested a preferable time window of late June to early August. The cited reasons for this timing were better (presumably shorter) dry time, large canopy to root mass, better translocation to the root system, better spray conditions, or cleaner canopies. Because the findings of this study are preliminary and the reasons for the preferred window of time somewhat speculative, it would be futile to try to extrapolate the timing to the San Francisco Estuary. However, the author emphasizes that it would be preferable to avoid viable seed production.

Canopy quality and integrity appeared to be very important. Areas where *Spartina* had a large leaf area to root mass (mid season) and where plants had not been previously compromised, *i.e.* had an undisturbed canopy, showed the best control results. These results suggest that pre-treatment crushing is not desirable for best results. One rather disappointing result of the study was the poor performance of hand applications with booms and hand guns. The manufacturer of Habitat® suggested that this might have been due to poor boom design, calibration and tuning and suggested the replacement of regular nozzles with so-called "air-induction drop tips" made from stainless steel. Finally, the author suggested that the drying time for Habitat® was longer than anticipated, leaving a narrower window than expected. The author concluded the use of imazapyr applied under the right conditions would deliver the level of control needed to eradicate *Spartina*.

Mixtures of Imazapyr and Glyphosate Herbicides

One shortcoming of imazapyr is that it is much slower acting than glyphosate; it takes several weeks to months for damages to plants to become visible. Because of the slower action of imazapyr, it is more difficult to evaluate the completeness of treatments, especially with many of the applications in the San Francisco Estuary occurring late in the season fairly close to the time of senescence of *Spartina* and natural browning. This precludes a follow-up application on spots or areas that were missed with the first application in the same year due to the rather short window of time available for treatment of many locations in the San Francisco Estuary (in 2005, July 1st through September 1st, at most locations). (Grijalva 04/05[54].) For example,

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[52] Hammond MER, The experimental control of Spartina anglica and Spartina × townsendii in estuarine saltmarsh, Ph.D. Thesis, University of Ulster, Northern Ireland, 2001.

[53] Kim Patten, WSU Long Beach, Spartina Regrowth in Willapa Bay in April 2005 as a Function of Herbicide Treatment in 2004, Preliminary Conclusions, via email, April 6, 2005.

[54] Personal communication with Erik Grijalva, Invasive Spartina Project, Berkeley, CA, April 2005.

treatment of breeding sites of the endangered California clapper rail is controlled by the breeding season, which extends from April 15th through September 1st. (Olofson 03/05.) However, imazapyr could potentially be used in combination with glyphosate, which acts considerably faster and would serve as a brown-down indicator. The addition of glyphosate to the tank mix would allow for better evaluation because brown-down would occur within two weeks, allowing for an additional application to be performed on those areas not treated properly. (Patten 03/05; Kerr 04/05[55].)

Glyphosate. Glyphosate herbicides are effective for the control of a large number of emerged aquatic nuisance species. (Monsanto 2000; Dow AgroSciences 2001.) However, its use for control of non-native *Spartina* is hindered by a number of factors that limit its efficacy under the tidal conditions inherent to estuaries. It requires long drying times (minimum 6 hours), which limits its efficacy in estuaries, where the diurnal tidal cycles leave only a small window of time for application, drying, and absorption by the plants. (Patten 03/05.) Glyphosate's efficacy is further reduced because it readily adsorbs to sediment particles. (*See* Section 3.1.6.) Once bound, it is inactivated and its herbicidal effect is lost. Because tidal waters often contain a high amount of suspended sediment, vegetation inundated by tides, such as *Spartina*, is frequently coated with a thin layer of sediment particles, which drastically reduces the efficacy of glyphosate herbicide applications. Consequently, even at high application rates of more than 16 lb glyphosate a.e./acre, the efficacy of glyphosate is highly variable and depends on local conditions. On non-native *Spartina*, glyphosate has been found to work most effectively when applied with the non-ionic surfactant R-11®. (Patten 03/05.) The surfactant R-11® is currently not approved in California for marine use and, as mentioned before, the ISP does not intend to use R-11® or other nonyl-phenol surfactants.

The use of glyphosate in an estuarine environment is further complicated because its application requires mixing of the formulation with freshwater. Glyphosate formulations can not be mixed with brackish or salt water. (Patten 03/05.) Because in many of the areas of the San Francisco Estuary freshwater is not readily available in the quantities required for glyphosate application, transportation of large quantities of freshwater to the sites would be required. (Olofson 03/05.) Aerial applications of glyphosate, carried out by helicopters, are also hampered because of the large spray volumes necessary to achieve satisfactory efficacy, which necessitate frequent refilling of the comparatively small tanks of helicopters. (Patten 03/05; Birk 04/05.)

[55] Personal communication with Drew Kerr, Invasive Spartina Project, Berkeley, CA, May 2005.

4. ECOLOGICAL RISK ASSESSMENT SUMMARY

The following sections address the potential ecological risks associated with the use of imazapyr and glyphosate herbicides for control of non-native Spartina in the San Francisco Estuary. The evaluation is based on a number of documents and risk assessments that evaluated the potential benefits and risks associated with the use of herbicides to control estuarine nuisance vegetation. The 2003 Programmatic EIS/EIR contains such an evaluation specifically for the San Francisco Estuary for control of non-native *Spartina* with glyphosate herbicides. Additional information can be found in the 1993 Final Environmental Impact Statement from Washington State ("WS FEIS 1993") on the use of glyphosate for noxious emergent plant management. (WS FEIS 11/93[56].) The 2003 Entrix report, a standard ecological risk assessment, evaluated the use of imazapyr for control of non-native, invasive *Spartina* for the estuarine environment in Washington State.

The sections below describe the ecological receptors and species of concern in the San Francisco Estuary, estimate environmental exposure concentrations for imazapyr applications, and a summarize and update the key information from the above-mentioned reports.

4.1 Ecological Receptors and Conceptual Exposure Model

The San Francisco Estuary provides a number of different salt marsh habitats, including tidal brackish marsh, estuarine beaches, brackish lagoons, and tidal salt marsh pans and ponds. These habitats support diverse, species-rich intertidal and subtidal ecological communities, including several species of concern[57], some listed as threatened or endangered[58] ("T&E") under

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[56] Washington State, Departments of Agriculture, Ecology, Natural Resources, Fisheries, and Wildlife and Noxious Weed Control Board, Environmental Impact Statement – Final, Noxious Emergent Plant Management, Element E: Environmental Effects of Glyphosate, Section 1, November 1993.

[57] The term *species of concern* refers to a plant or animal with declining populations and believed in need of concentrated conservation actions such as research, monitoring, or removal of threats, and given legal classification as threatened or endangered. The U.S. Fish and Wildlife Service ("U.S. FWS"), defines this term as those species listed in the periodic Birds of Conservation Concern report published by the Division of Migratory Bird Management; priority migratory bird species documented in the North American Waterbird Conservation Plan, United States Shorebird Conservation Plan, and Partners in Flight Bird Conservation Plan; species or populations of waterfowl identified as high, or moderately high, continental priority in the North American Waterfowl Management Plan; listed threatened and endangered bird species under 50 CFR 17.11; and Migratory Bird Treaty Act ("MBTA") listed game birds below desired population sizes.

[58] The term *threatened and endangered species* refers to those species that have been given special legal and protective designations by Federal or State government resource agencies. A Federally endangered species under the provisions of the ESA is in danger of extinction throughout all or a significant portion of its range. A Federally threatened species is likely to become an endangered species in the foreseeable future.

the Federal Endangered Species Act ("ESA"). (For a detailed description of the biological communities and a listing of the species of concern, consult the Programmatic EIS/EIR, Section 3.3.1 and Appx. F.) Estuarine plants, algae, animals, and bacteria are all potential receptors for exposure to herbicides. Humans are also potential receptors, particularly herbicide applicators, but also people who live or work close to marshland or who use treated marshland for recreation.

Application of imazapyr or mixtures of imazapyr with glyphosate would be executed in the same way as glyphosate applications, *i.e.* herbicide mixtures will be sprayed onto target plant surfaces, either manually with backpack sprayers or with spray equipment mounted on trucks, amphibious tracked vehicles, boats, or helicopters (broadcast sprayers or directed spray apparatus). In certain situations, pastes may be applied to cut stems or solutions wiped or painted on foliage. (*See* Section 3.1.5.) Therefore, the ecological receptors and species of concern occurring in the marshes in the San Francisco Estuary where imazapyr would be used to control non-native *Spartina* are identical to those identified in the Programmatic EIS/EIR for the application of glyphosate. (*See* Programmatic EIS/EIR, Section 3.3.1)

For effects on a biological receptor to occur, a receptor, exposure to the chemical of concern, and a complete exposure pathway must be present. An exposure pathway is only considered complete when all four of the following elements are present: a project-related source of the chemical; a mechanism of release of the chemical from the source to the environment; a mechanism of transport of the chemical to the ecological receptor; and a route by which the receptor is exposed to the chemical.

Based on the known properties of the herbicide glyphosate, potential methods of its application, and the ecological characteristics of the Estuary, the Programmatic EIS/EIR developed a conceptual exposure model and identified likely receptors and exposure pathways. Focusing on acute effects, this model included identification of primary and secondary herbicide sources, release mechanisms, exposure media, exposure routes, and potential ecological receptors. The Programmatic EIS/EIR identified potentially complete exposure pathways for non-target aquatic plants and algae through direct uptake, to aquatic and benthic invertebrates and fish through uptake and ingestion, and to birds and mammals through ingestion. Other pathways were deemed minor, insignificant, or incomplete. The inhalation pathway for birds and mammals was not quantified due to a lack of sufficient data. Exposure pathways for humans, primarily applicators, were deemed insignificant or incomplete. (Programmatic EIS/EIR, pp. 3.3-25–3.3-27, Figure 3.3-2.)

The 2003 Entrix report developed a similar conceptual model for imazapyr herbicide impacts to aquatic and terrestrial receptors in Willapa Bay and Padilla Bay in Washington State, accounting for the sources, pathways, and routes of exposure to the different trophic levels. In addition to the above identified, this model deemed the following pathways to be complete and potentially significant: for aquatic and benthic invertebrates and fish through respiration, for birds and marine mammals through dermal exposure and inhalation, and for terrestrial mammals through inhalation. The model also evaluated terrestrial invertebrates, reptiles, and amphibians and identified complete pathways through direct contact/dermal exposure, inhalation, and ingestion. (Entrix 10/03, pp. 20–22, Figures 2.3 and 2.4.)

4.2 Estimated Environmental Exposure Concentrations for Imazapyr Applications

For purposes of the estimating environmental exposure concentrations ("EECs"), the 2003 Entrix report assumed the use of the herbicide Arsenal®, which is identical with Habitat®. The following assumptions were used:

- Application of Arsenal® at the maximum concentration recommended for aquatic use. *i.e.* 6 pints Arsenal®/acre, equivalent to 1.5 pounds active ingredient (acid equivalents) per acre.
- A maximum of one application time per year until eradication is complete.
- Dilution of the neat herbicide formulation with water and surfactant prior to application. Surfactant added to the herbicide/water mixture to yield 1% of the spray solution applied.
- Three methods of herbicide application were considered including 1) hand-held sprayer unit, 2) boom-mounted sprayer, and 3) aerial sprayer. Spray volumes by these methods can vary from a minimum of 2.5 gal/acre to a maximum of 80 gal/acre.
- Herbicide quantity (mass) per unit area did not vary by spray volume (*i.e.* 1.5 lb/acre) but surfactant rates will, as they are normalized to spray volume. Ultra-low to low spray volumes of 2.5 to 20 gal/acre were assumed to be the most likely application rates, but risks of surfactant toxicity are also considered with high volume applications up to 80 gal/acre.

With the exception of the maximum spray volume, all assumptions apply equally for the Spartina Control Program. The most likely spray volumes to be used in the Estuary are 100 gal/acre for high-volume handheld applications, 20 gal/acre for low-volume directed sprayers, and 10-30 gal/acre for aerial applications with helicopters. (*See* Section 3.1.5.) (The active ingredient is applied at up to 1.5 lb/acre.) The higher maximum spray volume for manual applications results in higher application of surfactants than assumed in the 2003 Entrix report because surfactant rates are normalized to the spray volume not to the active ingredient. The resulting surfactant concentration is therefore 25%[59] higher than assumed in the 2003 Entrix report.

4.2.1 Concentrations in Water

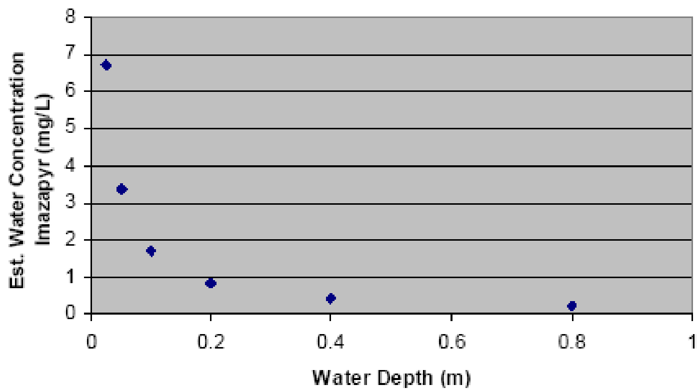
Herbicide mixtures may be indirectly released to surface waters by the incoming tide after application. (In the San Francisco Estuary rainfall is unlikely to occur during the planned application season.) The resulting concentrations in water will be affected by canopy

[59] 100/80 = 1.25.

interception of the applied herbicide, uptake into the plants, uptake into the root zone, and aerial drift.

The 2003 Entrix report developed a theoretical scenario for concentrations of imazapyr in water after application of 1.5 lb a.e./acre, the manufacturer-recommended maximum application rate, assuming no adsorption to sediment or vegetation, no foliar interception, and complete solubility of the herbicide in an incoming tide. This scenario is equivalent to application of the herbicide directly onto the sediment. Inset Figure 1 shows the modeled imazapyr concentrations in water above a unit area, which decrease exponentially with increasing depth.

Figure 1: Estimated water concentrations of imazapyr in tidal waters with no canopy interception and an application rate of 1.5 lb a.e./acre



From Entrix 10/03, p. 60; 1 m equals roughly 3 feet

One recent persistence study in Washington State investigated whether the herbicide would concentrate in the leading edge of the incoming tide as it moves over the treated site and continually dissolves herbicide from the sediment. Imazapyr herbicide was applied at the manufacturer-recommended rate of 1.5 lb a.e./acre directly onto a non-vegetated mudflat at the upper intertidal zone. The site was roughly 30 by 33 meters in size and aligned parallel with the tidal wetting front. Three hours later immediately following the first tidal flush, samples were collected 0.3, 6, and 60 meters beyond the upper tidal end of the site immediately after the incoming tide had reached the respective sampling site. The highest imazapyr concentration of 5.77 mg a.e./L, or 0.055 mg a.e./in^3 [60], was measured in 1-inch deep water at the upper tidal edge of the site. The average maximum concentration from three samples was 3.4 mg/L. (Patten 2003; Entrix 10/03, p. 61.) Thus, compared to the original application of 1.5 lb a.e./acre, or 0.11 mg a.e. onto a unit area of 1 square inch[61], the measured concentration in the first flush water was lower by a factor of about 2[62] and considerably lower than the theoretical worst-case calculations by the 2003 Entrix report. The concentration of imazapyr in water collected 6 and

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[60] (3.4 mg/L) / (61 in^3/L) = 0.055 mg/in^3

[61] (1.5 lb/acre) × (453,592 mg/lb) / (6,272,640 in^2/acre)= 0.108 mg/in^2

[62] (0.055 mg/in^3) / (0.11 mg/in^2) = 1.94/in

60 meters outside the treatment area was 99% lower than the maximum water concentration collected at the edge of the treatment area. The highest measured imazapyr concentration in sediment was 5.4 mg a.e./kg. No residues could be detected in water and sediment after 40 and 400 hours, respectively, with half-lives of <0.5 and 1.6 days, respectively, suggesting rapid dissipation of imazapyr from both water and sediment.

Under typical treatment conditions, the *Spartina* canopy will intercept the sprayed herbicide and will thus titrate the herbicide into the rising water. For aerial applications, the highest concentration of applied herbicide will be deposited in the upper canopy and hence will not be solubilized until the rising water reaches that portion of the canopy. In many cases, the upper portion of the canopy will not be inundated by the tide but will stay above it, thereby preventing the tide from washing off the herbicide. High interception rates reduce the potential exposure to aquatic receptors. In addition, a portion of the herbicide will be absorbed into the plant before the incoming tide washes of the remainder.

Foliar interception from canopies of a variety of grasses has been estimated at about 40%. (Entrix 10/03, p. 59.) Empirical results from Washington State indicate a canopy interception rate of about 75% for *Spartina* meadows. (Patten 2003.) The same foliar interception rate has been proposed by the manufacturer of imazapyr herbicides. (Mangels & Ritter 2000 in Entrix 10/03, p. 59.) For small stands of *Spartina*, which would be treated by manual application, the 40% interception value is more realistic because of the greater amount of edge around the clones. For Spartina meadows, which would be treated by aerial application, higher interception rates are more likely. Studies in grasslands suggest that 10% of the applied herbicide will drift off-site (or onto non-target vegetation) and the remaining 50% will be deposited onto the underlying sediment and be solubilized with the first flush. (USES 2.0 1998 in Entrix 10/03, p. 60.)

The San Francisco Estuary is home to a variety of different types of tidal marshes, some with hydraulic regimes that conceivably could result in higher imazapyr concentrations in water than modeled in the 2003 Entrix report. Of particular concern are tidal areas with little or slow exchange of water with the tides. Some marshes may be subject to slow laminar-flow flooding with the incoming tide rather than having turbulent conditions that allow for mixing of the herbicide in the water column. At such sites, the tides flood the channels and from there slowly “bleed” into the vegetated areas rather than proceeding in a lateral uniform flow up the shore. The leading edge of water, which slowly flows into the marsh, dissolves the herbicide from the sediment, potentially resulting in ever increasing concentrations as it continues to flow further inland. These types of marshes include, *e.g.*, diked marsh restoration areas with small outlets connecting to the Bay or the inner areas of larger marshes.

The ISP evaluated all marshes in the San Francisco Estuary to be treated with herbicide to identify such conditions. Most *Spartina*-infested marshes that will become inundated by tidal water following imazapyr application have a multitude of channels that will transport water directly from the San Francisco Bay before overbanking and causing lateral flow across the marsh. In such marshes, the channels themselves will not be treated. The maximum distance of lateral flow across a treated area before combining with flow from another direction was estimated to be about 100 feet.

To model the hypothetical worst-case concentration of herbicide that might arise in such a scenario, the following assumptions were made:

- Uniform spraying of herbicide across the entire marsh surface (but not in channels) at the highest manufacturer-recommended application rate of 1.5 lb imazapyr a.e./acre;
- 40% interception of herbicide by plant canopy and 60% of herbicide reaching sediment;
- No adsorption of the herbicide to sediment or absorption into vegetation;
- No evaporation of herbicide;
- No dilution through rain or other input of fresh water;
- The incoming tidal water overbanks from a channel and flows laterally across the surface of the marsh to a maximum distance of 100 feet;
- Herbicide from a unit area sediment (square foot) is instantly fully dissolved and mixed in the first unit volume (cubic foot) of water that flows through; and
- The entire amount of active herbicide that was deposited onto the sediment dissolves in the leading edge of the incoming tide water.

Based on these conservative assumptions and disregarding potential losses due to spray drift, the highest potential concentration in the leading unit volume of water of 1 cubic foot was determined to be 33.1 mg imazapyr a.e. /L. (*See* attached Table A-4.)

4.2.2 Residues in Plants and Animals

As discussed above (s*ee* Section 4.2.1), canopy interception rates will affect both plant residues and potential concentrations of the herbicide in water. Following application of 1 pound herbicide per acre onto tall grasses, maximum residual concentrations in plants were modeled at 87 mg/kg plant. A field experiment with the same application rate determined maximum concentrations of 29 mg/kg plant. (Hoerger & Kenaga 1972; Fletcher *et al.* 1984; both in Entrix 10/03, p. 60.) Extrapolated to the higher application rate proposed for *Spartina* control, 1.5 lb/acre, the estimated residue concentration shortly after spraying would be 130.5 mg/kg[63] based on the modeled residues and 43.5 mg/kg[64] based on the empirical results. No field data for *Spartina* control were available for review to compare against these residue estimates.

[63] 87 mg/kg × 1.5 = 130.5 mg/kg

[64] 29 mg/kg × 1.5 = 43.5 mg/kg

Imazapyr residues in plant material will change over time and this degradation has not been empirically determined in treated *Spartina*.

4.2.3 Sediment Concentrations

As previously mentioned (*see* Section 3.1.7), limited testing of marine sediment concentrations following imazapyr treatment of bare mudflats has been conducted in Washington State. (Patten 2003). The highest value measured in sediment was 5.7 mg/kg. This value is highly conservative in that the measurements were taken after the first tidal wash, and hence represent "acute" sediment conditions as opposed to more chronic sediment conditions. The half-life in estuarine sediments will be substantially less than the 12.2-day half-life determined in freshwater pond because of the tidal exchange of waters. However, due to the non-static nature of the estuarine environment, true sediment half-lives cannot be determined from empirical measurements and "dissipation" rates more accurately describe what is actually occurring in the estuarine environment—capturing the multiple mechanisms that reduce sediment concentrations over time. The dissipation study from Washington State (*see* Section 4.2.1) suggests complete dissipation of the herbicide from sediment in 400 hours with a half-life of 1.6 days. Approximately one fourth of the maximum detected concentration of imazapyr in sediment, 5.7 mg/kg, was detectable after roughly 4 days post treatment. The study found no persistence of imazapyr (or glyphosate) in sediment after application onto beds of Japanese eelgrass (*Zostera japonica*) and pickleweed. The treated beds were reinfested within 1 year of treatment. (Patten 2003.)

4.3 Toxicity of Imazapyr and Glyphosate

Categories for the qualitative ranking of ecotoxicity to mammals, birds, bees, and aquatic organisms based on LD_{50} or LC_{50} values according to U.S. EPA's criteria for ecological risk assessments are summarized in attached Tables A-5, A-6, and A-7.[65] This ranking scheme allows a qualitative comparison of the toxicity of the active ingredient and its formulations amongst species.

The following sections provide brief summaries of the acute, subchronic, and chronic toxicity[66] of imazapyr and glyphosate herbicides to mammals, birds, insects, reptiles and

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[65] No ecotoxicity categories exist for terrestrial reptiles and amphibians.

[66] *Acute toxicity* describes adverse effects occurring within a short time of administration of a single dose of a chemical, or immediately following short or continuous exposure, or multiple doses (typically 96 or 24 hours or less). *Subchronic* and *chronic toxicity* describe adverse effects occurring as a result of repeated daily dosing of a chemical, or exposure to the chemical, for part of an organism's lifespan (subchronic usually less than 10%; chronic usually more than 50%).

Various ways of measuring toxicity have been developed. Results from toxicity studies are typically provided as so-called effect concentrations ("EC") causing a certain percentage inhibition of a process. The most common scales used to determine the degree of toxicity include the median lethal dose ("LD_{50}") and the median lethal concentration ("LC_{50}") at which 50% death of the test organisms have occurred. The LD_{50} describes the acute oral or dermal toxicity while the LC_{50} describes acute inhalation toxicity. The amphibians, fish, aquatic invertebrates, and non-target vegetation. The sections further identify data gaps. Most studies regarding toxicity have been conducted with the parent compounds. Attached Tables A-8 through A-12 summarize toxicity studies for imazapyr and its isopropylamine salt from the 2003 Entrix and 2004 SERA reports and from the literature. Data on the toxicity of formulations as well as mixes with surfactants are provided where available.

Few studies have been conducted evaluating the combined toxicity of herbicide mixtures. A review of the literature shows that the occurrence of synergistic effects resulting from the application of herbicide mixtures is rare. For example, one comprehensive study of more than 400 combinations of pesticides showed that most had only additive or less than additive effects. Other studies also demonstrated the lack of synergistic effects. (Crockett 03/05[67].) The toxicity of imazapyr/glyphosate mixtures potentially used for control of non-native *Spartina* can therefore be derived from the individual compounds as described below.

4.3.1 Mammals

Imazapyr. Attached Table A-8 summarizes studies on the acute and subchronic mammalian toxicity to imazapyr and imazapyr isopropylamine salt (technical compounds and diluted solution). Based on U.S. EPA ecotoxicity criteria (*see* attached Table A-5), imazapyr is considered practically non-toxic to mammals via oral or dermal administration based on acute and chronic studies conducted with a variety of mammalian species. For example, the reported acute oral LD_{50} for technical imazapyr in rats is greater than 5,000 mg/kg body weight ("b.w.") Rats were observed to rapidly excrete imazapyr in urine and feces with no residues detected in their liver, kidney, muscle, fat, or blood. No observable effect was noted for any formulation of imazapyr administered dermally. Very few inhalatory studies were performed and none tested concentrations high enough to determine acute toxicity. Inhalatory effects at sublethal concentrations (<5 mg/L aerosol) were found with technical grade imazapyr resulting in slight

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former is expressed in milligram per kilogram ("mg/kg") body weight ("b.w.") while the latter is expressed as parts per million ("ppm") for gases and milligrams per cubic meter ("mg/m^3") of air or milligrams per liter ("mg/L") of water for liquids. The more toxic the chemical, the smaller the LD_{50} or LC_{50}. Other important toxicity values are the lowest-observable effect level ("LOEL") or concentration ("LOEC") and the no-observable effect level ("NOEL") or concentration ("NOEC").

[67] Attachment 'synergy-monsanto.doc' to email from Ron Crocket, Monsanto, to Peggy Olofson, Invasive Spartina Project, Re: Aquamaster/imazapyr manuscript, March 29, 2005.

Various ways of measuring toxicity have been developed. Results from toxicity studies are typically provided as so-called effect concentrations ("EC") causing a certain percentage inhibition of a process. The most common scales used to determine the degree of toxicity include the median lethal dose ("LD_{50}") and the median lethal concentration ("LC_{50}") at which 50% death of the test organisms have occurred. The LD_{50} describes the acute oral or dermal toxicity while the LC_{50} describes acute inhalation toxicity. The former is expressed in milligram per kilogram ("mg/kg") body weight ("b.w.") while the latter is expressed as parts per million ("ppm") for gases and milligrams per cubic meter ("mg/m^3") of air or milligrams per liter ("mg/L") of water for liquids. The more toxic the chemical, the smaller the LD_{50} or LC_{50}. Other important toxicity values are the lowest-observable effect level ("LOEL") or concentration ("LOEC") and the no-observable effect level ("NOEL") or concentration ("NOEC").

nasal discharge and congested lungs. Technical grade imazapyr and imazapyr isopropylamine salt were both found to be moderately irritating to rabbit eyes with complete recovery within 7 days. Technical grade imazapyr is reported as mildly irritating to rabbit skin. Commercial formulations of imazapyr appear to be less toxic via dermal exposure. (Entrix 10/03, p. 42-44.) Chronic and subchronic toxicity studies with imazapyr with dogs, mice, and rats did not suggest any systemic toxic or carcinogenic effects. (SERA 12/04.)

Glyphosate. Glyphosate has been determined to be practically non-toxic to mammals by ingestion with an acute oral LD_{50} of 5,600 mg/kg b.w. in rats. The no-observed-effect level ("NOEL") for chronic toxicity to rats has been determined at 362 mg/kg b.w./day (8,000 ppm) and LOEL at 940 mg/kg b.w./day (20,000 ppm). (USDA 1981; Monsanto 1983; both in WS FEIS 11/03.) The reported acute LD_{50} values for dermal effects range from >5,000 to 7,940 mg/kg for rabbits. Subchronic oral toxicity studies of glyphosate with rats and dogs indicate that oral does of up to 2,000 ppm do not significantly affect behavior, survival, or body weight. Laboratory studies of the chronic effects of glyphosate show that it is slightly to practically non-irritating to rabbits eyes. No significant reproductive, teratogenic, mutagenic, or carcinogenic effects from exposure to concentrations of up to 300 ppm were reported in 20-year laboratory studies with rats, dogs, rabbits, and mice.

4.3.2 Birds

Imazapyr. Only few toxicity studies exist for birds. Attached Table A-9 summarizes studies on the acute and subchronic toxicity of the imazapyr formulation Arsenal® (identical with Habitat®) to birds (mallard duck and bobwhite quail). No adverse effects were noted at imazapyr concentrations of up to 5,000 ppm in the diet. Based on the highest doses tested and the U.S. EPA ecotoxicity categories (*see* attached Table A-5), these results suggest that imazapyr is moderately or less toxic orally to birds. No data exist for the potential toxicity of imazapyr to shorebirds. (Fletcher 1983a,b,c,d in SERA 2004.) No studies exist on toxicity to raptors or on preening or inhalation exposure potentials.

Glyphosate. Glyphosate is no more than slightly toxic to birds. Several single-dose acute oral studies indicate that glyphosate is practically non-toxic to upland birds and only slightly toxic to waterfowl. (U.S. EPA 09/93.) Dietary exposure to glyphosate concentrations of up to 4,640 ppm diet did not result in mortality or treatment-related effects. Chronic exposure studies with glyphosate determined a no-observed-effect concentration ("NOEC") of 1,000 ppm in the diet. (Heydens 1991 in WS 11/93.)

4.3.3 Insects

Imazapyr. The only studies on the toxicity of imazapyr to insects are provided by studies with the honey bee. The acute contact LD_{50} for honey bees has been determined to be greater than 0.1 mg/bee. (Gagne *et al.* 1991 in Entrix 10/03, p. 45.) The oral LD_{50} was determined to be greater than 0.1 mg/bee. (Atkins & Kellum 1983 in SERA 12/04, p. 4-2.) These values indicate that imazapyr is practically non-toxic to insects according to the U.S. EPA ecotoxicity criteria. (*See* attached Table A-7.) Based on an average weight of 0.093 g/bee and making the very conservative assumption of 100% absorption, this would correspond to a lethal dose greater than 1,000 mg/kg b.w.[68] (SERA 2004, p. 4-2.)

Glyphosate. Glyphosate has been found to be practically nontoxic to honeybees. (U.S. EPA 09/93.) No other information on insects was found in the literature.

4.3.4 Reptiles and Amphibians

Imazapyr. Neither the published literature nor the files submitted by the applicant for registration of imazapyr (evaluated in 2004 SERA report) contain information regarding the toxicity of imazapyr to reptiles and amphibians,

Glyphosate. Pure glyphosate has been determined to be not very toxic to tadpoles of some Australian species. (Hileman 2005[69].) However, a recent study in a simulated pond ecosystem found that a glyphosate formulation for terrestrial use, Roundup®, caused a 70% decline in amphibian biodiversity and an 86% decline in the total mass of tadpoles. While the tadpoles of one frog species were completely unaffected, tadpoles of three other frogs and toads were completely or nearly completely eliminated. (Relya 2004[70].) Previous research had determined that the lethal ingredient in Roundup® was the cationic surfactant contained in the formulation, polyethoxylated tallowamine. (Hileman 2005.) However, due to their intolerance of saline conditions, amphibians are not expected in estuarine marshes.

4.3.5 Fish

Imazapyr. Attached Table A-10 summarizes toxicity studies for fish from the literature. As detailed in both the 2003 Entrix and 2004 SERA reports, a number of standard bioassays submitted to the U.S. EPA in support of the registration of imazapyr indicate very low toxicity to fish with 96-hr LC_{50} values greater than 100 mg/L in most studies. According to U.S. EPA's ecotoxicity classification for aquatic organisms (see Table A-6), these values classify imazapyr as practically non-toxic, the lowest category for addressing acute risk to aquatic organisms from use of chemicals. (U.S. EPA 04/05[71].) A recent study suggests that both Habitat® and Rodeo® have relatively low toxicity to juvenile rainbow trout. The LC_{50} determined for Arsenal®

[68] (0.1 mg imazapyr/bee) / (0.000093 kg b.w./bee) = 1,075 mg/kg b.w.

[69] Hileman B, Common Herbicide Kills Tadpoles, Chemical & Engineering News, vol. 83, no. 15, p. 11, 2005.

[70] Relya RA, The lethal impact of Roundup® on aquatic and terrestrial amphibians, Ecological Applications, 2005, vol. 15, p. 618, 2005.

[71] U.S. Environmental Protection Agency, Technical Overview of Ecological Risk Assessment, Analysis Phase: Ecological Effects Characterization, Ecotoxicity Categories for Terrestrial and Aquatic Organisms; http://www.epa.gov/oppefed1/ecorisk_ders/toera_analysis_eco.htm#Ecotox, accessed April 2, 2005.

(a terrestrial formulation identical to Habitat® that did not contain any surfactants) was determined at 22,305 mg imazapyr a.e./L. (King *et al.* 2004[72].)

One study reported much lower 96-hr LC_{50} values of 4.7 mg/L for Nile tilapia (*Tilapia nilotica*) and 2.7 mg/L for silver barb (*Barbus genionotus*). (Supamataya et al. 1981 in SERA 10/04.) Although the herbicide used was not specified, it is likely that a formulation was used rather than the technical grade active ingredient. Historically imazapyr herbicides contained surfactants and a formulation that removed the surfactant was only developed in 1992. (Birk 04/05.) The use of an herbicide containing surfactants might explain the considerably lower LC_{50} values. (*See* Section 4.4.2.) The 2004 SERA report used the lowest LC_{50} value from this study, 2.7 mg/L, for their risk assessment despite some reservations about the study due to the fact that they only had access to its abstract and because the species studied were not native to the U.S. Nevertheless, the 2004 SERA report assumed that, even though the study was not well documented, the response of these apparently sensitive species may well encompass the response of other sensitive species native to the U.S. (SERA 12/04, p. 4-22.) This conclusion is supported by a study that examined the comparative sensitivity of eight ESA-listed fish species to standard test organisms exposed to five different pesticides or metals in order to validate the use of surrogate species as a predictive tool in toxicological assessments. Based on their findings, the authors concluded that a safety factor of two would provide a conservative estimate in risk assessments for listed cold-water, warm-water and euryhaline fish species. (Sappington *et al.* 2000 in Entrix 10/03, p. 49.)

Glyphosate. Acute toxicity studies with warm and cold water fish indicate that technical glyphosate is slightly to practically non-toxic. (U.S. EPA 09/93.) Acute toxicity LC_{50} values were reported at 86 mg/L in rainbow trout, 120 mg/L in bluegill sunfish, and 168 mg/L in harlequin. (ExToxNet 04/05[73].) Chronic toxicity studies with a terrestrial formulation of glyphosate, Roundup®, found no significant adverse effects on growth, carcinogenicity, feeding, and agonistic behavior in rainbow trout fingerlings. The authors concluded that sublethal levels of the formulation are relatively non-toxic. (Morgan & Kiceniuk 1992 in WS FEIS 11/93.)

A recent study with the aquatic formulation Rodeo® determined the LC_{50} for juvenile rainbow trout at 782 mg glyphosate a.e./L, two orders of magnitude lower than found for the imazapyr herbicide Arsenal®, 22,305 mg imazapyr a.e./L. (King *et al.* 2004.)

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[72] King K, Curran C, Smith B, Boehm D, Grange K, McAvinchey S, Sowle K, Genther K, Highley R, Schaaf A, Sykes C, Grassley J, and Grue C, Toxicity of Rodeo® and Arsenal® Tank Mixes to Juvenile Rainbow Trout, Third International Conference on Invasive Spartina, San Francisco, California, November 8-10, 2004.

[73] ExToxNet is a cooperative effort of University of California-Davis, Oregon State University, Michigan State University, Cornell University, and the University of Idaho, Pesticide Information Profile for Glyphosate; http://extoxnet.orst.edu/, accessed April 5, 2005.

4.3.6 Aquatic Invertebrates

Imazapyr. Imazapyr has been found to have low toxicity to aquatic invertebrates. Attached Table A-11 summarizes aquatic invertebrate toxicity to imazapyr and its formulations. A study where *Daphnia* was exposed to an imazapyr formulation (~50%) produced a 48-hour EC_{50} concentration of 373 mg imazapyr a.e./L (Cyanamid 1997 in Entrix 10/03). Another study with Arsenal® (identical to Habitat®) with an unspecified surfactant determined a 48-hour LC_{50} of 350 mg Arsenal/L (79.1 mg imazapyr a.e./L) and a NOEC of 180 mg Arsenal/L (40.7 mg imazapyr a.e./L) for the freshwater flea (*Daphnia magna*), highlighting the potential effects of surfactants on aquatic toxicity. Other studies also reported 24 and 48-hour LC_{50} concentrations of greater than 100 mg/L, the highest dose tested ("HDT"), in static tests conducted with newly-hatched *Daphnia.* (Kintner & Forbis 1983 in SERA 12/04.) Chronic studies reported no adverse effects on survival, reproduction or growth of 1st generation *Daphnia* after 7, 14 and 21-days of exposure at concentrations up to 97.1 mg/L, the HDT. (Manning 1989 in SERA 12/04.). Testing with other invertebrate species that exhibit alternative life cycles has been limited to survival of pink shrimp (*Penaeus duorarum*) and growth studies with the Eastern oyster (*Crassostrea virginica*). Acute toxicity to pink shrimp was determined at LC_{50} >132 mg imazapyr a.e. /L, the HDT, which was also the NOEC. The EC_{50} for growth inhibition of the Eastern oyster was established at a concentration greater than 132 mg imazapyr a.e./L, with the NOEC set at this concentration, the HDT. (Mangels & Ritter 2000 in SERA 12/04.)

A recent microcosm study analyzing benthic macroinvertebrates in a logged pond confirmed the low toxicity of imazapyr to benthic freshwater macroinvertebrates. The study analyzed macroinvertebrate community composition, chironomid deformity rate, and chironomid biomass and concluded that imazapyr did not affect the macroinvertebrate community at the concentrations tested. The NOEC was determined to be greater than 18.4 mg/L (Fowlkes et al. 2003[74].)

Glyphosate. Glyphosate is only slightly toxic to practically non-toxic to marine and freshwater aquatic invertebrates. Acute toxicity for freshwater invertebrates varies from 545 to 780 mg/L for water flea (*Daphnia magna*), to 673 mg/L for mosquito 4th instar (*Anopheles quadrimaculatus*), to 1,157 mg/L for a leech (*Nephaelopsis obscura*). Acute toxicity for marine invertebrates were reported as greater than 10 mg/L for Atlantic oyster larvae (*Crassostrea virginica*), 281 mg/L for grass shrimp (*Palaemonetes vulgaris*), and 934 mg/L for fiddler crab (*Uca pugilator*). (ExToxNet 04/05; Henry 1992, Heydens 1991; both in SERA 12/04.) The wide variation in the aquatic toxicity of glyphosate has been attributed to the dilution water, temperature, formulation, and the amount of suspended sediment in the water. Toxicity appears to increase with temperature, and decrease with elevated pH and suspended sediment. (Schuette 1998). Field studies with glyphosate/surfactant applications to tidal mudflat communities in Washington State indicate low potential for adverse impacts, possibly due to

[74] Mark D. Fowlkes, Jerry L. Michael, Thomas L. Crisman, and Joseph P. Prenger, Effects of the Herbicide Imazapyr on Benthic Macroinvertebrates in a Logged Pond Cypress Dome, Environmental Toxicology and Chemistry, vol. 22, no. 4, pp. 900–907, 2003.

inactivation of glyphosate when adsorbed to sediment. (Kubena 1996 in Programmatic EIS/EIR, p. 3.3-30.)

4.3.7 Non-target Vegetation

Due to their engineered mechanism of action, imazapyr and glyphosate are toxic to a wide variety of plants. Native salt marsh plants, aquatic macrophytes, and algae in the Estuary waters where the herbicides would be applied could be negatively affected.

Imazapyr. Attached Table A-12 summarizes the toxicity of technical grade imazapyr and an herbicide/surfactant mixture to algae and aquatic plants. The most sensitive species appear to be aquatic macrophytes with reported EC_{25} values for duckweed (*Lemna gibba*) of 0.013 mg/L for growth and for common water milfoil (*Myriophyllum sibiricum*) of 0.013 mg/L for shoot growth and 0.0079 mg/L for root growth. (Hughes 1987; Roshon *et al.* 1999; both in SERA 12/04.) Aquatic algae appear to be substantially less sensitive. The most sensitive species of algae tested was a unicellular green algae (*Chlorella emersonii*) with an EC_{50} of about 0.2 mg/L for growth. Some algal species appear to be stimulated rather than inhibited by imazapyr concentrations of up to 100 mg/L. (Hughes 1987 in SERA 10/04.) Some species of plants, including aquatic plants, may develop resistance to imazapyr. Bioassays conducted on *Chlorella emersonii* indicated that resistant strains may be less sensitive by a factor of 10. (Landstein *et al.* 1993 in SERA 10/04.) Due to the infrequent application of imazapyr for control of *Spartina*, *i.e.* once per year, development of resistance to imazapyr is unlikely.

Recent studies conducted in Washington State also document the potential for imazapyr to impact non-target vegetation. Effects of imazapyr application on non-native Japanese eelgrass were compared to glyphosate application. For both herbicides, the eelgrass canopy was killed if herbicide was applied on dry eelgrass at low tide with imazapyr being more toxic. Application onto an eelgrass bed with a thin overlying film of water did not result in toxic effects. Within 12 months, all treated eelgrass beds had recovered. Persistence was not recorded in the sediment underlying these eelgrass beds. (Patten 2003.)

Glyphosate. In laboratory growth inhibition studies with submerged aquatic plants no adverse effects on the growth of elodea (*Elodea canadensis*), water milfoil (*Myriophyllum spicatum*), and wild celery (*Valisneria americana*) were found with glyphosate concentrations of up to 1 mg/L. (Forney & David 1981 in WS FEIS 11/93.) These results are consistent with the findings of other investigators who report that submerged plants are either resistant or affected only by very high glyphosate concentrations. (Evans 1978; Peverly & Crawford 1975; both in WS FEIS 11/93.) A large number of studies with a variety of green algae, blue-green algae, diatoms, and periphyton indicate that glyphosate is slightly toxic to practically non-toxic to most algae. Most algae tolerate concentrations of glyphosate greater than 1 mg/L. (WS FEIS 11/93.)

4.4 Inert Ingredient and Adjuvant Toxicity

The following sections discuss the toxicity of inert ingredients in commercial formulations and the toxicity of surfactants and colorants used in combination with imazapyr and glyphosate formulations.

4.4.1 Inert Ingredients

As mentioned above, neither Aquamaster® nor Rodeo® contain inert ingredients other than water. Habitat® contains a small amount of a weak acid, most likely acetic acid. The 2003 Entrix report summarized a number of studies on the toxicity of acetic acid, which is contained in small amounts in the Habitat® formulation. (Entrix 10/04, p. 52, Table 3-14.) From the acute LC_{50} for several studies with fathead minnow (*Pimephales promelas*), the toxicity of acetic acid to aquatic organisms can be categorized as slightly toxic. An inhalation study with mice indicates that acetic acid is practically non-toxic. Because acetic acid is present in small quantities in the formulation only, and its content in the tank mix will be even lower, risks from this ingredient are considered insignificant.

4.4.2 Adjuvants

Most toxicity testing of herbicides uses either the technical grade active ingredient or its formulations. However, toxicity to non-target organisms may change depending on the adjuvants contained in the tank mix. Many adjuvants can produce wide-ranging effects on physiological and metabolic processes and almost all of these effects can occur at low concentrations or doses. (Tu *et al.* 2001.) As discussed in Section 3.1.7, registration requirements for adjuvants are not as stringent as those for herbicides. Consequently, only limited information is available for most adjuvants.

Attached Table A-2 summarizes chemical properties, degradation pathways (where known), general toxicity rating, and acute toxicity of surfactants and colorants potentially used with Habitat® and glyphosate herbicides for control of *Spartina* in the San Francisco Estuary. Even though at the time being, non-ionic surfactants are not proposed for use by the ISP, they have been included in the table for completeness sake.

Surfactants

A number of surfactants were evaluated for their toxicity, including the non-ionic surfactants R-11®, X-77®, LI-700®, Liberate®, and Cygnet Plus; the crop-oil concentrate Agri-Dex®; the esterified seed oil Competitor®; and the organo-silicones Dyne-Amic® and Kinetic®.[75] Attached Table A-2 summarizes the general toxicity rating and the lowest reported

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[75] The categorization of surfactant classes is inconsistent and the names of surfactant classes are not necessarily intuitive regarding the content of the surfactant. For example, crop oil concentrates are not made from vegetable oils but from petroleum oils and not all surfactants with mainly non-ionic ingredients, *e.g.*, oils or silicones, are classified as non-ionic surfactants. To complicate the fact, surfactant

toxicity for these surfactants. Based on the limited testing available, all surfactants would be considered practically non-toxic to moderately toxic to aquatic organisms and practically non-toxic to mammals via oral administration. Most surfactants are moderate skin and eye irritants. (Entrix 10/03, pp. 52-55.) No studies regarding surfactant toxicity to birds were found in the literature.

The potential impact of surfactants on the toxicity of herbicides is clearly illustrated in several studies, which found that the toxicity of imazapyr and glyphosate herbicide tank mixes to aquatic organisms (fish and water flea) is more driven by the surfactant and its percentage in the tank mixture (herbicide formulation, water, plus surfactant) than by the herbicide itself. One study analyzed Arsenal® (identical with the aquatic formulation Habitat®) and Rodeo® with and without surfactants, as well as the surfactants alone. In all cases, the toxicity of the herbicides alone was found to be much lower, *i.e.* the LC_{50} much higher, than in combination with a surfactant. In most cases the surfactant by itself was considerably more toxic than the herbicide/surfactant combinations. (Smith *et al.* 2002, Henry 1992, both in Entrix 10/03, pp. 54/55; Mitchell *et al.* 1987a in WS FEIS 11/93.) Inset Table 1 summarizes the results of these studies for acute toxicity to rainbow trout.

Table 1: Acute toxicity of surfactants, herbicides, and herbicide/surfactant mixtures to rainbow trout

Surfactant	**LC_{50} (ppm)**	**Herbicide**	**LC_{50} (ppm)**	**Herbicide/ surfactant mixture**	**LC_{50} (ppm)[2]**
Agri-Dex®	271	Arsenal® Herbicide	77,716 concentrate 22,305 imazapyr a.e.	Arsenal® Herbicide + Agri-Dex®	479
Hasten®[3]	74			Arsenal® Herbicide + Hasten®	113
X-77	4.2	Rodeo®	782 glyphosate a.e.	Rodeo® + X-77®	130
LI-700®	17			Rodeo® + LI-700®	23
R-11®[1]	6.0			Rodeo® + R11®	5.4

References in Entrix 10/03.
[1] not proposed for use by ISP
[2] as surfactant
[3] esterified seed oil (Competitor® plus nonylphenol non-ionic surfactant)

These studies demonstrate that the toxicity of the herbicide/surfactant mixture is driven by the surfactant. The LC_{50} values for tank mixtures were typically two orders of magnitude lower, *i.e.* more toxic, than the pure formulation. This changes the ecotoxicity classification to address acute risk to non-target aquatic organisms from practically non-toxic (margin of safety two orders of magnitude) for the formulations to slightly toxic for the tank mixtures. Thus, depending on the surfactant selected, tank mixtures may pose a greater hazard to non-target species than the formulations tested.

A study with a glyphosate formulation/surfactant mixture (Rodeo®/X-77®) reported lethal concentrations for rainbow trout, Chinook salmon, and Coho salmon ranging from 680 to

mixtures often contain several ingredients belonging to different surfactant classes. They are typically, but not always, classified based on their main ingredient.

1,070 mg/L, 750 to 1,440 mg/L, and 600 to 1,000 mg/L, respectively, considerably higher than those reported for glyphosate. (Mitchell *et al.* 1987a in WS FEIS 11/93.) Other studies have also determined that the surfactants contained in terrestrial glyphosate formulations make the formulation more toxic compared the toxicity of glyphosate alone. (Schuette 1998.)

Colorants

The acute oral toxicity of Blazon® Blue, the colorant likely used by the ISP, to rats has been reported to be greater than 5,000 mg/kg. (Milliken Chemical 05/02[76].) Therefore, the colorant is practically non-toxic.

4.5 Relative Exposure and Risk Characterization

It is not feasible to estimate the exposure and risk for each of the hundreds of identified individual receptor species for which potentially complete exposure pathways have been identified. For wildlife receptors, evaluation of so-called "receptor guilds" can serve as a reasonable surrogate approach. This approach is based on the concept that each receptor is part of a group of potential receptors that function in similar ecological niches or "guilds." Species belonging to the same guild exhibit similar life histories and are therefore expected to have similar exposures to herbicide applications. Surrogate species for which reliable life history information and toxicological information is available are used for calculating risk. The results are then extrapolated to the entire guild as a whole. The fundamental assumption of this approach is that if negligible risk is determined for the surrogate species, then the entire guild is protected. (Entrix 10/03, pp. 18/19.)

Based on the above information, risks to ecological receptors can be characterized by integrating the potential effects and exposure to determine the ecological risk from the use of a herbicide and the likelihood of effects on aquatic life, wildlife, and plants based on various herbicide use scenarios. Frequently, the risk to ecological receptors is characterized numerically as a so-called risk quotient ("RQ"), which is calculated as the ratio of potential exposure to a select toxicity endpoint for a given species or surrogate species. The risk quotients are then compared to an agency's level of concern ("LOC"), which is specific to each category of organisms. An LOC is a tool to interpret potential risk to non-target organisms. In addition to the risk quotients for characterizing acute or chronic risk, U.S. EPA has published levels of concern for characterizing risks from pesticides to T&E species, which include additional factors of safety. (U.S. EPA 01/04[77].) The 2003 Entrix report considered risks adverse if the RQ exceeded 1. The following sections evaluate the risk quotients derived in the 2003 Entrix report additionally in light of the levels of concern for T&E species for species of concern found in the San Francisco Estuary. The toxicological endpoints typically used for calculating the RQ and levels of concern for interpreting risk quotients are summarized in attached Table A-13.

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[76] Milliken Chemical, Blazon® Blue Spray Pattern Indicator, Material Safety Data Sheet, May 7, 2002.

[77] U.S. Environmental Protection Agency, Overview of the Ecological Risk Assessment Process in the Office of Pesticide Programs, Endangered and Threatened Species Effects Determination, January 23, 2004.

Because the toxicity of herbicide mixtures is additive and synergistic effects are not likely, the risk quotients for an herbicide mixture would be the sum of the risk quotients determined for the individual exposure to each of the herbicides. (*See* Section 4.3.) The toxicity of glyphosate to wildlife and non-target vegetation from application in an estuarine environment has been extensively documented in the WS EIS 1993.

4.5.1 Mammals

Mammalian wildlife could be exposed to imazapyr through dermal, oral (ingestion) or inhalation routes. The dietary route is considered the most likely. Several species of concern are potentially present in or close to areas where non-native *Spartina* is distributed or where imazapyr herbicides could be applied. The Suisun ornate shrew (*Sorex ornatus sinuosus*) occurs in tidal brackish marsh plains with dense cover and the harbor seal (*Phoca vitulina richardi*) uses haul-outs on tidal marshes. (Programmatic EIS/EIR, Appx. F.) Other T&E species occurring close to areas where imazapyr herbicide would be sprayed include the salt marsh wandering shrew (*Sorex vagrans halicoetes*), which inhabits tidal salt marsh plains above the cordgrass zone, and the southern sea otter (*Enhydra lutris nereis*).

Imazapyr. Based on the EPA criteria outlined in attached Table A-13, the acute oral and dermal toxicity of technical imazapyr and imazapyr isopropylamine to mammals is categorized as practically non-toxic. None of the risk quotients estimated in the 2003 Entrix report exceeded levels of concern for acute risks to mammals for any of the species or exposure pathways modeled relative to the NOEL with the exception of the deer mouse spill scenario exposure (RQ deer mouse = 1.20). (Entrix 10/03, Table 5-1, p. 75.) Levels of concern for endangered mammals of 0.1 were exceeded for the spill scenario exposure for all mammals. (Entrix 10/03, Table 5-1, p. 75.) However, the spill scenario modeled (*i.e.*, where an animal would effectively drink undiluted spilled spray solution) is highly conservative and unlikely to be realized *in situ* because best management practices would be employed immediately to clean up any spilled herbicide and the disturbance of the cleanup action would discourage wildlife use of the area.

In addition, substantial conservatism was factored into this risk characterization. Because the dose ranges of imazapyr administered to mammals over the variety of tests performed have never yielded lethality, characterizing risk based on absolute lethal thresholds such as the LD_{50} is not possible. Thus, the 2003 Entrix report used NOELs for risk calculations. Most of the NOELs simply referenced the HDT and were not based on actual empirical findings from a dose-response curve. Clearly, using a NOEL HDT instead of an LD_{50} considerably overestimates potential risk. In addition, the doses for dietary and dermal exposure modeled in the 2003 Entrix report tended to overestimate conditions *in situ*. This is particularly true for chronic exposures because applications of herbicide would occur only once a year and tidal flushing over the treated area would result in the loss of the herbicide over time. These very conservative assumptions and toxicity values result in considerably overestimated risk quotients.

Since imazapyr does not bioaccumulate, and best management practices identified in the Programmatic EIS/EIR and adopted by the Conservancy as conditions of approval of the Spartina Control Program will prevent significant drift off-site and reduce spills, it can be reasonably assumed that no mammal species would be adversely affected by the use of an imazapyr herbicide at the manufacturer-recommended application rate of 1.5 lbs/acre (0.68 kg/acre) in San Francisco Estuary, even under worst-case exposure scenarios.

Glyphosate. Based on the reported acute, subchronic, and chronic glyphosate toxicities to rats, dogs, rabbits, and mice it appears unlikely that glyphosate will adversely affect mammals that inhabit or use emergent wetlands. (WS FEIS 11/93.)

4.5.2 Birds

Exposure to birds may occur via ingestion, contact, and inhalation. Several species of concern occur in the San Francisco Estuary where *Spartina* would be treated, including the Alameda, San Pablo, and Suisun song sparrows (*Melospiza melodia pusilla, M. melodia samuelis*, *M. melodia maxillaris*), the California black rail (*Laterallus jamaicensis coturniculus*), the California clapper rail (*Rallus longirostris obsoletus*), the California least tern (*Sterna antillarum brownii*), the California brown pelican (*Pelecanus occidentalis californicus*), the salt marsh common yellowthroat (*Geothylpis trichas sinuosa*), and the Western snowy plover (*Charadris alexandrinus nivosus*). The federally listed endangered California clapper rail is of particular concern because of its occurrence in native *Spartina* marshes where non-native *Spartina* and its hybrids could occur and be treated.

Imazapyr. Based on the U.S. EPA ecotoxicity classification , imazapyr is considered practically non-toxic to birds. (*See* Section 4.3.2.) None of the risk quotients for birds modeled in the 2003 Entrix report exceeded the level of concern for acute risks to birds of 0.5 or chronic risks of 1 with the exception of the drinking water spill scenario. Again, the spill scenario modeled is unlikely to be realized *in situ*. The disturbance associated with cleanup efforts employed by the ISP as described in the MMRP would effectively eliminate exposure of birds to the spill. For example, the MMRP requires hazing of birds until the spill is remediated. (MMRP, p. 7.) The risk quotient for acute risks to endangered birds of 0.1 was exceeded for the male scaup via dermal contact exposure (RQ = 0.17) and for the male mallard duck via dietary exposure (RQ = 0.11). Risk quotients for the bobwhite quail, a surrogate species for evaluating risks to the California clapper rail, were well below 0.1 for all exposure routes. Several factors contributed to a considerable overestimate of these risk quotients. First, because no studies were available that determined lethality, the risk quotients were based on NOELs. Second, the modeled doses considerably overestimated potential conditions *in situ* because imazapyr would only be applied once per year and dissipation from the environment was not factored into the calculations. In addition, research in Washington State suggests that shorebirds do not use non-native *Spartina* to forage, which reduces or eliminates their exposure via the ingestion pathway. (Patten & Stenvall 2002.) Therefore the risk assessment greatly overestimated risk associated with exposure to imazapyr. Risks to birds from exposure to imazapyr following treatment of *Spartina* are therefore considered insignificant.

Glyphosate. Based on the acute and chronic toxicity values for birds and the typical exposure rates for glyphosate herbicides, no adverse effects on gallinaceous or dabbling duck bird groups are expected due to application of glyphosate in the estuarine environment for control aquatic nuisance vegetation. (WS FEIS 11/93.) No lethal toxicity information is available for other bird groups that use wetland areas, such as perching birds or shorebirds. As discussed for imazapyr, risks from oral exposure to shorebirds are reduced or eliminated because they do not use non-native *Spartina* to forage. (Patten & Stenvall 2002.)

4.5.3 Insects

The 2003 Entrix report indicates that herbicide treatment in terrestrial environments has been shown to increase arthropod abundance, likely as a response to increased food supply to these detrivores from dead and decaying vegetation. Arthropods serve as a substantial, high-energy food source for terrestrial birds as well as waterfowl and shorebirds. The 2003 Entrix report concluded that a similar relationship is conceivable for decaying *Spartina*, arthropod abundance, and birds.

Imazapyr. Based on the U.S. EPA ecotoxicity classification for insects, imazapyr is practically non-toxic to bees. Exposure calculations for a worst-case scenario (spraying tank mix directly onto insects) resulted in an estimated direct contact exposure of 0.0335 mg/kg. The estimated NOEL for insects is 1,000 mg/kg (HDT) and the LD_{50} is greater than 1,000 mg/kg. Based on the resulting risk quotient, 2.23×10^{-5}, the risk to insects can therefore be characterized as insignificant.

Glyphosate. Glyphosate has been found to be practically nontoxic to honeybees. (U.S. EPA 09/93.) Risks to insects are expected to be insignificant.

4.5.4 Reptiles and Amphibians

Reptiles and amphibians may be exposed to herbicides via dietary consumption, inhalation and direct contact. Amphibians are particularly susceptible to contact exposure from direct spray of herbicides because of their thin skin, however, their exposure is unlikely due to their intolerance of saline conditions, which precludes their occurrence in areas where *Spartina* is distributed and would be treated. One reptile species of concern, the Northwestern pond turtle (*Clemmys marmorata marmorata*) occurs in tidal sloughs of the Suisun Marsh. (Programmatic EIS/EIR, Appx. F.) It is highly unlikely that this species would be present in areas of *Spartina* treatment. In general, the life history of reptiles and amphibians native to the San Francisco Estuary suggests that exposure is precluded because they would not be found in the brackish water and estuarine environment where *Spartina* would be treated.

Imazapyr. No studies regarding the toxicity of imazapyr to reptiles and amphibians were found in the literature. Although a formal risk calculation could not be conducted, the life history of reptiles and amphibians suggests that their exposure is unlikely. The 2003 Entrix report therefore considered the risks to reptiles and amphibians following treatment of non-native *Spartina* with imazapyr herbicides insignificant.

Glyphosate. No studies regarding the toxicity of glyphosate to reptiles were found. Several studies demonstrated high toxicity of glyphosate/surfactant combinations to amphibians. However, as with imazapyr, the risks associated with the treatment of non-native *Spartina* in the San Francisco Bay can be considered insignificant due to the life history of the amphibian and reptile species.

4.5.5 Fish

Several species of concern may be present in tidal sloughs of marshes potentially treated with imazapyr herbicides. These include the chinook Salmon (*Oncorhynchus tshawythscha*), steelhead trout (*Oncorhynchus mykiss*), the Delta smelt (*Hypomesus transpacificus*), , and the Sacramento splittail (*Pogonichthys macrolepidotus*).

Imazapyr. An empirical LC_{50} of 22,305 mg imazapyr a.e./L has been established for fish, which classifies the herbicide as practically non-toxic according to U.S. EPA standards. (The highest spray solution that would be applied to non-native *Spartina* is a 7.5% solution at an application rate of 10 gal/acre, containing approximately 18,000 mg imazapyr a.e./L[78], which is on the same order of magnitude as the established LC_{50}.) As discussed in Section 4.2.1, even under highly conservative exposure scenarios, the maximum imazapyr concentration in water is not expected to exceed 5.77 mg imazapyr a.e./L (the ISP modeling resulted in 33.1 mg/L). The resulting risk quotient for imazapyr, 2.6×10^{-4}, is three orders of magnitude below the acute LOC of 0.5 for fish. The risk for the highest modeled concentration in the edge of the incoming water, as described in Section 4.2.1, would result in an RQ more than two orders of magnitude below the acute LOC for fish. However, as discussed in Section 4.4.2, surfactants may greatly increase the toxicity of the formulation. Empirical LC_{50} values for an imazapyr herbicide mixture with Agri-Dex® and Hasten® (Competitor® plus nonylphenol non-ionic surfactant) have been determined at 459 ppm and 113 ppm (based on surfactant), respectively. If risk quotients are based on these toxicity values, they increase considerably. Inset Table 2 summarizes acute risk quotients for the highest measured environmental exposure concentrations in water and for the highest modeled concentration of 33.1 mg/L as discussed in Section 4.2.1.

[78] Habitat® contains 22.6% v/v imazapyr isopropylamine or 226 ml/L imazapyr as acid equivalent. The 7.5% spray solution for aerial applications at 10 gal/acre therefore contains: (226 ml imazapyr a.e./L Habitat®) × (imazapyr density 1.04 to 1.07 g/ml) × (6 pints Habitat®/10 gal water) × (gal/8 pints) × (1,000 mg/g) = 17,628 to 18,137 mg imazapyr a.e./L.

Table 2: Acute risk quotients for fish

Herbicide/Surfactant	LC_{50} rainbow trout	Acute RQ EEC[1] maximum measured concentration	EEC[1] ISP modeling[2]
Imazapyr a.e.	22,305 ppm	<0.001[4]	<0.001
Arsenal + 1% Agri-Dex®	459 ppm[3]	0.013[4]	0.074
Arsenal + 1% Hasten®	113 ppm[3]	0.051[4]	0.293

1 EEC = environmental exposure concentration
2 EEC ISP modeling = RQ maximum measured concentration × (33.1 mg/L) /(5.77 mg/L)
3 as surfactant
4 The RQs reported in the 2003 Entrix were higher by a factor of 10

Levels of concern for endangered fish of 0.05 would be marginally exceeded for the imazapyr/Hasten® surfactant combination for the highest measured concentrations in water. In case of the modeled EEC, both herbicide/surfactant combinations would exceed the LOC of 0.05. However, the presence of fish in the leading edge of an incoming tide, where these concentrations might occur, is highly unlikely. Further, the basis for the highest measured exposure value was extremely conservative in that the pesticide was applied directly to sediment with no interception by vegetation and collection of the sample only three hours later. The Spartina Control Program intends to apply pesticides with the outgoing tide, leaving a much longer window of time before the tide washes off any remaining herbicide from the sediment and foliage. Some degradation and uptake of the herbicide will occur, which will further reduce the concentration in water. As discussed in Section 3.1.7, the herbicide dissipates quickly in the tidal environment and no residues were detected at the treatment site 40 hours after application.

Exposures are relevant only for an acute exposure scenario. Due to the tidal exchange of waters, which results in dilution of the compound with each tide, imazapyr would quickly dissipate beyond detection. (Entrix 10/03. p. 78.) This conclusion is supported by dissipation experiments in Washington State, which showed that imazapyr effectively dissipated in water within about four to five tidal exchanges, or about 40 hours. (Patten 2002.) Complete tidal exchange of water in some marshes in the San Francisco Estuary may take considerably longer but chronic effects are not conceivable.

Based on the above discussion, the acute and chronic risk to fish due to application of imazapyr herbicides for control of non-native *Spartina* is considered insignificant.

Glyphosate. Glyphosate becomes quickly inactivated by adsorption to sediment and suspended particles in water. (*See* Section 3.1.6.) This makes the herbicide biologically unavailable for fish. The risk to fish due to the application of glyphosate has been considered insignificant at the application rates typical to treat non-native, invasive *Spartina*. (Programmatic EIS/EIR, p. 3.3-30.)

4.5.6 Aquatic Invertebrates

The aquatic invertebrate community in the San Francisco Estuary is to a large extent composed of non-native species. (Baye 04/05[79].) No species of concern occur in or close to areas where non-native *Spartina* would be treated with herbicides.

Imazapyr. The reported acute toxicity LC_{50} concentrations for technical-grade imazapyr for the freshwater flea (*Daphnia magna*) and the pink shrimp (*Penaeus duorarum*) are >100 mg/L. The reported acute EC_{50} concentration for growth inhibition of Eastern oysters is >132 mg/L. On the basis of these toxicity measurements, imazapyr would be considered practically non-toxic to both freshwater and marine invertebrates according to EPA ecoxicity screening criteria. No empirical results have been documented that establish lethal or sub-lethal effects such as growth inhibition. Thus, the measures of >100 and >132 mg/L can provide only screening values for a risk characterization. One study reported an LC_{50} of 71 mg/L for water flea after exposure to Arsenal mixed with an unidentified surfactant.

To differentiate risks from motile epibenthic[80] or pelagic[81] invertebrates from benthic infauna[82], the 2003 Entrix report calculated RQs using sediment pore water concentrations of 3.29 mg/L, the highest concentration measured in the Washington State study. Inset Table 3 summarizes acute risk quotients for pelagic and epibenthic invertebrates and benthic infauna based on these toxicity measures and the measured and estimated worst-case concentrations in surface water and sediment pore water.

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[79] Personal communication with Peter Baye, April 25, 2004.

[80] Organisms that are living on or above the sediment.

[81] Organisms that live in the water column, away from sediment.

[82] Benthic infauna lives in sediment within soft substrate areas such as shallow mud flats and sand flats. Most estuaries support large numbers of benthic infauna, including worms, bivalves and crustaceans. Benthic communities provide a significant food source for many species of fish. Wading birds also rely on benthic infauna to form an integral part of their diet.

Table 3: Acute risk quotients for marine invertebrates

Herbicide/Surfactant	LC_{50} *Daphnia magna*	Acute RQ: EEC[1] maximum measured concentration	Acute RQ: EEC[1] ISP modeling[2]
Epibenthic and pelagic invertebrates (surface water exposure)			
Imazapyr	>100 ppm	0.058	0.333
Arsenal + unidentified surfactant	79.1 ppm	0.073	0.419
Benthic infauna (sediment pore water exposure)			
Imazapyr	>100 ppm	0.033	0.189
Arsenal + unidentified surfactant	79.1 ppm	0.042	0.241

1 EEC = environmental exposure concentration
2 EEC ISP modeling = RQ maximum measured concentration × (33.1 mg/L)/(5.77 mg/L)

In all cases, the acute risk to aquatic invertebrates is below the LOC for acute risk for aquatic invertebrates. Even under the worst-case scenario of an accidental spill the impact would not affect biological diversity because the majority of the benthic community is non-native. Any potential impact regarding the availability of prey would be short-term only. Epibenthic and pelagic invertebrate communities will likely recover within a few tidal cycles. For infauna, it is known that even such intrusive disruptions as dredging cause only short-term biomass reduction. (Baye 04/05.)

Based on the above information, the risk to aquatic invertebrates for application of imazapyr herbicides and surfactants is considered insignificant.

Glyphosate. Impacts to aquatic invertebrates due to post-application water concentrations of glyphosate are unlikely due to glyphosate's rapid adsorption to sediment particles and inactivation. Field studies of benthic invertebrates in tidal mudflats revealed no short- or long-term effects. (*See* Section 4.3.6.) Based on these facts, risks to aquatic invertebrates are considered insignificant.

4.3.7 Non-target Vegetation

For both herbicides, the most significant risk appear to be impacts to non-target aquatic vegetation due to the herbicides' engineered mechanisms of action, which target protein synthesis in plants. Several species of concern occur in the brackish tidal marshes of the San Francisco Estuary where they are potentially affected by spray drift and concentrations of the herbicide in water including the Delta tule-pea (*Lathyrus jepsonii var. jepsonii*), the soft bird's beak (*Cordylanthus mollis* ssp. *mollis*, the Suisun marsh aster (*Aster lentus*), and the Suisun thistle (*Cirsium hydrophilum* var. *hydrophilum*). (*See* Programmatic EIS/EIR, Appx. F.)

Imazapyr. Inset Table 4 summarizes the acute risk quotients for non-target aquatic vegetation for the maximum measured concentration of 5.77 mg/L and the modeled concentration by the ISP of 33.1 mg/L. (*See* Section 4.2.1)

Table 4: Acute risk quotients for non-target aquatic vegetation

Herbicide/Surfactant	Species	EC_{50} Growth	Acute RQ: EEC[1] maximum measured concentration	Acute RQ: EEC[1] ISP modeling[2]
Algae				
Imazapyr technical grade	Green algae (*Selenastrum capricornutum*)	71 ppm	0.081	0.465
Arsenal + unidentified surfactant	Green algae (*Selenastrum capricornutum*)	14.1 ppm	0.409	2.346
Vascular plants				
Imazapyr technical grade	Duckweed (*Lemna gibba*)	0.0214 ppm	240	1,377
Arsenal + unidentified surfactant	Duckweed (*Lemna gibba*)	0.0216 ppm	152	872

1 EEC = environmental exposure concentration
2 EEC ISP modeling = RQ maximum measured concentration × (33.1 mg/L)/(5.77 mg/L)

Risks to algae from imazapyr are insignificant for the maximum measured water concentration and for the modeled highest potential concentration of 33.1 mg/L. However, when applied in combination with a surfactant, the risk quotient for algae increases above a factor of 2 for the modeled concentrations. However, any potential impact would be short-term only because of tidal mixing and dissipation of imazapyr. It is expected that algal communities will recover within a few tidal cycles from any adverse impacts.

Based on EC_{50} concentrations developed for duckweed, a floating vascular macrophyte, with both imazapyr technical grade and Arsenal with an unidentified surfactant, risks from herbicide concentrations in water to vascular plants such as pickleweed or the above-mentioned species of concern may be significant. Risk quotients greatly exceed the acute risk quotient of 1. The 2004 SERA report determined that off-site drift of imazapyr after ground broadcast or aerial applications with 1.25 lb/acre may cause damage to sensitive plant species at distances of up to 500 feet from the application site. The closer the plant is to the application site, the greater the likelihood of damage. (SERA 12/04, p. 4-26.) However, the impact of imazapyr herbicide use on non-target vegetation should be largely controllable by the use of best management practices identified in the Programmatic EIS/EIR and adopted by the Conservancy as conditions of approval of the Spartina Control Program that limit the potential for non-target vegetation exposure. In addition, the monoculture growth typical of *Spartina* reduces the potential for non-target plant exposure during herbicide application. Further, as discussed in Section 4.3.7, even direct spraying of the herbicide onto non-target vegetation does not result in long-term suppression of growth. While these effects are locally adverse, they are not considered to have overall significance.

Glyphosate. Glyphosate is ineffective on submerged aquatic vegetation and algae. It is likely that suspended organic matter or sediment interfere with glyphosate uptake by submerged plant tissue. Effects on non-target vegetation from application of glyphosate are considerable. However, effects, though locally important, are considered to be overall less than significant and further mitigable. (See Programmatic EIS/EIR, Section 3.3.)

4.5.2 Data Gaps and Uncertainties

The fundamental question in addressing the significance of the uncertainty in any risk assessment is the degree to which it could qualify the risk conclusions. The 2003 Entrix report summarized the uncertainties and data gaps associated with the ecological risk assessment for imazapyr herbicide use for control of non-native *Spartina*. Based on the most recent data on the toxicity, fate, and degradation of imazapyr, the risk assessment indicated that imazapyr has insignificant toxicity to aquatic and terrestrial wildlife, is not environmentally persistent, and does not bioconcentrate or bioaccumulate.

Uncertainties

Several uncertainties are inherent in the manner of preparation and conclusions of the ecological risk assessment presented in the 2003 Entrix report (and other ecological risk assessments). These include:

- *Information gaps* where sources or stressors are not identified or important aspects of the ecology are not known can affect risk conclusions. Although it is believed that the important potential sources of adverse effects have been addressed, it is possible that there are unmeasured or unconsidered chemical constituents in the estuarine environment that are contributing an unevaluated degree of risk to receptors in target areas.
- If relationships between sources and receptors are missing or incorrectly identified, risks could be under- or overestimated. To reduce this uncertainty, a *conceptual model* was developed that identified all known pathways (both complete and incomplete) and receptor trophic levels. The overall impact of this source of uncertainty on risk conclusions is unknown.
- *Uncertainty (safety) factors* used to derive tissue residue factors may not accurately reflect site conditions. However, the uncertainty factors applied were considered realistic based on data from various published studies. Since published tissue residue factors were not available for all receptors of interest, uncertainty factors were applied. Because the uncertainty factors applied were considered conservative, risk estimates were likely overestimated.
- The use of data from *laboratory versus field populations* introduces another source of uncertainty because species used in laboratory toxicity tests are not necessarily

subjected to the same degree of non-chemical related stresses as receptors in natural conditions. As such, cumulative effects of multiple stressors (including chemicals) are not necessarily the same. It is difficult to predict the effect on ecological risk assessment results since laboratory versus natural conditions may stress species differently. Due to likely differences in the health of laboratory populations and those inhabiting target areas, differences in genetic diversity (hence resistance to stressors), and possible impacts of non-chemical stressors, some unavoidable uncertainty exists when extrapolating laboratory derived data to field situations.

— The use of *surrogate species* also introduces uncertainty because the toxicological studies used species that are related to taxa present in the target areas, but are not identical. In general, the greater the taxonomic difference, the greater the uncertainty in application of laboratory toxicity data to receptors. It is not known whether laboratory test species or receptors in target areas are the most sensitive to a given chemical constituent.

— Finally, *feeding rates* were assumed not to vary with season, breeding condition, or with other local factors. Reported feeding rates undoubtedly vary with all of these factors because metabolic needs change as does food availability. Where possible, estimates of average feeding rates were derived from studies that reported for multiple seasons and areas to compensate for this potential uncertainty. As such, while uncertainty is introduced, the effect on the ecological risk assessment conclusions is unquantifiable.

(Entrix 10/03, p. 85.)

Data Gaps

While the risks to ecological receptors appear very low, several data gaps exist. No significant new data were identified for this report that would serve to eliminate some of the data gaps identified in the 2003 Entrix report. The following list summarizes the main data gaps that remain for the assessment of imazapyr use in the estuarine environments:

— Studies pertaining to the effect of imazapyr on aquatic or water-dependent species other than fish are limited;

— No studies examining the toxicity of imazapyr to amphibians and reptiles were discovered in the literature review, however, amphibians do not occur in the saline environment where *Spartina* is growing and the life history of reptiles does not indicate their occurrence where *Spartina* will be treated;

— No studies on the toxicity of imazapyr to marine fish typical of those areas where invasive *Spartina* is distributed in the San Francisco Estuary have been conducted;

— Specific data on the toxicity of imazapyr to sediment-associated organisms typical of northern temperate marine environments is generally lacking and represents a significant data gap;

- Residues of imazapyr in treated *Spartina*, and the degradation of the herbicide over time in plant tissue were not identified in the literature. Exposure calculations in the 2003 Entrix report therefore relied on estimated concentrations in the plant tissue. Empirical residues from plants would increase confidence in the exposure and risk estimates;
- Effects on the micorhizosphere and microflora in a treated estuary, which could affect nutrient dynamics, have not been explored. This subject area has not been investigated thoroughly for any herbicide used in an estuary setting;
- Effects on non-target salt-marsh plants native to areas non-native *Spartina* has colonized are poorly understood and only limited data on a few species have been reported;
- Persistence and stability of imazapyr in dead and decaying *Spartina* is not known. However, based on observations in Washington State, it is unlikely that leachate from decaying vegetation retains any herbicidal activity thereby potentially delaying the recovery of native salt marsh plants;
- Drift concentrations of imazapyr off-site by treatment method (*e.g.*, backpack, boom sprayer, etc.,) have not been quantified. However, worst-case scenario exposure conditions in direct application sites did not indicate significant risk;
- Effects on marine phytoplankton are unknown, however, studies with freshwater phytoplankton and the rapid dissipation of imazapyr in tidal water indicate a large margin of safety for adverse effects;
- Effects on sea-surface microlayer associated organisms and microflora in this surface water film are not known.

While the above data gaps represent some uncertainty, the existing information on the toxicity and fate of imazapyr is substantial and suggests that significant negative impacts would be unlikely in studies addressing the above data gaps—with the possible exceptions of effects on non-target vegetation.

5. HUMAN HEALTH RISK ASSESSMENT SUMMARY

The following summary of human health risks associated with the use of imazapyr herbicide in the San Francisco Estuary for control of non-native *Spartina* is based on information contained in the Programmatic EIS/EIR and data, procedures, and findings of a standard human health risk assessment for the use of imazapyr in forestry applications (2004 SERA report).

5.1 Potentially Exposed Populations and Sensitive Receptors

As mentioned above, application methods with the imazapyr herbicide would be identical to those previously identified for glyphosate. (Olofson 03/05.) Therefore, the potentially exposed populations and sensitive receptors from a human health perspective are identical to those described in the Programmatic EIS/EIR. (Programmatic EIS/EIR, p. 3.6-1.)

5.2 Risk Characterization for Imazapyr

The 2004 SERA report contained an exhaustive human health risk assessment for the application of imazapyr in forestry applications, which evaluated worst-case scenarios for both workers and members of the general public. Worst-case scenario application methods evaluated in the 2004 SERA report correspond to those expected for applications in the estuarine setting for control of non-native *Spartina*. (Applications in the Estuary will be performed by licensed applicators.) The exposure assessment scenarios presented in the 2004 SERA report were based on a typical forestry application rate of 0.45 lb/acre. Risk was characterized quantitatively using a risk quotient calculated as the ratio of the exposure estimate to the chronic reference dose ("RfD"). For both acute exposures (*i.e.*, accidental or incidental exposures) and general exposures (*i.e.*, daily exposures that might occur over the course of an application season), the chronic RfD of 2.5 mg/kg b.w./day derived by the U.S. EPA was used to characterize risk. The level of concern for the risk quotient at the typical application rate is 1. To compare the risk quotients from the 2004 SERA report to the application of imazapyr herbicide in the San Francisco Estuary, the level of concern must be adjusted to the maximum application rate. For all exposure scenarios, the estimated dose scales linearly with application rate. Thus, at the maximum application rate of 1.5 lb imazapyr a.e./acre, the resulting level of concern for evaluating the derived risk quotients is 0.3.[83] This level of concern was compared to the risk quotients presented in the 2004 SERA report to interpret the results for control of *Spartina* with imazapyr herbicide in the San Francisco Estuary.

5.2.1 Applicators

The highest risk quotient determined for workers based on general exposures was 0.03 for the upper range for broadcast ground spray. Thus, even at the highest application rate that might be used in the Estuary, the upper range of risk quotients is below the level of concern by a factor of 10.[84]

While the accidental exposure scenarios are not the most severe one might imagine (*e.g.*, complete immersion of the worker or contamination of the entire body surface for a prolonged period of time) they are representative of reasonable accidental exposures. The highest risk quotient for all evaluated accidental worker exposure scenarios was determined to be 0.006 (the upper range for a worker wearing contaminated gloves for 1 hour). Because the

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[83] (0.45 lb/acre) / (1.5 lb/acre) = 0.3

[84] 0.3 / 0.03 = 10

estimate of the absorbed dose is linearly related to the risk quotient, a scenario in which the worker wore contaminated gloves for about 167 consecutive hours[85], or a about 7 days, would be required to reach a level of concern (a risk quotient of one) at the application rate of 0.45 lb imazapyr a.e./acre evaluated in the 2004 SERA report. Adjusted to the application rate of 1.5 lb imazapyr a.e./acre proposed for *Spartina* control in the San Francisco Estuary, the risk quotient of 0.006 is below the level of concern, *i.e.* 0.3, by a factor of 50. Thus, at the highest application rate, a worker would have to wear contaminated gloves for 50 hours or 2 days to reach a level of concern. In other words, under a protective set of exposure assumptions, workers would not be exposed to levels of imazapyr that are regarded as unacceptable and no exposure scenario approaches a level of concern. Mitigation measures identified in the Programmatic EIS/EIR and adopted by the Conservancy as conditions of approval of the Spartina Control Program require appropriate protection and training of these workers. (Programmatic EIS/EIR, pp 3.6-7/8.)

The 2004 SERA report indicated uncertainties associated with these risk characterizations for workers due to the lack of experimental data on the dermal absorption kinetics of imazapyr and lack of worker exposure studies. However, uncertainties in the estimated dermal absorption rates and worker exposure rates were incorporated into the exposure assessment and risk characterization and these estimates would have to be in error by a factor of about 100 or more to impact this qualitative risk characterization. An additional factor of safety is introduced by the fact that the risk assessment presented in the 2004 SERA report specifically considered the effect of repeated exposure because it used the chronic RfD as an index of acceptable exposure even for acute exposure scenarios.

Imazapyr is mildly irritating to the skin and eyes. Quantitative risk assessments for eye irritation were not derived; however, effects on eyes likely only result as a consequence of mishandling the herbicide and can be prevented by wearing goggles.

5.2.2 General Public

Based on the available information and under the foreseeable conditions of application, there are no routes of exposure or scenarios suggesting that the general public will be at any substantial risk from longer-term exposure to imazapyr. Similarly, none of the evaluated acute risk scenarios, including consumption of contaminated vegetation and fish, acute contact exposure, and direct spray of a small child, resulted in risk quotients that exceeded the level of concern of 0.3 for the application rate of 1.5 lb imazapyr a.e./acre. The only exception was the arbitrary scenario of risks to the public associated with drinking contaminated water after an accidental spill into a small pond. Best management practices identified as mitigation measures in the Programmatic EIS/EIR and adopted by the Conservancy as conditions of approval of the Spartina Control Program (in addition to the improbability of people drinking from a pond and the probably unpleasant taste of the herbicide/surfactant) will effectively prevent such exposure.

[85] 1/0.006 = 166.7

6. SUMMARY AND CONCLUSIONS

This report evaluated the potential impacts to water quality, biological resources, and human health and safety associated with the proposed use of imazapyr herbicides for control of non-native, invasive *Spartina* cordgrass species and their hybrids in the San Francisco Estuary. The following sections summarize findings on the environmental fate and the potential ecological and human health risks for imazapyr applications in an estuarine environment and compare the risks relative to glyphosate applications. These sections are followed by a discussion of changes in environmental effects for the Spartina Control Program, approaches to minimize increased risk, and conclusions.

6.1 Summary of Findings on Environmental Fate of Imazapyr in Estuarine Environments and Impacts on Water Quality

Under typical environmental conditions, imazapyr is highly soluble in water. In aquatic systems, it is not expected to be biodegraded and volatilization from water or plant surfaces is insignificant. Imazapyr has a very low propensity to bioconcentrate. In water, it is subject to rapid photolysis with reported half-lives ranging from 3 to 5 days. In a number of field dissipation studies, imazapyr rapidly dissipated from the water with of 1.9 days and 12.8 days. No detectable residues of imazapyr were found in the water and sediment after 14 and 59 days, respectively. In estuarine systems, dilution of imazapyr in the incoming tides will contribute to its rapid dissipation and removal from the area where it has been applied. Measured maximum concentrations after application of 1.5 lb imazapyr a.e./acre onto a non-vegetated tidal mudflat, measured after three hours in the first tidal flush, were 5.77 mg/L in water, 5.7 mg/kg sediment, and 3.29 mg/L in pore water. The study demonstrated complete dissipation of imazapyr from the area within 40 hours from the water column and within 400 hours from sediment. This information suggests that imazapyr is not environmentally persistent in the estuarine environment.

6.2 Summary of Findings on Ecological and Human Health Risks of Imazapyr

The evaluation of using an imazapyr herbicide for control of non-native *Spartina* in the San Francisco Estuary was based on the data, procedures, and findings of a standard ecological risk assessment for use of imazapyr for control of non-native *Spartina* in an estuarine setting in Washington State (2003 Entrix report) and a standard human health risk assessment for the use of imazapyr in forestry applications (2004 SERA report). In addition, this report incorporated information from a comprehensive literature search and review of publications on ecological impacts, toxicity, and fate and transport of imazapyr and its formulations including potentially used adjuvants. Additional unpublished information was obtained from the ISP, industry representatives, researchers, and government.

6.2.1 Ecological Receptors

The 2003 Entrix report developed a realistic exposure scenario for the application of imazapyr herbicide on non-native *Spartina* in an estuarine ecosystem in Washington State. This report interpreted the results of the 2003 Entrix report for the San Francisco Estuary ecosystem taking into account local conditions and species of concern. Additionally, this report evaluated a higher concentration of imazapyr in water. In addition to evaluating risk quotients (exposure/toxicity) compared to levels of concern for the entire category, this report evaluated the risk quotients compared to levels of concern specifically for endangered species.

Mammalian wildlife could be exposed to imazapyr through dermal, oral (ingestion) or inhalation routes. The dietary route is considered the most likely. The oral and dermal toxicity of imazapyr to mammals is categorized as practically non-toxic. Based on the exposure scenario, the only potentially significant risk was identified for a spill scenario that assumed ingestion of undiluted spray solution by mammalian wildlife. This risk scenario is highly unlikely because best management practices set forth in the MMRP would ensure immediate cleanup of the spill and because the disturbance created by the cleanup efforts would discourage wildlife use of the area. Risks to mammals from exposure to imazapyr following treatment of *Spartina* are therefore considered insignificant.

Exposure to birds may occur via ingestion, contact, and inhalation. None of the acute or chronic scenarios was significant to birds with the exception of the drinking water spill scenario. Again, the spill scenario modeled is unlikely to be realized in the field. Risks to birds from exposure to imazapyr following treatment of *Spartina* are therefore considered insignificant.

Based on exposure calculations for a worst-case scenario (spraying tank mix directly onto insects) and the reported toxicity to bees (practically non-toxic), the risk to insects from exposure to imazapyr following treatment of *Spartina* is considered insignificant.

No studies regarding the toxicity of imazapyr to reptiles and amphibians were found in the literature and a formal risk calculation could not be conducted. However, amphibians cannot tolerate the salinity levels found in areas where non-native *Spartina* occurs and are therefore not at risk. The life history of those reptiles that might occur in the Estuary suggests that their exposure is unlikely. The risks to reptiles and amphibians following treatment of non-native *Spartina* with imazapyr herbicides are therefore considered insignificant.

Imazapyr is practically non-toxic to fish. However, the use of surfactants in the tank mixture may greatly increase the toxicity of the formulation to aquatic organisms. The acute levels of concern for fish were not exceeded for any of the surfactant/formulation mixtures tested. However, levels of concern for endangered fish could potentially be marginally exceeded for the highest measured and modeled concentrations in water. However, the presence of fish in the leading edge of an incoming tide, where these concentrations might occur, is highly unlikely. Further, the basis for the highest measured exposure value was extremely conservative in that the herbicide was applied directly to sediment with no interception by vegetation and collection of the sample only three hours later. The Spartina Control Program intends to apply herbicides with the outgoing tide, leaving a much longer window of time before the tide washes off any remaining herbicide from the sediment and foliage. Some degradation and uptake of the herbicide will occur, which will further reduce the concentration in water. Due to the tidal exchange of waters, which results in dilution of the compound with each tide, imazapyr would quickly dissipate beyond detection. This conclusion is supported by dissipation experiments in Washington State, which demonstrated that imazapyr effectively dissipated in water within about four to five tidal exchanges. Therefore, the acute and chronic risk to fish due to application of imazapyr herbicides for control of non-native *Spartina* is considered insignificant.

Imazapyr would be considered practically non-toxic to both freshwater and marine invertebrates. The acute risk to aquatic invertebrates from exposure to imazapyr in water was determined to be insignificant. Any potential impact from a spill would be short-term only. Epibenthic and pelagic invertebrate communities will likely recover within a few tidal cycles. Therefore, the acute and chronic risk to aquatic invertebrates due to application of imazapyr herbicides for control of non-native *Spartina* is considered insignificant.

In sum, the maximum proposed application rate of 1.5 lb imazapyr a.e./acre for control of *Spartina* in the Estuary did not result in aquatic concentrations or terrestrial doses that would pose significant risks to aquatic or terrestrial wildlife, even under the extremely conservative conditions modeled.

Because imazapyr is an effective herbicide, non-target plants that are inadvertently directly sprayed are likely to be severely damaged. These risks are particularly acute for vascular plants. Algae appear to be less sensitive to imazapyr than aquatic macrophytes. Off-site drift from the application site after ground-broadcast or aerial applications may cause damage to sensitive plant species at distances of up to 500 feet. Peak concentrations of imazapyr with the incoming tide could also result in adverse effects on aquatic macrophytes and non-target vegetation. However, the tidal exchange of water would rapidly dilute these concentrations to levels that do not cause acute damage to plants. The above-discussed studies demonstrated the rapid dissipation and lack of persistence of imazapyr in the estuarine environment. Longer-term concentrations of imazapyr in water are substantially below levels of concern and are not expected to result in adverse effects to non-target vegetation. Best management practices as identified in the Programmatic EIS/EIR and adopted by the Conservancy as conditions of approval of the Spartina Control Program will reduce the likelihood of effects on non-target vegetation.

Several significant data gaps were identified that introduce some uncertainty into the risk assessment. However, the existing information on the toxicity and fate of imazapyr is substantial and suggests that significant negative impacts would be unlikely in studies addressing these data gaps—with the possible exceptions of effects on non-target plants.

6.2.2 Human Health and Safety

The 2004 SERA report contained an exhaustive human health risk assessment for the application of imazapyr in forestry applications, which evaluated worst-case scenarios for both workers and members of the general public. Worst-case scenario application methods evaluated in the 2004 SERA report correspond to those expected for applications in the estuarine setting for control of non-native *Spartina*. This report scaled the effects from the lower application rates of imazapyr for forestry applications to the maximum application rate proposed for the Spartina Control Program.

Typical exposures to imazapyr did not lead to estimated doses that exceed a level of concern for either workers or members of the general public at the maximum application rate of imazapyr proposed for control of *Spartina* in the San Francisco Estuary. Based on the available information and under the foreseeable conditions of application, it can be reasonably concluded that workers or members of the general public will not be at any substantial risk from acute or longer-term exposure to imazapyr at the application rate of 1.5 lb/acre on non-native *Spartina*.

Mild irritation to the eyes can result from accidental splashing. This effect will be minimized or avoided by exercising care to reduce splashing and wearing goggles during the handling of the compound as required by the MMRP.

6.3 Comparison of Relative Ecological and Human Health Effects of Imazapyr versus Glyphosate and Associated Adjuvants

The ecological and human health effects of the use of glyphosate for control of non-native *Spartina* were addressed in the Programmatic EIS/EIR and thoroughly evaluated in an ecological and human health risk assessment on the use of glyphosate for control of emergent nuisance vegetation in aquatic wetlands in Washington State (WS FEIS 1993). These documents concluded that the use of glyphosate in aquatic systems presents limited risks to some ecological receptors.

Imazapyr has been demonstrated to be less toxic to aquatic organisms than glyphosate. For example, a direct comparison test with rainbow trout established an inherent acute toxicity of glyphosate to fish at more than 25-fold higher than for imazapyr. Given that the relationship between fish and aquatic invertebrate toxicity for a given chemical rarely differs by more than an order of magnitude, it is reasonable to expect a similar relationship to exist for aquatic invertebrates for the toxicity of glyphosate compared to imazapyr. On a unit compound basis, imazapyr is more effective than glyphosate for control of *Spartina* and is consequently applied at considerably lower application rates. The resulting risk from imazapyr to aquatic organisms is therefore considerably lower than that for glyphosate. In mixture with glyphosate herbicides, toxicity is expected to additive only and synergistic effects are not likely.

The aquatic formulations of both herbicides must be mixed with surfactants for use on post-emergent vegetation such as *Spartina*. The inherent risks of using either herbicide have been shown to increase significantly when mixed with surfactants. Risks associated with glyphosate/surfactant mixtures increase more drastically than those for imazapyr/surfactant mixtures for a number of reasons. First, most non-ionic surfactants that must be used with glyphosate are inherently more toxic to aquatic organisms than the methylated or esterified seed oils or silicone-based surfactants that can be used with imazapyr herbicides. (For example, the non-ionic surfactants R-11® and LI-700® were determined to be 5 times as toxic as the esterified seed oil Competitor®.) Second, glyphosate requires considerably higher spray volumes than imazapyr and surfactants are mixed proportionally to the spray volume, resulting in about twice as high surfactant concentrations for glyphosate tank mixes compared to imazapyr tank mixes. (*See* Tables A-3a and A-3bA.) A number of less toxic surfactants are available for use with imazapyr and have been demonstrated to be effective on *Spartina*.

Although glyphosate is highly soluble like imazapyr, it is not photolyzed in water and is readily adsorbed to suspended particles and sediment. Its fate in an estuarine environment is primarily determined by its strong adsorption to sediment particles and the rate of microbial degradation. Concentrations of glyphosate in rhizomes of treated *Spartina* have been shown to increase over several years after treatment. The residual biomass of Spartina could therefore slowly release glyphosate into the environment. Therefore, glyphosate is predicted to be more persistent than imazapyr in an estuarine environment.

In sum, due to the lower inherent toxicity of imazapyr to aquatic organisms, the ability to use less toxic surfactants, the lower application rates, and the more rapid dissipation from the environment, the use of an imazapyr herbicide in the estuarine environment presents an improved risk scenario for aquatic and terrestrial animals over the use of glyphosate herbicides.

Adverse effects of imazapyr to directly sprayed non-target vegetation may be higher compared to glyphosate due to the herbicide's higher efficacy. These risks are particularly pronounced for vascular plants. Because of the lower spray volumes used with imazapyr, impacts due to drift may be lower.

6.4 Changes in Environmental Effects

The imazapyr herbicide Habitat® will be used on as many as 1,500 acres per year of tidal wetlands for as many as four consecutive years to facilitate eradication of non-native *Spartina.*

Fewer adverse effects on aquatic and terrestrial animals are expected when using an imazapyr herbicide as compared to a glyphosate herbicide. Potential adverse effects from their combined use are also less than those expected for the use of a glyphosate herbicide alone. Due to its higher efficacy, the use of imazapyr instead of glyphosate may result in potentially increased adverse effects on non-target vegetation. In addition, effective *Spartina* eradication, which requires little or no retreatment allows for recolonization of treated sites with native species sooner than if multiple treatments have to be used over a number of years. Even so, it can take a number of years for the ecosystem to restabilize itself after treatment with either herbicide.

The higher efficacy of imazapyr for control of *Spartina* may result in decreased impacts due to potentially fewer applications over the years for the control of existing *Spartina* and a better rate of control than could be achieved with glyphosate alone, which, in turn, would slow the spread of *Spartina* through the Estuary. Fewer applications also imply fewer physical adverse impacts to the estuarine ecosystem due to trampling, compaction of sediment, and so forth.

6.5 Approaches to Minimize Increased Risk

The only potentially increased adverse effect due to the use of imazapyr instead of or in combination with glyphosate is the increased risk to non-target vegetation. This effect can be minimized by strictly adhering to the precautions identified in the Programmatic EIS/EIR and adopted by the Conservancy as conditions of approval of the Spartina Control Program and verified through the Conservancy's adopted MMRP. For example, off-site drift would be minimized by the adopted condition that requires ceasing application of imazapyr herbicides at wind speeds exceeding 10 mph. Other mitigation measures proposed in the MMRP include, for example, temporary covering of non-target vegetation with geotextiles, irrigation of oversprayed non-target vegetation, and establishment of buffer zones. (*See* MMRP, pp. 6-11.)

6.6 Conclusions

The overall weight of evidence from this analysis suggests that imazapyr herbicides can be a safe, highly effective treatment for control and eradication of non-native *Spartina* species in the San Francisco Estuary, offering an improved risk scenario over the existing treatment regime with glyphosate herbicides. Based on the evaluation presented in this report, it can be concluded with reasonable certainty that the use of Habitat® (or any other imazapyr herbicide for aquatic use) for the Spartina Control Program in the San Francisco Estuary, either by itself or in combination with glyphosate, will not result in any significant impacts that were not already identified in the Programmatic EIS/EIR for the use of glyphosate. From a CEQA perspective, the potential significant impacts to biological resources, and human health and safety due to imazapyr application, and mitigations required to reduce those impacts to less than significant levels, are encompassed in those impacts and mitigations previously identified for glyphosate application. Therefore, no additional mitigation is required for the use of imazapyr.

TABLES

Table A-1: Chemical description; degradation rates, products, and pathways; bioaccumulation ratings; and advantages and disadvantages of imazapyr and glyphosate herbicides for estuarine use

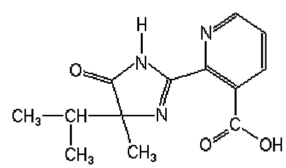
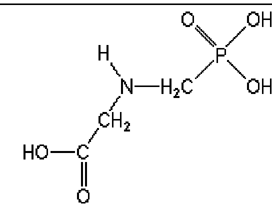
	Imazapyr	Glyphosate
Trade Name (Company)	Habitat® (Bayer Corporation)	Rodeo® (Dow Chemical Company) Aquamaster® (Monsanto Corporation)
Registration No.	81334-34-1	1071-83-6
Formulation	Aqueous solution of isopropylamine salt of imazapyr plus acidifier; active ingredient: 28.7% isopropylamine salt of imazapyr; equivalent to 22.6% imazapyr	Aqueous solution of isopropylamine salt of glyphosate; technical formulation contains 2,4-nitrosoglyphosate ("NNG") impurity; active ingredient: 53.8% glyphosate isopropylamine salt; equivalent to 48.0% glyphosate
Chemical name	IUPAC: (*RS*)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid CAS: 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-3-pyridinecarboxylic acid	IUPAC: *N*-(phosphonomethyl)glycine CAS: *N*-(phosphonomethyl)glycine
Chemical formula		
Formula	$C_{13}H_{15}N_3O_3$	$C_3H_8NO_5P$
Herbicide family	Imidazolinone	Organophosphorus
Mode of action	Systemic, broad-spectrum (non-selective); amino acid synthesis inhibitor, specifically, inhibits acetohydroxyacid synthase ("AHAS") aka acetolactase synthase ("ALS"), the first enzyme in the synthesis of branched-chain aliphatic amino acids (valine, leucine, and isoleucine) and as a result inhibits protein synthesis and cell growth	Systemic, broad-spectrum (non-selective); amino acid synthesis inhibitor; inhibits 5-enolpyruvylshikimate-3-phosphate synthase, needed by plants to synthesize chorismate, an intermediate metabolic product in the synthesis of aromatic amino acids
Molecular weight	261.28 g/mole imazapyr 320.42 g/mole imazapyr isopropylamine salt	169.08 g/mole glyphosate 228.22 g/mole glyphosate isopropylamine salt

Table A-1 contd.: Chemical description; degradation rates, products, and pathways; bioaccumulation ratings; and advantages and disadvantages of imazapyr and glyphosate herbicides for estuarine use

	Imazapyr	Glyphosate
Specific gravity	1.04–1.07	0.5
Minimum drying time	1 hour	6 hours
Highest proposed application rate	1.5 lb a.e./acre	10.8 lb/acre
Rate of kill	Very slow	Relatively slow
Volatility	Vapor pressure = 1.8×10^{-11} mm Hg Henry's Law constant of 7.1×10^{-17} atm m^3/mole No volatilization from dry soil surfaces; low volatilization of imazapyr from water or moist soil surfaces.	Extremely low vapor pressure, thus, negligible risk of movement through volatility
Solubility	Water: 11,272 mg/L	Water: ~12,000 mg/L
Soil organic carbon adsorption coefficient	K_{oc} = 8.81 Very low K_{oc} indicates low sorption potential.	K_{oc} = 24,000 Very high K_{oc} indicates tight sorption to most soils, suspended solids, and sediments in the environment.
Octanol/water partition coefficient	K_{ow} = 0.22, 1.3	K_{ow} = 0.0003
Degradation pathways	Slow anaerobic microbial degradation. No degradation under anaerobic conditions. Rapid photolysis in water.	Primarily degraded by microbes and fungi in soil or water, under both aerobic and anaerobic conditions. Photodegradation in water and soil are not expected to contribute significantly to glyphosate degradation.
Degradation products	Quinolinic acid	Aminomethylphosphonic acid ("AMPA"); further degraded to carbon dioxide and phosphate.
Half-life in soil	$t_{½}$ = 25–141 days	Average $t_{½}$ = 32 days, based on 47 agricultural and forestry studies. In most cases, >90% degraded within six months after application.
Half-life in benthic sediment	$t_{½}$ = <2 to 7 days	$t_{½}$ = >3 to 12 months

Table A-1 contd.: Chemical description; degradation rates, products, and pathways; bioaccumulation ratings; and advantages and disadvantages of imazapyr and glyphosate herbicides for estuarine use

	Imazapyr	Glyphosate
Half-life in water	No detectable degradation due to hydrolysis up to 30 days, pH 5-7 Average $t_{½}$ = 1-4 days (photolysis)	$t_{½}$ = 7–14 days
Bioaccumulation	BCF = 3; Low potential for bioaccumulation	BCF in fish after 10-14 day exposure period = 0.2 to 0.3 Low potential for bioaccumulation in aquatic animals; poorly absorbed when ingested by terrestrial mammals; any absorbed glyphosate is rapidly eliminated resulting in minimal tissue retention.
Advantages for estuarine use	– Rapid photolysis in water – Shorter minimum drying time than glyphosate – No adsorption to particles – Formulation can be mixed with salt water – Aerial applications require an order of magnitude lower spray volumes than glyphosate – Application is more cost-effective than application of glyphosate – Does not require use of non-ionic surfactants	– Low leaching potential due to strong sorption to soil/sediment particles
Disadvantages for estuarine use	– Increased adverse effects to non-target emerged vegetation due to higher efficacy on vascular plants	– Efficacy hindered by minimum drying time – Inactivated by adsorption to sediment particles – Formulation requires mixing with freshwater, which is not readily available – Aerial applications require large spray volumes, which require frequent refilling of helicopter tanks – Application is expensive – Requires use of non-ionic surfactants

Table A-2: Chemical properties, environmental fate, general toxicity rating, and toxicity of adjuvants

Adjuvant (Manufacturer)	Ingredients[1]	Chemical Properties	Degradation Pathways	General Toxicity Rating	Toxicity (lowest reported)
Non-ionic Surfactants ("NIS")					
R-11® (surface activator) (Wilbur-Ellis Company)	80% octylphenoxy polyethoxyethanol, 20% butanol and compounded silicone	– soluble in lipid and water – flammable – specific gravity = 1.0	Slowly biodegraded by progressive shortening of ethoxylate chain; intermediate breakdown products of polyethylene glycol (anti-freeze) and short-chain ethoxylates	Mammals: practically non-toxic orally, mild skin irritation possible Fish: Moderately toxic Other aquatic biota: slightly toxic	96-hr LC_{50}, rainbow trout 3.8 ppm[2] 96-hr LC_{50}, bluegill sunfish 4.2 ppm[2] 96-hr LC_{50}, juvenile rainbow trout 6 ppm[5] 48-hr LC_{50}, *Daphnia* spp. 19 ppm[3] LD_{50} oral, rabbit >5,840 mg/kg[2] LD_{50} dermal, rabbit >5,000 mg/kg[2]
X-77® (spreader activator) (Valent Corp.)	Alkylarylpoly (oxy-ethylene) glycols, free fatty acids, isopropyl alcohol	– soluble in lipid and water – flammable	Slowly biodegraded by progressive shortening of ethoxylate chain; intermediate breakdown products of polyethylene glycol (anti-freeze) and short-chain ethoxylates	Mammals: practically non-toxic orally Fish and other aquatic biota: moderately toxic	96-hr LC_{50}, rainbow trout 4.2 ppm[2] 96-hr LC_{50}, bluegill sunfish 4.3 ppm[2] 48-hr LC_{50}, *Daphnia* spp. 2 ppm[2] LD_{50} oral, rabbit >5,000 mg/kg[2] LD_{50} dermal, rabbit >5,000 mg/kg[2]
Liberate® (penetrating surfactant, deposition and drift control agent) (Loveland Industries, Inc.)	Phosphatidylcholine (lecithin), methyl esters of fatty acids, alcohol ethoxylate	– emulsifiable – specific gravity = 0.976	Biodegradation presumed rapid due to natural lecithin ingredients	Mammals: practically non-toxic orally, moderate skin irritation possible	96-hr LC_{50}, rainbow trout 17.6 ppm[1] NOEC, rainbow trout 12.5 ppm[1] 48-hr LC_{50}, *Daphnia magna* 9.3 ppm[1] NOEC, *Daphnia magna* 7.5 ppm[1] LD_{50} oral, rat >5,000 mg/kg[1] LD_{50} dermal, rat >5,000 mg/kg[1]
LI-700® (wetting and penetrating surfactant) (Loveland Industries, Inc.)	Phosphatidylcholine (lecithin), methylacetic acid, alkyl polyoxyethylene ether	– emulsifiable – not flammable – specific gravity = 1.03	Biodegradation presumed rapid due to natural lecithin ingredients	Mammals: practically non-toxic orally, causes skin and eye irritation Fish and other aquatic biota: practically non-toxic	96-hr LC_{50}, rainbow trout 17 ppm[2] 24-hr LC_{50}, rainbow trout 22 ppm[2] 96-hr LC_{50}, juv. rainbow trout 700 ppm[5] 96-hr LC_{50}, bluegill sunfish 210 ppm[2] 48-hr LC_{50}, *Daphnia* spp. 170 ppm[3] LD_{50} oral, rat >5,000 mg/kg[2] LD_{50} dermal, rat >5,000 mg/kg[2]
Cygnet Plus (Cygnet Enterprises)	75% d-limonene and related isomers, 15% methylated vegetable oil, 10% alkyl hydroxypoly oxyethylene; manufactured from natural limonene	– flammable – specific gravity = 0.87		Mammals: causes skin and eye irritation; Fish: slightly toxic Other aquatic biota: moderately toxic	NOEC, Ceriodaphnia dubia 3.0 ppm[4] 96-hr LC50 Ceriodaphnia dubia 6.6 ppm[4] NOEC, rainbow trout 30 ppm[4] 96-hr LC50, rainbow trout 45 ppm[4] NOEC, fathead minnow 15 ppm[4] 96-hr LC50, fathead minnow ppm[4]
Esterified Seed Oils ("ESOs") or Mehylated Seed Oils ("MSOs")					
Competitor® Wilbur-Ellis Company)	Ethyl oleate, sorbitan alkyl polyethoxylate ester, dialkyl polyoxy-ethylene glycol	– soluble in water – combustible – specific gravity = 0.9		Fish: slightly toxic Other aquatic biota: practically non-toxic	96-hr LC_{50}, rainbow trout 95 ppm[3] 48-hr LC_{50}, *Daphnia* spp. >100 ppm[3]

Table A-2 contd.: Chemical properties, environmental fate, general toxicity rating, and toxicity of adjuvants

Adjuvant (Manufacturer)	Ingredients[1]	Chemical Properties	Degradation Pathways	General Toxicity Rating	Toxicity (lowest reported)
Crop Oil Concentrates ("COC")					
Agri-Dex® (wetting and penetrating agent) (Helena Chemical Company)	Proprietary; heavy range paraffin-based petroleum oil with polyol fatty acid esters and polyethoxylyated derivatives	– dispersible in water as micelles – moderately flammable	Biodegradation presumed rapid	Mammals: practically non-toxic through oral ingestion, mild skin and eye irritant; Fish and other aquatic biota: practically non-toxic	96-hr LC_{50}, rainbow trout 271 ppm[2] 24-hr LC_{50}, rainbow trout 386 ppm[2] 96-hr LC_{50}, juv. rainbow trout 271 ppm[5] 48-hr LC_{50}, *Daphnia* spp. >1,000 ppm[3] LD_{50} oral, rat 5,010 mg/kg[2] LD_{50} dermal, rabbit >2,020 mg/kg[2]
Silicone-based Surfactants					
Dyne-Amic® (activator, spreader-sticker, wetting and penetrating agent, buffer) (Helena Chemical Company)	Organosilicone , methylated vegetable oil			Fish and other aquatic biota: slightly toxic	96-hr LC_{50}, rainbow trout 23.2 ppm[3] 48-hr LC_{50}, *Daphnia* spp. 60 ppm[3]
Kinetic® (spreader-sticker, wetting agent) (Helena Chemical Company)	Organosilicone , polyoxypropylene-polyoxyethylene copolymer			Fish and other aquatic biota: slightly toxic	96-hr LC_{50}, rainbow trout 13.9 ppm[3] 48-hr LC_{50}, *Daphnia* spp. 60.7 ppm[3]
Colorants					
Blazon® Spray Pattern Indicator "Blue" (Milliken Chemical)	Proprietary; 30% non-ionic polymeric colorant, 70% water	– pH = 7.0 – completely soluble in water – specific gravity = 1.07 – mildly acidic		Mammals: practically non-toxic orally; mild skin irritant; not mutagenic	LD_{50} rat >5,000 mg/kg[1]

[1] Manufacturer specimen labels
[2] Referenced in Entrix 10/03.
[3] Erik Johansen, Washington State Department of Agriculture, Memorandum Re: Summary of Acute Toxicity Data for Five Spray Adjuvants, February 4, 2004.
[4] Pacific Ecorisk, An Evaluation of the Acute Toxicity of "CYGNET PLUS" to *Ceriodaphnia dubia* (water flea), *Oncorhynchus mykiss* (rainbow trout), and *Pimephales promelas* (fathead minnow), December 10, 2004.
[5] King *et al.* 2004.

Table A-3a: Imazapyr herbicide mixture component concentrations and application rates for treatment of non-native *Spartina* in San Francisco Estuary

Application Method	Spray Volume	Formulation	Active Ingredient[1]	Surfactant[2]	Colorant
High volume handheld sprayer	100 gal/acre	0.52-0.75% solution 4-6 pints/100 gal	1-1.5 lb a.e./acre	0.25% v/v NIS with ≥70% a.i.; ~1% v/v MSO, ESO, or VOC; SBS according to label	3 qt/100 gal
Low-volume directed sprayer	20 gal/acre	0.75-1.5% solution 1.2-2.4 pints/20 gal	0.3-0.6 lb a.e./acre	0.25% v/v NIS with ≥70% a.i.; ~1% v/v MSO, ESO, or VOC; SBS according to label	3 qt/100 gal
Broadcast sprayer/ Aerial application	10-30 gal/acre	2.5-7.5% solution 6 pints/10-30 gal	0.5-1.5 lb a.e./acre	0.25% v/v NIS with ≥70% a.i.; ~1% v/v MSO, ESO, or VOC; SBS according to label	0.5-1.5 qt/acre

[1] Active ingredient in Habitat® is imazapyr isopropylamine salt; values expressed as imazapyr acid equivalent
[2] NIS = non-ionic surfactant; MSO = methylated seed oil; ESO = esterified seed oil; VOC = vegetable oil concentrate, SBS = silicone-based surfactant, %v/v = percentage based on volume by volume

Table A-3b: Glyphosate herbicide mixture component concentrations and application rates for treatment of non-native *Spartina* in San Francisco Estuary

Application Method	Spray Volume	Formulation	Active Ingredient[1]	Surfactant[2*]	Colorant
High volume handheld sprayer	100 gal/acre	1-2% solution 1-2 gal/100 gal	4-8 lb a.e./acre	≥0.5% v/v NIS with ≥50% a.i.	3 qt/100 gal
Low-volume directed sprayer	25-200 gal/acre	1-8% solution 1-8 gal/100 gal	1.35-10.8 lbs a.e./acre	≥0.5% v/v NIS with ≥50% a.i.	3 qt/100 gal
Broadcast sprayer/ Aerial application	7-40 gal/acre/ 7-20 gal/acre	4.5-7.5 pints/acre	2.25-3.75 lb a.e./acre	≥0.5% v/v NIS with ≥50% a.i.	0.5-1.5 qt/acre

[1] The active ingredient in Rodeo® and Aquamaster® is glyphosate isopropylamine salt; values are expressed as glyphosate acid equivalent
[2] NIS = non-ionic surfactant, %v/v = percentage based on volume by volume

Table A-4: Worst-case concentration of imazapyr herbicide dissolved in leading edge of incoming tide

Assumptions

Worst-case occurs on the leading edge of lateral flow from overtopped channel through an herbicide-treated marsh
Herbicide was uniformly sprayed across the entire marsh surface (but not in channels) at an application rate r = 15.6 mg a.e./sqft
The herbicide applied on a unit area (1 sqft) is therefore mass m = 15.6 mg a.e.
The herbicide dissolves completely in the incoming water
A percentage, p, of the herbicide sticks to the vegetation canopy, and does not dissolve in the first one foot of flow depth
Incoming tidal water overbanks channel and flows laterally across the surface of the marsh to a maximum distance D
Water flow across marsh (after it leaves channel) has a uniform depth d = 1ft
A percentage, s, of the active herbicide that was deposited onto the sediment surface dissolves into the water column
The dissolved herbicide is instantly fully dissolved in the first unit volume that flows through
No evaporation
No rain or other input of fresh water

Application rate

Habitat® label application rate: 4-6 pints per acre			Label indicates 2 pounds imazapyr acid equivalents per gallon Habitat®		
	6	pints/acre		1.5	lb a.e./acre
=	0.75	gal/acre	=	15.61	mg a.e./ft^2

Variables (p, D, and s can be varied):

r =	15.61	mg a.e./ft^2	Herbicide application rate
m =	15.61	mg a.e.	Initial mass of herbicide per unit area (per 1 ft^2)
p =	0%		Percentage of applied herbicide that is absorbed into vegetation canopy
d =	1	ft	Depth of water flow across marsh (1 ft allows unit volume calculations)
D =	100	ft	Distance of lateral flow across the marsh surface[a]
s =	60%		Percentage of herbicide reaching the sediment that resuspends into water column
C =	?		Concentration of herbicide in water column (mg a.e./ft^3)

Equation[b]

C = m × (1-p) × D × s = (mass per unit area) × (1-percent absorbed by plant canopy) × (percent dissolved in water column) × (number of units through which water flows)

Computed Concentration

C =	**m**	**1-p**	**D**	**s**	=	937 mg/ft^3
	15.61	100%	100	60%		**33.1 mg/liter**

Notes

a) Most *Spartina* infested marshes in the San Francisco Estuary that will become inundated by tidal water in the days following imazapyr application have a multitude of channels throughout the marsh that will transport water directly from the San Francisco Bay before overbanking and causing lateral flow across the marsh. In these marshes there would be a maximum of 100 feet of lateral flow through sprayed marsh before meeting with another flow.
b) Calculation does not take into account potential decay during period of time between spraying and water inundation nor any decay that might occur in water column once the herbicide is resuspended from sediment.

Table A-5: Ecotoxicity categories for acute toxicity of pesticides to wildlife[1]

Toxicity Category	Mammals		Birds	
	Acute Oral or Dermal LD_{50} (mg/kg)	Acute Inhalation LC_{50} (ppm)	Acute Oral LD_{50} (mg/kg)	Acute Inhalation LC_{50} (ppm)
Very highly toxic	<10	<50	<10	<50
Highly toxic	10-50	51-500	10-50	50-500
Moderately toxic	51-500	501-1000	51-500	501-1,000
Slightly toxic	501-2,000	1001-5000	501-2,000	1,001-5,000
Practically non-toxic	>2,000	>5,000	>2,000	>5,000

Table A-6: Ecotoxicity categories for acute toxicity of pesticides to aquatic organisms[1]

Toxicity Category	Fish or Aquatic Invertebrates Acute Concentration LC_{50} (mg/L)
Very highly toxic	<0.1
Highly toxic	0.1-1
Moderately toxic	>1-10
Slightly toxic	>10-100
Practically non-toxic	>100

Table A-7: Ecotoxicity categories for acute toxicity of pesticides to insects[1]

Toxicity Category	Concentration (µg/bee)
Highly toxic	<2
Moderately toxic	2 - 11
Practically non-toxic	>11

[1] U.S. EPA, Technical Overview of Ecological Risk Assessment, Analysis Phase: Ecological Effects Characterization, September 28, 2004.

Table A-8: Toxicity of imazapyr to mammals

Test Substance	Animal Species	Administration Route	Gender	LD_{50} or ED_{50}	Effect[3]	Testing Facility (Reporting Year)
Imazapyr technical	Rat	oral	♂	>5,000 mg/kg b.w.	NOEL	American Cyanamid Company (1983)[1]
			♀	>5,000 mg/kg b.w.	NOEL	
	Rabbit	dermal	♂	>2,000 mg/kg b.w.	NOEL	
			♀	>2,000 mg/kg b.w.	NOEL	
	Rat	inhalatory	♂	>1 ppm	ND	Food and Drug Research Laboratories (1983)[1]
			♀	>1 ppm (analytical)	ND	
AC 243,997 (93% pure)	Rat	inhalation	♂+♀	>1.3 ppm	L	Voss *et al.* (1983)[2]
Imazapyr isopropylamine technical (49.3% a.i.)	Rat	oral	♂	>10,000 ppm diet	DA	Medical Scientific Research, Laboratory (1983)[1]
			♀	>10,000 ppm diet	DA	
		intraperitoneal	♂	4,200 mg/kg b.w.	DA, B, A, S, CY, C, DBW	
			♀	3,700 mg/kg b.w.	DA, B, A, S, CY, C, DBW	
		subcutaneous	♂	>5,000 mg/kg b.w.	DA	
			♀	>5,000 mg/kg b.w.	DA	
		dermal	♂	>2,000 mg/kg b.w.	NOEL	
			♀	>2,000 mg/kg b.w.	NOEL	
	Mouse	oral	♂	>10,000 mg/kg b.w.	DA	
			♀	>10,000 mg/kg b.w.	DA	
		intraperitoneal	♂	3,450 mg/kg b.w.	DA, B, A, S, CY, C, DBW	
			♀	3,000 mg/kg b.w.	DA, B, A, S, CY, C, DBW	
		subcutaneous	♂	>5,000 mg/kg b.w.	DA, B, S	
			♀	>5,000 mg/kg b.w.	DA, B, S	

Table A-8 contd.: Toxicity of imazapyr to mammals

Test Substance	Animal Species	Administration Route	Gender	LD_{50} or ED_{50}	Effect[3]	Testing Facility (Reporting Year)
Imazapyr isopropylamine (25% a.i.)	Rat	oral	♂	>5,000 mg/kg b.w.	DA	American Cyanamid Company (1983)[1]
			♀	>5,000 mg/kg b.w.	DA	
	Mouse	oral	♂	>5,000 mg/kg b.w.	DA	American Cyanamid Company (1986)[1]
			♀	>5,000 mg/kg b.w.	DA	
	Rabbit	dermal	♂	>2,148 mg/kg b.w.	NOEL	American Cyanamid Company (1983)[1]
			♀	>2,148 mg/kg b.w.	NOEL	
	Rat	inhalatory	♂	>0.2	NOEL	Food and Drug Research Laboratories (1983)[1]
			♀	>0.2 (analytical)	NOEL	
Arsenal® 4-AS	Rat	inhalatory	♂+♀	>4.62 ppm	L	Hershman & Moore (1986)[2]
Chopper®RTU (NOS)	Rat	inhalatory	♂+♀	>3.34 ppm	L	Werley (1987)[2]

[1] cited in Entrix 10/03.
[2] cited in SERA 12/04, Appendix 1
[3] Acronyms: A = ataxia (loss of ability to coordinate muscular movement); B = blepharoptosis (drooping of upper eyelid); b.w. = body weight; C = convulsion; CY = cyanosis (bluish discoloration of skin and mucous membranes resulting from inadequate oxygenation of blood); DA = decreased activity; DBW = decreased body weight; ED_{50} = dose causing 50% inhibition of a process; L = lethality; LD_{50} = lethal dose, 50% kill; ND = nasal discharge; NOEL = no-observable-effect level (no toxic signs); NOS = not otherwise specified; S = sedation

Table A-9: Toxicity of imazapyr to birds

Test Substance	Species	Test (Observed Effect)	Result*
Arsenal® (identical with Habitat®)	Northern bobwhite quail	LD_{50}, 18-weeks dietary	>1890 mg/kg diet ~200 mg/kg b.w.
		NOEL, 18-weeks dietary	1890 mg/kg HDT ~200 mg/kg b.w.
		LD_{50}, 5-day acute dietary	>5000 mg/kg diet ~674 mg/kg b.w.
		NOEL, 5-day acute dietary	5000 mg/kg HDT ~674 mg/kg b.w.
	Mallard duck	LD_{50}, 18-weeks dietary	>1890 mg/kg diet ~200 mg/kg b.w.
		NOEL, 18-weeks dietary	1890 mg/kg diet ~200 mg/kg b.w.
		LD_{50}, 5-day acute dietary	>5000 mg/kg diet ~674 mg/kg b.w.
		NOEL, 5-day acute dietary	5000 mg/kg HDT ~674 mg/kg b.w.

* Fletcher 1983a, 1983b, Fletcher *et al*. 1984a, 1984b, 1984c, 1984d, 1995a, 1995b; all in SERA 12/04, Appendix 3

Table A-10: Toxicity of imazapyr and imazapyr herbicide/surfactant mixtures to fish

Test Substance + Surfactant	Animal Species	Test	Result	Reference
Arsenal® Herbicide (28.7% imazapyr) + Hasten	Rainbow trout, juvenile (*Oncorhynchus mykiss*)	96-hr LC_{50}	113 ppm surfactant	Smith *et al.* 2002[1]
Arsenal® Herbicide (28.7% imazapyr) + Agri-Dex®		96-hr LC_{50}	479 ppm surfactant	
Arsenal® Herbicide (28.7% imazapyr)		96-hr LC_{50}	77,716 ppm of concentrate 22,305 mg imazapyr a.e./L	Grue 2003[1] King *et al.* 2004
Arsenal® Concentrate (53.1 a.i. imazapyr)		96-hr LC_{50}	43,947 ppm of concentrate 23,336 mg imazapyr a.e./L	Grue 2003[1]
AC 243,997 with isopropylamine in water	Bluegill sunfish (*Lepomis macrochirus*)	96-hr LC_{50}	>1000 mg/L	Cohle & McAllister 1984a[2]
Arsenal® Herbicide (22.6% purity)		96-hr LC_{50}	180 mg/L	Cohle & McAllister 1984b[2]
AC 243,997 (99.5% purity)		96-hr LC_{50}	>100 mg/L	Kintner & Forbis 1983a[2]
Imazapyr NOS	Rainbow trout (*Salmo gairdneri*) Channel catfish (*Ictaluras punctatis*) Bluegill sunfish (*Lepomis macrochirus*)	96-hr LC_{50}	>100 mg/L	Peoples 1984[2] Gagne *et al.* 1994[2]
Arsenal® Herbicide (22.6% purity)	Rainbow trout (*Salmo gairdneri*)	96-hr LC_{50}	110 mg/L	Cohle & McAllister 1984c[2]
Arsenal® Herbicide (21.5% purity)		96-hr LC_{50}	>110 mg a.e./L	Drotter *et al.* 1995[2]

Table A-10 contd.: Toxicity of imazapyr and imazapyr herbicide/surfactant mixtures to fish

Test Substance + Surfactant	Animal Species	Test	Result	Reference
AC 342,997 (purity NOS)	Fathead minnow (*Pimephales promelas*)	NOEC LOEC MATC	120 mg a.i./L >120 mg/L >120 mg/L	Drotter *et al.* 1998[2]
AC 342,997 (99.6% purity)		28-day NOEC LOEC MATC	>118 mg a.i./L >118 mg a.i./L >118 mg a.i./L	Drotter *et al.* 1999[2]
AC 243,997 (99.5% purity)	Atlantic silverside (marine) (*Menidia menidia*)	96-hr LC_{50}	184 mg/L	Manning 1989a[2]
Imazapyr NOS	Nile tilapia (*Tilapia nilotica*)	24-hr LC_{50} 48-hr LC_{50} 72-hr LC_{50} 96-hr LC_{50}	4,670 µg/L 4,630 µg/L 4,610 µg/L 4,360 µg/L	Supamataya *et al.* 1981[2]
	Silver barb (*Barbus genionotus*)	24-hr LC_{50} 96-hr LC_{50}	2,706 µg/L 2,706 µg/L	

[1] cited in Entrix 10/03
[2] cited in SERA 12/04

Abbreviations: LC_{50} = lethal concentration, 50% kill; LOEC = lowest-observable-effect concentration; MATC = maximum allowable toxicant concentration; NOEC = no-observable-effect concentration (no toxic signs); NOS = not otherwise specified

Table A-11: Toxicity of imazapyr and imazapyr/surfactant mixtures to aquatic invertebrates

Test Substance	Species	Test (observed effect)	Result	Reference
Arsenal® Applicator's Concentrate (479 g imazapyr a.e./L)	Freshwater benthic macroinvertebrates	In-situ microcosm NOEC, (D, BM)	>18.4 mg/L (HDT)	Fowlkes *et al.* 2003
Arsenal®Herbicide (22.6% purity)	Freshwater water flea (*Daphnia magna*)	NOEC 48-hr LC_{50}	180 mg/L 350 mg/L	Forbis *et al.* 1984[2]
Arsenal® + unidentified surfactant		48-hr LC_{50}	79.1 mg imazapyr a.e./L	Cyanamid 1997[1]
Arsenal®		NOEC	40.7 mg imazapyr a.e./L	
		48-hr EC_{50} (?)	373 mg imazapyr a.e./L	
	Eastern oyster (*Crassostrea virginica*)	EC_{50} (G) NOEC	>132 mg imazapyr/L >132 mg imazapyr/L (HDT)	Mangels & Ritter 2000[1]
	Pink shrimp (*Penaeus duorarum*)	EC_{50} (S)	>132 mg imazapyr/L >132 mg imazapyr/L (HDT)	
AC 243,997 (technical)	Freshwater water flea (*Daphnia magna*) (<24 hours old)	24-hr LC_{50} 48-hr LC_{50}	>100 mg imazapyr a.e./L >100 mg imazapyr a.e./L	Kintner & Forbis 1983[2]
AC 243,997 (99.5% a.i.)	Freshwater water flea (*Daphnia magna*)	7, 14, 21-day NOEC (S/R/G)	97.1 mg/L (HDT, MATC)	Manning 1989[2]
AC 243,997 (purity NOS)	Grass shrimp (*Paleomonetes pugio)*	BCF	<1 (not calculable)	Drotter *et al.* 1996[2]
	Eastern oyster (*Crassosstrea virginica*)	BCF	<1 (not calculable)	Drotter *et al.* 1996[2]
AC 243,997 (99.6% purity)		EC_{50} (G)	>132 mg/L	Drotter *et al.* 1997[2]
AC 243,997 (99.5% purity)		96-hr EC_{50} (G)	>173 mg/L	Ward 1989[2]

[1] cited in Entrix 10/03
[2] cited in SERA 12/04, Appendix 4

Abbreviations: BM = biomass, D = deformity, S = survival; R = reproduction; G = growth; HDT = highest dose tested;
MATC = maximum allowable toxicant concentration

Table A-12: Toxicity of imazapyr and imazapyr/surfactant mixtures to non-target aquatic vegetation

Test Substance	Species	Test (Observed Effect)	Result	Reference
Technical grade imazapyr	Green algae (*Selenastrum capricornutum*)	EC_{50} (G) EC_{25} (G)	71 mg/L 78 mg/L	Hughes 1987[2] Mangels & Ritter 2000[1]
	Freshwater diatom *(Navicula pelliculosa)*	EC_{50} (G) EC_{25} (G)	>59 mg/L >59 mg/L	Mangels & Ritter 2000[1]
	Saltwater diatom (*Skeletonema costatum*)	EC_{50} (G) EC_{25} (G)	85 mg/L 42.2 mg/L	Hughes 1987[2]
	Blue-green algae (*Anabaena flos-aquae*)	EC_{50} (G) EC_{25} (G)	117 mg/L 7.3 mg/L	Mangels & Ritter 2000[1]
	Green algae (*Chlorella emersonii*)	EC_{50} (G)	0.2 mg/L	Landstein *et al.* 1993[2]
	Duckweed (*Lemna gibba*)	EC_{50} (G) EC_{25} (G)	0.024 mg/L 0.013 mg/L	Hughes 1987[2]
Arsenal®+ unidentified surfactant	Common water milfoil (*Myriophyllum sibiricum*)	EC_{25} (G shoots) EC_{50} (G shoots) EC_{25} (# roots) EC_{50} (# roots) EC_{25} (G roots) EC_{50} (G roots)	0.013 mg/L 0.032 mg/L 0.022 mg/L 0.029 mg/L 0.0079 mg/L 0.0099 mg/L	Roshon *et al.* 1999[2]
	Green algae (*Selenastrum capricornutum*)	EC_{50} (G) EC_{25} (G)	14.1 mg/L 8.36 mg/L	Mangels & Ritter 2000[1]
	Duckweed (*Lemna gibba*)	LC_{50} EC_{50} (G) EC_{25} (G)	24 ppb 0.0216 mg/L 0.0132 mg/L	Mangels & Ritter 2000 Mangels & Ritter 2000[1]

[1] cited in Entrix 10/03.
[2] cited in SERA 12/04, Appendix 4.

Abbreviations: S = survival; R = reproduction; G = growth; HDT = highest dose tested;
MATC = maximum allowable toxicant concentration

Table A-13: Toxicity endpoints for risk quotient calculation and levels of concern for interpretation of risk quotients

	Aquatic animals	Mammals	Birds	Aquatic vascular plants and algae	Non-endangered plants	Endangered plants
Assessment						
Acute	EC_{50} or LC_{50} acute toxicity	LD_{50} oral	LD_{50} oral	EC_{50}	EC_{25} seedling emergence and vegetative vigor	EC_{25} seedling emergence and vegetative vigor or NOEC
Chronic	NOEC early-life stage or full life-cycle tests	NOEC 2-generation reproduction	NOEC 21-week reproduction			
Levels of concern (risk quotient greater than)						
Acute risk	0.5	0.5	0.5	1.0	1.0	1.0
Acute restricted use	0.1	0.2	0.2			
Acute risk endangered species	0.05	0.1	0.1			
Chronic risk	1.0	1.0	1.0			

U.S. Environmental Protection Agency, Technical Overview of Ecological Risk Assessment, Analysis Phase: Ecological Effects Characterization and Risk Characterization, September 28th, 2004.