



FINAL

**Supplemental Environmental Impact
Statement for State of Washington
Aquatic Plant and Algae Management**

August 14, 2017

**Submitted to: Washington
Department of Ecology**

Prepared by: TRC Environmental

Ecology issued publication

To request ADA accommodation or materials in a format for the visually impaired, call Ecology at 360-407-7472, Relay Service 711, or TTY 877-833-6341.

Publication No. 17-10-020

SEPA No. 201704291

This page intentionally left blank



STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY

PO Box 47600 • Olympia, WA 98504-7600 • 360-407-6000

711 for Washington Relay Service • Persons with a speech disability can call 877-833-6341

**Final Supplemental Environmental Impact Statement for State of Washington
Aquatic Plant and Algae Management**

August 14, 2017

Environmental Review – This Final Supplemental Environmental Impact Statement (SEIS) is being distributed to tribes, agencies, organizations, and individuals with an interest in the Ecology proposal to modify or reissue the National Pollutant Discharge Elimination System (NPDES) general permits for the management of noxious weeds, algae and nutrients in and around waters of the State of Washington. This Final SEIS analyzes the potential environmental impacts of eight (8) new herbicides, algacides and nutrient inactivation products, updates information on the fifteen (15) herbicides and algacides currently allowed for use and provides a review and update of five alternative actions.

Washington State Department of Ecology Action Required – The proposed action that this Final SEIS supports is the discharge of herbicides, algacides and nutrient inactivation products in and around waters of the state through an NPDES discharge permit. The two permits that this Final SEIS supports are the Aquatic Plant and Algae Management NPDES General Permit and the Aquatic Noxious Weed Control NPDES General Permit.

Other Permits and Approvals Required – Applicators will also be required to obtain a license for aquatic application of registered pesticides from the Washington State Department of Agriculture. Authorization under a local (City or County) shoreline permit may also be required.

Public Review and Comment Opportunities – Tribal, agency, and public comments were invited on the proposed action and alternatives from May 8, 2017 through June 6, 2017. Comments received on the Draft SEIS can be found at http://www.ecy.wa.gov/programs/wq/pesticides/seis/risk_assess.html. Ecology's response to comments received can be found in the Responsiveness Summary: Appendix A.

Printed copies of the Final SEIS are available for review at the location indicated below.

Washington State Department of Ecology
Water Quality Program
300 Desmond Drive SE
Lacey, WA 98503

The Alternatives – The Final SEIS evaluates five (5) alternatives for implementing the proposed action to manage noxious weeds, algae and nutrients in and around waters of the State of Washington: 1) Use of an Integrated Pest Management (IPM) Approach, 2) No Action–Continuing Existing Management Practices, 3) Use of Chemical Methods Only, 4) Physical and Mechanical Control Methods, and 5) Biological Control Methods.

Alternative 1 (Integrated Pest Management) is the preferred alternative. Management of aquatic plants, algae and nutrients would combine the use of chemical treatments with existing biological, manual and mechanical methods of control to achieve the most effective control while minimizing use of these pesticides and nutrient inactivation products in the aquatic environment.

Key Environmental Issues – The Final SEIS provides a detailed discussion of potential non-target or unintended environmental effects to human health and the aquatic and surrounding ecosystem potentially associated with each of the alternatives discussed. This discussion includes all of the proposed herbicides and chemical agents as well as the currently registered herbicides and chemical agents. Each section provides a detailed discussion of potential mitigation measures needed to reduce or eliminate these environmental effects.

The Ecology Water Quality Program appreciates your interest in this proposal. If you would like more information about the proposed use of herbicides, algaecides or nutrient inactivation products to control aquatic plants, algae and nutrients in waters of the state of Washington, please contact Nathan Lubliner, Aquatic Plant Specialist, at nathan.lubliner@ecy.wa.gov or (360) 407- 7670.

Thank you.


Heather R. Bartlett
Water Quality Program Manager

Date: 8/10/17

Table of Contents

ACRONYMS	IV
FACT SHEET	VII
EXECUTIVE SUMMARY	X
REFERENCE GUIDE	XVI
1.0 INTRODUCTION AND BACKGROUND	17
1.1 INTRODUCTION TO ALTERNATIVES	17
1.1.1 <i>Criteria Used in the Analysis and Comparison of Alternatives</i>	18
1.2 SEPA DEFINITIONS OF MITIGATION.....	19
1.3 PROTECTION OF WETLANDS	19
1.4 ESA CONSIDERATIONS FOR EACH ALTERNATIVE METHOD	19
2.0 ALTERNATIVE 1: INTEGRATED PEST MANAGEMENT (IPM) (PREFERRED ALTERNATIVE)	20
2.1 IMPACTS AND MITIGATION	21
2.2 REFERENCES.....	22
3.0 ALTERNATIVE 2: NO ACTION	23
3.1 DESCRIPTION OF THE ALTERNATIVE	23
3.2 IMPACTS AND MITIGATION	23
4.0 ALTERNATIVE 3: USE OF HERBICIDES, ALGAECIDES AND CHEMICAL AGENTS	24
4.1 DESCRIPTION OF THE ALTERNATIVE	24
4.1.1 <i>Methodology for evaluating the eight proposed new herbicides and chemical agents</i>	24
4.2 EVALUATION OF AMINOPYRALID	26
4.2.1 <i>Registration Status</i>	26
4.2.2 <i>Description</i>	27
4.2.3 <i>Environmental and Human Health Impacts</i>	33
4.2.4 <i>Mitigation</i>	34
4.2.5 <i>References</i>	37
4.3 EVALUATION OF PROCELLACOR™ (FLORPYRAUXIFEN-BENZYL)	39
4.3.1 <i>Registration Status</i>	39
4.3.2 <i>Description</i>	40
4.3.3 <i>Environmental and Human Health Impacts</i>	47
4.3.4 <i>Mitigation</i>	50
4.3.5 <i>References</i>	52
4.4 EVALUATION OF TOPRAMEZONE.....	54
4.4.1 <i>Registration Status</i>	54
4.4.2 <i>Description</i>	54
4.4.3 <i>Environmental and Human Health Impacts</i>	57
4.4.4 <i>Mitigation</i>	61
4.4.5 <i>References</i>	64
4.5 EVALUATION OF PEROXYACETIC ACID/HYDROGEN PEROXIDE	65
4.5.1 <i>Registration Status</i>	65

4.5.2	Description	65
4.5.3	Environmental and Human Health Impacts	69
4.5.4	Mitigation	71
4.5.5	References.....	73
4.6	EVALUATION OF ALUMINUM SULFATE (ALUM)	75
4.6.1	Registration Status.....	75
4.6.2	Description	75
4.6.3	Environmental and Human Health Impacts	79
4.6.4	Mitigation	82
4.6.5	References.....	83
4.7	EVALUATION OF CALCIUM HYDROXIDE/OXIDE AND CALCIUM CARBONATE	86
4.7.1	Registration Status.....	86
4.7.2	Environmental Characteristics: Product Use and Chemistry.....	86
4.7.3	Environmental and Human Health Impacts	88
4.7.4	Mitigation	90
4.7.5	References.....	91
4.8	EVALUATION OF IRON AND IRON SALTS	93
4.8.1	Registration Status.....	93
4.8.2	Description	93
4.8.3	Environmental and Human Health Impacts	98
4.8.4	Mitigation	100
4.8.5	References.....	102
4.9	EVALUATION OF LANTHANUM-CLAY (PHOSLOCK®)	104
4.9.1	Description	104
4.9.2	Environmental and Human Health Impacts	108
4.9.3	Mitigation	110
4.9.4	References.....	112
4.10	UPDATE OF CURRENTLY REGISTERED HERBICIDES AND ALGAEICIDES IN WASHINGTON STATE	113
4.10.1	Tank Mixes, Inerts and Surfactants	113
4.10.2	2,4-D amine and ester	115
4.10.3	Bispyribac-sodium	119
4.10.4	Carfentrazone-ethyl.....	121
4.10.5	Diquat.....	125
4.10.6	Endothall (dipotassium salt) Herbicide.....	130
4.10.7	Flumioxazin	134
4.10.8	Fluridone.....	138
4.10.9	Glyphosate.....	141
4.10.10	Imazamox	146
4.10.11	Imazapyr.....	151
4.10.12	Penoxsulam	155
4.10.13	Triclopyr TEA.....	160
4.10.14	Endothall (mono salt) algaecide.....	164
4.10.15	Sodium Carbonate Peroxyhydrate (sodium percarbonate)	168
5.0	ALTERNATIVE 4: MANUAL AND MECHANICAL CONTROL METHODS.....	173
5.1	POTENTIAL IMPACTS AND MITIGATION MEASURES.....	173
5.1.1	Bottom barriers.....	173

5.1.2	<i>Diver assisted suction harvesting</i>	174
5.1.3	<i>Manual methods</i>	174
5.1.4	<i>Rotovation</i>	175
5.1.5	<i>Mechanical Harvesters and Cutters</i>	176
5.2	REFERENCES	176
6.0	ALTERNATIVE 5: BIOLOGICAL CONTROL METHODS	177
6.1	POTENTIAL IMPACTS AND MITIGATION MEASURES	177
6.1.1	<i>Plant Pathogens</i>	177
6.1.2	<i>Herbivorous Insects</i>	178
6.1.3	<i>Competitive plants</i>	180
6.1.4	<i>Plant Growth Regulators</i>	180
6.1.5	<i>Grass Carp</i>	180
6.1.6	<i>Investigations into Biocontrol of Flowering Rush</i>	181
6.2	REFERENCES	182

Table 1:	Proposed New and Currently Registered Aquatic Herbicides and Chemical Agents.....	xiv
----------	---	-----

Acronyms

°C	degrees Celsius
µg	microgram
ac	acre
ae	acid equivalents
ai	active ingredient
ALS	acetolactate synthase
alum	aluminum sulfate
APAM	Aquatic Plant and Algae Management
BMP	best management practices
BOD	biochemical oxygen demand
bw	body weight
Ca(OH) ₂	calcium hydroxide
Ca ²⁺	calcium ion
CET	concentration and exposure time
CHO/HGPRT	Chinese hamster ovary cell/hypoxanthine-guanine phosphoribosyl-transferase
CO ₂	carbon dioxide
CWA	Federal Water Pollution Control Act of 1972, known as the Clean Water Act
DO	dissolved oxygen
DNA	deoxyribonucleic acid
EC ₃	estimated concentration required to produce a 3-fold increase in draining lymph-node cell proliferative activity
EC ₅₀	effective concentration at which half of test organisms show a toxic, quantifiable response (e.g. growth or reproductive viability), used as a common metric in toxicity testing)
EDTA	ethylenediaminetetraacetic acid
EFED	Environmental Fate and Effects Division of the US Environmental Protection Agency
EIS	Environmental Impact Statement
EPA	United States Environmental Protection Agency
ESA	Endangered Species Act
EWM	Eurasian watermilfoil
FDA	United States Food and Drug Administration
Fe ²⁺	iron(II) ion, or ferrous ion
Fe ³⁺	Iron (III) ion, or ferric ion
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
fl oz	fluid ounces
FQPA	Food Quality Protection Act
g	gram
GRAS	Generally Regarded as Safe (used by FDA)
HED	Health Effects Division of the US Environmental Protection Agency

HP	hydrogen peroxide
HPPD	hydroxyphenylpyruvate dioxygenase
IARC	International Agency for Research on Cancer
IPM	integrated pest management
kg	kilogram
K _{oc}	organic carbon-normalized soil adsorption coefficient
K _{ow}	octanol-water partition coefficient
K _{sp}	solubility product constant
L	liter
LaCl ₃	lanthanum chloride
LaPO ₄	rhabdophane
lb	pound
LC ₅₀	lethal concentration at which 50% of the test population experiences mortality
LD ₅₀	lethal dose at which 50% of the test population experiences mortality
LOAEC	Lowest Observable Adverse Effect Concentration
LOEC	Low Observed Effect Concentration
log K _{ow}	octanol/water partition coefficient
m ³	cubic meter
mg	milligram
mL	milliliter
mm Hg	millimeter of mercury
NIEHS/NTP	National Institute of Environmental Health Sciences/National Toxicology Program
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
NPDES	National Pollutant Discharge Elimination System
OH ⁻	Hydroxide ion
OPP	Office of Pesticide Programs
PAA	peroxyacetic (peracetic) acid
pH	potential of hydrogen
PMRA	Pest Management Regulatory Agency
PO ₄ ⁻	phosphate ion
PPE	personal protective equipment
PRIA	Pesticide Registration Improvement Act
RCW	Revised Code of Washington
RfD	reference dose
SEIS	Supplemental Environmental Impact Statement
TGAI	technical grade active ingredient
T _{max}	time to maximum concentration

US	United States
USDA	United States Department of Agriculture
WDFW	Washington Department of Fish and Wildlife
WDNR	Washington Department of Natural Resources
WHO	World Health Organization
WSDA	Washington State Department of Agriculture

Fact Sheet

Project Title	State of Washington Aquatic Plant and Algae Management
Proposed Action	<p>The Proposed Action is for aquatic plant management. The action is defined as a non-project proposal under State Environmental Policy Act (SEPA) rules such that the Supplemental Environmental Impact Statement (SEIS) will be integrated with on-going agency planning and permitting procedures for aquatic herbicides. The purpose of this SEIS is to support SEPA review of the Aquatic Plant and Algae Management and Aquatic Noxious Weed Control National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permits. The goal is to update the information available in a previous EIS on chemicals currently allowed for use as well as review a number of new herbicides, algaecides and chemical agents to be considered for incorporation into future reissuances of the two permits. Additionally, herbicides and algaecides currently registered by WSDA were also reviewed, evaluated, and updated. New information on pesticide use patterns, non-chemical aquatic plant, and algae management options is sought, and updates of the evaluation of impacts to the environment. The recommended alternative is an integrated aquatic plant management approach using the most appropriate mix of vegetation control methods that may include biological, manual/mechanical, and chemical methods.</p>
Lead Agency	Washington State Department of Ecology
Responsible Official	Heather R. Bartlett Program Manager, Water Quality Program
Contact person	Nathan Lubliner, Project Manager, Water Quality Program
Licensees, Permits	<p>The list below reflects permits required for various plant management alternatives discussed in this document, including use of aquatic herbicides, rotoation, dredging, manual and biological control methods. Not all permits listed below are required for all activities discussed in this document. Requirements may change; please check with resource agencies to determine permit requirements for a particular project.</p>
Washington Department of Ecology	<p>Aquatic Plant and Algae Management National Pollutant Discharge Elimination System General Permit</p> <p>Aquatic Noxious Weed Control National Pollutant Discharge Elimination System General Permit</p>

Washington Department of Fish and Wildlife	Hydraulic Project Approval Permit
Local	Shoreline Substantial Development Permit (Shoreline Management Act) in certain locales
Federal	US Army Corps of Engineers Section 404 Permit
Contract Authors and Principal Contributors	<p>Jeremy Pratt, Vice President and Project Manager, TRC 2701 First Ave, Suite 400 Seattle, WA 98121 MS Washington State University (Environmental Science) BS The Evergreen State College (Interdisciplinary Studies)</p> <p>Allan Chartrand, DABT, Lead Author and Principal Scientist MSPH University of California, Los Angeles (Toxicology) BS University of California, Berkeley (Biology)</p> <p>Shannon Luoma, Assistant Project Manager, TRC BA Ohio University (Political Science)</p> <p>Water Quality Program Department of Ecology P.O. Box 47600 Olympia, WA 98504-7600</p> <p>Nathan Lubliner, Aquatic Plant Specialist, Water Quality Program, WA Dept of Ecology</p> <p>Derek Rockett, Senior Nonpoint Specialist, Water Quality Program, WA Dept of Ecology</p> <p>Fran Sant, Environmental Review Coordinator, Shorelands and Environmental Assistance Program, WA Dept of Ecology</p> <p>Kathleen Emmett, Technical Services Unit Supervisor, Water Quality Program, WA Dept of Ecology</p> <p>Jenifer Parsons, Aquatic Plant Specialist, Environmental Assessment Program, WA Dept of Ecology</p> <p>Erik Johansen, Policy Assistant, Registration and Licensing Services Program, WA Department of Agriculture</p> <p>Mark A. Heilman, Ph.D., Senior Aquatics Technology Leader, SePRO Corporation: Review of Florpyrauxifen-benzyl section</p>
Agency Authors and Principal Contributors	

Location of Background Data	Water Quality Program Department of Ecology P.O. Box 47600 Olympia, WA 98504-7600
--------------------------------	--

Executive Summary

This Supplemental Environmental Impact Statement (SEIS) provides further Washington State Environmental Policy Act (SEPA) review on the Washington Department of Ecology Aquatic Plant and Algae Management and Aquatic Noxious Weed Control National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permits. This SEIS updates and revises information from Ecology's previous Final EIS (1980) and SEIS's prepared between 2000 and 2012 to: (1) update information on herbicides, algaecides and other chemical agents currently allowed for use; (2) review eight (8) new herbicides, algaecides and other chemical agents considered for incorporation into future reissuances of the two permits; (3) incorporate new information on pesticide use patterns, non-chemical aquatic plants, and algae management options; (4) address potential cumulative and synergistic interactions among chemicals.

Additional tools and technologies are needed for control of noxious aquatic plants and weeds in Washington State. The approval of new herbicides can improve control of weed species not optimally addressed by currently registered compounds. The goal is to enhance selectivity to reduce impacts to non-target plant and animal species, reduce use rates, and further mitigate risk of potential herbicide resistance development. Selectivity to protect non-target native aquatic vegetation and longevity of control are key criteria in the management of invasive aquatic plants. Efforts are currently under way to find newer, more selective, systemic modes of actions with short exposure time requirements for in-water partial site treatment of major target aquatic weeds (e.g. floating plants such as water hyacinth, or submersed species such as hydrilla, Eurasian watermilfoil, and pondweed).

Aquatic plants are a valuable component of aquatic ecosystems and habitats within Washington State, and often require protection. These plants provide refugia (cover), habitat, and food sources for many species of aquatic invertebrates, fish, and wildlife. They can, however, limit certain waterbody uses. Invasive (non-native) or native rooted and floating plants, for example, can degrade water quality, impair fisheries, block water intakes that support domestic or agricultural purposes, and also interfere with navigation, recreation, and aesthetics. In addition, noxious or invasive aquatic plant species such as Eurasian watermilfoil, a common pest species in Washington State, can form dense stands that may pose safety or navigation problems for swimmers and boaters, impair critical aquatic habitat, and degrade wildlife habitat by out-competing native species or changing water chemistry. Numerous other noxious weed species impair both freshwater and estuarine water bodies, and can also affect protected wetlands. The most problematic submerged weeds in the Pacific Northwest include: Eurasian watermilfoil (EWM, (*Myriophyllum spicatum*, a perennial), hybrid milfoils, including variable leaf milfoil, hydrilla (*H. verticillata*), curlyleaf pondweed (*P. crispus*, annual), and flowering rush (*B. umbellatus*, perennial). Other emergent and potential target aquatic plants include Brazilian elodea (*E. densa*), parrotsfeather (*M. aquaticum*), purple loosestrife (*Lythrum salicaria*), and phragmites (*Phragmites australis*). Typical use patterns for managing these species would include lakes, reservoirs, slow moving rivers and streams, as well as irrigation canals.

ECOLOGY'S WATER QUALITY PROGRAM AND ITS REGULATORY AUTHORITY

Ecology is the delegated authority responsible for implementing the State Water Pollution Control Act (RCW 90.48) and the federal Clean Water Act (CWA). Under these provisions, Ecology's Water Quality

Program receives requests for permits from various businesses and entities to use herbicides and other control methods to manage excessive native and invasive noxious aquatic weed species, including algae, for a wide variety of water bodies and wetlands. In response to these requests and in accordance with the provisions of the SEPA, Ecology determined that aquatic plant management by chemical methods may have significant adverse environmental impacts, and that an Environmental Impact Statement (EIS) was necessary. Under these requirements, Ecology complied with SEPA by conducting an environmental review of both the Aquatic Plant and Algae Management (APAM) and the Aquatic Noxious Weed Control National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permits.

The two permits are located at

http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/noxious/noxious_index.html
and

http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology's Final EIS (FEIS) for aquatic plant management, which addressed the application of aquatic herbicides to freshwater bodies within Washington State, was originally prepared in 1980. In light of new information and to update the original document, a Final Supplemental EIS (SEIS) for Freshwater Aquatic Plant management was completed by Ecology's Water Quality Program in February 2001 (Publication No. 00-10-040; www.ecy.wa.gov/pubs/0010040.pdf). This document updates the February 2001 document and is formally designated as a supplement to that SEIS.

The Washington State Department of Agriculture (WSDA) is charged with registering pesticides for distribution in the State, regulating pesticide use and pesticide applicator licensing, and along with the State Noxious Weed Control Board, controlling noxious plants within the State. The Washington State Department of Fish and Wildlife (WDFW) is charged with issuing Hydraulic Project Approvals (HPAs) to implement various physical and mechanical methods and with protecting fish and wildlife and critical habitats within the State. As Ecology does not have the resources to develop individual risk assessments for each new active herbicide, algaecide, or phosphate inactivating agent for aquatic plant treatments in Washington State, it must rely on a variety of other scientific and technical data sources, including United States Environmental Protection Agency (US EPA) risk assessments of new and proposed aquatic herbicide products. Risk assessments prepared by other states, Canada, or other private entities were also incorporated into this SEIS evaluation.

Part of SEPA review requirements include an alternatives analysis for both chemical and non-chemical aquatic plant management approaches. The alternatives analysis included an evaluation of the following aquatic plant control alternatives:

- Alternative 1: Integrated Pest Management (IPM) techniques, *see Section 2*;
- Alternative 2: No Action, *see Section 3*;
- Alternative 3: Herbicides, Algaecides and Chemical Agents (new and proposed: topramezone, aminopyralid, rinskor (Procellacor™), peroxyacetic acid/hydrogen peroxide, lanthanum clay (Phoslock), iron, aluminum sulfate/alum, calcium hydroxide/oxide) and currently registered chemical agents (see below) *see Section 4*;

- Alternative 4: Physical and Mechanical Control Methods (bottom barriers, suction (diver) dredging, manual methods [hand-pulling, raking, cutting], rotovation, and mechanical harvesters), *see Section 5*; and
- Alternative 5: Biological Control Methods (plant pathogens, herbivorous insects, competitive plants, plant growth regulators, grass carp), *see Section 6*.

CONDUCTING THE ALTERNATIVES ANALYSIS

Each of the five alternatives were qualitatively evaluated based on the data and evidence available, and the alternatives analysis identified Alternative 1, use of IPM techniques, as the preferred alternative. The IPM approach is the only alternative that considers each individual aquatic noxious weed problem or algal bloom independently and evaluates a range of chemical and non-chemical alternatives available to treat plants or algae. Some infestations or blooms may be amenable to alternative methods such as physical or mechanical removal (e.g. bottom barriers, cutters, rotovation, mechanical harvesting) or biological control methods, while other problems may be much more complex and require a stronger mode of treatment or control such as herbicides, algaecides, or phosphorus inactivation agents. The IPM approach is especially important given the growing scientific and societal concerns and continually improving environmental data regarding potential impacts to human health and the environment from the use of aquatic herbicides, algaecides, and other agents. Our enhanced understanding of the role of wetlands and other critical habitats and the need to consider and control nutrient and sediment loading within a total watershed also improves our understanding of some of the non-target effects of herbicides and related chemical agents.

In the event that chemical control methods such as herbicides may be required, each agent will be individually evaluated for a number of selection criteria before final selection and application or treatment. These criteria will include target efficacy, non-target effects, human health and ecological hazard or risk, short- and long-term toxicity, potential effects to endangered plant and animal species as well as their habitats, label restrictions, mitigation requirements, the need for post-treatment monitoring, and other key factors. These factors are evaluated for each new chemical addressed in this SEIS. Another key selection criteria is the actual benefit that the treatment method brings to the receiving water environment.

As an example, in the event of a dense watermilfoil infestation, there is often a safety, habitat, navigational, or other problem, and using the preferred alternative, part of the selection process would be to choose a chemical agent or non-chemical approach that would alleviate the problem and thus benefit the ecosystem, somewhat independently of the non-target effects of the agent in question. The most effective IPM-based treatment strategies are site-specific rather than generic, and consider both the short- and long-term implications of all treatment strategies considered and selected, whether chemical or non-chemical.

Even under an IPM-based management program, unavoidable adverse impacts may occur that will restrict beneficial water uses. The development of a lake or aquatic plant management plan will allow for and promote use prioritization by involved stakeholders while maintaining, improving, and protecting the designated uses of a specific waterbody. Management plans help to ensure that proven control methods will be implemented for long term management of the waterbody and that problems

such as nutrient enrichment and sediment loading, which often contribute to accelerated plant and algal growth, are addressed. Use of an integrated management approach will further this goal through the selection of the control or management method that will yield maximum aquatic plant control while minimizing undesirable impacts to human health and the environment.

METHODOLOGY FOR EVALUATING THE EIGHT PROPOSED NEW HERBICIDES AND CHEMICAL AGENTS

Results of the technical evaluation of the eight chemical agents (see Table 1) proposed for use in controlling noxious plant and algal species are reported in this SEIS. The evaluation procedure is presented in this SEIS as follows. Initially, a general description of each herbicide or chemical agent is provided, along with a summary of its registration status with EPA, WSDA, and other regulatory agencies. This is followed by a more detailed discussion of its chemical (including efficacy-related) and environmental fate properties, together with any relevant field investigations or monitoring studies which could illustrate its effectiveness in the field. An overview of acute, subchronic, and chronic toxicological properties is provided and evaluated, including human, mammalian, and ecotoxicological characteristics, covering effects to fish, birds, invertebrates, plants and algae, as available. This toxicological evaluation considers both full life-cycle and food web impacts to non-target species, and where available, information on one-time vs. repeated applications of the chemical agent or herbicide, as well as impacts on numbers, diversity and habitat of species of plants and animals.

Following this presentation of technical and environmental data, a discussion on human health and environmental impacts is provided, including impacts to human health, ecological risk or hazard, and potential effects to the earth, water, plant, and other aspects of the environment as appropriate. This discussion considers both label-specified exposure scenarios and off-site transport such as aerial drift and/or surface runoff. Based on these potential impacts, each evaluation discusses possible label restrictions and proposed mitigation measures relating to swimming or recreational uses, required mitigation for addressing effects to habitats and non-target plants, endangered plant and animal species (including salmonids), and fisheries and fish consumption. Finally, post-treatment monitoring requirements and recommendations are provided for each of the chemical agents under evaluation, with references used and cited for each evaluation provided for each.

UPDATE OF CURRENTLY REGISTERED HERBICIDES AND CHEMICAL AGENTS IN WASHINGTON STATE

There are currently 14 herbicides registered for aquatic use in Washington State (see Table 1). These are discussed in detail in Section 4.10 and include the following: 2,4-D (amine and ester), bispyribac-sodium, carfentrazone ethyl, diquat, endothall (dipotassium salt and mono (N,N-dimethylalkylamine) salt), flumioxazin, fluridone, glyphosate, imazamox, imazapyr, penoxsulam, triclopyr (triethylamine salt), and sodium carbonate peroxyhydrate. Previous reviews for each of these currently registered aquatic herbicides are updated using a similar approach to the new or proposed herbicide or chemical agent evaluation discussed above. Generally more information is already available for these currently registered chemicals, and as such the emphasis is on updating previous studies, data, and information collected since the time of registration rather than acquiring new information on these chemicals. Again, for each of these herbicides and chemical agents the SEIS discusses mitigation requirements and label

restrictions needed to limit or eliminate potential adverse effects to human health or the environment. References used to evaluate each of the proposed chemical ingredients are listed at the end of the section for each chemical agent or herbicide.

Table 1 shows the proposed and currently registered aquatic herbicides, algaecides, and phosphorus-inactivating agents, including active ingredients and trade names, evaluated under this SEIS document. Note that use of commercial, trade, and formulation details are provided as examples only and do not constitute an endorsement of that product by the Department of Ecology.

Table 1 Proposed New and Currently Registered Aquatic Herbicides and Chemical Agents

Proposed herbicide or chemical agent	Type	Commercial, Trade Names and Formulations
Aminopyralid	Selective systemic herbicide	Milestone®, Capstone®, Opensight®
Florpyrauxifen-benzyl/Procellacor™	Selective systemic herbicide	Procellacor™
Topramezone	Selective systemic herbicide	Oasis®
Peracetic acid/hydrogen peroxide	Broad-spectrum disinfectant/algaecide	GreenClean™
Aluminum sulfate (alum)	Phosphorus inactivating agent	alum
Calcium hydroxide	Phosphorus inactivating agent	"slaked lime"
Iron salts	Phosphorus inactivating agent	iron salts
Lanthanum clay-Phoslock®	Phosphorus inactivating agent	Phoslock®
Currently registered herbicides and algaecides		
2,4-D amine & ester	selective systemic herbicide	AquaKleen®, Navigate®
Bispyribac-sodium	Broad-spectrum systemic herbicide	Tradewind™
Carfentrazone-ethyl	Narrow-spectrum Contact herbicide	Stingray™
Diquat	Broad-spectrum Contact herbicide	Reward®
Endothall dipotassium salt	Broad-spectrum Contact herbicide	Aquathol®
Flumioxazin	Broad-spectrum Contact herbicide	Clipper™
Fluridone	Systemic herbicide	Sonar®
Glyphosate	Systemic herbicide	Rodeo®, Pondmaster®
Imazamox	selective systemic herbicide	Clearcast®
Imazapyr	Broad spectrum, Systemic herbicide	Arsenal™, Habitat
Penoxsulam	Broad-spectrum systemic herbicide	Galleon SC™
Triclopyr TEA	Selective, Systemic herbicide	Renovate®, Garlon 3A®

Endothall mono(N,N-dimethylalkylamine) salt	Broad-spectrum algaecide	Hydrothol®191
Sodium carbonate peroxyhydrate	Fast-acting broad-spectrum algaecide	GreenClean™, Pak 27™

Reference Guide

Each of the references provided in this DSEIS also identify information sources by the following 11 categories, as required by RCW 34.05.272:

1. Peer review is overseen by an independent third party.
2. Review is by staff internal to Department of Ecology.
3. Review is by persons that are external to and selected by the Department of Ecology.
4. Documented open public review process that is not limited to invited organizations or individuals.
5. Federal and state statutes.
6. Court and hearings board decisions.
7. Federal and state administrative rules and regulations.
8. Policy and regulatory documents adopted by local governments.
9. Data from primary research, monitoring activities, or other sources, but that has not been incorporated as part of documents reviewed under other processes.
10. Records of best professional judgment of Department of Ecology employees or other individuals.
11. Sources of information that do not fit into one of the other categories listed.

1.0 Introduction and Background

This Supplemental Environmental Impact Statement (SEIS) provides further SEPA review on the Washington Department of Ecology Aquatic Plant and Algae Management (APAM) and Aquatic Noxious Weed Control National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permits. This SEIS updates and revises information from Ecology's previous Final Environmental Impact Statement (FEIS) (1980) and other supplemental EIS's (SEIS's) issued between 2000 and 2012 to: (1) update detailed technical information on herbicides and algaecides currently allowed for use; (2) review eight (8) new herbicides, algaecides and chemical agents considered for incorporation into future reissuances of the two permits; (3) incorporate new information on pesticide use patterns, non-chemical aquatic plants, and algae management options; (4) address potential cumulative and synergistic interactions among herbicides, algaecides and chemical agents.

Additional tools and technologies are needed for control of noxious aquatic plants and weeds in Washington State. Permit applications are normally submitted for herbicide applications, with permit coverage often being maintained for multiple years, permitting herbicide treatments for the same water bodies for multiple years. For Ecology's noxious weed NPDES permit, only limited agents working under the WSDA permit coverage would apply each year to use pesticides. The permit holder WSDA maintains coverage for the entire duration of the permit (5 years). For the APAM permit, a permittee can maintain coverage until the permit is reissued (up to 5 years) and if they send in a renewal letter (including a Notice of Intent [NOI] update) they will be automatically covered under the reissued permit.

The approval of new herbicides can improve control of weed species not optimally addressed by currently registered compounds. The goal would be to enhance selectivity, reduce use rates, and further mitigate risk of potential herbicide resistance development. Selectivity to native aquatic vegetation and longevity of control are key criteria in the management of invasive aquatic plants. Efforts are currently under way to find new selective, systemic chemistries and modes of actions with short exposure time requirements for in-water partial site treatment of major target aquatic weeds such as hydrilla and Eurasian watermilfoil.

1.1 INTRODUCTION TO ALTERNATIVES

This alternatives analysis updates information on alternative methods for control of aquatic vegetation, including both chemical and non-chemical aquatic plant management. The preferred alternative is Integrated Pest Management (IPM). The following aquatic plant control alternatives are described below:

- Alternative 1: Integrated Pest Management (Preferred Alternative);
- Alternative 2: No Action (continuing current practices);
- Alternative 3: Use of Herbicides, Algaecides and Chemical Agents (topramezone, aminopyralid, rinskor (Procellacor™), peroxyacetic acid/hydrogen peroxide, aluminum sulfate/alum, iron salts, calcium hydroxide/oxide, and lanthanum clay (Phoslock);
- Alternative 4: Physical and Mechanical Control Methods; and
- Alternative 5: Biological Control Methods.

Each of these alternatives represent management or control actions available to an applicant or agency for aquatic plant management. A variety of actions may be required to implement these aquatic plant management alternatives, often involving multiple agencies. As examples, these actions may include Ecology's issuance of an NPDES permit to allow for application of herbicides to waters of the state; or action by WDFW to allow the use of grass carp or other methods for the purpose of biological control. Issuance of HPA permits from WDFW may also be required for hand pulling, raking, harvesting, diver dredging, weed rollers, rotoation and bottom barrier installation, or other physical or mechanical methods. Local governments may require substantial development shoreline permits for mechanical or chemical treatment projects. The US Army Corps of Engineers may require Section 404 of the Clean Water Act (CWA) and/or Section 408 of the Rivers and Harbors Act of 1899 (as amended) permits for suction dredging and rotoation projects.

1.1.1 Criteria Used in the Analysis and Comparison of Alternatives

State surface water quality regulations and standards (RCW 90.48; WAC Chapter 173-201A) provide Ecology with both the authority and responsibility to establish criteria for waters of the State, to protect designated beneficial uses, and to regulate various activities, including those related to aquatic plant control. These beneficial uses include recreational activities (e.g. swimming, boating, and fishing), public water supply, stock watering, irrigation and other water rights, fish and shellfish rearing and harvesting, habitat for spawning, wildlife habitat, navigation, and other designated uses. A short-term modification of water quality standards cannot be permitted if water quality degradation interferes with or becomes injurious to designated water uses that standards have been established to protect, or causes harm to the environment. In the discussion below, elements of the environment (under WAC 197-11-444) that are most likely to be significantly affected by each alternative are emphasized. Accordingly, each alternative is evaluated for potential short- and long-term effects to designated beneficial uses as well as more general effects to human health or the environment, including:

- The extent to which the alternative potentially affects the designated beneficial uses of a particular water body;
- Potential adverse environmental impacts, especially to ESA listed species, critical habitats and wetlands;
- The actual benefit that the treatment method brings to the receiving water environment;
- The need for mitigation and/or post-treatment monitoring;
- Potential adverse human health effects; and
- The degree to which any specific method or methods effectively controls a particular plant problem, such as those aquatic plants designated as noxious or invasive.

Because of the complexity and variability of water bodies, their beneficial uses and the types of management needed, distinct mitigation is applied on a case-by-case basis to the various management alternatives. If adverse environmental impacts cannot be avoided or mitigated in the use of an alternative, its use may be severely restricted, curtailed, or disallowed.

1.2 SEPA DEFINITIONS OF MITIGATION

Several types of environmental mitigation are defined by SEPA (WAC 197-11-768), listed below in order of preference:

1. Avoid the impact altogether by not taking a certain action or part of an action;
2. Minimize impacts by limiting the degree or magnitude of the action and its implementation by using appropriate “best management practices” or other approaches, or by taking affirmative steps to avoid or reduce impacts;
3. Rectify the impact by repairing, rehabilitating, or restoring the affected environment;
4. Reduce or eliminate the impact over time by preservation and maintenance operations during the life of an action; and
5. Compensate for the impact by replacing, enhancing, or providing substitute resources or environments.
6. Monitoring the impact and taking appropriate measures.

Different elements of each of the types of mitigation listed above may be incorporated into Ecology’s NPDES discharge permits to assure that the appropriate mitigation measures are implemented.

1.3 PROTECTION OF WETLANDS

Wetlands serve a variety of essential ecological functions in Washington State, and the overall goal of wetland protection is “no net loss” of wetland function and acreage. Where possible, improvement and enhancement of wetland integrity and quality is encouraged by Ecology, WDFW, and other agencies. Ecology has extensive requirements for protecting and maintaining wetlands in Washington State, such as those which meet the criteria of the Washington Natural Heritage Program (79.70 RCW), wetlands which served as critical habitat for ESA-listed species, rare wetlands with irreplaceable ecological function, and a variety of other criteria. Wetland quality must be maintained and protected unless it can be demonstrated that the impact is unavoidable and necessary. If such a determination is made, wetland losses and degradation are required to be offset through compensatory or other mitigation such as restoration, creation, wetland enhancement, or related approaches.

1.4 ESA CONSIDERATIONS FOR EACH ALTERNATIVE METHOD

The federal Endangered Species Act (ESA) requires that listed species be protected along with their critical habitats. Such listings may affect aquatic plant control projects throughout the State. Obtaining a permit from Ecology for the application of herbicides does not exempt an applicator from “take” liability, defined under ESA as to “harass, harm, pursue, hunt, shoot, wound, kill, trap, capture or collect, or to attempt to engage in such conduct” with respect to an ESA- listed species (16 U.S.C. Section 1532(19)). Ecology requests identification of rare plants and potential impacts to animals and waterbody uses, and the permit further clarifies that the permittee may not violate state or federal ESA provisions.

2.0 Alternative 1: Integrated Pest Management (IPM) (Preferred Alternative)

Alternative 1, Integrated Pest Management (IPM), is the preferred alternative. IPM is favored over other alternatives because it is the only alternative that considers each individual aquatic noxious weed problem or algal bloom independently and evaluates a range of chemical and non-chemical alternatives available to treat plants or algae. Some infestations or blooms may be amenable to alternative methods such as physical or mechanical removal (e.g. bottom barriers, cutters, rotovation, mechanical harvesting) or biological control methods, while other problems may be much more complex and require a stronger mode of treatment or control such as herbicides, algaecides, or phosphorus inactivation agents. IPM is especially important given the growing scientific and societal concerns, as well as continually improving environmental data, regarding the impacts of aquatic herbicides and their potential impacts to human health and the environment. Our enhanced understanding of the role of wetlands and critical habitats and the need to consider and control nutrient and sediment loading within a total watershed also improves our understanding of some of the non-target effects of herbicides and related chemical agents.

Use of IPM techniques is consistent with State guidelines for 1997 Integrated Pest Management (found at 17.15 RCW; <https://app.leg.wa.gov/rcw/default.aspx?cite=17.15&full=true>). Ecology recognizes that each management scenario is highly individualized and recommends planning when determining whether to use chemical and/or non-chemical aquatic plant control methods, in order to avoid deleterious ecological or environmental effects associated with management or treatment of aquatic plants and algae.

Consistent with Ecology's 1992 FSEIS, in which IPM is the preferred alternative, a Washington State statute known as the IPM "law" (RCW 17.15) states that it is the policy of Washington State and all agencies with pest control responsibilities to follow the principles of IPM. This statute provides definitions, discusses current IPM practices and procedures, and provides guidelines for IPM training and coordination. Developing an integrated aquatic plant management plan requires consideration of all available management and control methods. Under this alternative, each lake or surface water system is evaluated to determine the extent and underlying causes of aquatic plant and/or algae infestations or problems as well as the most effective and environmentally sound control strategy for correction and long-term management.

This approach incorporates the most effective combinations of biological, mechanical, physical, and chemical control methods available, which is intended to eliminate the need for further action against many nuisance aquatic plants (Bottrell 1979). This concept is based on the premise that no single control method will by itself be completely effective, and that a variety of biological, physical, mechanical, and/or chemical methods are integrated into a cohesive plan developed to provide long-term control of unwanted aquatic plants. If nuisance plant species cannot be adequately controlled using non-chemical methods at levels needed to support designated beneficial uses, the addition of chemical control methods (e.g. herbicides) to the management strategy may become necessary in targeting noxious or nuisance species. This Supplemental EIS evaluates both new and proposed as well as currently registered herbicides and chemical agents (Alternative 3) as important additional tools for aquatic plant management. It is well

understood that when herbicides, algacides, and other chemical agents are added to a management strategy arsenal, the selection of the herbicide, label-specified dosages, seasonal considerations, treatment times, and numerous other factors must be carefully considered to avoid or eliminate environmental or human health impacts.

The IPM approach is most effective not only for one-season treatments but rather for multi-year (often three to five year) aquatic plant treatment plans (Gibbons *et al.* 1994, Bottrell 1979). Proposed integrated management planning should be set up so that affected communities, stakeholders, and interest groups can offer comments on proposed management strategies where potential uses or interests in a given water body or watershed may conflict. Plans would help lake managers evaluate how plants that provide fisheries or wildlife habitat should be controlled or eradicated to improve aesthetics or recreational use of a water body.

The *Citizen's Manual for Developing Integrated Aquatic Vegetation Management Plans* (IAVMP Manual, Gibbons *et al.* 1994) provides detailed guidance for developing integrating management plans for watersheds, lakes, or other water bodies. Components that need to be addressed in formulating such an integrated plan include:

- identification of the target nuisance or noxious aquatic plant or algal species;
- establishing management objectives in supporting designated beneficial uses;
- preserving recreational and restoration goals for the watershed or water body;
- identifying candidate (mechanical and physical, chemical, biological) control methods;
- evaluating impacts and providing mitigation measures; and
- incorporating public involvement and education.

2.1 IMPACTS AND MITIGATION

The overall ecological, human health, and ecosystem-level impacts of aquatic plant control methods selected for use, including the actual impact of removing targeted plant species, must be assessed as part of the overall IPM plan and evaluation. Most alternatives have the potential to cause some adverse environmental impacts. Even subtle ecological manipulations may affect the entire ecosystem, possibly aggravating one problem in the attempt to resolve another. Integrated pest management manipulates ecosystems to control nuisance or noxious plant species while avoiding and minimizing disruptions of the larger watershed or ecosystem. Thus, all proposed management techniques, both individually and in combination, must be carefully considered in an ecological context both before and after use of aquatic plant controls. This may require development of a monitoring strategy to ensure that the plan is effective and considers impacts of various control methods at selected sites on both target and non-target species. The IPM plan would include applicable mitigation measures. Such measures should be incorporated in the final integrated management plan, and both monitoring requirements and mitigation measures should be incorporated, as appropriate, into the final action plan. Mitigation measures proposed on an individual basis throughout this SEIS document for chemical, biological, and physical/mechanical control methods should be incorporated into the overall mitigation strategy on a case-specific basis and are discussed further in each section below.

2.2 REFERENCES

- Bottrell, D. 1979. Integrated Pest Management. Council on Environmental Quality. #041-011-00049-1, US Government Printing Office, Washington, D.C. 120 p. [1]
- WA State Department of Ecology (Ecology). 2000. Ecology Water Quality Program. April 2000. Washington's Water Quality Management Plan to Control Nonpoint Source Pollution, Publication No. 9926. <http://www.wa.gov/ecology/biblio/9926.html>. [3]
- Ecology 2000. Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides. July 2000. Ecology Publication No. 00-10-040. [3]
- Ecology 2000. Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides: Appendix E 1992 SEIS Appendices: Grass Carp Supplement, Copper Compounds, Fluridone Human Health Risk Assessment, Fluridone Aquatic Risk Assessment, Glyphosate Risk Assessment, 1992 SEIS Responsiveness Summary. <https://fortress.wa.gov/ecy/publications/publications/0010040.pdf>. [3]
- Gibbons, M., H. Gibbons, Jr., M. Sytsma. 1994. A Citizen's Manual for Developing Integrated Aquatic Vegetation Management Plans, WATER Environmental Services, Inc. Ecology Publication No. 93-93. <https://fortress.wa.gov/ecy/publications/documents/93093.pdf>. [3]

3.0 Alternative 2: No Action

3.1 DESCRIPTION OF THE ALTERNATIVE

The No Action alternative means that Ecology would continue to issue water quality permit coverages and grant funds for aquatic plant control as currently practiced. Ecology would continue to protect designated beneficial uses to the extent possible, as well as to continue funding aquatic plant management activities through the Aquatic Weed Management Fund. There are significant limitations to continuing this approach. For example, if new or “improved” aquatic herbicides or other chemical agents are not assessed or subsequently permitted, opportunities to incorporate new, improved, narrow-spectrum, selective herbicide or other formulations for aquatic plant control that may be less harmful to human health and the environment, as well as potentially less costly, will not be available within Washington State. These limitations could result in more uncontrolled, invasive, noxious plant and algal infestations in Washington State waters.

Moreover, the Washington Legislature directed Ecology to expand certain chemical application sections of the 1992 SEIS to make it more responsive for the application of newer, improved, commercially available herbicides, and to evaluate their use with the most recent research available (Engrossed Substitute Senate Bill 5424, effective May 1999).

3.2 IMPACTS AND MITIGATION

If Ecology were to simply continue current practices by selecting the No Action alternative, it could find itself at odds with a legislative directive. If current practices are to be maintained, integrated plant management would not be able to incorporate newer, improved chemical and non-chemical methods that can more effectively control target plant species while avoiding or minimizing non-target effects. This could result in less efficient, effective, and/or environmentally unsound control practices, when more improved practices could support both effective control and reduced unintended environmental or human health impacts. A key principle of integrated pest management is that a variety of potentially unrelated treatment methods are approved and available, which is more effective at preventing target plant species from developing resilience or tolerance to repeated use of specific treatments.

4.0 Alternative 3: Use of Herbicides, Algaecides and Chemical Agents

4.1 DESCRIPTION OF THE ALTERNATIVE

As discussed earlier in this SEIS, herbicides, algaecides, and chemical agents such as phosphorus deactivating agents may be very effective in helping to control or eliminate nuisance or noxious plant species, and are frequently incorporated into IPM-oriented treatment plans. The emphasis in using such chemical agents is to identify those herbicides and chemical agents which are effective at lower doses than traditional herbicides or other chemicals, or are more narrow-spectrum (i.e. they are more selective than traditional herbicides in controlling target species while causing fewer non-target effects), or are less persistent or bioaccumulative than traditional agents, or which have other desirable characteristics typical of “later generation” herbicides or algaecides.

To that end, eight proposed herbicides and chemical agents were subjected to a detailed impact analysis and technical evaluation under Alternative 3. These chemical agents are: 1) aminopyralid; 2) Procellacor™; 3) topramezone; 4) peroxyacetic acid/hydrogen peroxide; 5) aluminum sulfate/alum; 6) calcium hydroxide/oxide; 7) iron salts; and 8) lanthanum clay (Phoslock).

Toxicological effects to human and non-human receptors is a key component of this SEPA review. A common practice within toxicology is the principal of species surrogacy, which allows for evaluation of species for which actual testing has not been performed. This practice was widely used as part of this toxicological evaluation. For example, human subjects are not normally used to evaluate carcinogenicity of a given compound, so surrogate species (e.g. rats, mice, etc.) would be used instead to complete the evaluation.

4.1.1 Methodology for evaluating the eight proposed new herbicides and chemical agents

For the review and impact evaluation of the eight new herbicides, algaecides, and other chemical agents listed above, which are proposed for use in controlling noxious aquatic plant and algal species, a methodology was developed for the systematic impact evaluation of each chemical which is consistent with EPA Office of Pesticide Programs (OPP) ecological and human health risk assessment guidelines:

- Ecological: <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/overview-risk-assessment-pesticide-program#ecological>.
- Human health: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/overview-risk-assessment-pesticide-program#human_health.

First, a general description of the herbicide or chemical agent and a summary of its registration status with EPA and other agencies was provided. Then a more detailed discussion of its chemical (including efficacy-related) and environmental fate properties was provided, along with any relevant field investigations or monitoring studies which could illustrate its effectiveness in the field. This included an analysis of mobility and transport potential for each herbicide or chemical agent. Following this discussion, an overview of the toxicological properties was provided, including a review and evaluation of human, mammalian, and ecotoxicological characteristics, including acute and chronic effects to fish, birds, invertebrates, other biota, including higher plants and algal species. This included a discussion of effects to phytoplankton and zooplankton species, and these biota form an important foundational basis

for the aquatic food web. This toxicological evaluation considered both full life cycle and food web impacts to non-target species, and where available, information on one-time vs. repeated applications of the chemical agent or herbicide, as well as impacts on numbers, diversity and habitat of species of plants and animals. In some cases, where outdoor field trials such as mesocosm or microcosm studies were available, these studies were included in the overall impact evaluation of these materials. No quantitative risk assessment was actually performed, as the available literature was adequate to assess key exposure scenarios to both human and ecological receptors, including aquatic and sediment exposures, terrestrial soils, drinking water or groundwater, and off-site exposures potentially occurring with aerial drift surface water runoff, or other exposure pathways.

Following this detailed evaluation of technical information and environmental laboratory and field data (where available), an analysis and discussion on human health and environmental impacts was provided, including impacts to human health, ecological risk or hazard, and potential effects to the earth (soils and sediments, including agriculture), water (surface water, drinking water, groundwater), plant (including non-target species), and other potential environmental exposure pathways as appropriate. Based on these potential impacts, each evaluation concluded with a discussion on label restrictions and proposed chemical-specific mitigation measures relating to swimming or recreational uses, required mitigation for addressing effects to habitats and non-target plants, endangered plant and animal species, and fisheries and fish consumption. Finally, post-treatment monitoring requirements and recommendations were provided for each of the chemical agents under evaluation. References cited for each evaluation were provided at the end of each individual section.

This evaluation and review provided special consideration to salmonid and other listed species under the Endangered Species Act, as well as to their designated critical habitats. Each such species is comprised of many stocks and populations that vary from one another in their genetic makeup, life history, and other characteristics. Native salmonids in Washington State that have been listed or are proposed for listing include Chinook salmon, Coho salmon, chum, sockeye, steelhead (anadromous form of rainbow trout), coastal cutthroat trout, and bull trout.

4.2 EVALUATION OF AMINOPYRALID

4.2.1 Registration Status

Aminopyralid-containing herbicides, including Milestone®, Capstone®, and Opensight®, are registered for use on rights-of-way, industrial sites, non-irrigation ditch banks, and a variety of natural areas (e.g. wildlife management areas, campgrounds), as well as grazed areas in and around these sites (Dow, 2016). Aminopyralid herbicides are labeled for use on pastures around industrial sites without grazing restriction. There are no current in-water registrations for aminopyralid nationally, and current registrations only address applications to the water body's edge, where overspray, drift, or surface water runoff could potentially cause effects to the adjoining surface water body. Aminopyralid herbicides provide systemic control of a variety of target plant species with reasonable tolerance of grasses and other non-target species. Aminopyralid is currently classified by the EPA as a Reduced Risk herbicide due to low toxicity to birds, fish, mammals, and aquatic invertebrates, as well as a generally favorable environmental profile. It has been shown to be effective and is approved for controlling broadleaf vegetation. It is used to control weed, vine and brush target species such as tropical soda apple, musk thistle, Canada thistle, spotted knapweed, diffuse knapweed, yellow star thistle and Russian knapweed.

The EPA registration for aminopyralid specifies application at 7 fl oz aminopyralid acid equivalents per acre per year on rangeland, grassland and non-crop land areas (lower rate of 0.57 fl oz/ac/yr for wheat crop areas) (EPA OPPTS, 2005). There are no in-water aquatic uses anywhere in the United States (US), including Washington State, and none are currently proposed. An aquatic registration would expand the utility of aminopyralid-containing herbicides by allowing control of invasive or other weedy plant species along shorelines or banks of water bodies, but the new label would not include control of submersed aquatic plants. It would, however, expand uses to sites currently covered under Ecology's NPDES permit requirements.

Field research trials in ponds and flowing water systems have been conducted to collect data to support the potential addition of aquatic uses to aminopyralid product labels (see discussion below). This research has generally been designed to establish food tolerances for fish and shellfish, and to define herbicide dissipation in water and sediment over time. According to label specifications, aminopyralid cannot be applied around or directly to wetlands, drainage areas, lakes, ponds, shorelines, rivers and other sensitive aquatic areas. Carefully applied buffer zones around aquatic areas and water bodies must be implemented to avoid off-site transport such as drift, runoff, or overspray.

Aminopyralid was suspended from use in the UK from 2008-2009 due to problems associated with the use of aminopyralid-contaminated animal manure. Crops were reportedly damaged by aminopyralid, causing malformation and discoloration. In 2009, use of aminopyralid was reinstated in the UK after the registrant (Dow AgroSciences) initiated an aminopyralid stewardship program on how to address contaminated animal manures (discussed further below). This highlights the importance of assuring that aminopyralid or other persistent herbicides or pesticides would not be allowed to cause non-target exposures via manure or other pathways to susceptible plant or animal species.

4.2.2 Description

Milestone® is the primary trade name for aminopyralid herbicide products sold in the US. There are several trade names in the UK, including Banish and Forefront. Aminopyralid is a pyridine carboxylic acid active ingredient that provides systemic control of target plant species with favorable tolerance by non-target grasses and other species.

4.2.2.1 Environmental Characteristics: Product Use and Chemistry

The pure state of the active ingredient aminopyralid (4-amino, 3,6-dichloropyridine-2-carboxylic acid) is an off-white odorless powder which is classified as a pyridine carboxylic acid herbicide. It is quite water soluble (2.48 g/L at 18°C) when compared to many other herbicides. It decomposes upon melting, and has a vapor pressure at 20 degrees Celsius (°C) of about 7.0×10^{-7} millimeters of mercury (mm Hg), which together with a low Henry's Law constant suggests that this is not a volatile material. The K_{ow} at 19°C is calculated to be 0.2, varying slightly with pH. This value strongly suggests that this material has no propensity to bioaccumulate into organic matrices such as biological tissue. The commercial herbicide Milestone® contains two pounds of the TGA1 of aminopyralid technical acid per gallon of solution (Dow, 2013, 2008). In surface soil, EPA has reported a half-life of 103 days, in topsoil a half-life of 72 days, which is somewhat long-lived, and in water a rapid half-life of 0.6 days has been reported, based on photolysis as the key degradation pathway (EPA OPPTS, 2005).

Aerobic microbial degradation is the primary route of breakdown of aminopyralid in soils. Field results show the rate of degradation as an average half-life of 34.5 days for eight North American sites and 25 days for four European sites (Dow, 2016). Laboratory experiments showed an average soil-water partition coefficient (K_{oc}) of 108 L/kg, suggesting weak sorption and some potential for mobility in soils, but field experiments indicated only limited mobility in soils. No degradation metabolites of concern were produced in any of these studies.

Field studies (cited in EPA, 2005) showed that aminopyralid had a very rapid half-life in water (0.6 d due to photolysis) but was stable to direct hydrolysis and in anaerobic sediment-water systems. In aerobic sediment-water systems, degradation proceeded slowly, with observed total system half-lives of 462 to 990 days. The degradation resulted in the formation of non-extractable residues and no other major products. Under aerobic conditions, degradation of aminopyralid in five different soils resulted in the production of no significant degradation products. Half-lives ranged from 31.5 to 533.2 days, and yielded a half-life of 103.5 days, which was subsequently used by EPA for its risk assessment. Two field dissipation studies (performed in California and Mississippi) indicated that aminopyralid is likely to be non-persistent and relatively immobile in the field. Half-lives of 32 and 20 days were determined, with minimal leaching below the 15 to 30 cm horizon depth. The nature of aminopyralid metabolism and residue in both plants and animals is well understood based on extensive laboratory testing by Dow AgroSciences (summarized in Dow 2013 and Miller 2005). For example, based on a residue study of a lactating goat, the tolerance expression in milk, meat and meat-byproducts was the unchanged, unmetabolized parent compound, aminopyralid.

4.2.2.2 Environmental Mobility and Transport

Due to its very short half-life in water and low K_{ow} , aminopyralid is not expected to bioconcentrate in fish or other biological tissue. According to water flow and aquatic life studies conducted by Dow

AgroSciences (e.g. Dow, 2013; Peterson *et al.*, 2013), aminopyralid dissipates through flowing water ecosystems in 120 days or less leaving no residue in the water, sediment or aquatic species living tissues (see discussion below). Due to the relatively low toxicity of the chemical, also summarized below, and its relatively short half-lives in water, aminopyralid is not expected to cause or contribute to groundwater contamination or other leaching, is not expected to be mobile in groundwater, and is generally not persistent within the aquatic environment (Dow, 2013; EPA, 2005). Its residual action is intended to alleviate the need for repeat applications, resulting in a reduction in the amount of herbicide required for weed control. Aminopyralid has been determined to be nearly non-toxic to animals at the registered application rates, compared to alternative herbicides, as it is less likely to impact both terrestrial and aquatic species.

Due to its unique mode of action, EPA has not designated a common mechanism of toxicity finding for aminopyralid with any other herbicides or pesticides, unlike other pesticides for which EPA has followed a cumulative risk approach based on a common mechanism of toxicity. Moreover, aminopyralid does not appear to form toxic metabolites as part of the degradation process. EPA's efforts to determine which chemicals have a common mechanism of toxicity to evaluate the cumulative effects of such chemicals are described by the policy developed by EPA's Office of Pesticides Programs concerning common mechanisms and procedures for cumulative effects determination (<http://www.epa.gov/pesticides/cumulative>).

4.2.2.3 Field Surveys and Investigations

Several field studies were conducted as part of research trials in support of registration submissions to EPA. Peterson *et al.* (2013) reported on field studies conducted in multiple states on ponds ranging in size, using Milestone® herbicide at 7 fl oz/ac applied on pond banks, with intentional overspray into adjacent water bodies. Water sediment samples were collected prior to application as well as periodically following the application.

Dissipation of aminopyralid was calculated from residues in water and sediment samples. Caged organisms included catfish, bluegill sunfish, and freshwater clams collected prior to and following application to evaluate for potential persistence and bioconcentration/bioaccumulation. Data was collected to determine concentrations of aminopyralid in tissues, and whether these concentrations were present at levels that could harm people or animals feeding on these contaminated prey organisms.

Results of this pond study (Peterson *et al.*, 2013) indicated that dissipation of aminopyralid residues occurred with more than 99% of the applied herbicide dissipating within 120 days following treatment. No residues were found to accumulate in water, sediment, or biological tissue. Results of a 120-day flowing water dissipation study conducted (cited by Peterson *et al.*, 2013) in both Oregon and Florida indicated that dilution was a major route of dissipation at the Oregon site and dissipation occurred to non-quantifiable levels in less than 2 hours following application. In Florida, degradation was the major route of dissipation. Dissipation to non-quantifiable levels in both locations was similar.

These studies concluded that registration will support use of aminopyralid products for invasive or other weedy plant control on shorelines, including stream or river banks, with minimal impacts to the aquatic environment. As noted above, no in-water registrations for this compound have been proposed.

Assuming registration approval, labels are not expected to include restrictions on water use either recreational or for livestock following application. Similarly, at the time of writing, the proposed labeled use will not include the inside banks of irrigation ditches or for submersed aquatic plant control.

4.2.2.4 Bioconcentration and Bioaccumulation

As noted above, the K_{ow} , a frequently used metric for assessing bioconcentration and bioaccumulation potential, is calculated to be only 0.2, which strongly suggests that aminopyralid has little or no propensity to bioaccumulate into organic matrices such as biological tissue. The pond studies cited above indicated that rapid dissipation of aminopyralid residues occurred with more than 99% of the applied herbicide dissipating within 120 days following treatment, and that no residues were found to accumulate in water, sediment, or biological tissue.

4.2.2.5 Toxicological Profile

EPA (EPA OPPTS, 2005) has classified aminopyralid as a Reduced Risk herbicide that is deemed to be safer at applicable levels than most other alternatives. EPA has classified aminopyralid TGAi as a toxic chemical (signifying Danger) due to acute eye irritation caused by the raw chemical. Milestone® as an end-use product is classified by EPA as a chemical requiring “caution” for acute oral and dermal toxicity, with reportedly no measurable adverse effects on neurotoxicity, mutagenicity, and has been classified as “not likely” to be a carcinogen (EPA OPPTS, 2005).

Aminopyralid technical (TGAi) is known to cause acute eye irritation and long term eye damage. Upon contact, the eye should be thoroughly flushed and visiting a physician is recommended (EPA OPPTS, 2005; Dow, 2008). Therefore, aminopyralid technical should be avoided in direct use with aquatic environments because of a material increase of risk to the human (and presumably mammalian or other wildlife) eye caused by swimming into the treated area. Milestone® as a formulated end-use product has been shown not to cause the same acute eye irritation due to much lower concentrations of the TGAi, and therefore would be much safer to apply near aquatic environments with less hazard or risk to eyes of people, mammals, or other wildlife.

Mammalian and Human Toxicity

Aminopyralid is expected to cause very few short- or long-term ecological risks when associated with proper label-specified use of the product Milestone®. As discussed below, studies have shown aminopyralid to be “practically non-toxic” for small mammals, birds, predators, fish, bees, earthworms and other invertebrates. According to lethal dose studies, most animal species that would come into contact with aminopyralid in a treated area (rats, moles, birds, earthworms etc.) would need to come into contact with 5,000-40,000 times the normal dose to reach that species’ LD₅₀ value, defined as the concentration at which 50% of test organisms will experience mortality. Aminopyralid is not expected to bioconcentrate, bioaccumulate, contaminate groundwater or have persistent negative environmental effects (WSDOT, 2006; EPA, 2005).

Regarding potential occupational exposures, based on labeled uses, the occupational exposure is expected to be short- or intermediate-term with no long-term exposure expected. The application of Milestone® to control weeds in wheat, rangeland, pastures, non-cropland, and natural recreation areas is recommended by using broadcast treatment with ground and aerial equipment for wheat, and with

hand-spray and spot treatments for all other uses. Available toxicological information suggests that dermal exposures do not produce any adverse systemic effects; therefore, EPA did not include dermal exposures into the estimation of occupational risk to workers (EPA OPPTS, 2005). Short- and intermediate-term oral and inhalation exposures are regulated based on observed effects seen in a developmental rabbit toxicity study, for which a No Observable Apparent Effect Level (NOAEL) of 104 mg/kg/day was determined (summarized below). The highest potential occupational exposure was estimated by EPA to be mixer-loaders working on aerial applications of 0.11 lb /A, for up to 1,200 ac applied per day.

EPA conducted a risk assessment for aminopyralid, as summarized by Miller (EPA OPPTS, 2005). This is required by the 1996 Food Quality Protection Act (FQPA), wherein EPA assesses the potential for concurrent exposure to aminopyralid via oral, dermal and inhalation routes of exposure. This aggregate exposure considers all potential non-occupational exposure pathways, including residues in food, drinking water and residential exposure from indoor/outdoor non-crop uses. Based on available toxicological information (summarized below), dermal exposures do not result in any adverse systemic effect; therefore, dermal exposures were not included into the estimation of aggregate risk. Short- and intermediate-term oral and inhalation exposures are regulated based on observed effects from the developmental rabbit toxicity study, also summarized below. Non-crop uses did not address any indoor use; therefore, both handler and post-application inhalation exposures are expected to be negligible.

Based on aminopyralid's low acute toxicity, a reference dose (RfD), a toxicity-based benchmark used to estimate risk or hazard from non-carcinogenic toxicity, was not required, but a chronic RfD for aminopyralid was calculated to be 0.5 mg/kg/day, and was used to calculate potential human health risks. This value is based on the NOAEL of 50 mg/kg/day in the rat combined chronic toxicity/carcinogenicity study with a 100-fold uncertainty factor to account for interspecies extrapolation and intraspecies variability. EPA conducted a chronic exposure analysis using the tolerance levels for wheat grain and meat commodities, and conservatively assuming 100% of crops were treated with aminopyralid. Based on results of this risk assessment, the estimated exposures to US population and relevant sensitive sub-population groups were all at least 3 orders of magnitude below the RfD.

The EPA exposure and aggregate (multi-pathway) risk assessment involved development of estimated environmental concentrations for potential chronic exposures to humans in surface water and groundwater. Results showed that the chronic estimated water concentrations will be protective of potential exposures via surface or ground water sources of drinking water. These aminopyralid concentrations were incorporated into the margin of error for exposure calculations, and EPA concluded that there is reasonable certainty that no harm to human health will result from aggregate exposures, including drinking water. Post-application exposure via inhalation is not expected to occur. Potential human exposures considered include dietary exposure to food and drinking water, short-term incidental oral exposure, and possible short-term oral exposure of children to treated campgrounds.

General Ecotoxicity Profile

"Practically non-toxic" is EPA's least toxic category, and aminopyralid was classified accordingly by EPA for tests to birds, fish, honey bees, earthworms and aquatic invertebrates. Among herbicides, aminopyralid has very low toxicity when used in the label-specified concentrations for non-target

species, and as noted above, aminopyralid has shown a very low toxicity profile for humans. Following is a discussion of toxicity to specific test species. While aminopyralid is slightly toxic to oysters, algae, and aquatic vascular plants, anticipated environmental concentrations resulting from the use of aminopyralid herbicides for weed control is expected to be orders of magnitude below any levels of concern established by EPA for these species (see more specific discussions for ecotoxicology below). Dow (2016) reported on basic acute mammalian toxicity testing conducted for aminopyralid as the TGA1. Three acute tests for rats using the oral, dermal, and inhalation pathways, respectively, show LD₅₀ values of greater than 5,000 mg/kg (oral and dermal) and greater than 5.5 mg/L (inhalation). Dermal and eye irritation studies were conducted for rabbits, and results showed a negative result for dermal irritation and “irritating” for rabbit eye. A skin sensitization test for guinea pigs was conducted and results showed no sensitization for this test.

Similarly, Dow (2016) reported on chronic mammalian toxicity testing conducted for aminopyralid. A 2-year chronic feeding study of rats showed that aminopyralid was not carcinogenic, and reported an NOAEL of 50 mg/kg-day (higher for females). A teratogenicity (birth defects) study on rats showed that aminopyralid was not teratogenic, and reported NOAEL values for both maternal and fetal development of 1,000 mg/kg-day. A reproductive study on rats was also conducted, evaluating fertility, delivery and number of offspring for second generations following exposure to aminopyralid at the highest doses tested. Results showed that aminopyralid did not cause reproductive effects, with reported NOAEL values for both parental and reproductive endpoints of 1,000 mg/kg-day.

Two chronic dog studies were conducted, one over 90-days and another over 1-year (summarized in Miller 2005 and Dow 2013). Data from the 90-day toxicity study produced a NOAEL of 282 mg/kg-day for males and 232 mg/kg-day for females based on slight diffuse hyperplasia and hypertrophy of the mucosal epithelium of the stomach. The 1-year chronic toxicity study produced a NOAEL of 99 mg/kg/day for males and 93 mg/kg/day for females based on thickening of the stomach, slight lymphoid hyperplasia of the gastric mucosa, and slight chronic mucosal inflammation.

Acute and chronic neurotoxicity in rats was evaluated by Dow (2013). No evidence of neurotoxicity or neurological effects was reported, with a reported NOAEL value of 1,000 mg/kg-day. Three separate tests for mutagenicity (Ames testing (in vitro), Chinese hamster ovary cell/hypoxanthine-guanine phosphoribosyl-transferase (CHO/HGPRT) (in vivo), and mouse micronucleus (in vivo) were conducted. These tests included chromosome aberrations, gene mutations, and deoxyribonucleic acid (DNA) repair and damage. Aminopyralid was negative except for in vitro chromosome aberration assay using rat lymphocytes, which occurred only at cytotoxic concentrations and thus should not be a concern. Other than the one positive response, these mutagenicity tests reported uniformly negative results for aminopyralid.

Regarding metabolism and clearance, a metabolism study using rats indicated that aminopyralid was excreted unchanged, suggesting little or no uptake or metabolism. A separate cattle feeding study showed aminopyralid cleared from the digestive system within three days. Repeated administration of aminopyralid to cattle did not indicate any tendency to bioconcentrate or bioaccumulate in tissue (EPA, 2005; WSDOT, 2006; Toxnet, 2012).

Fish Ecotoxicity

Several acute fish toxicity tests were conducted for aminopyralid as the TGAi, as reported by Dow (2013) and EPA (EPA OPPTS, 2005). Tests were conducted for rainbow trout and bluegill producing 96-hour LC₅₀ values of greater than 100 mg/L for both species, and a 96-hour LC₅₀ value of 120 mg/L for sheepshead minnow. Fathead minnow (*P. promelas*) testing was also conducted, and both a No Observed Effect Concentration (NOEC) and a Low Observed Effect Concentration (LOEC) were determined (1.36 mg/L and 2.44 mg/L, respectively). In addition to these fish species, a 96-hour LC₅₀ of greater than 95.2 mg/L was determined for the Northern leopard frog (an amphibian). Each of these values are indicative of very low toxicity for these test species.

Avian Toxicity

Dow (2016) reported avian toxicity testing conducted for aminopyralid as the TGAi. Tests were conducted for birds using the oral and dietary pathways, and reported LD₅₀ values were 2,250 mg/kg for bobwhite quail (oral administration), greater than 5,625 mg/kg (dietary administration) for both bobwhite quail and mallard duck. In addition, an LOEC value of 640 mg/kg was determined for bobwhite quail, and a NOEC value of 2,623 mg/kg for mallard duck. Each of these values is uniformly indicative of very low toxicity to these two avian species.

Invertebrate Ecotoxicity

Both acute and chronic toxicity tests were conducted for several species of aquatic invertebrates, using aminopyralid as the TGAi. These tests were conducted for common, widely accepted test organisms using commonly measured responses other than lethality, such as growth or reproductive viability. Three acute tests were performed; for the daphnid *D. magna* (48-hour EC₅₀ was reported to be greater than 100 mg/L with a NOEC of greater 102 mg/L, which was the highest concentration tested), and for a mysid shrimp a 96-hour EC₅₀ was reported as greater than 100 mg/L as well. Both of these values are regarded as very slightly toxic. The eastern oyster indicated a 48-hour EC₅₀ value of greater than 89 mg/L, which is regarded as slightly acutely toxic. A chronic growth and reproduction test was done for *D. magna*, which produced a NOEC of 100 mg/L, and the midge *Chironomus* was tested for chronic toxicity, and results showed a NOEC value of 130 mg/L. Both of these values are indicative of very slight chronic toxicity associated with the TGAi aminopyralid.

Two terrestrial invertebrates, the honey bee and earthworm, were also tested for acute toxicity. Results indicated a 48-hour LD₅₀ of 100 micrograms (µg) per bee for acute contact, and a 48-hour LD₅₀ of greater than 120 µg/bee for acute oral administration. A 14-day LC₅₀ of greater than 1,000 mg/kg soil was determined for the earthworm. All of these values are indicative of very low toxicity to invertebrates.

Data Gaps

EPA (EPA OPPTS, 2005) reported the following data gaps with the registrant-submitted data, and requested the following:

- Uncertainties were noted in the determinations of soil half-life and chronic effects on birds;
- Completed enforcement method of analysis to show that analytical method differentiates between aminopyralid, picloram and clopyralid;

- The analytical method needs to be validated by EPA's specialty laboratory;
- Storage stability data should be submitted for grass forage and hay reflecting up to approximately 15 months of frozen storage;
- A repeated aerobic soil metabolism study should be completed;
- A repeated avian reproduction study using bobwhite quail should be submitted;
- A repeated Tier II aquatic plant growth study using blue-green algae should be submitted.

4.2.3 Environmental and Human Health Impacts

4.2.3.1 Earth

Soil and Sediments

Under aerobic soil conditions, degradation of aminopyralid in five different soils resulted in the production of non-extractable residues. Half-lives ranged from 31.5 to 533.2 days in 5 soils. For risk assessment purposes, EPA used a half-life of 103.5 days, reflecting moderately slow degradation. Aminopyralid is only weakly sorbed to soil, with a laboratory Freundlich adsorption isotherm study with eight US and European soils yielding very low dissociation constants for soils. As noted above, adsorption K_{oc} values were reflective of very weak sorption to soils. Two field dissipation studies (also summarized above) from California and Mississippi indicated that aminopyralid is likely to be relatively non-persistent and relatively immobile in the field. Half-lives of 32 and 20 days were determined, with minimal leaching below the 15 to 30 cm soil depth.

Agriculture

No impacts on recreational or livestock use of water following application are expected to be required. Labeled use will not include the inside banks of irrigation ditches or submersed aquatic plant control. Precautions and restrictions on use of water treated with Milestone® for irrigation will likely be included on the new label, although a timeframe for this new label is not yet known. There is a prohibition on aminopyralid-treated hay to be exported from the US. Also, when treating areas with aminopyralid herbicides in and around roadside or utility rights-of-way that could be grazed or planted to forage, label precautions would apply regarding harvesting hay, using manure from animals grazing on treated areas, or rotating treated areas to sensitive crops.

4.2.3.2 Water

Surface Water and Runoff

In water, the primary route of degradation of aminopyralid is photolysis, with half-lives under standard conditions reported to be 0.6 day, indicating rapid degradation in surface water. It is stable to direct hydrolysis and in anaerobic sediment-water systems, with total system half-lives of 462 to 990 days. However, as predicted by the low soil-water K_{oc} , partitioning into sediment is minor and aminopyralid is largely soluble and available for photodegradation (photolysis). This degradation resulted in the formation of non-extractable residues with no other major breakdown products.

The discussion on basic chemical properties and environmental fate suggests that due to aminopyralid's low vapor pressure (about 7.0×10^{-7} mm Hg) and low Henry's Law constant, this is not a volatile material.

As with any aerially sprayed herbicide, susceptible non-target plants could be injured via physical spray drift, and spray application practices should minimize drift to desirable and vulnerable plant species. In addition, aminopyralid is very soluble and only weakly binds to soil, so surface water runoff is possible with this material. These characteristics are included on the product label.

Groundwater and Public Water Supplies

Groundwater contamination potential for aminopyralid is considered to be low due to its low use rates, moderate field degradation rates, and limited mobility as observed in field studies. This information was used and verified by Dow AgroSciences in conducting simulations for potential groundwater contamination, which indicated minimal leaching potential below 15 to 30 cm, as discussed in Section 4.2.3.1.

4.2.3.3 Wetlands

Impacts of aminopyralid could occur to non-target sensitive plant species in wetlands, but impacts to fish, invertebrates, birds, and mammalian species are expected to be minimal due to low acute and chronic toxicity profiles. Bioconcentration or bioaccumulation within the wetland is not likely to occur.

4.2.3.4 Plants

Higher Plants (Including Crops) and Algae

Aminopyralid is toxic to (efficacious for) the treatment broadleaf (dicot) plants including all target plants identified on the product label. As required by EPA and other agencies, acute phytotoxicity testing was conducted on a number of non-target aquatic plant and algae species using a quantifiable physiological response such as growth (Peterson *et al.*, 2013). Aminopyralid was tested with freshwater green algae (72-hour half maximal effective concentration (EC₅₀) of 30 mg/L, No Effect Concentration (NOEC) of 23 mg/L) and cyanobacteria (120-hour EC₅₀ of 27 mg/L), as well as diatoms (96-hour EC₅₀ of 14 mg/L, NOEC of 6 mg/L) and the vascular plant duckweed (*L. gibba*), 14-day EC₅₀ of 88 mg/L, NOEC of 44 mg/L). All of these results would be classified as slightly toxic.

Aminopyralid has consistently shown a relatively high level of tolerance on a wide range of grasses, with more than 20 different grass species evaluated in field trials from 1999 to 2004 (Dow, 2016).

Aminopyralid was applied at rates up to two times the maximum labeled use rate and few impacts were recorded to these grassy species.

4.2.3.5 Habitat

Based on available toxicity information, aminopyralid is not acutely or chronically toxic to most animal species, but can be somewhat toxic to non-target plant species, which could affect critical habitat. Also, aminopyralid is relatively persistent in soils and sediments, which is part of critical habitat, and therefore this potential impact should be considered when registering or applying aminopyralid herbicides to areas where critical aquatic habitat is present.

4.2.4 Mitigation

Dow AgroSciences administers a stewardship program teaching farmers how to properly use animal manure contaminated with aminopyralid. Aminopyralid passes through animals unchanged, as

discussed above, but the manure containing aminopyralid herbicide can damage the growth of crops such as potatoes, tomatoes, lettuce and beans. Therefore, this stewardship program is intended to keep the manure in a life cycle where it will affect target and non-sensitive crop species such as wheat and corn, but not affect the sensitive non-target crops (Dow, 2013).

In regular application, aminopyralid requires no special mitigation in non-crop land areas. In the event of a spill either large or small, all normal spill containment and clean procedures would apply. However, aminopyralid requires no special cleanup procedure or follow up mitigation measures.

4.2.4.1 Use Restrictions

Following registration approval, labels are not expected to include restrictions on recreational or livestock use of water following application. Similarly, labeled use will not include the inside banks of irrigation ditches or for submersed aquatic plant control. There is currently a prohibition on aminopyralid-treated hay to be exported from the US.

As discussed above, Milestone® as an end-use product is typically non-toxic to non-target species. Therefore, it does not warrant special protocols, restrictions, or other mitigation measures to prevent non-target exposures, in addition to those standard restrictions such as recommending that no berries or other edible vegetation should be eaten from the treated area.

The discussion above on field research trials conducted in ponds and flowing water systems lends support to the potential addition of aquatic uses of aminopyralid products. However, at the time of writing the current FIFRA label(s) for aminopyralid states that it should not be applied around or directly to wetlands, drainage areas, lakes, ponds, shorelines, rivers and other sensitive aquatic areas. Carefully applied buffer zones around aquatic areas and water bodies must currently be practiced to avoid off-site transport such as drift or overspray.

4.2.4.2 Swimming and Skiing

Due to the potential for eye irritation, it may be prudent to limit swimming, skiing, or other direct contact water uses during or immediately following aminopyralid application near the water's edge. However, it is important to note that studies have largely been performed with the aminopyralid TGA1 rather than the formulated end-use product, and concentrations occurring in surface waters would not be expected to approach thresholds that could cause eye or skin irritation in swimmers.

Moreover, Ecology requires that treatments are prohibited with pesticides that have water use restrictions on the FIFRA label that restrict public water use during the opening week of fishing season or during tribal fisheries, WDFW Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. They further require that permittees must minimize treatments that restrict public water use during weekends.

4.2.4.3 Irrigation, Drinking and Domestic Uses

Following registration approval, aminopyralid labels are not expected to include restrictions on recreational or livestock use of water following application. Similarly, labeled use will not include the inside banks of irrigation ditches or for submersed aquatic plant control. Precautions and restrictions on use of water treated with Milestone® for irrigation will likely be included on the new label.

The Ecology APAM permit at the time of this writing requires that if the product label has potable water use restrictions and the treatment occurs in water bodies with municipal or community drinking water intakes, the applicant must obtain and submit written consent to the treatment from the municipality or community. When there are potable water restrictions on the label and the treatment is within the setback distance listed on the product label, the permittee must not apply any chemical until it has notified people who withdraw potable water from the waterbody. If requested by the affected water user(s), the permittee must provide an alternative potable water supply until the intake water tests at or below the concentration specified for that pesticide in the product label for potable water. If requested by an affected water user, the permittee must provide at least 2 weeks advance notice of pending treatments.

Anyone withdrawing water under a legal water right or claim for irrigation or livestock watering purposes may request an alternate water supply during the treatment if the label has restrictions for those uses and the treatment is inside the setback distance listed on the product label. The permittee must provide an alternative water supply until the intake water tests at or below the irrigation restriction concentration or livestock drinking water concentration on the label or until the time interval specified on the label has elapsed. If requested by an affected water user, the permittee must provide at least 2 weeks advance notice of pending treatments.

4.2.4.4 Roadsides or Utility Rights-of-way

When treating areas with aminopyralid herbicides in and around roadside or utility rights-of-way that could be grazed or planted to forage, it is recommended that important label precautions apply regarding harvesting hay, using manure from animals grazing on treated areas, or rotating treated areas to sensitive crops.

4.2.4.5 Fisheries and Fish Consumption

Fish consumption is not expected to be affected by aminopyralid application, as the material is not persistent in surface water, is not acutely or chronically toxic to fish, and does not bioconcentrate or bioaccumulate in fish or shellfish tissues.

4.2.4.6 Endangered Species

Based on available toxicity information, aminopyralid is not acutely or chronically toxic to potentially vulnerable ESA-listed animal species, but it is relatively persistent in soils and sediments where prey organisms reside, which is part of critical habitat, and therefore this should be considered when applying aminopyralid herbicides to areas where critical aquatic habitat is present. In addition, aminopyralid can be somewhat toxic to non-target plant species, which may be part of critical habitat requiring protection under ESA requirements.

Concerning where additional requirements for discharges to water bodies where sensitive, threatened, or endangered plants could be present, based upon the current permit at the time of this writing, before issuing permit coverage, Ecology will determine whether such plant species are present in the proposed treatment area. If present, for aquatic plant control projects, the permit requires a plant survey and implementation of mitigation measures if the rare plant is found.

4.2.4.7 Wetlands or Non-Target Plants

FIFRA product labels at the time of writing for aminopyralid herbicides state that they are not to be applied in or adjacent to a wetland, and buffer zones need to be carefully delineated prior to application.

As stipulated by Ecology for the APAM permit at the time of this writing, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation.

4.2.4.8 Post-treatment Monitoring

Label-specified post-treatment monitoring will likely be required, probably both short- and long-term. Monitoring may be required in Washington State in compliance with NPDES water quality permits issued by Ecology. Both short- and long-term post-treatment monitoring are commonly required for the purpose of evaluating non-target effects from a toxic herbicide such as aminopyralid. For Ecology, this post-treatment monitoring would be required under their APAM and/or NPDES discharge permit, and would be a permit condition requiring monitoring to determine potential non-target impacts. These requirements will be incorporated into both label and permit requirements, as appropriate, in conjunction with pesticide registration and permit requirements prior to application.

4.2.5 References

- Dow AgroSciences Co. (Dow). 2016. Aminopyralid Family of Herbicides.
http://msdssearch.dow.com/PublishedLiteratureDAS/dh_0949/0901b803809493a6.pdf?filepath=ivm/pdfs/noreg/010-50805.pdf&fromPage=GetDoc. [1]
- Dow. 2013. Aminopyralid Stewardship. <http://www.dowagro.com/en-us/range/forage-management/aminopyralid-stewardship>. [9]
- Dow. 2008. Product Safety Assessment: Aminopyralid.
http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_096d/0901b8038096dbd0.pdf?filepath=productsafety/pdfs/noreg/233-00376.pdf&fromPage=GetDoc. [1]
- Peterson, et al. 2013. Research Studies Support Aquatic Labeling of Aminopyralid.
<http://webcache.googleusercontent.com/search?q=cache:http://techlinenews.com/articles/2013/research-studies-support-aquatic-labeling-of-aminopyralid>. [9]
- Toxnet. 2012. Aminopyralid. Toxicology Data Network, Hazardous Substances Database. National Library of Medicine. <https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7939>. [1]
- US Environmental Protection Agency (EPA). Office of Prevention, Pesticides, and Toxic Substances (OPPTS). 2005. Pesticide Fact Sheet. Conditional Registration: Aminopyralid. August 10. [5]

Washington State Department of Ecology (Ecology). 2016. Aquatic Plant Management: Plant Herbicides. <http://www.ecy.wa.gov/programs/wq/plants/management/aqua028.html>, WA State Dept. of Ecology. [3]

Washington State Department of Transportation (WSDOT). 2006. Aminopyralid: Roadside Vegetation Management Herbicide Fact Sheet. <https://www.wsdot.wa.gov/NR/rdonlyres/CD6D91AC-D382-4E5D-AF1E-50C52C34484F/0/Aminopyralid.pdf>. [1]

4.3 EVALUATION OF PROCELLACOR™ (FLORPYRAUXIFEN-BENZYL)

NOTE: GEI Consultants, Inc. executed a confidential non-disclosure agreement with SePRO Corporation to obtain and review proprietary studies and data. SePRO is working in partnership with Dow AgroSciences to develop this technology for aquatic weed control. In the absence of peer-reviewed journal articles or other scientific literature, these studies—many of which were performed in support of EPA's Office of Pesticide Programs (OPP) registration requirements—were used to prepare the evaluation of the candidate aquatic herbicide.

4.3.1 Registration Status

PROCELLACOR™ (Procellacor™) Aquatic Herbicide (2-pyridinecarboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoro-, phenylmethyl ester also known as Rinskor™; common name: florpyrauxifen-benzyl) has not yet been registered nationally by the EPA or in Washington State by the WSDA under 15.58 Revised Code of Washington (RCW). This SEIS provides technical, environmental, and other information required by Ecology to determine whether to add Procellacor™ to existing water quality NPDES permits, which will allow this herbicide to be discharged to the waters of the State as allowed under the Clean Water Act.

Procellacor™ (florpyrauxifen-benzyl) was granted Reduced Risk status by EPA under the Pesticide Registration Improvement Act (PRIA) Version 3 (<https://www.epa.gov/pria-fees/pria-overview-and-history#pria3>) in early 2016 (Denny, Breaux, 2016; also see notification letter at Attachment A) because of its promising environmental and toxicological profiles in comparison to currently registered herbicides utilized for partial treatment of hydrilla, invasive watermilfoils, and other noxious plant species. EPA concluded that the overall profile appeared more favorable when compared to the registered alternatives for the proposed use patterns for these noxious species, and that the reduction in risk pertaining to human health was the driving factor in this determination. As discussed later in the document, Procellacor™ shows excellent selectivity with few or limited impacts to native aquatic plants such as aquatic grasses, bulrush, cattail, pondweeds, naiads, and tapegrass. In its review, EPA also noted that the overall profile for the herbicide appears favorable when compared to currently registered alternative herbicides (e.g. 2,4-D, endothall, triclopyr) for this aquatic use pattern. Procellacor™ represents an alternative mode of chemical action which is more environmentally favorable than currently registered aquatic herbicides. Florpyrauxifen-benzyl would be expected to offer improvements in IPM for control of noxious aquatic weeds. The alternative mode of action should also help to prolong the effectiveness of many aquatic herbicide solutions by offering a new rotation or combination alternative as part of herbicide resistance management strategies.

The new candidate aquatic herbicide is under expedited review from EPA under the PRIA per the Reduced Risk status designation discussed above, with an anticipated registration date of summer 2017. As part of the review, EPA's OPP is also currently conducting human health and ecological risk assessments with an expected date of release in late spring 2017. This SEIS document relies on information currently available at this time, much of which necessarily is limited to data provided by Dow AgroSciences and SePRO Corporation in developing and testing the herbicide. It can be revised with more updated information following the release of EPA review information as well as other peer-reviewed literature expected to be released later in 2017. Dow AgroSciences has also concurrently

applied to EPA for registration of the florpyrauxifen-benzyl active ingredient for weed control in rice paddies. The initial Procellacor™ formulation is expected to be a 300 g TGA/L suspension concentrate. Control of hydrilla and invasive watermilfoils can be achieved at in-water spot/partial treatment rates of 10 to 50 µg a.i./L with Procellacor™, as opposed to rates of 1,000 to 5,000 µg a.i./L for endothall, 2,4-D, and triclopyr (Getsinger 2016, Beets and Netherland 2017a *in review*, Netherland et al 2017 *in prep*).

This analysis considers florpyrauxifen-benzyl's (Procellacor™'s) mode of action, efficacy, and range of in-water treatment concentrations required to achieve control across different water exchange / exposure scenarios. The review discusses results of mesocosm and other field studies conducted in partial site and whole pond treatments, described in more detail below.

To help expedite development and future adoption of the technology, SePRO has been working with numerous partners and collaborators to conduct experimental applications to confirm field efficacy on a variety of target aquatic vegetation, as well as to document non-target effects or impacts. As an unregistered product that does not have a federal experimental use permit, EPA guidelines require that field testing be limited to one acre or less of application per target pest species and that uses of water potentially affected by this application such as swimming, fishing, and irrigation be restricted. The discussion below provides a summary of the herbicides' physical properties, mammalian and ecotoxicological information, environmental fate, and other requirements for EPA registration. Most of these studies have been conducted by Dow AgroSciences and SePRO Corporation in fulfillment of EPA's OPP pesticide registration requirements under FIFRA (as represented by Heilman 2016). As noted above, few peer-reviewed publications have yet been released, although more are expected later in 2017 and beyond.

4.3.2 Description

Procellacor™ is the aquatic trade name for use of a new active ingredient (florpyrauxifen-benzyl), which is one chemistry in a novel class of herbicides known as the arylpicolinates. The primary end-use formulation anticipated for in-water application at time of registration is a 300 g active ingredient/liter suspension concentrate, but other aquatic use formulations are being considered for registration shortly after the initial EPA decision.

Aquatic herbicides are grouped by contact (controls plant shoots only) vs. systemic (controls entire plant), and by aqueous concentration and exposure time (CET) requirements. In general, contact products are quicker acting with shorter CET requirements, while systemic herbicides are slower acting with longer CET requirements. In light of this, Procellacor™ is quick-acting, has relatively short CET requirements, is systemic, and requires low application rates compared to other currently registered herbicides. Moreover, it has shown short persistence in both water and sediment relative to currently registered herbicides such as endothall, 2,4-D, and triclopyr, is species-selective, and has minimal non-target effects to both plant and animal species. Its effective chemical mode of action and high selectivity for aquatic invasive and noxious plants provides a significant impetus for its development and eventual registration. Procellacor™ has demonstrated this selective, systemic activity with relatively short CET requirements on several major aquatic weed species, including hydrilla and invasive watermilfoils. Netherland and Richardson (2016) and Richardson *et al.* (2016) investigated the sensitivity of numerous aquatic plant species to the compound, and provided verification of Procellacor™'s activity on key

invasives and greater tolerance by the majority of native aquatic plants tested to date. Additional government and university research has documented high activity and different selectivity patterns relative to possible impacts to non-target aquatic vegetation compared to other currently registered, well-documented herbicides such as triclopyr, endothall, and/or 2,4-D (Beets and Netherland 2017a *in review*, Beets and Netherland 2017b *in prep*, Haug and Richardson 2017 *in prep*).

4.3.2.1 Environmental Characteristics: Product Use and Chemistry

Procellacor™ shows excellent activity on several major US aquatic weeds including hydrilla (*H. verticillata*) and multiple problematic watermilfoils (*Myriophyllum spp.*), including Eurasian (EWM) and hybrid Eurasian (*M. spicatum* X *M. sibiricum*), parrotsfeather (*M. aquaticum*), and variable-leaf milfoil (*M. heterophyllum*). Procellacor™ provides a new systemic mode of action for hydrilla control and a new class of auxin-mimic herbicide chemistry for selective management of invasive watermilfoils. It also has in-water or foliar herbicidal activity on a number of noxious emergent and floating aquatic plants such as water hyacinth and invasive floating hearts (*Nymphoides spp.*). Procellacor™ has low application rates (50 µg/L or less) for systemic activity with short CET requirements (12 – 72 hours depending on rate and target weed) allowing for spot and/or partial in-water applications. For such treatments, Procellacor™ provides selective control with several hundred times less herbicide use versus current in-water, spot treatment herbicides such as endothall (5,000 µg/L maximum use rate for dipotassium salt form) and 2,4-D (4,000 µg/L maximum use rate). Procellacor™ also appears to show high selectivity with few impacts to native aquatic plants such as aquatic grasses, bulrush, cattail, pondweeds, naiads, and tapegrass (see discussion on selectivity below).

Procellacor™ is effective in controlling hydrilla, and offers a new pattern of selectivity for removing hydrilla from mixed aquatic-plant communities. The strong activity of this new alternative mode of action supports its development for selective hydrilla control. Mesocosm studies summarized by Heilman (2016) and in preparation or under active review for peer-reviewed publication have shown that control of standing biomass of hydrilla and EWM can be achieved in two to three weeks, with high activity even on 2,4-D and triclopyr-tolerant stands of hybrid EWM (Beets and Netherland 2017a *in review*, Netherland et al. 2017 *in prep*). Multiple small-scale laboratory screening studies were conducted to support both target weed activity and regulatory consideration of potential effects of Procellacor™ on non-target aquatic vegetation. The test plant EC₅₀ response (herbicide concentration having 50% effect) to static exposures of Procellacor™ was determined for 12 different plant species: the general EC₅₀ range was approximately 0.11 µg/L to greater than 81 µg/L (Netherland and Richardson, 2016; Richardson *et al.*, 2016). Similar small-scale comparative efficacy testing of Procellacor™ vs. 2,4-D and triclopyr on multiple invasive watermilfoils confirms orders of magnitude greater activity with Procellacor™ versus the older auxin herbicides, including activity on hybrid EWM with documented tolerance to the older herbicides (Beets and Netherland 2017b *in prep*). These findings are promising for Procellacor™, as they support significantly lower herbicide application rates combined with a favorable environmental profile, discussed in more detail below.

4.3.2.2 Environmental Mobility and Transport

Procellacor™/Rinskor is known to have low water solubility (laboratory assay of TGA1: 10 to 15 µg/L at pH 5 to 9, 20°C), low volatility (vapor pressure approx. 10⁻⁷ mm Hg), with moderately high partition

coefficients (log K_{ow} values of approximately 5.4 to 5.5), which describe an environmental profile of low solubility and relatively high affinity for sorption to organic substrates.

The environmental fate of the herbicide in soil and water has been characterized as part of the registration package and is well understood. The parent compound is not persistent and degrades via a number of pathways including photolysis, aerobic soil degradation, aerobic aquatic degradation, and/or hydrolysis to a number of hydroxyl, benzyl-ester, and acid metabolites. In aerobic soil, Procellacor™ degrades moderately quickly, with half-lives ranging from 2.5 to 34 days, with an average of 15 days. Anaerobic soil metabolism studies also show relatively rapid degradation rates, with half-lives ranging from 7 to 15 days, and an average of 9.8 days. The herbicide is short-lived, with half-lives ranging from 4 to 6 days and 2 days, respectively, in aerobic and anaerobic aquatic environments, and in total water-sediment systems such as mesocosms. These half-lives are consistently rapid compared to other currently registered herbicides such as 2,4-D, triclopyr, and endothall. Degradation in surface water is accelerated when exposed to sunlight, with a reported photolytic half-life in laboratory testing of 0.07 days.

In two outdoor aquatic dissipation studies, as summarized by Heilman (2016), the SC formulation of the herbicide was directly injected into outdoor ponds at nominal rates of 50 and 150 µg/L as the active ingredient. Water phase dissipation half-lives of 3.0 – 4.9 days were observed, which indicates that the material does not persist in the aquatic environment. With conditions similar to wetland and marsh habitat, results from another field dissipation study in rice paddies that incorporated appropriate water management practices for both wet-seeded and dry-seeded rice (also reported by Heilman 2016) resulted in aquatic-phase half-lives ranging from 0.15 to 0.79 days, and soil phase half-lives ranging from 0.0037 to 8.1 days. These results do not indicate a tendency to persist in the aquatic environment. The herbicide can be classified as generally immobile based on soil log K_{oc} values in the order of 10^{-5} , and suggest that the potential for off-site transport is minimal. This is consistent with numerous observations that Procellacor™ undergoes rapid degradation in the soil and aqueous environments via a number of degradation mechanisms, summarized above.

4.3.2.3 Field Surveys and Investigations

A human health and ecological risk assessment is currently being conducted by EPA Office of Pesticide Programs. Results of this assessment are expected to be released during spring of 2017 (Denny, 2016), and these conclusions will either support or refute data already collected for Procellacor™. There are no preliminary findings to report, but based on the current understanding of available environmental fate, chemistry, toxicological, and other data, there is little to no cause for concern to human health or ecotoxicity for acute, chronic, or subchronic exposures to Procellacor™ formulations.

4.3.2.4 Bioconcentration and Bioaccumulation

A fish bioconcentration factor study and magnitude of residue studies for clam, crayfish, catfish, and bluegill support that, as anticipated from its physical chemistry and organic affinity, Procellacor™/Rinskor will temporarily bioaccumulate but is rapidly depurated and/or metabolized within freshwater organisms within 1 – 3 days after exposure to high concentrations (150 µg/L or higher). Based on these findings and the low acute and chronic toxicity to a wide variety of receptor organisms, summarized below, bioconcentration or bioaccumulation are not expected to be of concern for the

Procellacor™ aquatic use. EPA's forthcoming human health and ecological risk assessment will include exposure scenarios that will help to further clarify and refine the understanding of bioconcentration or bioaccumulation potential for Procellacor™.

4.3.2.5 Toxicological Profile

Mammalian and Human Toxicity

Extensive mammalian toxicity testing of Procellacor™ has been conducted by the proposed registrant, and results have shown little evidence of acute or chronic toxicity. Acute mammalian toxicity testing for Procellacor™ showed very low acute toxicity by oral or dermal routes (LD₅₀ values greater than 5,000 mg/kg). Acute toxicity is also reported low via the inhalation route of exposure (LC₅₀ value greater than 5.2 mg/L). Procellacor™ is reported not to be an irritant to eyes or skin and only demonstrated a weak dermal sensitization potential in a mouse local lymph node assay (EC₃ of 19.1%).

Absorption, distribution, metabolism, and elimination profiles have been developed for Procellacor™. In summary, Procellacor™ has demonstrated rapid absorption (T_{max} of 2 hours), with higher absorption rates at lower doses (36 to 42% of the administered dose), rapid hydrolysis, and rapid elimination via the feces (51 to 101%) and urine (8 to 42%) during the first 24 hours following administration to laboratory mammals. In general, the lower doses tested would be more representative of levels potentially encountered by people, mammals, or other organisms.

Based on laboratory testing, Procellacor™ is not genotoxic, and there was no treatment-related toxicity even up to the highest doses tested in the acute, short-term, two generation reproduction or developmental toxicity studies or in the acute or subchronic neurotoxicity studies. Chronic administration of the herbicide did not show any carcinogenicity potential and did not cause any adverse effects in mice, rats or dogs, at the highest doses tested. In summary, studies conducted in support of EPA registration indicate there is little or no concern for acute, short term, subchronic or chronic dietary risk to humans from Procellacor™ applications. Tests have shown no evidence of genotoxicity/carcinogenicity, immunotoxicity, neurotoxicity, subchronic or chronic toxicity, reproductive or developmental toxicity, and only showed evidence of low acute toxicity.

Several studies conducted on both mice and rats, over the course of 1-2 years have indicated no treatment-related (post-necropsy) clinical observations or gross histopathological lesions. An 18-month mouse study was conducted, and no chronic toxicity, carcinogenicity, or other adverse effects were observed, even in those male and female mice receiving the highest doses tested. A 1-year dog study is also ongoing; similar to the above mammalian toxicity tests, no treatment-related toxicity or pathology has yet been observed during this study. Reproductive, developmental, and endocrine toxicity (immunotoxicity) has also been tested, and results of all these tests showed no evidence of toxicity. Although no specific human testing has been conducted for Procellacor™, based on extensive laboratory testing on mammalian species, little to no acute or chronic toxicity would be expected in association with environmental exposures.

General Ecotoxicity

Procellacor™ has undergone extensive ecotoxicological testing and has been shown to be nearly non-toxic to birds in acute oral, dietary, and reproduction studies. Similar to the mammalian testing

summarized above, no toxicity was observed for avian, fish, or other species exposed to the herbicide in acute and long-term studies, with endpoints set at the highest concentration tested, which are well above those actually released as part of label-specified application of Procellacor™. As would be expected for an herbicide, toxicity has been observed to certain sensitive terrestrial and aquatic plants (see plant discussion below).

As noted above, the TGAi of Procellacor™ exhibits low water solubility, and in laboratory aquatic ecotoxicity studies, the highest concentration of TGAi that could be dissolved in the test water (or functional solubility) was approximately 40-60 µg/L in freshwater. The acute and/or chronic endpoints for freshwater fish and invertebrates are generally at, or above, the limit of functional solubility. Additional evaluations indicate a lack of toxicity of the aquatic end-use product (greater functional solubility than the TGAi) and metabolites up to several orders of magnitude above the typical in-water use rates of Procellacor™ (50 µg/L or less).

Fish Ecotoxicity

A variety of fish tests have been conducted in cold and warm water fish species using the TGAi as well as the end-use formulation and various metabolites. Acute toxicity results using rainbow trout (*O. mykiss*, a standard cold water fish testing species) indicated LC₅₀ values of greater than 49 µg/L, and greater than 41 µg/L for fathead minnow (*P. promelas*, a standard warm water species). The pure TGAi would not be expected to be released into the environment, and comparable acute ecotoxicity testing was performed for carp using an end-use formulation for Procellacor™. Results indicate an LC₅₀ value of greater than 1,900 µg/L for carp (*C. carpio*), indicating much lower acute toxicity potential. A marine toxicity test was identified, where sheepshead minnows (*C. variegatus*) were tested for acute toxicity, and a LC₅₀ value of greater than 40 µg/L was produced, which is comparable to freshwater species tested for acute toxicity. This value is indicative of slight acute toxicity potential if environmental concentrations were to be present at these levels, which is unlikely. Comparable acute ecotoxicity testing using various Procellacor™ metabolites indicated LC₅₀ values uniformly greater than 1,000 µg/L, indicating a minimal potential for acute toxicity from metabolites. Salmonid toxicity data also indicated no overt toxicity to juvenile rainbow trout at limit of solubility for both the TGAi and end-use formulation at the maximum application rate (40 µg/L). If fish were to occupy a plant-infested littoral zone that was treated by Procellacor™, no toxic exposure would be expected to occur, as toxicity thresholds would not be exceeded by the concentrations predicted to be allowed for use by the FIFRA label.

Fish toxicity testing, in addition to that summarized above, has been planned and is currently under way for sensitive and ESA-listed aquatic species and habitat considerations in the Pacific Northwest, as reported by Grue (2016 and 2017). The emphasis for this aquatic toxicity testing is on salmonid species (Chinook salmon, bull trout, coho salmon, etc.), which are the most frequently listed and probably the most representative fish species in the Northwest under ESA. The most commonly accepted surrogate fish test species for salmonids is the cold water salmonid rainbow trout (*O. mykiss*), but to help alleviate additional uncertainty, this additional testing will use age- and species- appropriate salmon species, and is intended to replicate pre-registration toxicity tests with trout using environmentally representative exposure concentrations. Test endpoints include acute mortality, growth, and other sublethal and behavioral endpoints (e.g. erratic swimming, on-bottom gilling, etc.) to evaluate more subtle toxicological effects potentially associated with Procellacor™. Preliminary results from this testing

indicate little to no effects associated with exposure to florypyrauxifen-benzyl, and a final report on this work will be forthcoming later in 2017.

This testing will screen comparable treatments to the trout testing (0, 40 and 80 µg/L Procellacor™, with the latter being well in excess of anticipated maximum labeled use rate). Testing will follow standard guidelines (ASTM, 2002; EPA, 1996) as did the earlier testing (e.g. Breaux, 2015), to ensure comparability. Results from this additional testing are expected to become available by late spring 2017, and will be useful in expanding our understanding of the toxicological properties of Procellacor™ when used in salmon-bearing waters.

Avian Toxicity

As noted above, Procellacor™ has been shown to be of low acute and chronic toxicity to birds as shown in a series of acute oral, dietary, and reproduction studies (Breaux, 2015). Little to no toxicity was observed for avian species exposed to the herbicide in both acute and longer-term chronic studies, with the highest test concentrations exceeded expected labeled rates, a common practice in laboratory toxicology. Bird testing was conducted to include standard test species including mallard duck (*A. platyrhynchos*), the passerine (songbird) species zebra finch (*T. guttata*), and bobwhite quail (*C. virginianus*). Tests involved oral administration for acute and chronic testing and reproductive studies, eggshell thinning, life cycle testing, and other endpoints. In summary, acute oral testing using bobwhite quail and zebra finch yielded LD₅₀ values of greater than 2,250 mg/kg-day for both species. Two five-day acute dietary tests were also conducted, which both yielded LC₅₀ values of greater than 5,620 mg/kg-day. Subchronic reproductive tests were also conducted for bobwhite quail and mallard ducks both yielded NOEC values of 1,000 mg/kg in the feed. All of these results are highly indicative of little to no toxicity to each of the avian species tested.

No amphibian or reptile toxicity testing was required by EPA Office of Pesticide Programs registration requirements, or conducted as part of the testing regimen for Procellacor™. EPA guidelines generally assert that avian testing is an adequate surrogate for amphibian or reptile testing, and invertebrate and mammalian test results are available as well to support projection of minimal toxicity of Procellacor™ to amphibians or reptiles.

Invertebrate Ecotoxicity

Acute and chronic testing of Procellacor™ with honey bees, the only insect species tested, has indicated no evidence of ecotoxicity to this species (Breaux, 2015). Concerning aquatic invertebrates, acute testing was performed for both the daphnid *D. magna* and the midge *Chironomus* sp. Tests were conducted using both the TGAI and end-use formulation for Procellacor™, as well as various metabolites. Acute toxicity results for the TGAI using *D. magna* indicated LC₅₀ values of greater than 62 µg/L, and greater than 60 µg/L for *Chironomus*. This is generally consistent with acute toxicity testing conducted for the freshwater amphipod *Gammarus* sp., for which a NOEC value of 42 µg/L was developed. These results are indicative of little to no acute toxicity to these species. Comparable acute ecotoxicity testing was performed for *D. magna* using a Procellacor™ end-use formulation, and results indicated an LC₅₀ value of greater than 80,000 µg/L, also indicating negligible acute toxicity potential. Acute ecotoxicity testing using various metabolites of the herbicide indicated LC₅₀ values uniformly greater than 980 µg/L, with most values exceeding 10,000 µg/L, indicating little to no potential for acute toxicity for the metabolites.

Life cycle testing was also completed for a freshwater (*D. magna*) for both the TGAI and metabolites, and results showed a Lowest Observable Adverse Effect Concentration (LOAEC) and an NOAEC of 38 µg/L (both endpoints) showing low toxicity potential for the TGAI in an artificial scenario of static exposure using a renewal protocol design. The spot/partial use pattern of the herbicide and instability of TGAI under natural conditions project to a lack of chronic exposure to aquatic fauna. Comparable testing with metabolites showed LOAEC/NOAEC values both exceeding 25,000 µg/L, indicating negligible levels of toxicity for metabolites. Whole sediment testing using the TGAI for a freshwater invertebrate (chironomid midge) was also conducted for acute (10 day) and chronic (28 day) duration. The chronic test spiked water overlying sediments to a target concentration as the means to initiate exposure. Results of the whole sediment testing indicated an acute 10-day LOAEC of 10.5 mg ai/kg sediment and 28-day NOEC level of 78.5 µg/L (overlying water target concentration), which would generally be indicative of very low to negligible aquatic ecotoxicity.

Additionally, acute screening was recently performed by North Carolina State University (Principal Investigator: Dr. Greg Cope, cited as Buczek *et al.* 2017) on the juvenile life stage of a representative freshwater mussel (*L. siliquoides*) with the TGAI, a primary metabolite (acid metabolite), and two TEP / formulations (the SC above and a 25 g/L EC formulation). The study showed no toxicity to juvenile mussels in any test with formulated results showing No Effect Concentrations (NOEC) that were 25 – 50 times greater than anticipated maximum application rate for the new herbicide (Cope *et al.* 2017 *in prep*).

Although the proposed registration for Procellacor™ in Washington State will be for freshwater application, it is possible that Procellacor™ would be applied near marine or estuarine habitats for weed control. Acute toxicity testing, using TGAI, conducted on the eastern oyster (*C. gigas*) produced an NOEC of greater than 24 µg ai/L and a comparable NOEC value for mysid shrimp (*M. bahia*) of greater than 26 µg ai/L, both the highest rates tested due to solubility limits with assays. Comparable NOEC values developed for primary aquatic end-use formulation were greater than 1,100 and 1,350 µg/L as formulated product (>289 and >362 µg/L as active ingredient), respectively, for the oyster and shrimp.

Marine invertebrate life cycle testing was conducted using the TGAI on a mysid shrimp) and a chronic NOAEC of 7.8 µg/L (LOAEC of 13 µg/L) was developed, which is potentially indicative of chronic toxicity to marine or estuarine invertebrates if these sustained concentrations were attained in environmental settings. Acute NOECs for oyster and mysids tested with the TGAI were set at the highest mean measured rate of tested material. There were no adverse effects noted in those studies. There are potential unknowns with possible effects with acute exposures to concentrations greater than 24-26 µg/L, but range finding-finding toxicity testing demonstrated that this range of concentrations were the highest limits to maintain solubility of TGAI in the assays.

In practice, due to rapid degradation of the TGAI in the field, rapid dilution from spot applications (main use pattern), and not labelling for estuarine and marine sites will mitigate any chance of acute exposures to marine invertebrates above the range of mid-20 µg/L. Chronic toxicity results for mysid shrimp do suggest possible chronic effects at 7.8 µg/L, with extended exposures to the TGAI. Again, however, the use pattern is not intended for estuarine/marine application with the initial labelling. The use pattern in freshwater is spot/partial treatments with negligible chance of sustained TGAI concentrations migrating downstream to estuarine habitat even if the freshwater site was in close

proximity to an estuarine area. In general, the labeled freshwater use for spot/partial applications (high dilution potential) to control noxious freshwater aquatic plants and the rapid degradation of the TGA1 suggest minimal risk to marine and estuarine invertebrates following application to a nearby freshwater site. Metabolite testing with marine species yielded NOECs of greater than 25,000 µg/L, indicating negligible toxicity.

Data Gaps

No data gaps have been identified for the basic environmental profile, including environmental fate, product chemistry, toxicology and ecotoxicology, and field studies required by EPA for pesticide registration. However, a number of recent trials are currently in review (e.g., Beets and Netherland 2017a) or in preparation for publication (e.g. Beets and Netherland, 2017b, Netherland *et al.* 2017, Haug *et al.* 2017). These, along with the continued use of Procellacor™ under a variety of plant management scenarios, will add valuable information that can be incorporated into the product labels, improved treatment profiles and potentially required mitigation measures.

4.3.3 Environmental and Human Health Impacts

4.3.3.1 Earth

Soil and Sediments

Procellacor™ has moderately high measured K_{ow} and K_{oc} partition coefficients, with log K_{ow} and K_{oc} values of approximately 5.4 to 5.5, or about 10^{-5} , which supports low solubility and demonstrates a relatively high affinity for sorption to organically enriched substrates such as soils or sediments. However, as noted above, in aerobic soil Procellacor™ degrades quickly, with half-lives ranging from 2.5 to 34 days, with an average of 15 days. Anaerobic soil metabolism studies are similar, showing relatively rapid degradation rates with half-lives ranging from 7 to 15 days, and an average of 9.8 days. This rapid degradation in the soil and sediment environment strongly suggests low persistence in these media. Due to the low acute and chronic toxicity described below, low to negligible impacts are expected in soils and sediments adjoining Procellacor™ treatment areas. The herbicide can be classified as largely immobile based on soil log K_{oc} values in the order of 10^{-5} , and that potential for off-site transport would be minimal.

Agriculture

At anticipated use concentrations, irrigation or flooding of crops with water treated with Procellacor™ are not expected to damage crops or non-target wild plants, except under scenarios not addressed in the forthcoming EPA label.

Terrestrial Land Use

At anticipated use concentrations, water reentry or swimming in water treated with Procellacor™ is not expected to cause dermal, eye, or other irritation or toxicity to human or wildlife species.

4.3.3.2 Water

Surface Water and Runoff

Procellacor™ is known to have low water solubility (about 15 µg/L in lab testing) and the parent compound is not persistent and is known to quickly degrade via a number of well-established pathways. As discussed above, the herbicide is short lived in aerobic and anaerobic aquatic environments in a total water-sediment system. When exposed to direct sunlight, degradation in surface water is even more accelerated, with a reported photolytic half-life as little as 0.1 days.

The two outdoor aquatic dissipation studies summarized above further support this rapid dissipation and low impact. Both studies show that when Procellacor™ was directly injected into outdoor freshwater ponds at nominal rates of 50 and 150 µg/L, very rapid water-phase dissipation half-lives (3 to 4.9 days) were observed. These characteristics strongly suggest that the potential for off-site transport or mobility is minimal. As noted above, Procellacor™ undergoes rapid degradation in both soil and aqueous-phase environments via a number of degradation mechanisms.

No use for aquatic vegetation management in marine or estuarine water using Procellacor™ will be labeled at this time in Washington State (Heilman, 2016).

No specific studies or exposure scenarios were identified where drift or runoff were specifically investigated, but the forthcoming EPA risk assessment for Procellacor™ is expected to address these scenarios. For drift, the low vapor pressure (approximately 10^{-7} mm Hg) indicates that the material is not prone to volatilize following application, thus minimizing drift potential, and the low water solubility, low acute and chronic toxicity, along with minimal potential for persistence suggest that potential hazards associated with surface water runoff would be minimal.

Groundwater and Public Water Supplies

Few studies have yet been completed for groundwater, but based on known environmental properties concerning mobility, solubility, and persistence, Procellacor™ is not expected to be associated with potential environmental impacts or problems in groundwater.

In laboratory aquatic ecotoxicity studies, the highest concentration of TGA1 that could be dissolved in the test water (or functional solubility) was approximately 40-60 µg/L in freshwater and 20-40 µg/L in saltwater. This is due to the low water solubility of the active ingredient and limits the range for which these toxicity tests can be conducted. This finding suggests that the water chemistry of Procellacor™ would limit potential environmental impacts to groundwater or surface water.

Impacts to public water supplies are expected to be low to negligible based on the low solubility, low persistence, and low acute and chronic toxicity of Procellacor™. Section 4.3.4 discusses possible measures or best management practices (BMPs) that could be used to further reduce potential impacts to public water supplies. The Ecology permit has mitigation that requires permittees to obtain an approval letter for this treatment prior to obtaining coverage under the permit.

4.3.3.3 Wetlands

The habitat and aquatic structure found in rice paddies is similar to those in a wetland and marsh environments, making the studies reported by Heilman (2016a) and Netherland and Richardson (2016) important tools for this analysis. The wetland and marsh study, discussed above in Section 4.3.2.2., incorporated appropriate water management practices for both wet-seeded and dry-seeded rice, and reported rapid aquatic-phase half-lives ranging from 0.15 to 0.79 days, and soil phase half-lives were also rapid, ranging from less than 0.01 to 8.1 days.

4.3.3.4 Plants

Algae

Limited ecotoxicity testing using a growth endpoint was conducted for two species of freshwater algae, including a diatom and green algae. These tests showed EC₅₀ values using the TGA of greater than 40 and 34 µg/L, respectively (solubility limit of assays). These results indicate that Procellacor™ is generally not toxic to green algae, freshwater diatoms, or blue-green algae at the anticipated label rate. Metabolite testing showed little toxicity to these algae, with no EC₅₀ value less than 450 µg/L. Comparable growth testing was also conducted using the end-use formulation for aquatic algal plant growth, and results showed an EC₅₀ greater than 1,800 µg/L (480 µg/L as active), with a NOAEC of 420 µg/L of formulation (111 µg/L as active), again showing a lack of toxicity to algae within anticipated label use rates. A comparable test of the TGA was performed for cyanobacteria (blue-green algae), and results showed an EC₅₀ of greater than 45 µg/L, with a calculated NOAEC value of 23.3 µg/L, showing little evidence of toxicity for any of these species.

Higher Plants and Crops

Procellacor™ is known to have strong herbicidal activity on key target aquatic invasive species, and testing shows that many native plants are able to tolerate Procellacor™ at exposure rates greater than what is necessary to control key target invasives. Data collection is still underway for specific toxicity to non-target plant species. Initial results of a 2016 collaborative mesocosm study conducted in Texas, for which results will be formally available later in 2017 indicate favorable selectivity by Procellacor™ of multiple invasive watermilfoils in the presence of representative submersed aquatic native plants (Netherland *et al.* 2017 *in prep*). Aquatic native plants challenged in this study included tapegrass, Illinois pondweed, American pondweed, waterweed, and water stargrass. Using aboveground biomass as a response endpoint, no significant treatment effects were observed with tapegrass or American/Illinois pondweed. Similarly, no statistically significant treatment effects were observed with stargrass, although injuries were observed at higher rates and exposures, although it was much more tolerant than the two target milfoil species. Other mesocosm studies have shown similar responses in white water lily with other non-target species including Robbins pondweed, American pondweed, and multiple bladderwort species showing little or no discernible impact. Richardson *et al.* (2016) and Haug and Richardson (2017 *in prep*) report that Procellacor™ provides a new potential for selectivity for removing hydrilla from mixed aquatic-plant communities. They recommend that further research should be conducted to further characterize observed patterns of selectivity.

4.3.3.5 Habitat

Impacts to critical habitat for aquatic plant or animal species are expected to be minimal, and may benefit critical habitat overall by supporting plant selectivity. Procellacor™ is generally of a low order or acute and chronic toxicity to plants and animals and generally does not persist in the environment. Due to its documented selectivity, Procellacor™ would allow many native non-target plants to thrive and thus enhance quality habitat. Removing noxious aquatic plants creates open spaces in the littoral zone that may be recolonized by not only native plants but other invasive plant species.

For example, when left unchecked, dense stands of unwanted weeds such as watermilfoil, parrotsfeather, hydrilla, or numerous other noxious plant species can negatively impact critical salmonid or other habitat used at all life stages, as well as habitats to a wide variety of plant and animal species, including vulnerable life stages. Stands of invasive weeds can reduce water flow and circulation, thus impeding navigation for migrant salmonids. Such stands can also provide ambush cover for predatory species such as bass, which prey on critical juvenile and other salmonid life stages. Moreover, noxious plants may outcompete native plant species, thus reducing overall biodiversity and reducing overall habitat quality. Dense stands may also be conducive to creating warmer water (through reduced circulation and dissolved oxygen sags), and could become subject to wide fluctuations in water quality (e.g. temperature, dissolved oxygen (DO)) on a diurnal/seasonal basis.

4.3.4 Mitigation

4.3.4.1 Use Restrictions

Procellacor™ should only be used for the control of aquatic plants in accordance with label specifications. No data gaps have been identified for the basic environmental profile required by EPA for pesticide registration, although continued use of Procellacor™ under a variety of plant management scenarios will add valuable information that can be incorporated into improved treatment profiles and possible mitigation measures. For potential future irrigation with Procellacor™-treated water, final EPA labeling will include guidance on appropriate water use. Such restrictions can be refined once the human health and ecological risk assessment currently being conducted by EPA are released in spring 2017. The proposed label language is expected to reflect fewer application-related restrictions than other herbicides. Lower levels of personal protective equipment (PPE) for workers will be required, which is consistent with lower use rates, lower water use restrictions, and minimal effects to crops or other non-target species.

4.3.4.2 Swimming and Skiing

Recreation activities such as swimming, water skiing and boating are expected to be unaffected by applications or treatments using Procellacor™ herbicide formulations.

4.3.4.3 Irrigation, Drinking and other Domestic Water Uses

Ecology's Aquatic Plant and Algae permit provides specific mitigation measures for irrigation water and water rights. Following registration, however, no water use restrictions are anticipated for the product use label except for some forms of irrigation. Any such restrictions will be specified on the final label language in collaboration with EPA.

Drinking water is not expected to be affected by Procellacor™ applications.

4.3.4.4 Fisheries and Fish Consumption

Neither fisheries nor human fish consumption are expected to be affected by application of Procellacor™ herbicides. If there is potential to impact listed salmonid species (e.g. salmon, steelhead, bull trout, etc.) Ecology would enforce a fish timing window that would be protective of those species. Guidance for such timing windows are found at:
http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/permitdocs/wdfwtiming.pdf.

4.3.4.5 Endangered Species

Data are limited for specific listed threatened or endangered species under the ESA, however, a number of carefully designed and relevant laboratory toxicity tests for endangered species are currently under way, as discussed above. These tests will increase available testing data and enhance our understanding of how to more effectively protect non-target listed and vulnerable species, with particular emphasis on ESA-listed salmonid species such as salmon species, steelhead, and bull trout.

4.3.4.6 Wetlands or Non-Target Plants

Ecology's APAM permit outlines specific restrictions on what can be treated in wetlands. For example, in identified wetlands, the APAM specifies that the permittee "may treat only *high use areas* to provide for *safe recreation* (e.g., *defined swimming corridors*) and boating (e.g., *defined navigation channels*) in *identified and/or emergent wetlands*. The permittee must also limit the treated area to protect native wetland vegetation. However, final mitigation measures and best management practices concerning potential effects to beneficial or desirable wetland plant species will be developed in conjunction with testing on higher plants, some of which may occur in wetlands.

In general, effects to wetlands are anticipated to be minimal. Toxicity to fish, invertebrates, wildlife, and non-target plants would not generally be expected, and persistence (and thus food chain effects) would also be minimal. No specific toxicity testing was required or conducted for amphibians or reptiles which are ubiquitous in wetlands, but test results from invertebrate, avian, mammalian and other test species would be expected to serve as representative surrogate species for amphibians and reptiles.

Regarding potential impacts to rare or endangered plants occurring in wetlands, Ecology uses the Washington Department of Natural Resources (WDNR) Natural Heritage Site guidelines to determine if rare plants are likely to occur in the treatment area. If rare plants may be present at the treatment site, Ecology would require a field survey, and if such plants are found mitigation would be required.

4.3.4.7 Post-treatment Monitoring

EPA, Ecology, and other agencies routinely require both short- and long-term post-treatment monitoring for the purpose of evaluating non-target effects from herbicides such as Procellacor™. For Ecology, this post-treatment monitoring would be required under the permit, and would be a permit condition requiring monitoring to determine potential non-target impacts. These requirements will be incorporated into both label and permit, as appropriate, in conjunction with pesticide registration prior to application.

4.3.5 References

- American Society of Testing and Materials (ASTM). 2002. Standard Guide for Conducting Acute Toxicity Tests on Test Materials with Fish, Macroinvertebrates, and Amphibians. ASTM Designation E 729-96, reapproved 2002. [1]
- Beets J., and M. Netherland. 2017a. Mesocosm Response of Crested Floating Heart, Hydrilla, and Two Native Emergent Plants to a New Arylpicolinate Herbicide. Journal of Aquatic Plant Management - in prep. [1]
- Beets J., and M. Netherland. 2017b. Response of Eurasian and Hybrid Watermilfoils to Five Auxin-Mimic Herbicides. Journal of Aquatic Plant Management - in prep. [1]
- Breaux, N.T. (Dow AgroSciences LLC). 2015. Laboratory Studies Performed in Support of EPA Requirements: Ecotoxicology (Study #49677885), Environmental Fate (Study #49677884), Toxicology, (Study #49677882), Ecotoxicology (Study #030093_49678019), Environmental Fate Study #030093_49678018), Residue Analysis (Study #030093_49678017), Toxicology (Study #030093_49678016), and Product Chemistry (Study #030093_49678014). [9]
- Buczek, S., J. Archambault, and W. Cope. 2017. Evaluation of the Acute Toxicity of Multiple Forms of Procellacor™ Aquatic Herbicide to a Freshwater Mussel. In prep. [9]
- Denny, D., Branch Chief, EPA Office of Chemical Safety and Pollution Prevention, to Breaux, Dr., Regulatory Leader for Dow AgroSciences. 2016. Reduced Risk Decision for Rinskor Aquatic Uses. February 8. [letter [10]]
- Getsinger, K. 2016. Potential Procellacor™ Use Patterns for Controlling Submersed Invasive Plants in Pacific Northwest Waterbodies. UW-SAFS Herbicide Salmonid Presentation. October 25. [9]
- Grue, C. 2016. Confirming the Safety of the New Herbicide for Salmon-Bearing Waters. UW-SAFS Herbicide Salmonid Presentation. October 25. [9]
- Haug E. and R. Richardson. 2017. Mesocosm evaluation of the efficacy and selectivity of Procellacor for *monoecious hydrilla* control. Journal of Aquatic Plant Management in prep. [1]
- Heilman, M. (SePRO/Dow AgroSciences LLC). 2016. Efficacy, Fate, and Toxicology Associated with Selective Control of Invasive Aquatic Weeds. UW-SAFS Herbicide Salmonid Presentation. October 25. [9]
- Netherland, M., and R. Richardson. 2016. Evaluating Sensitivity of Five Aquatic Plants to a Novel Arylpicolinate Herbicide Utilizing an Organization for Economic Cooperation and Development Protocol. Weed Science. Volume 64: p. 181-190. [1]

- Netherland M., M. Heilman, J. Beets, and B. Willis. 2017. Mesocosm Response of Multiple Invasive Watermilfoils and Representative Native Submersed Plants to several Concentration – Exposure Times of Procellacor Aquatic Herbicide. *Journal of Aquatic Plant Mgt*, in prep. [1]
- Richardson, R., E. Haug, and M. Netherland. 2016. Response of Seven Aquatic Plants to a New Arylpicolinate Herbicide. *Journal of the Aquatic Plant Management Society*. Volume 54: p. 26-31. [1]
- US Environmental Protection Agency (EPA). Office of Prevention, Pesticides, and Toxic Substances (OPPTS). 1996. Ecological Effects Test Guidelines: OPPTS 850.175, Fish Acute Toxicity Testing, Freshwater and Marine. EPA 712-C-96-118. April. [1]

4.4 EVALUATION OF TOPRAMEZONE

4.4.1 Registration Status

Topramezone has historically been a conditionally registered herbicide for control of broadleaf and grassy weeds, and is also applied post-emergence to field crops such as corn, sweet corn and popcorn through ground or aerial application. It has an aquatic registration in Washington state for Oasis® Aquatic Herbicide for control of floating aquatic plants (e.g. water hyacinth [*E. crassipes*]), submersed aquatic plants (e.g. hydrilla [*H. verticillata*]), and a variety of other aquatic weeds and noxious plants.

4.4.2 Description

4.4.2.1 Environmental Characteristics: Chemistry (including efficacy) and Environmental Fate

Topramezone is a selective, systemic herbicide that shows effective herbicidal activity in controlling against broadleaf weeds and grasses as well as a number of aquatic plant species. The labeled rate for Impact® is 0.5 to 1.0 fl oz/ac, which is a maximum labeled rate of 0.22 lb/active ingredient/acre. The label specifies these restrictions: not applying the material within 45 days of corn harvest, not grazing or feeding treated corn forage, silage, fodder, or grain for at least 45 days following application. There are also label-specified rotational crop restrictions. In addition to this label, SePro has developed an aquatic label for the aquatic herbicide formulation Oasis® (29.7% active ingredient topramezone), which shows herbicidal activity against floating aquatic plants such as water hyacinth, and submersed aquatic plants such as hydrilla, pondweed, Eurasian milfoil, and bladderwort. The labeled rate for Oasis® foliar application is 4 to 16 fl oz/acre. The SePRO label (<http://cru66.cahe.wsu.edu/~picol/pdf/WA/60613.pdf>) has irrigation restrictions, guidance for aerial drift management, and including a drift reduction advisory.

The efficacy (effectiveness) of topramezone results from the inhibition of the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD) enzyme in target plants (Grossman and Ehrhardt, 2007). Following treatment in sensitive plants, carotenoid pigment formation, membrane structure and photosynthesis is disrupted.

Topramezone (SC formulation) is commonly used on sweet corn, white popcorn, and other varieties grown by hybrid growers because it provides a unique mode of action to control grasses and broadleaf weeds, when few other herbicide options are available. Oasis® has shown activity on fluridone-resistant biotypes of dioecious hydrilla found in Florida. Topramezone has been shown to be effective as a resistance management tool, for growers experiencing target species resistance and tolerance to triazine herbicide and acetolactate synthase (ALS)-inhibitor herbicides (EPA OPPTS, 2005c). Topramezone may be useful to field corn growers as a resistance management tool, and would be the only HPPD enzyme inhibitor available for post-emergent application that would not have the same label restrictions as would the other classes of herbicides.

4.4.2.2 Environmental Mobility and Transport

Topramezone can be somewhat persistent in aerobic soils (half-life >125 days). It is relatively water-soluble, with a solubility (at 20°C) of 0.98 grams (g) per liter(L) at potential of hydrogen (pH) 5, 15 g/L at pH 7, both values suggesting that topramezone is quite water soluble. Its measured vapor pressure is 1×10^{-12} hPa, suggesting that the material is largely non-volatile and not prone to aerial drift associated with

overspray or other applications. Concerning sorption and partitioning to organically enriched substrates, the measured octanol-water partition coefficient ($\log K_{ow}$) values for topramezone range from -0.81 (pH 4), -1.52 (pH 7), and -2.34 (pH 9), all suggesting that this material does not strongly sorb to organically enriched substrates but tends to remain in aqueous solution. Studies of the metabolites of topramezone show that topramezone is not extensively metabolized in ruminants, poultry, or other organisms (EPA OPPTS, 2005c).

Post-treatment dissipation of topramezone in the environment appears to be predominantly controlled by time-dependent adsorption and desorption. Adsorption/desorption studies indicate that topramezone may be quite mobile in some soils and sediments, but increasing non-extractable residue concentrations over time suggests time-dependent sorption behavior. Intact residues of topramezone may remain associated with the humic material and/or mineral components in soils and potentially accumulate from season to season. Slow desorption may free topramezone residues and extend phytotoxicity in soils. Neither abiotic hydrolysis nor direct photolysis in water nor photolysis on soil appear to be significant dissipation routes for topramezone. Concerning environmental degradation, abiotic hydrolysis and direct photolysis in water are not important transformation pathways, but microbially mediated biotransformation is an important pathway for biodegradation (EPA OPPTS, 2005b).

4.4.2.3 Bioconcentration and Bioaccumulation

As noted above in the Section 4.4.2.2, measured $\log K_{ow}$ values for topramezone range from -0.81 (pH 4), -1.52 (pH 7), and -2.34 (pH 9), which indicate that topramezone is not likely to partition to tissue or strongly sorb to organically enriched substrates. No bioconcentration or bioaccumulation factors for this compound were identified in the literature sources reviewed.

4.4.2.4 Toxicological Profile

Mammalian and Human Toxicity

Topramezone has demonstrated low acute toxicity to humans via the oral, dermal, and inhalation routes. An acute oral toxicity study conducted in rats produced a lethal dose (LD_{50}) value of greater than 2,000 milligrams (mg) per kilogram(kg) per day in both males and females, and a similar acute dermal study also conducted in rats produced an LD_{50} value of greater than 2,000 milligrams per kilogram (mg/kg)-day (also in both males and females). An acute inhalation study in rats produced lethal concentration (LC_{50}) values of greater than 5.05 mg/L. Each of these values are regarded as slightly toxic.

Topramezone is regarded as a slight eye and dermal irritant, but not a skin sensitizer, based on eye and skin irritation studies on rabbits, as well as a dermal sensitizer study on guinea pigs. Following oral administration in mammals, topramezone is rapidly absorbed and excreted via urine and feces. It is an inhibitor of 4-HPPD; this results in elevated serum tyrosine levels, but no thresholds have been developed to determine levels at which elevated tyrosine levels would result in detrimental or adverse effects. Elevated tyrosine from topramezone has been shown to cause adverse effects in the eye, liver, kidney, pancreas, and thyroid (EPA OPPTS, 2005c). Concerning mammalian dose-response studies of topramezone, there is a concern about elevated tyrosine levels based on studies of treated rates and mice. Two other common herbicides causing “tyrosinemia” are mesotrione and isoxaflutole. The EPA’s

Health Effects Division (HED) examined the potential for cumulative tyrosine-related effects for these three herbicides, and concluded that individual risk characterizations for all three herbicides were overstated, and that cumulative exposures are unlikely to pose a concern (EPA OPPTS, 2005b).

Concerning chronic toxicity to mammals, a number of subchronic and chronic toxicity studies have been conducted for topramezone, including prenatal, subchronic oral and dermal exposures, reproduction and fertility, and developmental toxicity (as summarized in EPA 2005b). No chronic effects were observed in mammals up to 4,000 mg/kg, based on a two-generation toxicity study on laboratory rats. Numerous acute and chronic neurotoxicity studies in rats, in addition to a long-term developmental study in rats, showed no evidence that topramezone can cause neurotoxicity. A reproductive toxicity study in rats did not demonstrate adverse reproductive effects; however, eight developmental toxicity studies in rats and rabbits showed slightly increased incidences of skeletal variation and alterations in skeletal ossification sites (EPA OPPTS, 2005b).

Mutagenicity studies conducted on the technical active ingredient (topramezone) and its major metabolites did not demonstrate any significant mutagenic potential. Post-treatment histopathological evaluations of test animals showed slight dose-dependent increases of adverse effects in the thyroid (follicular cell hyperplasia) in rats and dogs, liver (hepatocellular hypertrophy and focal necrosis) in rats and mice, and eyes (chronic keratitis) in rats. Increased incidences of thyroid follicular cell adenomas and adenoma and/or adenocarcinomas combined were observed in the carcinogenicity study in rats of both sexes. Based on the preponderance of evidence from these and other studies, however, in accordance with EPA's 2005 *Final Guidelines for Carcinogen Risk Assessment*, the EPA's HED classified topramezone as "not likely to be carcinogenic to humans at doses that do not alter rat thyroid hormone homeostasis". HED determined that quantification of human cancer risk would not be required since the calculated No Observed Adverse Effect Level (NOAEL) (0.4 mg/kg-day) for non-cancer risk assessment is not expected to alter thyroid hormone homeostasis or result in thyroid tumor formation.

General Ecotoxicity Profile

Toxicity testing of topramezone was conducted on a variety of standard animal test species, including birds, mammals, terrestrial invertebrates (e.g. honey bees, earthworms), fish species (both freshwater and marine/estuarine), and estuarine/marine invertebrates. These tests generally showed little to no toxicity. However, the estuarine and marine invertebrates showed moderate toxicity and there was some evidence of chronic toxicity to freshwater fish using growth as a toxicity endpoint (see *Fish Ecotoxicity* discussion, below). Metabolites were apparently nontoxic to both freshwater fish and invertebrates. Testing using the formulated end-use product Oasis® was largely nontoxic to honey bees, terrestrial invertebrates, and freshwater fish and invertebrates.

Fish Ecotoxicity

Chronic effects were apparent for freshwater fish with a non-lethal, chronic endpoint, which is reduced growth (length and weight) in fish at 9.01 mg ai /L, which is expected to be well above environmental concentrations associated with topramezone applications. Estimated chronic effects for estuarine/marine fish are uncertain because no chronic data were submitted by the registrant; therefore, the No Observed Adverse Effect Concentration (NOAEC) value was derived based on the

assumption that the freshwater and estuarine/marine fish are of equal sensitivity. Metabolites tested were reportedly nontoxic to freshwater fish.

Avian Toxicity

Acute toxicity of topramezone was not found to be problematic in birds (EPA OPPTS, 2005a), but there is uncertainty for *chronic* toxicity in birds. A chronic toxicity study of bobwhite quail reproduction using the TGA1 produced reduction in the ratio of number hatched to live embryos (a measure of hatchability) at the highest treatment level (1,012 mg ai/kg dry weight). Similarly, a mallard duck reproduction study showed significant reductions in hatchling body weight (bw) and female weight gain at all three treatment levels. However, these treatment levels using the TGA1 are expected to be well below expected environmental concentrations following treatment with the formulated product (e.g. Oasis®). As noted in the section on ecological risk (Section 4.4.34), EPA OPPTS (2005c) concluded that ecotoxicity concerns, including avian toxicity, are not expected to be problematic in association with treatment of this product.

Invertebrate Ecotoxicity

Acute toxicity testing using the formulated end-use product Topramezone SC™ was largely nontoxic to honey bees and other tested terrestrial invertebrates (EPA OPPTS, 2005c), although estuarine and marine invertebrates showed moderate toxicity. Metabolites of topramezone tested were reportedly nontoxic to both freshwater fish and invertebrates.

Toxicology Data Gaps

EPA believes the toxicology database for topramezone to be essentially complete, and there are no concerns for pre- or post-natal toxicity, mutagenicity, or neurotoxicity in mammals (EPA OPPTS, 2005b). Based on the quality of the exposure data submitted, EPA determined that the tenfold safety factor to protect infants and children could be removed. They further concluded that by using screening-level assessments, acute and chronic exposures/risks associated with topramezone would not be underestimated. The dietary drinking water assessment utilized exposure values and associated modeling parameters which provided conservative, health-protective, high-end estimates of water concentrations. Also, there are no residential uses of topramezone, so this exposure scenario did not need to be addressed.

4.4.3 Environmental and Human Health Impacts

4.4.3.1 Earth

Soil and Sediments

As noted above in Section 4.4.2.2, topramezone can be quite persistent in aerobic soils with a half-life greater than 125 days. Some adsorption/desorption studies indicate that topramezone may be mobile in some soils and sediments, but non-extractable residues increase over time, which suggests time-dependent sorption behavior. Topramezone residues may remain intact in soils, sorbed or associated with humic materials and/or mineral components in soils, and thus pose a potential for seasonal accumulation. Slow desorption may free topramezone residues from soils, thus potentially contributing to phytotoxicity in soils.

Agriculture

Environmental Impacts to non-target species associated with agriculture treatments using topramezone on corn has been somewhat problematic. Accordingly, the Impact® herbicide label specifies several use restrictions (see Section 4.4.2.4), including not applying topramezone within 45 days of corn harvest, not grazing or feeding treated corn forage, silage, fodder, or grain for at least 45 days following application. There are also label-specified rotational crop restrictions. Following these label restrictions and other mitigation procedures, impacts to agriculture are expected to be slight.

Terrestrial land Use

There are currently no residential registrations for topramezone. Accordingly, impacts to terrestrial land use are expected to be minimal.

4.4.3.2 Water

Surface Water, Runoff, and Aerial Drift

Aerial drift and surface water runoff were identified as potential routes of exposure to topramezone residues in aquatic ecosystems (EPA OPPTS, 2005c), and for non-target terrestrial plants. Incidental residues of topramezone may also be present in irrigation water and may be phytotoxic to irrigated non-target plants. In addition, soils containing residues of topramezone have the potential to be transported offsite by aerial drift, airborne dust or soil erosion. Recommendations for rotational crop intervals of more than 18 months suggest that residues of topramezone in soil are still active and may cause injury to sensitive, non-target plants.

Concerning the possibility of aerial drift associated with topramezone, the aquatic label Oasis® includes detailed restrictions on avoiding spray drift (Section 4.4.4.1), including an aerial drift reduction advisory detailed on the label. If these label specifications are followed, the potential impact for drift associated with topramezone applications is expected to be mitigated.

Groundwater and Public Water Supplies

As noted in the *Data Gaps* section of 4.4.2.4, above, EPA conducted a human health risk assessment which addressed drinking water exposures to topramezone via both surface water and groundwater exposure scenarios. Conclusions from this risk assessment, based on health-protective, conservative estimates and input parameters, were that no risks or concerns were evident in association with dietary and drinking exposure to topramezone. In addition, there are no registered or anticipated residential applications for topramezone, which further diminishes the likelihood of adverse exposures associated with water, food, soils, aerial drift, or other pathways.

Water and Shoreline Use

Impacts to receiving water and shoreline use are expected to be negligible as long as label specifications are followed, and is consistent with the findings from EPA's risk assessment for topramezone (EPA OPPTS, 2005c).

4.4.3.3 Human Health Hazards and Risk

Topramezone has demonstrated low acute toxicity to humans via the oral, dermal, and inhalation routes (more detail provided in Section 4.4.2.4). It is a slight eye and dermal irritant, but not a skin sensitizer. Following oral administration, topramezone is rapidly absorbed and excreted via urine and feces. Topramezone is an inhibitor of 4-HPPD; this results in elevated serum tyrosine levels. While no thresholds have been developed to show levels at which elevated tyrosine levels would result in detrimental or adverse effects, elevated tyrosine from topramezone has been shown to cause adverse effects of various test species (EPA OPPTS, 2005c) (see discussion in Section 4.4.2.2 above). Histopathological evaluations have shown potential adverse effects in the thyroid of rats and dogs, pancreas in rats, liver in rats and mice, and eyes of in rats. A reproductive toxicity study in rats did not demonstrate adverse reproductive effects, but developmental toxicity studies in rats and rabbits have shown increased incidence of skeletal changes. Animal studies have consistently shown that some skeletal variations may be associated with 4-HPPD inhibitor herbicides such as topramezone.

As previously discussed in Section 4.4.2.2 above, mutagenicity studies conducted on technical topramezone and its major metabolites showed little to no mutagenic potential. EPA's HED classified topramezone as "Not likely to be carcinogenic to humans at doses that do not alter rat thyroid hormone homeostasis". They determined that quantification of human cancer risk is not required since the NOAEL for non-cancer risk assessment is not expected to alter thyroid hormone homeostasis or result in tumor formation.

Hazard and risk assessments were conducted in relation to this registration application and tolerance petition for topramezone on corn. Results of these assessments suggest that its use, consistent with the proposed labeling measures, will be protective of both public health and the environment. The risk assessment was a joint review by the Pesticide Management Regulatory Agency (PMRA) of HED and EPA's Environmental Fate and Effects Division (EFED). HED's review used conservative exposure assumptions, including tolerance level residues and 100 percent crop-treated exposure assumptions, in both the acute and chronic risk analyses. Aggregate exposures to the general public are based on food plus water exposure scenarios derived from potential exposure to topramezone.

Consideration of risks to pesticide applicators, handlers, and other agricultural workers were also considered. HED determined that short- and intermediate-term exposures may occur. Since topramezone may be applied only twice per year, long-term exposures are not expected from the proposed uses. No more than a 30-day exposure is expected for most handlers, although it may be possible for commercial applicators to experience intermediate-term exposures (1-6 months). Mixer and loaders should use protective gloves as required on the Topramezone SC™ label registered under Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA); if precautions are taken, HED's concerns would be addressed. An acute and chronic dietary exposure analysis was conducted using a dietary exposure evaluation model, which incorporates food consumption data from the United States Department of Agriculture (USDA) 1994-1996 and 1998 Nationwide Continuing Surveys of Food Intake by Individuals. This assessment considered accumulated exposure to topramezone for each route of exposure, with assumed tolerance-level residues for key food groups with proposed topramezone tolerances.

Concerning assessment of human health risk for both dietary exposure and topramezone in drinking water, EPA determined that insufficient monitoring exposure data has been collected to complete a comprehensive or quantitative risk assessment for these pathways (EPA OPPTS, 2005a). Thus, drinking water concentration estimates for both surface water and groundwater were made using modeling based on data on the physical characteristics of topramezone. In addition, the Oasis® label has an application rate limit when working in waterbodies with potable water intakes. Because topramezone is not registered for any uses that could result in residential exposures, the aggregate risk is the sum of the risk from food and water, which are not of concern based on findings from EPA's EFED risk assessment. HED (EPA OPPTS, 2005a) further concluded that no residue chemistry, toxicology, or occupational or residential exposure data requirements would be problematic in terms of exceeding tolerance levels for residues of topramezone.

4.4.3.4 Ecological Risk

EPA's EFED has reviewed this proposed registration of topramezone and concluded that plants, including both non-target terrestrial and aquatic vascular plants, are directly at risk from the proposed use of topramezone on corn. This potentially includes federally listed endangered plant species. Regarding ecological risk to specific animal species including acute and chronic risks to avian, mammalian, fish, invertebrate (including insect) exposures, EPA concluded that no levels of ecological concern were exceeded and therefore risks are expected to be negligible. In addition, EPA concluded that non-vascular aquatic plants (e.g. algae, diatoms, etc.), are not believed to be at risk, as modeled exposure concentrations in water were below thresholds of concern. However, some growth effects were observed in an avian laboratory study (see Avian Toxicity discussion in Section 4.4.2.4) that creates uncertainty as to the potential for chronic toxicity and effects. As noted in Section 4.4.4.6 below, EPA has specific task forces that will help to implement mitigation measures as needed to eliminate or mitigate risks to non-target plants associated with topramezone.

4.4.3.5 Wetlands

Topramezone would not be expected to cause or contribute to impacts to animal species inhabiting wetlands due to its low toxicity to mammals, invertebrates, and birds. Uncertainty does exist concerning chronic effects to both invertebrates and birds, some of which may inhabit wetlands. Topramezone does not appear to bioaccumulate or bioconcentrate in the environment, although residues in soils may be persistent. As discussed in Section 4.4.4.2, there is a tendency for topramezone to cause toxicity to some species of broadleaf or grassy non-target plant species, and potential impacts to non-target plants could be an issue.

4.4.3.6 Plants

Algae

EPA EFED concluded that non-vascular plants such as algae are not likely to be harmed by topramezone, as the herbicidal activity of the material is focused on metabolic pathways occurring in vascular plants.

Higher Plants and Crops

As noted in Section 4.4.2.4 above, EPA's EFED has conducted an ecological risk assessment for both plant and animal non-target receptors associated with topramezone exposures, and concluded that plants, including terrestrial and aquatic vascular plants are directly at risk from the proposed use of topramezone on corn. They further concluded that this risk could include federally listed endangered plant species.

Concerning phytotoxicity, the most significant toxicity identified during testing were on non-target plant species. For aquatic plants, toxicity was higher on vascular than non-vascular plants. Vascular plants are more sensitive to the technical grade active ingredient (TGAI) topramezone than to Topramezone SC™ (formulated topramezone) or to metabolites. The most pronounced effects on frond counts were observed for topramezone TGAI. All terrestrial plants showed toxic effects from TGAI exposure in seedling emergence and vegetative vigor studies, but at varying degree depending on the species and exposure concentrations. In seedling emergence and vegetative vigor studies, monocots were observed to be less sensitive than dicots. The most sensitive plants to seedling emergence were ryegrass (monocot) and cabbage (dicot). The most sensitive plants to vegetative vigor were onion (monocots) and soybeans (dicots). Dry weight, a measure of plant growth, appeared to be the most sensitive toxicity endpoint. However, phytotoxic growth effects, such as effects on shoot height, were also observed.

4.4.3.7 Habitat

Topramezone is not expected to cause or contribute to environmental problems in animal or plant habitat wetlands due to its low toxicity to animal species and its lack of bioconcentration or bioaccumulation potential. Moreover, topramezone shows little to no toxicity to both invertebrates and fish, which form the key prey base for salmonids (e.g. salmon, steelhead, bull trout) in the Pacific Northwest. Despite the low toxicity potential, the persistence of topramezone in soils is moderate and could have some longer-term impacts to critical habitat, especially to plant species. As discussed above in Section 4.4.3.6, in the *Higher Plants and Crops* discussion, topramezone may cause toxicity to some non-target plant species, and it would be prudent to consider possible impacts to sensitive non-target vegetation in streams, lakes, wetlands, and other water bodies due to the phytotoxic properties of topramezone.

4.4.4 Mitigation

4.4.4.1 Use Restrictions

The Impact° herbicide label (EPA OCSF, 2016) specifies several key use restrictions, also summarized above, which are intended to mitigate potential impacts associated with agricultural use of topramezone. These include not applying the material within 45 days of corn harvest, not grazing or feeding treated corn forage, silage, fodder, or grain for at least 45 days following application. There are also label-specified rotational crop restrictions.

Topramezone SC™ has a unique mode of action to control target grasses and broadleaf weeds, when few other herbicide options are available. Growers have concerns with conventional herbicides such as triazine due to ALS-inhibitor resistance and weed tolerance, that use of topramezone is expected to mitigate. Topramezone is therefore useful to field corn growers as a resistance management tool, and

would be the only HPPD inhibitor available for post-emergent applications with minimal label restrictions.

The Oasis® label (<http://cru66.cahe.wsu.edu/~picol/pdf/WA/60613.pdf>) contains a variety of restrictions concerning aquatic applications. These include irrigation restrictions, hydroponic and greenhouse or nursery farming, food crops, turf, and non-food/feed crops. In addition, there is an advisory on application of topramezone to exposed or dewatered sediments, and detailed restrictions on avoiding spray drift, including an aerial drift reduction advisory detailed on the label.

4.4.4.2 Swimming and Skiing

Swimming, water skiing, or other human recreational uses are not expected to be problematic in association with topramezone applications, as topramezone is water soluble and generally non-toxic to humans and mammals. Moreover, Ecology prohibits treatments with pesticides that have water use restrictions on the FIFRA label that would restrict public water use during the opening week of fishing season or during tribal fisheries, Washington State Department of Fish and Wildlife (WDFW) Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. They further require that permittees must minimize treatments that restrict public water use during weekends.

4.4.4.3 Irrigation, Drinking and Domestic Uses

As noted in above in Section 4.4.3.3, EPA OPPTS (2005c) conducted a human health risk assessment which addressed drinking water exposures to topramezone via both surface water and groundwater exposure pathways. Conclusions from this risk assessment, based on health-protective, conservative estimates and input parameters, were that topramezone posed no risks or concerns in association with dietary and drinking water exposures. In addition, there are no registered or anticipated residential applications for topramezone, which further diminishes the likelihood of adverse exposures associated with drinking water. The Oasis® label currently allows for in-water treatment and Ecology may consider topramezone for inclusion in the Aquatic Plant and Algae Management (APAM) permit which would allow for in-water treatment. The label has rate restrictions where potable water intakes occur and inclusion in the APAM permit would allow impacted water rights holders to request potable, irrigation or domestic water rights for the duration of the impact. Ecology's APAM permit also requires a letter of approval from a community or municipal water supply prior to application.

4.4.4.4 Roadsides or Utility Rights-of-way

Concerning possible application of topramezone to roadsides or utility rights-of-way, applicants would need to use the aquatic formulation of topramezone (Oasis®). When treating areas of corn or other crops with topramezone herbicides in and around roadside or utility rights-of-way that could be grazed or planted to forage, important label precautions would apply regarding runoff to irrigation ditches or streams, harvesting hay, using manure from animals grazing on treated areas, and/or rotating treated areas to sensitive crops.

4.4.4.5 Fisheries and fish consumption

Concerning impacts or potential mitigation for protection of fisheries, the permittee must comply with appropriate WDFW timing windows to protect salmon, steelhead, and bull trout populations as well as priority habitats and species. WDFW may periodically update this table as new information becomes

available or on request from Ecology. The timing table is available at:

http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying treatments to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, the WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations.

Fish consumption is not expected to be an issue as topramezone does not bioaccumulate and would not be expected to be present in edible fish or shellfish tissue.

4.4.4.6 Endangered Species

There is no anticipated hazard from topramezone to Endangered Species Act (ESA)-listed animal species of concern such as fish or mammals, but potential hazards could occur to non-target endangered plant species. EPA's Endangered Species and Spray Drift Task Forces will suggest and implement mitigation measures as needed to eliminate or mitigate risks to non-target plants associated with this material.

Concerning additional requirements for discharges to water bodies where sensitive, threatened, or endangered plants could be present, before issuing permit coverage under Ecology's APAM NPDES General Permit, Ecology would determine whether such plant species are believed to be present in the proposed treatment area. For aquatic plant control projects with suspected rare plant populations, the permittee must submit a detailed plant survey and implement appropriate mitigation measures if rare plants are found.

4.4.4.7 Wetlands or Non-Target Plants

As noted above, topramezone would not be expected to cause or contribute to environmental problems in wetlands due to its low toxicity to animal species and failure to bioaccumulate in the environment. As discussed in Section 4.4.3.4, however, there is a tendency for topramezone to cause toxicity to some species of broadleaf or grassy non-target species, and it would be prudent to consider possible mitigation measures for protection of wetlands due to the phytotoxic properties of topramezone.

As stipulated by Ecology for the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to allow for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed above in *Endangered Species*.

4.4.4.8 Post-treatment Monitoring

EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from herbicides such as topramezone. For Ecology, this post-treatment monitoring would be required under the water quality permit, and would be a permit condition requiring monitoring to determine potential non-target impacts, especially to non-

target plant species. These requirements will be incorporated into both label and permit requirements, as appropriate, in conjunction with pesticide registration and permit requirements prior to application.

4.4.5 References

- BASF Corp. 2005. Topramezone (BASF 670H) Herbicide. Tier II Drinking Water Assessment. D314642. March. [9]
- BASF Corp. 2002. The Determination of Residues of Topramezone and Metabolites in Soil using Liquid Chromatography -Mass Spectrometry (MS) or MS. BASF Study No. 62466, Reg. Doc. 2002/5002831. [9]
- Environmental Protection Agency (EPA). Office of Prevention, Pesticides, and Toxic Substances (OPPTS). 2005a. Amendment to the Human Health Risk Assessment New Active Ingredient (Topramezone) for Uses on Corn (Field, Pop, Seed, Sweet). DP 290075. [1]
- EPA. OPPTS. 2005b. Topramezone in and on Corn: Summary of Analytical Chemistry and Residue Data. May. https://www3.epa.gov/pesticides/chem_search/cleared_reviews/csr_pc_123009_11_may_05_a.pdf. [9]
- EPA. OPPTS. 2005c. Pesticide Fact Sheet: Topramezone, Conditional Registration. EPA Chemical Code 123009. https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_PC-123009_10-Aug-05.pdf. [1]
- EPA. Office of Chemical Safety and Pollution (OCSF). 2016. Product Label for Topramezone; Label Amendment for Fallow Land Application Use. https://www3.epa.gov/pesticides/chem_search/ppls/005481-00524-20160922.pdf. [1]
- Grossman, K. and T. Ehrhardt. 2007. On the Mechanism of Action And Selectivity of the Corn Herbicide Topramezone: A New Inhibitor of 4-Hydroxyphenylpyruvate Dioxygenase. Pest Management Science. Volume 63 (5): p. 429-439. [1]
- SePro Corp (SePro). 2015. Safety Data Sheet – Oasis® Herbicide. http://www.sepro.com/documents/Oasis_MSDS.pdf. [1]
- SePro. Undated. Specimen Label – Oasis® Aquatic Herbicide. https://s3-us-west-1.amazonaws.com/www.agrian.com/pdfs/Oasis_Aquatic_Label.pdf. [1]
- Washington State Department of Agriculture (WSDA). 2014. *Non-agricultural Pesticide use in Puget Sound Counties*. Publ. No. AGR PUB 103-409. <http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx>. [1]

4.5 EVALUATION OF PEROXYACETIC ACID/HYDROGEN PEROXIDE

4.5.1 Registration Status

Peroxyacetic acid, also known as peracetic acid (PAA) and hydrogen peroxide (HP) were first registered in the US as pesticides in 1977 and 1985, respectively for use as disinfectants, sanitizers and sterilants. Joint cooperation between EPA and the US Food and Drug Administration (FDA) gives the EPA primary regulatory jurisdiction over peroxy compounds such as PAA and HP. PAA and HP have a wide variety of current registrations with EPA (EPA 2016). These include at least seven registrations for a variety of compounds containing PAA and HP as water disinfectants, for food processing such as washing and peeling of produce, bleaching, sanitizing food contact surfaces, and removal of algae and bacteria from food products. In general, PAA and HP are classified by the FDA as Generally Regarded as Safe (GRAS), suggesting that these materials are considered safe to use in food applications. GreenClean 5.0® is also registered by EPA, and is a broad spectrum algaecide and bactericide (containing 5.3 percent PAA as the active ingredient) used for water disinfection of ponds, lakes, and other water bodies. In Washington State, Ecology maintains a fresh fruit packing Industry General Permit (WAG435031) for PAA as a chemical additive for use on apples and other produce.

4.5.2 Description

4.5.2.1 Environmental Characteristics: Product Use Pattern and Chemistry

Both hydrogen peroxide and peroxyacetic acid are highly reactive oxidizers that form a number of associated compounds with varying physical and chemical properties. For example, peroxyacetic acid and sodium percarbonate are organic addition compounds that are also reactive oxidants and/or break down to hydrogen peroxide. As noted above, PAA and HP are used for a wide variety of applications, including as antimicrobial solutions for use as stormwater and wastewater disinfectant, and are powerful oxidizers or disinfectants similar to chlorine, but without some of chlorine's deleterious side-effects. These compounds are used as bactericides, algaecides, fungicides, in food processing (see registrations summarized above), as oxidants in preparing epoxy compounds, bleaching agents, and for sterilization. Although they are not persistent in the environment, while in concentrated form or in storage they are considered highly reactive and even explosive, and therefore are normally stored in diluted form to reduce these hazards. PAA and HP are freely soluble (1,000 g/kg), both are highly volatile, with a vapor pressure of 14.8 mm Hg at 25°C (PAA). PAA also has K_{ow} of -0.9, which indicates that PAA is incapable of bioaccumulation or bioconcentration, HP also has no capacity for bioaccumulation or bioconcentration. A vapor pressure for HP was measured at 5 mm Hg at 30°C, which is comparable to the vapor pressure for PAA (ACGIH, 1991; NCBI, 2008, MDEP, 2010). Biosafe (2016) specifies that GreenClean Liquid 5.0 is classified as an organic peroxide that will not detonate in a cavitated state, does not deflagrate, only shows a low, or no effect if heated when confined, and has low or no explosive power.

Application of PAA and HP formulations can be made in several ways, depending on the products used. In general, these products are most effective when application is made while algae are not yet well established and when growth first begins to appear. Both sunlight and higher temperatures enhance the effect so application early in the day under calm, sunny conditions is best. In water bodies with floating mats of algae, the best results are obtained by breaking up the mats either before or during product

application. Dead and/or floating plant material should be removed before it sinks and decays as an accumulation of decaying matter will provide additional nutrients to the water that will stimulate regrowth of algae and further blooms. These products may be applied via either a spot treatment or a whole-lake treatment. Methods of application vary with the formulation and include, for liquid products, spot application directly over the infested area on the water surface from a boat or shore or injection via a piping system. For granular forms of the product, broadcast application by hand or via a mechanical spreader, spreading the product in burlap bags dragged behind a boat or aerially, via conventional aerial application equipment (BioSafe, 2008, 2016; MDEP, 2010).

4.5.2.2 Environmental Mobility and Transport

Howard (EnviroTech, 2003a) investigated the environmental fate and impact of Perasan™ in soil. Several peroxygen-based compounds in agricultural applications were monitored for 9 days in soils, and soil acidification was observed. Soil pH values dropped from pH 6.2 to pH 4.7 immediately after treatment, but reverted to normal pH levels within 9 days, presumably due to degradation of the acetate ion. After 13 minutes, less than 1 percent of the dose originally applied remained in treated soils.

Howard (EnviroTech, 2003b) investigated the decay kinetics of PAA and HP in a variety of water matrices. He calculated half-lives in three types of water, of varying hardness and including seawater, and found that half-lives ranged from 12 minutes to 30 hours, suggesting that neither PAA nor HP persist in surface water following application. Generally speaking, HP degrades rapidly due to its many degradation pathways. In fact, HP solutions are often mixed with a number of stabilizers to slow the degradation process, including mineral acids to maintain an acidic solution, as well as complexing/chelating agents. Both PAA and HP are freely soluble in water, so could be mobile if released into groundwater or other water sources, but due to the rapid degradation kinetics this material is not likely to transport off-site.

4.5.2.3 Field Surveys and Investigations

Several studies report on the efficacy and relatively low toxicity of HP (as summarized by MDEP 2010) when used at high concentrations to treat parasites in farmed or hatchery fish for very short time periods (i.e., typically 1 hour or less). Some studies found, however, that toxicity of HP appears to be temperature-related. For example, one study (Kierner and Black, 1997) recommended that HP at these high concentrations should not be applied to waters at water temperatures higher than about 14°C due to potentially much-increased toxicity; the cause of this disparity is unknown. They recommend that HP water treatments would best be conducted during winter for this reason, although lakes and ponds in the Northwest typically experience algal blooms during summer months when these waterbodies are much warmer, often exceeding temperatures of 21°C or more. Nonetheless, based on this finding it appears that application of high concentrations of hydrogen peroxide-based products during warmer weather may not be prudent, assuming the concentrations are comparable, even for short periods of time, due to this elevated temperature-related toxicity. Most applications of this product, throughout the US, use rates well below the specified maximum either as surface treatments or along lake margins for filamentous algae or cyanobacteria, and maintaining these lower concentrations should help to minimize any temperature-related increases in toxicity (Warmuth, 2017 - Personal Observation).

4.5.2.4 Toxicological Profile

In general, both peroxyacetic acid and hydrogen peroxide can be acutely toxic to both humans and to animal and plant species. A variety of studies on both mammals and aquatic species support this conclusion, and are summarized below. Regarding chronic toxicity, however, the material is known to dissipate quickly in the aquatic environment and would not be expected to persist long enough to cause any harmful chronic or subchronic exposures.

Mammalian and Human Toxicity

Both PAA and HP cause severe irritation to eyes, skin, and the respiratory tract upon direct exposure, and may cause permanent damage. An estimated human oral lethal dose is a range of 50 to 500 mg/kg, which is about one teaspoon for a 150-pound person. However, although an oral exposure to PAA could be toxic or lethal, a much more likely exposure would be via inhalation or direct contact with the skin or eyes as an occupational exposure. There is also some evidence that prolonged exposure to PAA causes lung cancer in test animals, and potentially liver and kidney cancers as well (EPA CEPP, 1987; Greene, 2013). However, in evaluations which consider the overall preponderance of evidence for human carcinogenicity associated with HP, both the European Union and International Agency for Research on Cancer (IARC) have concluded that there is insufficient information to classify HP as to its carcinogenicity to humans (ATSDR, 2002; ECJRC, 2003). Similarly, although several studies on developmental and reproductive toxicity associated with PAA and HP have been conducted, the overall evidence for this type of toxicity is regarded as inadequate for both compounds (ATSDR, 2002).

Several acute studies of PAA have been performed on test mammal species. Results of an acute rat oral study yielded an LD₅₀ value of 4,080 mg/kg bw for a 5 percent solution, and 330 mg/kg for a 7 percent solution of PAA as the active ingredient. An acute rabbit oral toxicity study yielded an LD₅₀ value of 1,410 mg/kg bw for a 10 percent solution. Each of these values is dramatically higher than any environmental concentration of PAA expected to occur in association or following algaecide treatments in ponds or lakes, and would thus serve to be protective of both mammalian and human health.

Several acute inhalation studies for PAA and HP were identified as well for test mammal species. Results of three acute rat inhalation studies yielded LC₅₀ values of 476 mg/cubic meter (m³) (60-minute exposure), 1,972 mg/m³ (4-hour exposure), and 204 mg/m³ (4-hour exposure). A similar study of mice inhalation yielded an LC₅₀ value of 512 mg/m³, showing relative consistency between test species. It was frequently observed that the animals experienced extreme respiratory irritation at levels well below those causing acute lethality. A study of HP using rats showed that lethality of HP is about ten-fold less acutely toxic than PAA. These studies further document that PAA and HP are acutely toxic when inhaled, a pathway that could be experienced as an occupational exposure. It is noted that the label addresses both worker safety and PPE requirements. Moreover, following aquatic application of PAA and HP, there should be little concern about inhalation exposure.

General Ecotoxicity Profile

Product labels for various PAA and HP-based products warn that formulations are toxic to birds, fish, invertebrates, bees and other beneficial insects (Biosafe, 2008, 2016). However, no quantitative acute toxicity information was found in the available literature for these endpoints. Importantly, dangers to

the aquatic environment associated with PAA treatments are expected to be limited due to the key chemical properties summarized above, including high volatility, low persistence, and inability to bioaccumulate. Nonetheless, several label restrictions have been added as part of EPA registrations (see Section 4.5.4.1), such as to eliminate drift to blooming crops or weeds while pollinating insects are present. Another label restriction specifies that PAA-containing effluent should not be discharged to water bodies unless a NPDES permit is in force; another recommends that PAA should not be applied directly to treated, finished drinking water (BioSafe, 2016).

The discussion below addresses the ecotoxicity to several plant and animal species. Several chronic studies of PAA and HP to fish and other organisms were reviewed, but it is clear that PAA and HP dissipate so quickly that chronic exposures generally do not occur, and would not be expected to occur in the aquatic environment.

Fish Ecotoxicity

Several acute studies of PAA and HP have been performed on test fish species. Results of a fathead minnow (*P. promelas*) acute study yielded a 96-hour LC₅₀ value of 16.4 mg/L. Results of an acute test on the cyprinid fish the ide (*L. idus*) yielded a 72-hour LC₅₀ value of 35 mg/L. Results of a channel catfish (*I. punctatus*) acute study yielded a 96-hour LC₅₀ value of 37.4 mg/L. In addition to these studies, ten other acute studies using an array of freshwater fish were conducted (MDEP, 2010), which reported a range of LC₅₀ values from 0.35 mg/L to 3.3 mg/L, which is generally consistent with the data summarized above. In addition, several chronic studies of PAA and HP to fish were reviewed, but as noted above, PAA and HP dissipate so quickly that chronic exposures generally do not occur, and would not be expected to occur in the aquatic environment.

Avian Toxicity

No avian toxicity tests were identified as part of the literature review, although the labels (BioSafe 2008, 2016) specify that PAA and HP product as a concentrate is toxic to birds, although formulated products when used as directed would have little likelihood of harming birds.

Invertebrate Ecotoxicity

Several acute studies of PAA and HP have been performed on test invertebrate species. Results of a 48-hour acute test using a daphnid (*D. pulex*), which would generally be among the zooplankton inhabiting an aquatic site, yielded an EC₅₀ value of 2.4 mg/L. Results of another acute test using another daphnid species (*D. magna*) yielded a 24-hour EC₅₀ value of 2.3 mg/L. Results of another acute test using an amphipod (*Gammarus sp.*) yielded a 96-hour EC₅₀ value of 4.4 mg/L. Results of another acute test using a freshwater snail (*Physa sp.*) yielded a 96-hour EC₅₀ value of 17.7 mg/L. A single study of *D. magna* in which EC₅₀ values were calculated 1, 4, and 48 hours following administration of PAA and HP shows EC₅₀ values of 10.7 mg/L, 5.37 mg/L, 5.37 mg/L, and 5.37 mg/L, respectively. These concentrations are generally very consistent, and indicate that the acute toxicity to these organisms occurs soon after exposure begins, and supports the supposition that PAA and HP will dissipate very quickly after in-water treatments.

Phytotoxicity

Few studies on the phytotoxicity of PAA and HP were identified in this literature review. Several fumigation studies testing HP toxicity in vascular plants (wheat, Norway spruce and red beech) indicated reversible effects on assimilation and photosynthesis in wheat plants. Effects on trees were more severe and included effects on internal needle and leaf structure. However, there were no EC₅₀ or NOEC values determined in these studies (ECJRC, 2003). Another study conducted with HP on the algae *C. vulgaris* indicated an EC₅₀ of 2.5 mg/L and a NOEC of 0.1 mg/L (MDEP, 2010). Given that herbicide products such as PAA and HP products are formulated to control and treat algae, the effect levels cited above are generally consistent within the range of dose levels used for these products.

4.5.3 Environmental and Human Health Impacts

4.5.3.1 Earth

Soil and Sediments

PAA and HP are proposed for treatment to ponds, lakes, and other water bodies in Washington State to remove algae, bacteria (including cyanobacteria), and fungus. From the water column, thus improving water quality. This material is highly soluble and not persistent in water soils, or sediments, or the water column. Accordingly, treatments using PAA and HP as algaecides would not be expected to cause or be associated with adverse effects to lake sediments.

Agriculture

The type of application under discussion is in-water application to lakes or ponds for the purposes of controlling aquatic algae, so no agricultural impacts are expected.

Terrestrial Land Use

The type of application under discussion is in-water application to lakes or ponds for the purposes of controlling aquatic algae, so no terrestrial land use impacts are expected.

4.5.3.2 Water

Surface Water and Runoff

Because PAA and HP are acutely toxic in the aquatic environment to a variety of species, short-term effects could occur, and it is important that treatments be conducted in strict accordance with label and permit specifications. PAA and HP may be used as a “shock treatment” to the water, and overall recovery in the aquatic environment will occur quickly. Longer-term effects to aquatic ecosystems associated with use of PAA and HP in controlling aquatic algae, should be insignificant or negligible so long as label and permit requirements are followed.

Groundwater and Public Water Supplies

In-water treatments applying PAA or HP to lakes or ponds are not expected to cause any effects to groundwater or to public water supplies. Label restrictions provide that these compounds should not be added to finished drinking water or drinking water sources, and both WSDA’s registration and Ecology’s permit requirements will focus on algal control to surface water bodies.

Water and Shoreline Use

As noted above, in-water treatments of PAA and HP for algal control to lakes or ponds are not expected to cause long-term effects to the water column of treated lakes or ponds, or to impact shoreline uses of these water bodies.

4.5.3.3 Human Health Hazards

As discussed above in Section 4.5.2.4, PAA and HP can cause acute toxicity through direct contact or inhalation exposure, and long-term exposure to humans could be carcinogenic. However, label specifications and Ecology's permit will require that humans avoid contact immediately following "shock treatments" by PAA and HP, allowing the material to dissipate before humans can be exposed. These mitigation measures and BMPs will be important in preventing human exposures associated with these treatments. Regarding occupational exposures, it is important that pesticide applicators and other workers follow prescribed FIFRA label precautions and wear appropriate PPE when applying.

4.5.3.4 Ecological Risk

As discussed above regarding fish and avian toxicity under Sections 4.5.2.4, PAA and HP are acutely toxic to aquatic organisms such as fish, invertebrates, plants, and birds, but as with the discussion on human exposure, the material does not persist in the aquatic environment and a rapid recovery of non-target aquatic organisms to pre-treatment levels would be expected.

4.5.3.5 Wetlands

Because of their powerful oxidizer and algaecidal behavior, PAA and HP could cause short-term effects to species inhabiting wetlands if label and permit specifications are not followed, although these effects would be expected to be short-term in nature. Environmental concentrations will be carefully considered as part of label-specified dose calculations prior to the in-water algal control treatments, and these concentrations are not expected to contribute to or cause long-term adverse impacts to plants or animals within a wetland environment.

4.5.3.6 Plants

Higher Plants (Including Crops) and Algae

As noted in the *Invertebrate Ecotoxicity* discussion in 4.5.2.4, few studies on the phytotoxicity of PAA and HP were identified, although fumigation studies testing HP toxicity in vascular plants indicated reversible effects on assimilation and photosynthesis. A study conducted with HP on algae showed that the effect levels observed are reversible and short-lived, and toxicity levels are generally consistent within the range of dose levels used for PAA and HP products used for algae control.

4.5.3.7 Habitat

As discussed above, PAA and HP are not expected to cause longer-term effects to aquatic habitats. In fact, administration of these algaecides to the aquatic lake or pond environment over the long term is more likely to benefit and improve habitat, water quality, and the aquatic environment in general. No long-term ecotoxicity would be expected due to label and permit restrictions, although temporary reductions in prey species such as phytoplankton, zooplankton, fish, invertebrate, and other aquatic

species could occur over the short term prior to ecosystem recovery. Some of these affected organisms are important prey species for protected species such as salmonids, and adverse effects may temporarily occur following these algal control applications. Environmental concentrations will be carefully considered per label specifications as part of dose calculations prior to the in-water treatments, and thus PAA and HP residues over time are expected to quickly attenuate, and not to contribute to or cause long-term adverse impacts to aquatic habitats within these water bodies.

4.5.4 Mitigation

4.5.4.1 Use Restrictions

PAA and HP are acutely toxic to insects, other invertebrates, birds and fish (see above discussion regarding *General Ecotoxicity Profile in Section 4.5.2.4*), and as such it is important to administer label and permit restrictions in association with algal control treatments. As noted above, several label restrictions have been added as part of EPA registration, for example, to eliminate drift to blooming crops or weeds while pollinating insects are present (EPA, 2016). Another label restriction specifies that PAA-containing effluent should not be discharged to water bodies unless a NPDES permit is in force, which Ecology would routinely enforce as part of its permitting requirements. Other restrictions concern application to surface water bodies as an algaecide, and include treating along shore and proceeding outward in ponds or lakes allow fish or other aquatic life to move into untreated areas. It is further recommended to not apply PAA-containing algaecides directly to treated, finished drinking water reservoirs or other sources (BioSafe, 2016), although these products are NSF/ANSI 60 Certified for potable water reservoir treatment for reservoirs or lakes that will eventually be drawn into a potable water facility for treatment and processing.

4.5.4.2 Swimming and Skiing

PAA and HP may be acutely toxic to humans either via oral or inhalation exposures (see above discussion regarding *General Ecotoxicity Profile in Section 4.5.2.4*), although these materials are widely used in the food production industry for a variety of purposes. Thus, as long as in-water treatments are administered in accordance with label specifications, and no recreational exposures are allowed immediately following treatments, impacts to swimming or other recreational aquatic activities are not expected. Moreover, Ecology prohibits treatments with pesticides that have water use restrictions on the FIFRA label that would restrict public water use during the opening week of fishing season or during tribal fisheries, WDFW Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. Ecology further requires that permittees must minimize treatments that restrict public water use during weekends.

4.5.4.3 Irrigation, Drinking and Domestic Uses

As noted in above in the Section 4.5.3.2, there are no registered or anticipated residential applications for these materials, which further diminishes the likelihood of adverse exposures or the need for mitigation associated with drinking water.

4.5.4.4 Fisheries and Fish Consumption

The potential for toxicity to various life stages of fish is possible due to the relatively high acute ecotoxicity of PAA and HP, application of an appropriate WDFW timing window to protect salmon,

steelhead, and bull trout populations as well as priority habitats and species should be considered. WDFW may periodically update this table as new information becomes available or on request from Ecology. The timing table is available at:
http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water algal treatments such as PAA and HP to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations. Fish consumption is not expected to be an issue with these compounds, or require any mitigation, because PAA and HP in any of their chemical forms do not bioaccumulate and would not be present in edible fish or shellfish tissue.

4.5.4.5 Endangered Species

The potential for toxicity to various life stages of fish, including ESA-protected salmonids such as steelhead, salmon, and bull trout, is possible due to the relatively high acute ecotoxicity of PAA and HP, but label restrictions, and timing windows will be implemented for protection of these fisheries as well as their critical habitats. EPA may suggest mitigation measures to be implemented as a label requirement to eliminate or mitigate risks to non-target plants associated with these algal control treatments.

Concerning additional requirements for discharges to water bodies where sensitive, threatened, or endangered plants could be present, before issuing permit coverage, Ecology will determine whether such plant species may be present in the proposed treatment area. If rare plants are potentially present, for aquatic plant control projects, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures.

4.5.4.6 Wetlands or Non-Target Plants

As discussed above, there is a potential for short-term effects to occur to wetlands in association with PAA and HP treatments. It is therefore important that label and permit specifications be carefully followed, and these effects would be expected to be limited and temporary in nature. Environmental concentrations will be carefully considered as part of dose calculations prior to the in-water algal control treatments to further minimize these impacts. There is a possibility that PAA and HP could affect some non-target aquatic vascular plants, and it would be prudent to consider possible mitigation measures for protection of wetlands due to these potentially phytotoxic properties.

As stipulated by Ecology for the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed above in Section 4.5.4.5.

4.5.4.7 Post-treatment Monitoring

Post-treatment monitoring in aquatic water bodies is important and is strongly recommended, and should be incorporated into both label and permit requirements in association with use of these algaecides. EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from algal control compounds such as PAA and HP. For Ecology, this post-treatment monitoring would be required under their APAM and/or NPDES discharge permit, and would be a permit condition requiring monitoring to determine potential non-target impacts, especially to non-target plant species.

4.5.5 References

- American Council for Governmental Industrial Hygienists (ACGIH). 1991. Hydrogen Peroxide. 6th ed: p. 782-783. [1]
- Agency for Toxic Substances and Disease Registry (ATSDR). 2002. U.S Department of Health and Human Services, Public Health Services (DHHS/PHS). ToxFAQsTM for Hydrogen Peroxide. April. [1]
- Biosafe Systems, Inc. (BioSafe). 2016. Safety Data Sheet and Product Label, GreenClean Liquid[®] 2.0 and 5.0. [1]
- BioSafe. 2008. GreenClean Pro[®]: Granular Algicide/Fungicide. Specimen Label. [9]
- Clayton, G, and F. Clayton. 1982. Patty's Industrial Hygiene and Toxicology; Volumes 2A, 2B, and 2C: Toxicology. 3rd edition, John Wiley & Sons, New York. [1]
- Cooke, G.D. 1993. Restoration and Management of Lakes and Reservoirs, Second Edition. Lewis Publ. [1]
- EnviroTech Chemical Services (EnviroTech). 2003a. The Environmental Fate and Impact of PerasanTM in Soil. [9]
- EnviroTech. 2003b. Decay Kinetics of Peracetic Acid and Hydrogen Peroxide in a Variety of Water Matrices. [9]
- European Commission Joint Research Centre (ECJRC). 2003. European Union Risk Assessment Report. Hydrogen Peroxide. 2nd Priority List. Volume: 38: Luxembourg. [1]
- Galvin, J. and C. Farr. 1993. Patty's Industrial Hygiene and Toxicology: Organic Peroxides. Volume 2a: Toxicology: p. 527-597. [1]
- Greene, S. 2013. Sittig's Handbook of Pesticides and Agricultural Chemicals – Technology and Engineering. <https://books.google.com/books?isbn=0815519036>. [1]
- Hazardous Substances Data Bank (HSDB). 1997. Peracetic Acid. Toxnet, Specialized Information Services, U.S. National Library of Medicine, Bethesda, MD: [online]. <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~T7RRWD:1>. [1]

- Kiemer, M., and K. Black. 1997. The Effects of Hydrogen Peroxide on the Gill Tissues of Atlantic Salmon (*Salmo salar*). *L. Aquaculture*. July 1, 1997; 153(3-4): p. 181-189. [1]
- Massachusetts Department of Environmental Protection (MDEP). 2010. Hydrogen Peroxide, Peracetic Acid, and Sodium Percarbonate. MDEP Dept. of Agricultural Resources. Oct. 2010. p. 17. [1]
- NCBI (National Center for Biotechnology Information). 2008. Peracetic Acid Acute Exposure Guideline Levels. <https://www.ncbi.nlm.nih.gov/books/NBK220001>. Accessed October 2016. [1]
- US Environmental Protection Agency (EPA). 2016. ECOTOX Database. <http://cfpub.epa.gov/ecotox/>. [1]
- EPA. 2006. Evaluation of EnviroTech Submission for Peroxyacetic Acid Wastewater End-Use Formulation. p. 10. [9]
- EPA. Chemical Emergency Preparedness Program (CEPP). 1987. Chemical Profile: Peracetic Acid. Washington DC. [1]
- Wagner, K. 2001. Management Techniques within the Lake or Reservoir. *Managing Lakes and Reservoirs*. North American Lake Management Society, the Terrene Institute and U.S. EPA. [1]
- Warmuth, Tom. Personal observations on the use pattern of peroxyacetic acid/hydrogen peroxide. Submitted as comment on the draft SEIS. 2017. [11]
- Washington State Department of Ecology (Ecology). 2016. Ecology's Coverage under Fresh Fruit Packing Industry General Permit WAG435031 – Chemical Additives (Including Peracetic Acid). WDOE, August. [2]

4.6 EVALUATION OF ALUMINUM SULFATE (ALUM)

4.6.1 Registration Status

Alum is currently approved for registration by the EPA Office of Pesticide Programs (EPA OCSP, 2016; EPA OPP, 2016) both as a phosphorus deactivation agent (under the CWA 311(b)(2)(A) and as an inert material under FIFRA 25(b). It is also allowed under 40 CFR 180.920 for use in pesticide formulations applied to growing crops.

4.6.2 Description

Alum is a widely used coagulant and has been used to treat water for centuries. Aluminum sulfate is used for papermaking; hide preservation and tanning, and food processing; as a dye additive; and in pharmaceutical applications. Aluminum hydroxide, a related form, is commonly used as an antacid in over-the-counter treatments. The establishment of wastewater discharge limits under the CWA for suspended solids, biochemical oxygen demand (BOD) and phosphorus contributed to a rapid increase in use of alum in the wastewater treatment industry. It is a largely nontoxic chemical commonly used in water treatment plants to clarify drinking water. Its success in precipitating and deactivating phosphorus from both wastewater and drinking water led to successful lake restorations in eutrophic lakes by the 1970's (Cooke and Kennedy, 1981; Lind, 1997).

In eutrophic lakes, alum is commonly used to reduce and deactivate the nutrient phosphorus in the water column. Reducing phosphorus concentrations can improve water quality by increasing water clarity and limiting the availability of nutrients for algae production. Phosphorus originates from a number of sources, including discharge of manmade fertilizers into lakes and ponds. It may be released from bed sediments under anoxic conditions when lakes stratify and oxygen is depleted from the lower layer. Thus, even when external sources or discharges of phosphorus have been controlled, internal recycling of phosphorus can continue to support explosive algal growth. Increased nutrient loading, particularly phosphorus, accelerates the eutrophication process in lakes and ponds, thus reducing habitat viability, ecosystem function, and recreational value. Frequent and pervasive algal blooms, low water transparency, noxious odors, dissolved oxygen depletion, and fish kills frequently accompany eutrophication.

Lake rehabilitation efforts may initially involve targeting external sources of phosphorus and can include encouraging the use of phosphorus-free fertilizers; improving agricultural practices, reducing urban run-off; and restoring vegetation buffers around waterways. Lake researchers have learned that lakes are slow to recover even after excessive phosphorus inputs have been eliminated (Lind, 1997). Lake or pond sediments become phosphorus-rich and can continue to deliver excessive amounts of phosphorus to the overlying water column. When dissolved oxygen levels are depleted in the bottom portion of the water column, thus creating anaerobic conditions, large amounts of phosphorus trapped in the bottom sediments may be released into the overlying water, a process known as internal nutrient recycling.

4.6.2.1 Environmental Characteristics: Product Use and Chemistry

On contact with water, alum forms a fluffy aluminum hydroxide precipitate known as a floc. Aluminum hydroxide binds with phosphorus to form an aluminum phosphate compound that is insoluble in water under most conditions. As a result, the bound phosphorus can no longer be taken up as a nutrient by

algae or other organisms. As the floc settles to the bed sediments, some phosphorus is removed from the water column. The floc also tends to attract and sorb to suspended particles in the water, precipitating on the lake bottom and clarifying lake water. Once on the lake bottom, the floc forms a layer that serves as a phosphorus barrier by binding phosphorus as it is released from bottom sediments.

It is important to maintain a stable water pH in association with treatments using alum. A standard practice is to maintain the water pH between 6 and 7.5 during treatment, which helps to prevent the ionization of aluminum, which can be toxic in the aquatic environment. Buffered alum is effective in maintaining this balance. Cooke *et al.* (2005) reports that adding sodium aluminate as a buffering agent at a 2:1 ratio is effective in treating phosphorus without affecting pH. He further recommends post-treatment monitoring for pH, alkalinity, and phosphorus. Influent water quality parameters are also important to ensure accurate dosage and buffering agents.

4.6.2.2 Environmental Mobility and Transport

Alum tends to inhibit environmental transport because it permanently settles as an insoluble floc to the bottom layer of sediments, which, if left undisturbed is largely chemically inert, non-reactive, and immobile in lake-bottom environments. It is worth noting, however, that this bottom layer may be resuspended or disturbed by boating or other disturbances, and is thus an imperfect barrier to internal re-loading of phosphorus to the system.

4.6.2.3 Field Surveys and Investigations

A number of limnological case studies have been conducted using alum to inactivate lake phosphorus. Cooke *et al.* (2005) evaluated the effectiveness and longevity of treatments on 21 lakes across the US, and concluded that the treatments were effective in six of nine shallow lakes, controlling phosphorus for about 8 years on average. Applications in stratified lakes were highly effective and long-lasting. This study found that percent reduction in controlling internal phosphorus loading was consistently above 80 percent. However, findings indicated that alum treatment of lakes with high external loadings of phosphorus was not as effective, and that other treatment strategies may be needed.

4.6.2.4 Toxicological Profile

In general, a variety of studies on both mammals and aquatic species indicate that alum is of low acute and chronic toxicity. Some of these studies are summarized below. Based on these studies, Cooke *et al.* (1978) adopted 50 µg ai/L as a safe upper limit for post-treatment dissolved aluminum concentrations. Kennedy and Cooke (1982) found that, based on solubility, dissolved aluminum concentrations, regardless of dose, would remain below 50 µg ai/L in the pH range 5.5 to 9.0. They concluded that a concentration post-treatment in this pH range would be considered environmentally safe with respect to aluminum toxicity. This is consistent with EPA guidelines for alum application, which require that the pH remain within the 5.5-9.0 range.

Mammalian and Human Toxicity

Alum is generally regarded as largely non-toxic to mammals and humans, although elemental aluminum may be neurotoxic at high concentrations. Human health concerns associated with alum or aluminum in

general have generally not been problematic because aluminum concentrations in lake water have normally been within EPA drinking water standards shortly after alum treatments (Cooke, 1993; Wagner, 2001). In addition, drinking water treatment facilities frequently process water that includes alum as a water clarifier before filtration, and the drinking water supply would likely exceed drinking water standards for aluminum for a short time after treatment with alum.

There have been reports that aluminum could be associated with Alzheimer's disease (e.g. UHN Daily 2017), which could be a concern for introducing aluminum into the environment.. While it is true that "free" aluminum has toxic properties, it is also reactive and does not normally remain in its ionic form in the environment. There are no known systemic effects associated with alum, and testing has shown that alum is not genotoxic, mutagenic, or carcinogenic (Toxnet, 2002).

A number of acute, subchronic, and chronic studies have focused on neurotoxicity and developmental toxicity of aluminum and alum. Aluminum is known to be neurotoxic but these effects are generally only seen at much higher dosages than what is administered as alum (e.g. Clayton and Clayton, 1982). For example, an embryonic fetal development study conducted on rats found that developmental effects (e.g. morphological deformities on both embryonic and fetal development) were observed at exposure doses greater than 3.0 µg/mL, (Clayton and Clayton 1982).

Several acute studies of alum have been performed on test mammal species. Results of two oral acute rat studies yielded LD₅₀ values of 5,000 and 1,930 mg/kg bw. Two mouse oral toxicity studies yielded somewhat lower LD₅₀ values of 730 and 980 mg/kg bw, and an oral acute toxicity study using guinea pigs produced an LD₅₀ values of 490 mg/kg bw. Each of these values is dramatically higher than any environmental concentration of alum expected to occur in association or following alum treatments.

Regarding acute or occupational exposures, alums are acidic compounds which may cause irritation in eyes, on mucous membranes, in the respiratory tract, and on abraded skin if direct exposure occurs (e.g. to workers in association with alum treatments). Alum can cause occupational asthma. Symptoms following ingestion range from irritation, mild cramping and nausea to severe vomiting and hemorrhagic gastroenteritis depending on the concentration and the amount ingested. Anhydrous alum and dried alum are more irritating than other forms of alum (Toxnet, 2002).

General Ecotoxicity Profile

Studies conducted to determine the toxicity of aluminum to aquatic biota are summarized below. A detailed study conducted by Narf (1990) on freshwater benthic macroinvertebrates (insects) assessed the long term impacts on two softwater and three hardwater Wisconsin lakes. Narf (1990) found that benthic insect populations either increased or did not change in benthic diversity following treatment with alum. He also reported that any fish-related toxicity associated with alum treatments have been primarily documented in softwater lakes, with the toxicity occurring from the pH itself rather than the chemical effects of alum. However, many softwater lakes have been successfully treated with alum, when treatments are pH buffered. Kennedy and Cooke (1982) reported that post-treatment concentrations of alum below 50 mg ai/L are generally regarded as environmentally safe with respect to aluminum toxicity.

Fish Ecotoxicity

Freeman and Everhart (1971) used flow-through bioassays to determine a NOEC for dissolved aluminum of approximately 52 µg ai/L on rainbow trout (*O. mykiss*). Similar results have been observed for salmon. Findings from Cooke *et al.* (1978) were consistent, as they adopted 50 µg ai/L as a safe upper limit for post-treatment dissolved aluminum concentrations. As discussed below, this concentration of dissolved aluminum is not expected to be attained under representative environmental ranges of pH levels. Narf (1990) reported that any fish-related toxicity associated with alum treatments have been primarily documented in softwater lakes, although when lakes are successfully treated with alum treatments they are normally pH buffered.

Several acute studies of alum have been performed on test fish species. Results of a rainbow trout (*O. mykiss*) acute study yielded a 144-hour LC₅₀ value of 91 µg/L. Results of two perch (*P. fluviatilis*) acute studies yielded 120-hour and 144-hour LC₅₀ values of 661 and 454 µg/L, respectively. Results of two fathead minnow (*P. promelas*) acute studies yielded 192-hour and 96-hour LC₅₀ values of 19.3 mg/L and 33.9 mg/L, respectively. A 10-day LC₅₀ study on roach (*R. rutilus*), 48 hour study on mosquitofish (*G. affinis*), and 48 hour study on brook trout (*S. fontinalis*), yielded wide-ranging LC₅₀ values of 100 µg/L, 69 mg/L, and 4 to 4.4 mg/L, respectively. Many of these toxicity values (as reported by Toxnet 2002) used lower pH values which allowed aluminum to become ionized and therefore more toxic, which would not be the case in the treated lakes or other water bodies in Washington state. As noted above, Kennedy and Cooke (1982) found that dissolved aluminum concentrations, regardless of dose, would remain below 50 µg/L in the environmentally applicable pH range 5.5 to 9.0, and reported that a concentration post-treatment in this pH range would be considered environmentally safe with respect to aluminum toxicity, as aluminum would not become ionized and therefore bioavailable or toxic within this range.

Avian Toxicity

No toxicity studies were identified for aquatic birds likely to inhabit lakes that could be treated for alum, but Huff *et al.* (1996) reported on two experiments using young chickens based on using alum as a litter treatment. They concluded that alum can be toxic to young chicks at high concentrations, but that the toxicity is based on aluminum, not aluminum hydroxide or alum, which are insoluble and therefore are neither likely to be bioavailable nor potentially toxic. Moreover, concentrations tested are well above any expected environmental concentrations likely to occur in or around lakes or ponds following alum treatment.

Invertebrate Ecotoxicity

Several acute studies of alum have been performed on test aquatic invertebrate species. Results of two aquatic sowbug (*A. aquaticus*) acute studies yielded 48-hour EC₅₀ values of 6,570 and 4,370 µg/L. Results of two amphipod (*C. pseudogracilis*) acute studies yielded 96-hour and 48-hour LC₅₀ values of 12,800 and 9,190 µg/L, respectively. Results of a caddisfly (*H. angustipennis*) larval 96-hour EC₅₀ study yielded an EC₅₀ value of 2,265 – 2,637 µg/L. A 24-hour EC₅₀ study on zebra mussels (*D. polymorpha*) yielded an EC₅₀ value of 130.5 µg/L. While wide-ranging, each of these values (Toxnet, 2002) represents concentrations considerably higher than expected aquatic concentrations of aluminum sulfate expected to occur in association or following alum treatments. Similar to the discussion above, Kennedy and Cooke (1982) found that dissolved aluminum concentrations, regardless of dose, would remain below 50

mg Al/L in the pH range 5.5 to 9.0, and reported that a concentration post-treatment in this pH range would be considered environmentally safe with respect to aluminum toxicity, because aluminum would not be ionized and would therefore not be toxic within this range.

Regarding field studies of aquatic invertebrates, according to Cooke *et al.* (1993), the most detailed study of the impact of alum treatments on freshwater benthic macroinvertebrates (insects) was that of Narf (1990), described above. Narf found that benthic insect populations were not reduced in benthic diversity following treatment with alum.

Phytotoxicity

Several studies of effects of aluminum sulfate were identified for terrestrial vascular plants (e.g. soybeans), but this literature review did not include any species of aquatic vascular plants, especially non-target species. However, several field studies were reviewed (e.g. Zarini *et al.*, 1983), and although alum treatments administered to eutrophic lakes for phosphorus inactivation produced obvious effects to algae and phytoplankton, no reports of adverse effects to vascular plants were identified.

Sulfate

Excessive amounts of sulfate ions in surface waters can have a negative impact to aquatic life. Water Quality Standards for Surface Water do not provide numeric water quality criteria for sulfate in Washington State. EPA sets a secondary drinking water standard for sulfate, which is not health threatening, mandatory or enforceable, at 250 mg/L, due to taste and odor.

The toxicity of sulfate ions has been shown to be linked to water hardness (Elphick *et. al.* 2011). They propose a tiered water quality guideline for sulfate to protect aquatic life based upon water hardness.

Water Hardness	Proposed Aquatic Life Guideline for Sulfate
Soft water (10–40 mg/L hardness)	129 mg/L sulfate
Moderately hard water (80–100 mg/L)	644 mg/L sulfate
Hard water conditions (150–250 mg/L)	725 mg/L sulfate

Data presented in this table are from: Elphick *et. al.* 2011.

4.6.3 Environmental and Human Health Impacts

4.6.3.1 Earth

Soil and Sediments

Alum forms an insoluble floc following treatment which settles on bed sediments of lakes or ponds following treatment, but this floc is chemically stable, non-toxic, and largely inert, so would not be expected to cause or be associated with adverse effects to lake sediments.

Agriculture or Land Use

The type of application under consideration is in-water application for phosphorus inactivation, so no agricultural or land use impacts are expected.

4.6.3.2 Water

Surface Water and Runoff

Concerning longer-term effects to aquatic ecosystems associated with alum treatments, Zarini *et al.* (1983) studied the effects of alum at a concentration of 6 mg/L as ionic Al^{3+} on freshwater plankton and water quality, using microcosm enclosures in a shallow eutrophic lake. Soon after the aluminum addition, dramatic modifications of the physical, chemical and biological characteristics were detected. However, several days after the beginning of the experiment the microcosms began to recover, with the exception of phosphate concentration and zooplankton structure. In a similar study, as reported by Toxnet (2002), after addition of alum to a eutrophic lake in order to inactivate and reduce phosphate levels, zooplankton levels dropped drastically, but two months after treatment, these levels had recovered to higher than initial zooplankton levels. Cladoceran (e.g. daphnid) levels dropped from 45% of total zooplankton determined 1 day before treatment to 20% of total zooplankton measured 15 days later. In general, each of these studies indicate that aquatic zooplankton and other biota rapidly recover after the addition of alum, and as such non-target effects are minimal and reversible.

Groundwater/Public Water Supplies

In-water treatments of alum to lakes or ponds are not expected to cause any effects to groundwater or to public water supplies. This is due to the fact that alum is largely non-toxic, and forms an insoluble floc that is unlikely to enter or to impact drinking water supplies.

Water and Shoreline Use

In-water treatments of alum to lakes or ponds are not expected to cause any long-term effects to the water column of treated lakes or ponds, or to impact shoreline uses of these water bodies. Alum is largely non-toxic in the aquatic environment (see Section 4.6.3.3, below), and forms an insoluble floc that is unlikely to remain in the water column over time. In addition, the reduction of free reactive phosphorus in the waterbody would reduce the occurrence of toxic algae blooms, thereby reducing health risks to humans and allowing for more primary contact uses of the waterbody.

4.6.3.3 Human Health Hazards and Risk

As discussed above in Section 4.6.2.4, human health concerns concerning drinking water are expected to be non-problematic, as are direct exposures such as direct contact or oral ingestion associated with swimming or other recreational uses. Although metallic aluminum may be neurotoxic or cause other forms of toxicity to humans at elevated concentrations, the form of aluminum used in in-water lake or pond treatments following an alum application, aluminum hydroxide, is accepted by FDA as a food additive. Free aluminum is not expected to occur in environmental concentrations following alum applications, and as such is not expected to cause adverse impacts to the aquatic environment. As noted above, the reduction of free reactive phosphorus in the waterbody would reduce the occurrence of toxic algae blooms, thereby reducing health risks to humans and allowing for more primary contact uses of the waterbody.

4.6.3.4 Ecological Risk

As discussed in both General and Fish Ecotoxicity in Section 4.6.2.4, above, alum is not expected to cause long-term ecotoxicity in the receiving water environment, although temporary reductions in phytoplankton, cyanobacteria, and/or zooplankton levels may be observed following alum applications (see Zarini *et al.*, 1983). The more toxic form of free aluminum is not expected to occur in environmental concentrations in pH-buffered receiving waters following alum applications, and as such is not expected to cause long-term adverse impacts to plants or animals within the aquatic environment.

4.6.3.5 Wetlands

Similar to the discussion above on ecological risk, alum is not expected to cause long-term ecotoxicity in the aquatic or within a wetlands environment, although temporary reductions in phytoplankton and/or zooplankton levels may be observed following alum applications (see Zarini *et al.*, 1983). Environmental concentrations will be carefully considered as part of label-specified dose calculations performed by the permittee prior to the in-water alum treatments, and these concentrations are not expected to contribute to or cause long-term adverse impacts to plants or animals within a wetland environment.

4.6.3.6 Aquatic Plants and Algae

The goal of phosphorus deactivation treatments in eutrophic water bodies using alum is to reduce the abundance of aquatic algae, cyanobacteria, and phytoplankton through nutrient deactivation rather than direct herbicidal activity. Although several studies of effects of alum and alum were reviewed for terrestrial vascular plants (e.g. soybeans), no toxicity values were identified for aquatic vascular plants, especially non-target plant species. It is known, however, that alum is not directly phytotoxic (Toxnet, 2002). Several field studies (e.g. Zarini *et al.*, 1983) indicated that alum treatments administered to eutrophic lakes produced obvious effects to algae and phytoplankton, but no reports of adverse effects to vascular plants were identified.

4.6.3.7 Habitat

Alum is not expected to cause longer-term effects to aquatic habitats. In fact, administration of alum to the aquatic lake or pond environment for the purpose of phosphorus deactivation is more likely to benefit and improve the environment. As discussed above, alum is not expected to cause long-term ecotoxicity in the aquatic environment, although temporary reductions in phytoplankton and/or zooplankton levels, which are important prey species for protected species such as salmonids, may temporarily occur following alum applications. Alum concentrations in sediment will occur as a chemically stable and largely inert form of aluminum hydroxide and alum, which will continue over time to “scavenge” residual phosphorus and thus improve water quality, although the use of aluminum sulfate (alum) potentially adds excess sulfates to the aquatic system, which themselves are nutrients and which may be transformed to the more toxic form (sulfides) under reducing conditions. Environmental concentrations will be carefully calculated by the permittee as part of dose calculations prior to the in-water alum treatments, post-treatment monitoring will be conducted as required by Ecology, and thus alum residues over time are not expected to contribute to or cause long-term adverse impacts to aquatic habitats within these water bodies.

4.6.4 Mitigation

4.6.4.1 Use Restrictions

A major use restriction recommended for the in-water use of alum will be to carefully control treatments according to label specifications to generate environmental concentrations that are effective in phosphorus inactivation, but not high enough to cause or contribute to aluminum toxicity, even if effects are temporary in nature.

When using aluminum sulfate, a test of water hardness may be needed to determine the appropriate guideline to protect aquatic life. Based upon water hardness, setting a limit to the amount of sulfate ion discharged may be appropriate.

4.6.4.2 Swimming and Skiing

Alum is not directly toxic to humans, and aluminum hydroxide is even used in edible products (e.g. as antacids; see discussion above). So long as in-water treatments are administered in accordance with label specifications, no impacts to swimming or other recreational aquatic activities are expected. Moreover, Ecology prohibits treatments that have water use restrictions that would restrict public water use during the opening week of fishing season or during tribal fisheries, WDFW Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. Ecology further requires that permittees must minimize treatments that restrict public water use during weekends.

4.6.4.3 Irrigation, Drinking and Domestic Uses

As noted above in Section 4.6.3.2, alum is not expected to impact groundwater or drinking water supplies. In addition, there are no registered or anticipated residential applications for alum, which further diminishes the likelihood of adverse exposures or the need for mitigation associated with drinking water.

4.6.4.4 Fisheries and Fish Consumption

The potential for toxicity to various life stages of fish is minimal due to the low ecotoxicity of alum, although a decrease in zooplankton as a prey source (see Section 4.6.3.7) has been identified. Before application the permittee must determine whether the NPDES permit requires implementation of WDFW timing windows to protect salmon, steelhead, and bull trout populations as well as priority habitats and species. WDFW may periodically update this table as new information becomes available or on request from Ecology. The timing table is available at:
http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water treatments such as alum to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations. Fish consumption is not expected to be an issue with alum or require any mitigation, because alum in any of its forms does not bioaccumulate and would not be present in edible fish or shellfish tissue.

4.6.4.5 Endangered Species

There is no anticipated hazard from alum to ESA-listed animal species of concern such as fish or mammals, but it is not known whether potential hazards could occur to non-target endangered plant species. EPA may suggest mitigation measures to be implemented as needed to eliminate or mitigate risks to non-target plants associated with alum treatments.

Prior to issuing permit coverage for discharges to water bodies where sensitive, threatened, or endangered plants could be present, Ecology will determine whether such plant species may be present in the proposed treatment area. For aquatic plant control projects where rare plants are potentially present, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

4.6.4.6 Wetlands or Non-Target Plants

As discussed above, alum would not be expected to cause or contribute to environmental problems in wetlands due to its low toxicity to animal species and the fact that it does not bioaccumulate in the environment. However, there is a possibility that alum could affect some non-target aquatic vascular plants, and it would be prudent to consider possible mitigation measures for protection of wetlands due to these potentially phytotoxic properties.

As stipulated by Ecology for the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed above in Section 4.6.4.5.

4.6.4.7 Post-treatment Monitoring

As noted above, Cooke *et al.* (2005) recommended post-treatment monitoring for pH, alkalinity, and phosphorus. Influent water quality parameters are also important to ensure accurate dosage and buffering agents. Moreover, EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from a phosphorus-deactivating agent such as alum. For Ecology, this post-treatment monitoring would be required under their APAM and/or NPDES discharge permit, and could include a condition requiring monitoring to determine potential non-target impacts, especially to non-target plant species. These requirements may be incorporated into the permit requirements, as appropriate.

4.6.5 References

- Clayton, G. and F. Clayton. 1982. Patty's Industrial Hygiene and Toxicology. Volumes 2A, 2B, and 2C: Toxicology. 3rd edition, John Wiley & Sons, New York. [1]
- Cooke, G., E. Welch, S. Peterson, and S. Nichols. 2005. Restoration and Management of Lakes and Reservoirs. Third Ed. Taylor and Francis Group, Publ. [1]

- Cooke, G. and R. Kennedy. 1981. Precipitation and Inactivation of Phosphorus as a Lake Restoration Technique. EPA-600/3-81-012. [1]
- Cooke, G., et al. 1978. Effects of Diversion and Alum Application on Two Eutrophic Lakes. EPA-600/3-81-012. [1]
- Elphick, J. R., Davies, M., Gilron, G., Canaria, E. C., Lo, B., and Bailey, H.C. 2011. An Aquatic Toxicological Evaluation Of Sulfate: The Case For Considering Hardness As A Modifying Factor In Setting Water Quality Guidelines. Environmental Toxicology and Chemistry. Vol. 30, No. 1, pp. 247–253.
- US Environmental Protection Agency (EPA). Office of Chemical Safety and Pollution (OCSP). 2016. Inert Ingredients Eligible for FIFRA 25(b) Pesticide Products. [5]
- EPA. Office of Pesticide Programs (OPP). 2016b. Output Reporting. Alum/Aluminum Sulfate. https://iaspub.epa.gov/sor_internet/registry/substreg/searchandretrieve/advancedsearch/externalSearch.do?p_type=CASNO&p_value=10043-01-3#. [5]
- Freeman, R. and W. Everhart. 1971. Toxicity of Aluminum Hydroxide Complexes in Neutral and Basic Media to Rainbow Trout. Transactions of the American Fisheries Society 100: p. 644-658. [9]
- Herrera Environmental Consultants. 2003. Green Lake Alum Treatment Study. Prepared for Seattle Dept. of Parks & Recreation: p. 43. [4]
- Huff, W., et al. 1996. Evaluation of the Toxicity of Alum in Young Broiler Chickens. Poultry Science 75: p. 1359-1364. [1]
- Kennedy, R. and Cooke, G. 1982. Control of Lake Phosphorus with Aluminum Sulfate: Dose Determination and Application Techniques. Water Resources Bulletin 18: p. 389-395. [1]
- Lind, C. 1997. Phosphorus Inactivation: Chemical Precipitants and Strategies. North American Lake Management Society (NALMS) Annual Conference. [9]
- Narf, R. 1990. Interaction of Chironomidae and Chaoboridae (Diptera) with Aluminum Sulfate Treated Lake Sediments. Lake Reserv. Manage. 6: p. 33-42. [1]
- Rydin, E., B. Huser and E. Welch. 2000. Amount of Phosphorus Inactivated by Alum Treatments in Washington Lakes. Limnol. Oceanogr. 45: p. 226-230. [1]
- Toxnet. 2002. National Library of Medicine Toxnet Database, Alum <https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+5067>. [1]
- University Health News (UHN) Daily. 2017. Seven pieces of evidence linking aluminum with Alzheimer’s Disease <http://universityhealthnews.com/daily/memory/aluminum-linked-to-alzheimers-disease/> [11]

- Wagner, K. 2001. Management Techniques within the Lake or Reservoir. Managing Lakes and Reservoirs. North American Lake Management Society, the Terrene Institute and US EPA. [9]
- Wisconsin Department of Natural Resources (WDNR). 2003. Alum treatments to control phosphorus in lakes. March. http://dnr.wi.gov/lakes/publications/documents/alum_brochure.pdf. [1]
- Welch, E. and G. Cooke. 1999. Effectiveness and Longevity of Phosphorus Inactivation with Alum. J. Lake and Reserv. Mgt. 15: p. 5-27. [1]
- Welch, E. and J. Jacoby. 2001. On Determining the Principal Source of Phosphorus Causing Summer Algal Blooms in Western Washington Lakes. Lake and Reservoir Management 17: p. 55-65. [1]
- Zarini, et al. 1983. Effects Produced by Aluminum in Freshwater Communities Studies by the Enclosure Method. Environ. Technol. Letters 4(6): p. 247-256. [9]

4.7 EVALUATION OF CALCIUM HYDROXIDE/OXIDE AND CALCIUM CARBONATE

4.7.1 Registration Status

Calcium hydroxide is on list 4 of the EPA's list of inert pesticide ingredients of minimal concern (under 40 CFR 180.910; EPA OPP 2002). EPA recently registered calcium hydroxide as a terrestrial pesticide under a Section 18 (emergency exemption label in the state of Hawaii.), the purpose of which is to manage the invasive coqui frog and greenhouse frog (label found at: http://hawaii.gov/hdoa/pi/pest/PEST_Calcium_Hydroxide_Section_18_label.pdf). EPA deleted calcium oxide from its list of hazardous substances in 1979. Under 40 CFR 180.910, residues of calcium hydroxide are exempted from registration requirements when used in accordance with good agricultural practice as inert (or occasionally active) ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest.

4.7.2 Environmental Characteristics: Product Use and Chemistry

Calcium hydroxide (Ca(OH)_2) has many uses including the production and manufacturing of building materials and the treatment of wastewater and biosolids. Calcium hydroxide neutralizes phosphorus and nitrogen in wastewater and animal wastes. EPA specifically prescribes the use of lime treatment for human wastewater sludge and as such, calcium hydroxide routinely enters waters through sewage treatment plant discharges (McClain 2005). Calcium hydroxide has uses in the dairy industry, the sugar industry, and in baking (e.g. tortillas are often made with lime treatment).

Calcium hydroxide (CAS No. 471-34-1), also known as "slaked lime", is a colorless crystal or white powder created when calcium oxide (lime or quicklime) is mixed ("slaked") with water. It is relatively soluble in water, and solutions are basic (alkaline). At ambient temperature, calcium hydroxide dissolves in water with a highly acidic pH of 1.2. It is quite soluble at 1.7 g/L at 20°C. Calcium hydroxide freely ionizes in water to form calcium ion (Ca^{2+}) and hydroxide (OH^-), forming a medium to strong base.

Calcium hydroxide was originally used as a soil amendment to supply calcium to crops. It was found, however, that calcium hydroxide can be harmful to soil biota, and that the same benefits of calcium as a soil amendment can be obtained through gypsum or mined limestone. Calcium hydroxide can also raise pH to prevent pipe corrosion.

Key aquatic uses of calcium hydroxide include use as a flocculant to improve water quality through removal of smaller particles, and use as a disinfectant in wastewater and sewage in water (Prepas *et al.*, 2001; Chambers *et al.*, 2001). When calcium hydroxide or calcium carbonate is added to eutrophic lakes or ponds, total phosphorus is reduced or removed, thus reducing algal biomass. Treatment of such eutrophic ponds, lakes or other water bodies may be achieved through relatively high levels of slaked lime (about 210 mg/L for 65 hours), which generally leads to the elimination of unwanted aquatic algae within approximately one month. It is believed that this activity is achieved when a short-term increase in pH lowers concentrations of carbon dioxide (CO_2) and bicarbonate ion, which are needed for biosynthesis. Robertson *et al.* (1992) reported a similar finding, in which calcium hydroxide acted as a disinfectant against *Cryptosporidium* oocysts in water supplies through high pH (alkalinity). They further reported that calcium hydroxide would not be effective if pH values were below 6.

When used to treat wastewater, consistent with its aquatic chemistry (NOSB, 2002), calcium hydroxide would react with carbon dioxide, and an insoluble, nonreactive form of calcium carbonate would remain, which would remove a significant but unknown fraction from the overall algal biomass present in the system. In aquatic ecosystems, calcium hydroxide also binds to phosphorus, an important biological nutrient, thus rendering the nutrient unavailable and incapable of causing or contributing to eutrophication in the system. This phosphorus inactivation process reduces the risk of algal blooms in ponds or lakes, and is thus a valuable tool for managing eutrophication and other processes in lakes and ponds.

4.7.2.1 Environmental Mobility and Transport

Calcium hydroxide is soluble in water, but does not accumulate in soils, or bioaccumulate or bioconcentrate in biological tissue. It does not degrade by photolysis, but rather is neutralized by the absorption and binding of CO₂. Some potential for leaching to soils exists, which is similar to the natural leaching process of calcium from soils (NOSB, 2002).

4.7.2.2 Toxicological Profile

Based on available data, calcium hydroxide is generally of low internal acute and chronic toxicity to a wide variety of test animals, including humans. It is even used as food additive for pH control, and as a texturing, firming and anticaking agent (Toxnet, 2002). In fact, the FDA allows calcium hydroxide as a food additive and is classified as GRAS (Toxnet, 2002). However, on contact with high concentrations of calcium hydroxide (Ca(OH)₂) it is a severe skin and eye irritant and could pose problems to workers handling the material or applying it for in-water treatment for phosphorus management. Given that calcium hydroxide is a relatively strong base, it may be seriously corrosive and cause permanent eye damage with prolonged exposure (reported with as little as a 10% solution). Unprotected exposure to calcium hydroxide can cause severe skin irritation, chemical burns (also known as “lime burns”) to mucous membranes, blindness, and lung damage (Richardson and Gangolli, 1993; Toxnet, 2002). Calcium hydroxide dusts are an important industrial hazard.

Mammalian and Human Toxicity

As noted above, calcium hydroxide is generally of low toxicity, with two reported oral LD₅₀ values of 7,340 and 7,300 mg/kg bw, respectively, in rats and mice (NOSB, 2002). Calcium hydroxide has been classified by the National Institute of Environmental Health Sciences/National Toxicology Program (NIEHS/NTP) (2002) as a non-carcinogen. Concerning genotoxicity or mutagenicity, calcium hydroxide showed no cytotoxic effects on human cells. No genotoxicity, measured as DNA strand breaks, was seen at the highest tested concentration (Toxnet, 2002).

A three month chronic toxicity test was conducted using rats that were treated with two different levels of calcium hydroxide (50 mg/L and 350 mg/L) via drinking water. This long-term exposure to Ca(OH)₂ in drinking water reportedly led to aggression, restlessness, reduced food intake and blood changes in test animals. Internal morphologic changes were observed in the liver, kidneys and stomach, with swelling in the small intestine (as reported by European Chemical Commission (ECC) in 2000).

Acute cases of oral poisoning or spills affecting human eyes and skin, due to accidental or intentional overexposure to calcium hydroxide, were not found as part of the literature review. Based on available

data, the use of calcium hydroxide in aquatic environments would not be expected to cause adverse effects to the public as long as label specifications are followed (McClain 2005).

General Ecotoxicity Profile

Calcium hydroxide causes little to no acute or chronic toxicity to tested plant or animal species, based on a review of the published calcium hydroxide toxicology literature reviewed.

Fish Ecotoxicity

Six fish acute toxicity tests conducted on the western mosquitofish (*G. affinis*), as reported by Toxnet (2002) and ECC (2000), yielded a range of LC₅₀ values, with all values reported to be at least 160,000 µg/L, which is highly suggestive of little to no toxicity to fish. Two additional acute ecotoxicity tests (Toxnet, 2002) using fish yielded LC₅₀ values ranging from 339,000 mg/L to 240,000 mg/L, which is consistent with other reported values. These concentrations indicate little to no toxicity to fish, and these concentrations are expected to be well above any environmental concentrations potentially occurring during in-water Ca(OH)₂ treatments.

Avian Toxicity

A single acute toxicity test was identified using redwing blackbird (*A. phoenicius*), which yielded an oral LD₅₀ value of 111 mg/kg, suggesting very low toxicity to birds (NOSB, 2002).

Invertebrate Ecotoxicity

One acute toxicity test for sand shrimp was identified, in which a LC₅₀ value of 158,000 µg/L for 96 hours, which is indicative of very low toxicity to this invertebrate test species (ECC, 2000).

Phytotoxicity

Two acute toxicity tests for blue-green algae were identified. EC₅₀ values were developed of 66,000 µg/L for 1.5 hours and 84,000 µg/L for 22-hour exposures, respectively. Both of these values were indicative of very low toxicity to these test species.

4.7.3 Environmental and Human Health Impacts

4.7.3.1 Earth – Soil and Sediments

As noted above, Ca(OH)₂ is quite soluble in water, and does not accumulate in soils, or bioaccumulate or bioconcentrate in biological tissue. Some potential for leaching to soils exists, but proposed phosphorus inactivation treatments will be in-water, which is expected to preclude the possibility of soil leaching. Ca(OH)₂ can bind with phosphorus and carbon dioxide in soils, thus neutralizing the calcium, which is a natural element.

Agriculture or Land Use

Proposed in-water treatments for phosphorus inactivation are not expected to impact agriculture or terrestrial land use.

4.7.3.2 Water

Surface Water and Runoff

If calcium hydroxide is used in the treatment of wastewater or biosolids, the majority of it is expected to be discharged with wastewater into natural receiving water bodies. Consistent with its aquatic chemistry (NOSB, 2002), calcium hydroxide would react with carbon dioxide, and an insoluble, nonreactive form of calcium carbonate would remain. In aquatic ecosystems, calcium hydroxide also binds to phosphorus, an important biological nutrient, thus rendering it unavailable and incapable of causing or contributing to eutrophication in the system. This phosphorus inactivation process reduces the risk of algal blooms in ponds or lakes and is thus beneficial to aquatic environments where eutrophication is a problem. In addition, calcium is largely non-toxic, except for its pH effects. Based on available data, the use of calcium hydroxide in the treatment of wastewater, as long as label specifications are followed, would not be expected to cause or contribute to impacts or adverse effects on aquatic ecosystems.

Groundwater/Public Water Supplies

No information was available for calcium hydroxide in groundwater or in public water supplies, but neither are anticipated to be problematic with regard to in-water phosphorus management treatments using $\text{Ca}(\text{OH})_2$, as long as label and permit specifications are followed (McClain 2005).

4.7.3.3 Human Health Hazards and Risk

As noted above, little or no toxicity has been identified in association with calcium hydroxide, except for effects associated with direct contact such as eye and skin irritation due to the corrosive nature of calcium hydroxide. As long as pH considerations are met, workers and pesticide applicators wear the appropriate PPE, and label specifications for environmental concentrations and worker protection are followed, no problems or impacts to human health are expected.

4.7.3.4 Ecological Risk

As noted above, little or no ecotoxicity has been identified in association with calcium hydroxide, and no ecological risk or hazard would be expected, as long as pH considerations are met and label specifications for environmental concentrations are followed.

4.7.3.5 Wetlands

Little to no impacts to wetlands would be expected, as long as pH considerations are met and label specifications for environmental concentrations are followed.

4.7.3.6 Plants

Algae

Algae species would be a common target for calcium hydroxide due to its phosphorus inactivation properties, albeit via indirect control rather than direct action as an algaecide. As such, non-target algal species would also be at potential risk for impacts associated with these in-water treatments.

Higher Plants

Aquatic plants, such as vascular plants, rely in part on the availability of nutrients such as phosphorus, and as such, some would be potentially impacted by treatments using calcium hydroxide. Section 4.7.4, *Mitigation*, below discusses possible mitigation measures to avoid such impacts.

4.7.3.7 Habitat

Aside from the potential impacts discussed above related to non-target algal and vascular plant species, impacts to the aquatic habitat are expected to be minimal.

4.7.4 Mitigation

4.7.4.1 Use Restrictions

A major use restriction recommended for the in-water use of calcium hydroxide would be to carefully control treatments according to label specifications to generate environmental concentrations that are effective in phosphorus inactivation, but not high enough to cause corrosive or high pH (alkalinity-related) effects to the environment, even if effects are temporary in nature.

4.7.4.2 Swimming and Skiing

Calcium hydroxide is not toxic to humans, is used as a food additive (see discussion above), and as long as in-water treatments are administered in accordance with label specifications, no impacts to swimming or other recreational aquatic activities are expected. Ecology requires that permittees must minimize treatments that restrict public water use during weekends.

4.7.4.3 Irrigation, Drinking and Domestic Uses

Calcium hydroxide may be discharged with treated wastewater into natural receiving water bodies. It is largely non-toxic, except for its pH effects. No information was specifically identified for calcium hydroxide in groundwater or in public water supplies, but neither should be problematic with regard to in-water phosphorus management treatments using $\text{Ca}(\text{OH})_2$, and mitigation measures may not be required.

4.7.4.4 Fisheries and Fish Consumption

Concerning impacts or potential mitigation for protection of fisheries, before application the permittee must, if indicated by the APAM permit, comply with appropriate WDFW timing windows to protect salmon, steelhead, and bull trout populations as well as priority habitats and species. WDFW may periodically update this table as new information becomes available or on request from Ecology. The timing table is available at:

http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water treatments such as calcium hydroxide to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and any affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations.

Fish consumption is not expected to be an issue because calcium hydroxide does not bioaccumulate and would not be expected to be present in edible fish or shellfish tissue.

4.7.4.5 Endangered Species

There is no anticipated hazard from calcium hydroxide to listed animal species of concern such as fish or mammals, but potential hazards could occur to non-target endangered plant species. Once the registration is under review, EPA's Endangered Species and Spray Drift Task Forces may suggest and implement mitigation measures as needed to eliminate or mitigate risks to non-target plants associated with calcium hydroxide.

Prior to issuing permit coverage for discharges to water bodies where sensitive, threatened, or endangered plants could be present, Ecology will determine whether such plant species may be present in the proposed treatment area. For aquatic plant control projects where rare plants are potentially present, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

4.7.4.6 Wetlands or Non-Target Plants

As noted above, calcium hydroxide would not be expected to cause or contribute to environmental problems in wetlands due to its low toxicity to animal species and the fact that it does not bioaccumulate in the environment. However, there is a tendency for calcium hydroxide to affect some non-target algal or vascular plant species, and it would be prudent to consider possible mitigation measures for protection of wetlands due to these potentially phytotoxic properties.

For example, as stipulated by Ecology in the general requirements of the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. Ecology requires that the permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed in Section 4.7.4.5.

4.7.4.7 Post-treatment Monitoring

EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from a phosphorus-deactivating agent such as calcium hydroxide. For Ecology, this post-treatment monitoring could be required under their APAM and/or NPDES discharge permit, and would be a permit condition requiring monitoring to determine potential non-target impacts, especially to non-target plant species.

4.7.5 References

Chambers, P., et al. 2001. The Effects of Lime Addition on Aquatic Macrophytes in Hard Water: in situ and Microcosm Experiments. *Freshwater Biology* 46(1): p. 1121-1138. [1]

Ecology. 2011. Non-project EIS – Aquatic Invasives. Publ. No. 10-10-010.
<http://www.ecy.wa.gov/biblio/1010010.html>. [3]

- European Chemicals Bureau (ECB). 2000. Compilation of Available Data on Calcium Hydroxide. [1]
- ClearTech Industries, Inc. 2009. Material Safety Data Sheet (MSDS) for Calcium Hydroxide: Chemical and Product Information. Saskatoon, SK, Canada: p. 7. [1]
- McLain, K. 2005. Draft human and environmental risk assessment of calcium hydroxide.
http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/lakes/RISK%20ASSESSMENT%20OF%20CALCIUM%20HYDROXIDE.pdf. [3]
- National Organic Standards Board (NOSB). 2002. NOSB Technical Advisory Panel Review: Calcium Hydroxide. Organic Material Review Institute: p. 15. [1]
- NOSB. 1995. Draft Minutes of the National Organic Standards Board Full Board Meeting. Orlando Florida April 24-29. USDA –NOP: p. 40-44. [9]
- National Institute of Environmental Health Sciences/National Toxicology Program (NIEHS/NTP). 2002.
<http://ntp-server.niehs.nih.gov/>. [1]
- Prepas, E., et al. 2001. Long-term Effects of Successive Ca(OH)₂ and CaCO₃ Treatments on the Water Quality of Two Eutrophic Hard Water Lakes. *Freshwater Biology* 46(1): p. 1089-1103. [1]
- Richardson, M. and S. Gangolli. 1993. The Dictionary of Substances and their Effects. Royal Society of Chemistry. UK. [1]
- Robertson, L., et al. 1992. Survival of *Cryptosporidium Parvum* Oocysts under Various Environmental Pressures. *Appl. & Environ. Microbiol.* 58 (11): p. 3494 - 3500. [1]
- Toxnet. 2002. National Library of Medicine Toxnet Database: Calcium Hydroxide.
<https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+919>. [1]
- US Environmental Protection Agency (EPA). Office of Chemical Safety and Pollution (OCSF). 2016. Inert Ingredients Eligible for FIFRA 25(b) Pesticide Products. [5]
- EPA. Office of Pesticide Programs (OPP). 2002. Output Reporting: Calcium Hydroxide.
<http://www.cdpr.ca.gov/cgi-bin/epa/mkepa3.pl?chems=075601>. [5]

4.8 EVALUATION OF IRON AND IRON SALTS

4.8.1 Registration Status

Iron salts (the two most common of which are ferric sulfate and ferric chloride) are currently approved for registration by the EPA Office of Pesticide Programs (2016a, 2016b) both as a phosphorus deactivation agent (under FIFRA) and as an inert material (iron oxide) under 40 CFR 180.910.

4.8.2 Description

Iron is one of the most abundant metals in the Earth's crust, is the second most common metal on earth, and is an essential nutrient for all life. It is found in natural fresh waters at levels ranging from 0.5 to 50 mg/L. Iron may also be present in drinking-water as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution. As reported by the World Health Organization (WHO, 2003), the WHO International Standards for Drinking Water suggested that concentrations of iron greater than 1.0 mg/L in drinking water would markedly impair its potability. Iron stains laundry and plumbing fixtures at levels above 0.3 mg/L, and there is usually no noticeable taste at iron concentrations below 0.3 mg/L. Concentrations of 1–3 mg/L can generally be acceptable for people drinking anaerobic well water. EPA's recommended organoleptic (i.e. not based on toxicity) national drinking water guideline for total iron is 0.3 mg/L.

Iron salts are commonly used as chemical coagulants, somewhat similar to alum, but are considerably less expensive. Coagulation-based water treatment is a common approach for treatment of surface waters and is usually done by coagulating salts of aluminum or iron with raw water under controlled conditions to form a solid flocculent metal (iron) hydroxide. Typical coagulant doses are 4–10 mg/L as iron, with the optimum dose determined as that which achieves adequate removal of color and turbidity; the optimum pH can be selected in a similar manner (WHO, 2003).

The establishment of wastewater discharge limits under the CWA for suspended solids, biochemical oxygen demand (BOD), and phosphorus contributed to an increase in use of iron salts in the wastewater treatment industry. Iron is a largely nontoxic chemical commonly used in water treatment plants to clarify drinking water. Its success in precipitating and deactivating phosphorus (i.e. as soluble reactive phosphorus) from both wastewater and drinking water led to its use in lake restoration in eutrophic lakes by the 1970's (Cooke and Kennedy, 1981; Lind, 1997). As an alternative to the use of iron salts, elemental, zero-valence iron has been used in water treatment. The surface of the finely granulated iron particles is chemically reactive and thus combines with phosphates to form an insoluble iron phosphate and/or combine with hydroxyl ions to form iron hydroxide or iron oxyhydroxide floc, which adsorbs phosphate ions and removes phosphorus from solution.

In eutrophic lakes, alum or iron may be used to reduce and deactivate the nutrient phosphorus (i.e. as soluble reactive phosphorus) in the water column. Reducing phosphorus concentrations can improve water quality by increasing water clarity and limiting the availability of nutrients for algae production. Phosphorus originates from a number of sources, including discharge of manmade fertilizers into lakes and ponds. It may be released from bed sediments under anoxic conditions when lakes stratify and oxygen is depleted from the lower layer. Thus, even when external sources or discharges of phosphorus have been controlled, internal recycling of phosphorus can continue to support explosive algal growth.

Increased nutrient loading, particularly phosphorus, accelerates the eutrophication process in lakes and ponds, thus reducing habitat viability, ecosystem function, and recreational value. Frequent and pervasive algal blooms, low water transparency, noxious odors, dissolved oxygen depletion, and fish kills frequently accompany eutrophication.

Lake researchers have learned that lakes are slow to recover even after excessive phosphorus inputs have been eliminated (Lind 1997). Lake or pond sediments become phosphorus-rich and can continue to deliver excessive amounts of phosphorus to the overlying water column. When dissolved oxygen levels are depleted in the bottom portion of the water column, thus creating anaerobic conditions, large amounts of phosphorus trapped in the bottom sediments may be released into the overlying water, a process known as internal nutrient recycling.

4.8.2.1 Environmental Characteristics: Product Use and Chemistry

Iron compounds are ubiquitous and used as chemical catalysts, pigments, drugs, as well as use in agriculture, nutrition, mining, processing of iron ores, metallurgy, and leather tanning. Iron is a natural constituent of all foods of plant or animal origin, and occurs in foods as iron oxides, inorganic and organic salts, and organic complexes.

The environmental geochemistry of iron is complex, especially in the aquatic environment. Common oxidation states of iron under environmental conditions are Fe^{+2} and Fe^{+3} , with the +3 oxidation state favored under normal oxidizing conditions. In general, iron cations in solution are attracted to the negatively charged surfaces of soil particles, and Fe^{3+} are known to be strongly retained by naturally occurring humic and fulvic acid fractions separated from soils. Adsorption of iron depends on soil organic matter and pH; an increase in either of these factors will usually increase adsorption. The mobility of iron ions in soils and sediments is influenced as well by redox potential, with iron being more mobile under reducing than oxidizing conditions. Chelating agents may enhance the mobility of iron in soils. Iron ions are prone to be retained on organic matter found in the aquatic environment. Iron ions with bound water molecules are normally expected to hydrolyze or form complexes in the aquatic environment. Above pH 2 colloidal gels are formed, producing a precipitate of red-brown hydrous iron oxide (rust). In the presence of complexing anions, such as chloride, the hydrolysis of Fe^{3+} is more complicated and can result in a variety of complexes. Fe^{2+} ions normally oxidize to Fe^{3+} under most environmental conditions. Iron hydroxide (+2 oxidation state) is precipitated from solution by basic conditions, and may be rapidly oxidized to the hydrated iron oxide (+3, also known as rust). The Fe^{2+} ion is also oxidized by other common oxidants, such as nitrite and nitrate. Fe^{2+} and Fe^{3+} ions can form complexes with a variety of environmental ligands containing halides, nitrogen, oxygen, phosphorus, or sulfur donor groups.

Two common iron salts used in surface water treatments are ferric sulfate and ferric chloride. Ferric sulfate is a reliable, well-documented, high quality coagulant used to enhance water quality. Since it dissolves slowly, the dry ferric sulfate needs to be dissolved prior to use, generally on shore. Dosage fluctuations and treatment excursions can occur through variations in strength. Ferric chloride is the most widely used among iron salts for water treatment, second only to alum in the volume of water treated in North America (Lind 1997). Potentially phytotoxic heavy metals are potential contaminants in ferric chloride, and testing should be done beforehand to ascertain the purity of this material. Both

ferric sulfate and ferric chloride react with phosphorus to form ferric phosphate, thus inactivating phosphorus, although ferric sulfate is often preferable to ferric chloride due to its superior removal of turbidity from the water column. As noted above, an alternative to use of iron salts is elemental, zero-valence iron, administered as finely ground iron powder. Use of elemental iron rather than iron salts does not introduce additional sulfate or chloride anions into the receiving water body.

Regarding which coagulant to use (i.e. alum vs. iron), this will depend largely on project goals and desired long term effects. Both iron and aluminum effectively precipitate and thus deactivate phosphorus. Iron phosphate precipitate will, under anoxic (negative redox) conditions in sediments or the water column, tend to resolubilize and release soluble reactive phosphorus back into the water column. Iron is itself a plant nutrient and can contribute to the proliferation of algal growth. This re-release of iron phosphates can be a “burst” of nutrient enrichment for algae and macrophytes. In contrast, aluminum phosphate from alum will not release the nutrient back into the water column regardless of sediment redox. Cooke and Kennedy (1981) also reported that phosphorus is released during the reduction of ferric hydroxide and other iron complexes, and therefore iron is not a suitable long-term agent for phosphorus deactivation. Therefore, alum/aluminum sulfate would generally be preferable, and for low alkalinity systems a combination alum/aluminate or alum/soda ash treatment would be recommended. Partially neutralized aluminum compounds or buffered alums are available and provide some convenience to handling two chemicals (Lind 1997). Hupfer *et al.* (2009) also provided a comparative analysis and discussion on ferric salts vs. aluminum-based or other compounds in German lakes for the purposes of phosphorus inactivation.

4.8.2.2 Environmental Mobility and Transport

As noted above, iron cations in solution are attracted to the negatively charged surfaces of soil particles. Adsorption of iron depends on soil organic matter and pH; an increase in either of these factors will usually increase adsorption. The mobility of iron ions in soils is influenced as well by redox potential, with iron being more mobile under reducing than under oxidizing conditions. Based on laboratory studies, environmental concentrations of ethylenediaminetetraacetic acid (EDTA), a common chelating agent, typically found in aquatic systems are unlikely to contribute to iron (or other metal) solubilization and mobilization from aquatic sediments. The iron precipitate thus inhibits environmental transport because it complexes with a variety of environmental ligands, is limited in solubility, and as such is inert, largely non-reactive, and immobile in the water column and in lake bottom environments.

4.8.2.3 Field Surveys and Investigations

A number of limnological case studies have been conducted to examine the effectiveness of using iron to inactivate phosphorus in surface waters (Wagner, 2001; Welch and Jacoby, 2001; Cooke and Kennedy, 1981). Molot *et al.* (2014) examined the roles of P, N, and Fe regulating algal bloom processes. They found that the availability of iron as Fe^{2+} is key to regulating the ability of cyanobacteria to grow and potentially bloom. Fe^{2+} (e.g. following treatment) diffusing from anoxic (reducing) sediments thus become a major source of iron as a nutrient for cyanobacteria growth. They found that when light and temperature are suitable for such growth, bloom onset is regulated by internal Fe^{2+} loading which in turn is itself regulated by redox processes, unlike alum or other forms of phosphorus inactivation.

4.8.2.4 Bioconcentration and Bioaccumulation

Bioconcentration factors for iron in aqueous phase (i.e. in equilibrium with sediments) and bioaccumulation factors (in biological tissue) were calculated for a wide variety of aquatic invertebrates, macrophytes, fish species, and other organisms, and in general iron was generally found to be prone not to either bioconcentrate or bioaccumulate (as reported by Toxnet, 2005).

4.8.2.5 Toxicological Profile

In general, iron has been very well studied and a variety of studies on both mammals and aquatic species indicate that iron is of low acute and chronic toxicity. Some of these studies are summarized below.

Mammalian and Human Toxicity

Human ingestion of less than 40 mg/kg of iron does not tend to cause significant toxicity, although mild gastro-intestinal irritation may develop. It is widely used in foods as it is an essential nutrient, and is regarded by the FDA as safe to consume. However, at higher concentrations, inhalation of ferric salts as dusts and mists can be irritating to the respiratory tract, and ferric salts are regarded as skin irritants. High ingested doses can lead to iron poisoning, which produces severe liver damage. Hepatocytes contribute to the homeostasis of iron by extracting this essential metal by a receptor-mediated process and maintaining a reserve of iron within the storage protein ferritin. Mammalian studies have shown that chronic exposure of excess levels of iron (50 mg to 100 mg/day) can result in various pathologies to liver, pancreas, and can cause diabetes mellitus. The cytotoxicity of free iron is attributed to its function as an electron donor for the formation of reactive oxygen species, which initiate destructive oxidative stress reactions. At high doses, chronic hepatic accumulation of excess iron in cases of hemochromatosis may be associated with a spectrum of hepatic disease including a >200-fold increased risk for liver cancer. Repeated animal studies with iron and iron salts have not caused cancers except with very high doses of iron.

The mechanism of action for iron toxicity is that it interferes with oxidative enzymes, releases hydrogen with formation of ferric hydroxides, and leads to the accumulation of lactic acid from anaerobic metabolism which can result in severe metabolic acidosis. Ferrous irons catalyze lipid peroxidation which can cause disruption of mitochondrial membranes and the Krebs cycle. Iron also shunts electrons from the electron transport system by acting as an electron sink. The result is the production of a metabolic acidosis.

General Ecotoxicity Profile

A variety of acute and chronic studies conducted for vertebrates, invertebrates, and plant species have shown that iron toxicity is generally very low. Studies conducted to determine the toxicity of iron to aquatic biota are summarized below.

Fish Ecotoxicity

Several acute studies of iron have been performed on test fish species. Results of a channel catfish (*I. punctatus*) acute study in 1959 using seven different time exposures (ranging from 1 hour to 96 hours) yielded LC₅₀ values all exceeding 500 mg/L. Results of a common carp (*C. carpio*) acute study yielded a

96-hour LC₅₀ value of 0.56 mg/L. The former study used static exposures while the latter, more recent study (1995) using carp, used static renewal exposures, and thus is probably more representative of actual toxicity and exposure to test fish.

Avian Toxicity

No avian toxicity studies were identified as part of the literature review for aquatic birds likely to inhabit lakes potentially treated for iron, but iron is not believed to be directly toxic, and it is highly unlikely that birds would be exposed to high enough concentrations of iron to experience acute or chronic toxicity.

Invertebrate Ecotoxicity

Several acute studies of iron have been performed on test aquatic invertebrate species. Results of a mayfly (*L. marginata*) chronic study yielded a 24-day LC₅₀ values of 73.07 mg/L. Results of two other mayfly subchronic food consumption studies yielded 5-day and 24-day EC₅₀ values of 8.48 and 50.1 mg/L, respectively. Another test using the unicellular dinoflagellate *G. splendens* yielded a 48-hour EC₅₀ value of 17.5 mg/L. Each of these values (as reported by Toxnet, 2005) provides evidence that iron is not likely to be directly toxic to sensitive invertebrate test species, even at high concentrations. These test concentrations are likely considerably higher than any environmental concentrations of iron expected to occur in association with or following treatments.

Phytotoxicity

Several acute studies of iron have been performed on test plant species to assess phytotoxicity. Results of a phytoplankton (haptophyte) chronic study of population growth inhibition yielded a 48-hour EC₅₀ value of 8.5 mg/L. Results of a duckweed (*L. minor*) subchronic growth inhibition study yielded 96-hour EC₅₀ value of 3.7 mg/L. Each of these values (as reported by Toxnet, 2005) provides evidence that iron is not likely to be directly toxic to sensitive plant species, even at high concentrations.

Sulfate and Chloride

When iron salts are used the potential toxicity of the chloride or sulfate ions must be taken into consideration. Chloride in surface waters can be toxic to many forms of aquatic life. Aquatic species of concern include fish, macroinvertebrates, insects, and amphibians. Elevated chloride levels can threaten the health of food sources and pose a risk to species survival, growth, and/or reproduction (New Hampshire Department of Environmental Services:

<https://www.des.nh.gov/organization/divisions/water/wmb/was/salt-reduction-initiative/impacts.htm>).

Limits to the discharge of chloride ions is given in the Water Quality Standards for Surface Water: WAC 173-201A-240. Chloride has an aquatic life criteria of 860 mg/L for a 1 hour average not to be exceeded more than once every three years and 230 mg/L for a 4 day average not to be exceeded more than once every three years.

The current Aquatic Plant and Algae Management Permit, which allows for the use of chloride containing products for nutrient inactivation, does not allow the Permittee to violate Surface Water Quality Standards (Permit Special Condition S3.A.1). EPA sets a secondary drinking water standard, which is not health threatening, mandatory or enforceable, at 250 mg/L, due to salty taste.

Excessive amounts of sulfate ions in surface waters can have a negative impact to aquatic life. Water Quality Standards for Surface Water do not provide numeric water quality criteria for sulfate in Washington State. EPA sets a secondary drinking water standard for sulfate, which is not health threatening, mandatory or enforceable, at 250 mg/L, due to taste and odor.

The toxicity of sulfate ions has been shown to be linked to water hardness (Elphick et. al. 2011). They propose a tiered water quality guideline for sulfate to protect aquatic life based upon water hardness.

Water Hardness	Proposed Aquatic Life Guideline for Sulfate
Soft water (10–40 mg/L hardness)	129 mg/L sulfate
Moderately hard water (80–100 mg/L)	644 mg/L sulfate
Hard water conditions (150–250 mg/L)	725 mg/L sulfate

4.8.3 Data presented in this table are from: Elphick et. al. 2011. Environmental and Human Health Impacts

4.8.3.1 Earth

Soil and Sediments

Iron salts used for phosphorus inactivation are not toxic to organisms in soils or sediments, and resulting iron complexes will be non-toxic, and largely non-reactive, so would not be expected to cause or be associated with adverse effects to lake sediments or adjoining soils.

Agriculture or Land Use

The type of application under consideration is in-water application for phosphorus inactivation, therefore no agricultural or land use impacts are expected.

4.8.3.2 Water

Surface Water and Runoff

Concerning longer-term effects to aquatic ecosystems associated with iron treatments, Holdren *et al.* (2001) reported that although use patterns of aluminum-based and iron-based treatments are comparable, aluminum at low pH is more likely to cause aquatic toxicity than iron. In general, studies indicate that acute and chronic toxicity of iron to aquatic biota is minimal and should not be problematic. However, as discussed in Section 4.8.2.1, the reversible complexation behavior of iron is prone to release phosphorus over time, which then allows both phosphorus and iron to serve as nutrient substrate for resilient species such as cyanobacteria.

Groundwater and Public Water Supplies

In-water treatments of iron salts to lakes or ponds are not expected to cause any effects to groundwater or to public water supplies. This is due to the fact that iron and derivatives are largely non-toxic, and in fact are frequently used to treat drinking water supplies (further discussed above in Section 4.8.2).

Water and Shoreline Use

In-water treatments of iron or iron salts to lakes or ponds are not expected to cause any long-term effects to the water column of treated lakes or ponds, or to impact shoreline uses of these water bodies. Iron is largely non-toxic in the aquatic environment (see discussion in Section 4.8.2.5), is not prone to environmental transport, bioconcentration, or other properties that could impact water or shoreline use.

4.8.3.3 Human Health Hazards

As discussed above in Section 4.8.2.5, human health concerns regarding iron in drinking water are expected to be non-problematic, as are direct exposures such as direct contact or oral ingestion associated with swimming or other recreational uses. Although metallic iron may be acutely or chronically toxic to humans at elevated concentrations, the concentrations as well as the chemical forms of iron following a treatment are not expected to be problematic. Ionic forms of iron (Fe^{2+} or Fe^{3+}) will not be favored under environmental conditions encountered during these treatments, and as such is not expected to cause adverse impacts to the aquatic environment.

4.8.3.4 Ecological Risk

As discussed in Section 4.8.2.5, iron is not acutely or chronically toxic to a wide variety of test organisms, and as such is not expected to cause short- or long-term ecotoxicity in the receiving water environment. However, as discussed in Section 4.8.2.1, the reversible complexation behavior of iron is prone to release phosphorus over time, which then allows both phosphorus and iron to serve as nutrient substrate for resilient and potentially harmful species such as cyanobacteria, which can lead to eutrophication of the receiving water body, which would be harmful to the aquatic ecosystem.

4.8.3.5 Wetlands

If applied according to label specifications, iron is not expected to cause long-term ecotoxicity in the aquatic or within a wetlands environment. Environmental concentrations would be carefully considered as part of label-specified dose calculations performed by the permittee prior to the in-water iron treatments, and these concentrations are not expected to contribute to or cause long-term adverse impacts to plants or animals within a wetland environment.

4.8.3.6 Plants

Higher Plants (Including Crops) and Algae

Toxicity tests reviewed for higher plants indicate little chance for acute or chronic toxicity associated with iron. Target species for phosphorus deactivation treatments in eutrophic water bodies using iron are aquatic algae and phytoplankton, and non-target algal species may be at risk. It is known that iron is not directly phytotoxic (Toxnet, 2005). Several field studies indicated that iron treatments administered to eutrophic lakes produced obvious effects to algae and phytoplankton, but no reports of short- or long-term adverse effects to vascular plants were identified (Holdren *et al.*, 2001).

4.8.3.7 Habitat

Iron is not expected to cause short- or long-term effects to aquatic habitats. In fact, administration of iron and iron salts to the aquatic lake or pond environment for the purpose of phosphorus deactivation is more likely to benefit and improve aquatic habitats and the aquatic environment overall. As discussed above, iron is not expected to cause long-term ecotoxicity in the aquatic environment, although temporary reductions in phytoplankton and/or zooplankton levels, which are important prey species for protected species such as salmonids, may temporarily occur following applications. In addition, iron concentrations in sediment will be largely chemically stable and non-reactive iron complexes, which will thus improve water quality. Environmental concentrations would be carefully calculated by the permittee as part of dose calculations prior to the in-water iron treatments. Iron does not bioconcentrate or bioaccumulate, and thus iron residues over time are not expected to contribute to or cause long-term adverse impacts to aquatic habitats within these water bodies.

4.8.4 Mitigation

4.8.4.1 Use Restrictions

A major use restriction recommended for the in-water use of iron and iron salts will be to carefully control treatments according to label specifications to generate environmental concentrations that are effective in phosphorus inactivation, but not high enough to cause or contribute to iron toxicity, even if effects are temporary in nature. It is further recommended that pH be carefully monitored so iron will not ionize, which is its most toxic and bioavailable form, although it is not very toxic within the aquatic environment.

Ensure that chloride ion concentrations resulting from the application of ferric chloride do not exceed the aquatic life criteria given in the Water Quality Standards for Surface Water: WAC 173-201A-240. The current Aquatic Plant and Algae Management Permit, which allows for the use of chloride containing products for nutrient inactivation, does not allow the Permittee to violate Surface Water Quality Standards (Permit Special Condition S3.A.1). When iron salts are used that contain sulfate, a test of water hardness may be needed to determine the appropriate guideline to protect aquatic life. Based upon water hardness, setting a limit to the amount of sulfate ion discharged may be appropriate.

4.8.4.2 Swimming and Skiing

Iron and iron salts are not directly toxic to humans, and are even used in edible products (see discussion above). So long as in-water treatments are administered in accordance with label specifications, no impacts to swimming or other recreational aquatic activities are expected. Based on available data, it is recommended that no swimming or other recreational activities be allowed immediately following in-water treatments by iron or other similar compounds. Ecology further requires that permittees must minimize treatments that restrict public water use during weekends.

4.8.4.3 Irrigation, Drinking and Domestic Uses

As noted in Section 4.8.3.2, iron or iron salts are not expected to impact groundwater or drinking water supplies. In addition, there are no registered or anticipated residential applications for iron, which further diminishes the likelihood of adverse exposures or the need for mitigation associated with drinking water.

4.8.4.4 Fisheries and Fish Consumption

The potential for toxicity to various life stages of fish is minimal due to the low ecotoxicity of iron and its derivatives. Before application the permittee must, if indicated by the APAM permit, comply with appropriate WDFW timing windows to protect salmon, steelhead, and bull trout populations as well as priority habitats and species. WDFW may periodically update this table as new information becomes available or on request from Ecology. The timing table is available at:

http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water treatments such as iron to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations. Fish consumption is not expected to be an issue with iron or iron salts or require any mitigation, because iron in any of its forms does not bioaccumulate and would not be present in edible fish or shellfish tissue.

4.8.4.5 Endangered Species

There is no anticipated hazard from iron or iron salts to listed animal species of concern such as fish or mammals, but it is not known whether potential hazards could occur to non-target endangered plant species. EPA may suggest mitigation measures to be implemented as needed to eliminate or mitigate risks to non-target plants associated with iron treatments.

Prior to issuing permit coverage for discharges to water bodies where sensitive, threatened, or endangered plants could be present, Ecology would determine whether such plant species have the potential to occur in the proposed treatment area. For aquatic plant control projects where such plant species do have the potential to occur, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

4.8.4.6 Wetlands or Non-Target Plants

As discussed above, iron or iron salts would not be expected to cause or contribute to environmental problems in wetlands due to its low toxicity to animal species and the fact that it does not bioaccumulate in the environment. However, as discussed in Section 4.8.2.1, the reversible complexation behavior of iron is prone to re-release phosphorus over time, which then allows both phosphorus and iron to serve as nutrient substrate for resilient and potentially harmful species such as cyanobacteria, which can lead to eutrophication of the receiving water body, which in turn would be harmful to the aquatic ecosystem, including non-target plants and animals.

As stipulated by Ecology for the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed in Section 4.8.4.5.

4.8.4.7 Post-treatment Monitoring

Post-treatment monitoring for water quality, turbidity, pH, alkalinity, phosphorus and other water quality parameters is important in association with iron treatment. Part of the rationale for both short- and long-term post-treatment monitoring would be to determine whether iron and/or phosphorus would be re-released into the receiving water and would thus become susceptible to eutrophication or cyanobacteria or similar blooms.

Moreover, EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from a phosphorus-deactivating agent such as iron. For Ecology, this post-treatment monitoring would be required under their APAM and/or NPDES discharge permit, and would be a permit condition requiring monitoring to determine potential non-target impacts. These requirements will be incorporated into both label and permit requirements, as appropriate, in conjunction with pesticide registration and permit requirements prior to application.

4.8.5 References

- Clayton, G. and F. Clayton. 1982. Patty's Industrial Hygiene and Toxicology. Volumes 2A, 2B, and 2C: Toxicology. 3rd edition, John Wiley & Sons, New York. [1]
- Cooke, G.D. 1993. Restoration and Management of Lakes and Reservoirs. Second Edition. Lewis Publ. [1]
- Cooke, G. and R. Kennedy. 1981. Precipitation and Inactivation of Phosphorus as a Lake Restoration Technique. EPA-600/3-81-012. [1]
- Elphick, J. R., Davies, M., Gilron, G., Canaria, E. C., Lo, B., and Bailey, H.C. 2011. An Aquatic Toxicological Evaluation Of Sulfate: The Case For Considering Hardness As A Modifying Factor In Setting Water Quality Guidelines. Environmental Toxicology and Chemistry. Vol. 30, No. 1, pp. 247–253. [1]
- Holdren, C., et al. 2001. Managing Lakes and Reservoirs. EPA, N. American Lake Mgt. Society and Terrene Institute. EPA 841-B-01-006. [1]
- Hupfer, M., et al. 2009. Evaluation of a Well-established Sequential Phosphorus Fractionation Technology for Use in Calcite-rich Lake Sediment. Limnol. Oceanogr. 7: p. 399-410. [1]
- Lind, C. 1997. Phosphorus Inactivation: Chemical Precipitants and Strategies. North American Lake Management Society (NALMS) Annual Conference. [9]
- Molot, L., et al. 2014. A Novel Model for Cyanobacteria Bloom Formation: The Critical Role of Anoxia and Ferrous Ion. Freshwater Biology (in press): p. 18. [9]
- Toxnet. 2005. National Library of Medicine Toxnet Database, Iron Compounds.
<https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7348>. [1]
- US Environmental Protection Agency (EPA). Office of Pesticide Programs (OPP). 2016. Registration Review Schedules – Pesticide Reevaluation. <https://www.epa.gov/pesticide-reevaluation/registration-review-schedules>. [5]

- EPA. Office of Drinking Water (ODW). 1991. Guideline Manual for the Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources. Contract NO. 68-01-6989: p. 580. [1]
- Wagner, K. 2001. Management Techniques within the Lake or Reservoir. Managing Lakes and Reservoirs. North American Lake Management Society, the Terrene Institute and US EPA. [1]
- Welch, E. and J. Jacoby. 2001. On Determining the Principal Source of Phosphorus Causing Summer Algal Blooms in Western Washington Lakes. Lake and Reservoir Management 17: p. 55-65. [1]
- World Health Organization (WHO). 2008. Guidelines for Drinking Water Quality. 3rd Ed. WHO, Geneva, 668 p. http://www.who.int/water_sanitation_health/dwq/fulltext.pdf. [1]
- WHO. 2003. Iron in Drinking-water: Background for Preparation of WHO Guidelines for Drinking-water Quality. Geneva, World Health Organization, WHO/SDE/WSH/03.04/8. [1]

4.9 EVALUATION OF LANTHANUM-CLAY (PHOSLOCK®)

4.9.1 Description

Phoslock® is a patented phosphorus-locking material containing lanthanum (5%), a naturally occurring earth element, embedded inside a clay matrix (~95%). It was developed to remove the nutrient phosphorus from water bodies to improve and restore water quality. It is produced through an ion exchange process whereby lanthanum ions displace sodium ions within the clay matrix. The formulation process absorbs lanthanum into a non-toxic carrier such that the lanthanum retains its capacity to bind phosphate when applied to aquatic environments and results in a non-toxic mineral that becomes an inert component of the sediment. It has been used in the US since 2010 and internationally over the past ten years in water resource restoration programs to inactivate and remove free reactive phosphorus and to help restore water quality. Typical application rates are < 150 mg/L, with applications occurring either as a single event or over several days. They may also be split over a season or multiple seasons depending on the water body restoration and management objectives.

In eutrophic lakes, lanthanum may be used to reduce and deactivate the nutrient phosphorus in the water column. Reducing phosphorus concentrations can improve water quality by increasing water clarity and limiting the availability of nutrients for algae production. Phosphorus may be released from bed sediments under anoxic conditions when lakes stratify and oxygen is depleted from the lower layer (Welch and Jacoby, 2001). Thus, even when external sources or discharges of phosphorus have been controlled, internal recycling of phosphorus can continue to support explosive algal growth. Increased nutrient loading, particularly phosphorus, accelerates the eutrophication process in lakes and ponds, thus reducing habitat viability, ecosystem function, and recreational value. Frequent and pervasive algal blooms, low water transparency, noxious odors, dissolved oxygen depletion, and fish kills frequently accompany eutrophication. Investigators have learned that lakes are slow to recover even after excessive phosphorus inputs have been eliminated (Lind, 1997). Lake or pond sediments become phosphorus-rich and can continue to deliver excessive amounts of phosphorus to the overlying water column. When dissolved oxygen levels are depleted in the bottom portion of the water column, creating anaerobic conditions, large amounts of phosphorus trapped in the bottom sediments may be released into the overlying water as part of an internal nutrient recycling process.

4.9.1.1 Environmental Characteristics: Product Use and Chemistry

Following an application of lanthanum clay, the lanthanum ions sorbed to the clay matrix react preferentially with free phosphate anions in the water column of lakes and ponds, thus inactivating and removing free reactive phosphorus and rapidly forming a highly stable, insoluble mineral complex. The resulting mineral complex becomes integrated as an inert component into the bottom sediments of the water body and is thus rendered non-bioavailable. Due to the specificity of lanthanum to phosphate, as long as binding sites are available, it will continue to bind and inactivate new incoming phosphorus from internal and external sources.

Lanthanum is a naturally occurring element and can occur in many forms. One such form, lanthanum chloride (LaCl_3) can be potentially toxic to aquatic organisms due to the dissolution of high levels of free lanthanum into water after application, which precludes use of lanthanum chloride as an acceptable treatment for phosphorus (DOI USGS, 1984). However, when lanthanum is applied to surface waters in

the form of Phoslock, the risk of potential lanthanum toxicity to aquatic organisms becomes negligible due to the unique formulation of Phoslock® (i.e., it is absorbed to the clay matrix) and the limited potential for exposure to free lanthanum. When applied to water, lanthanum associated with the clay in Phoslock® preferentially and rapidly binds with phosphate ion (PO_4^-), forming a highly stable mineral called rhabdophane (LaPO_4). This resulting rhabdophane complex has a very low solubility ($K_{sp} < 10^{-27}$) and is not reactive or influenced by changes in pH or redox reactions in bottom sediments.

Laboratory studies with lanthanum demonstrated that no lanthanum was released within 24 hours when granular Phoslock® (10 mg/L) was dissolved in de-ionized water; and only a small concentration of lanthanum (3% of the total lanthanum in Phoslock®) was released from the 10 mg/L concentration of Phoslock when dissolved in low alkalinity natural water or synthetic soft water (SePro, 2012). Even if the total amount of lanthanum applied to a system following an application became readily available in water, the margin of safety associated with preventing non-target lanthanum toxicity is very high. A field investigation demonstrating this chemical behavior is discussed below in Section 4.9.1.4.

4.9.1.2 Environmental Mobility and Transport

While free lanthanum can be used in tests to assess toxicity to organisms, lanthanum as it is formulated in Phoslock®, (or bound as rhabdophane), does not occur in a “free” state and is therefore unlikely to become available or achieve concentrations of toxicological concern in the aquatic environment. The phosphorus removal capacity of Phoslock® does not change drastically under different chemical or environmental conditions (binding to phosphates over a pH range of 4 to 11, including both aerobically and anaerobically). Since it rapidly settles to bottom sediments, the potential exposure duration to organisms in the water column is relatively short. Also, due to the unique formulation of Phoslock®, the lanthanum remains sorbed to the clay until it is displaced by phosphates, and subsequently only disassociates a minimal amount of free lanthanum to the water.

4.9.1.3 Field Surveys and Investigations

In addition to a number of laboratory studies showing that lanthanum is not readily soluble or bioavailable in water, free lanthanum levels were measured in a German lake (as reported by SePro, 2012) following an application dose of 75 mg/L Phoslock®. This application resulted in a peak level of 0.130 mg La^{+3} /L shortly after application and low phosphate concentrations (less than 20 mg/L). Toxicity tests following this lake treatment revealed an EC_{50} of 103 mg La^{+3} /L zooplankton (*D. magna*) and EC_{50} of 150 mg La^{+3} /L for fish eggs (*D. rerio*). This study demonstrates the effectiveness of Phoslock® and shows that the peak levels of measured La^{+3} concentrations in the lake following application were approximately 800 and 1,150 times lower than the EC_{50} concentrations for zooplankton and fish eggs, respectively.

4.9.1.4 Bioconcentration and Bioaccumulation

Concerning bioconcentration and bioaccumulation potential for lanthanum, the risk via consuming lanthanum in fish harvested from Phoslock®-treated water following its application was shown to be negligible in a fish health investigation conducted after three successive applications of Phoslock® in a New Zealand lake (Landman *et al.*, 2007). The lake monitoring report demonstrated slight bioaccumulation of lanthanum in trout and koura, but only in the liver and hepatopancreas tissues rather than edible flesh and muscle following the application of Phoslock®. This is consistent with

pharmacologic findings that the main excretion route for absorbed lanthanum in humans or mammals is via the liver into bile. The field study also demonstrated that lanthanum was depurated from these tissues within a few months and that concentrations of lanthanum returned to baseline before another application one year later, suggesting a biological capacity to depurate lanthanum (Landman *et al.*, 2007). Fish liver and hepatopancreas tissues are not generally consumed by humans, and even consumption of large quantities of fish liver and hepatopancreas tissues harvested from a Phoslock-treated waterbody would be expected to pose negligible risk to human health. Concerning bioconcentration, lanthanum is a naturally occurring substance and SePro (2012) reports that lanthanum residues do not bioconcentrate within sediments following these treatments.

4.9.1.5 Toxicological Profile

As noted above, when lanthanum is applied to surface waters in the form of Phoslock®, the risk of potential lanthanum toxicity to aquatic organisms is negligible due to the formulation of Phoslock® (absorbed to the clay matrix) and a limited potential for exposure to free lanthanum). When applied to water, lanthanum associated with the clay in Phoslock® preferentially and rapidly binds with PO₄⁻ to form a highly stable mineral (rhabdophane, LaPO₄), and this resulting complex has very low solubility, is not reactive or influenced by changes in pH or redox reactions in bottom sediments, and is therefore non-bioavailable and non-toxic.

In general, lanthanum has been very well studied and a variety of studies on both mammals and aquatic species generally indicate that it is of low acute and chronic toxicity. Some of these studies are summarized below.

Mammalian and Human Toxicity

Phoslock is not considered hazardous by the US Occupational Health and Safety Administration hazard communication standard (29 CFR 12910.1200). Neither Lanthanum nor the clay used in the formulation are listed on the EPA Toxic Substances Control Act inventory list. No human risk has been associated with contact of Phoslock®, with the main potential for human exposure occurring during the application process. Due to some small particulates in the formulation, there could be some potential eye irritation and inhalation for applicators and handlers associated with an application. Applicators and handlers should follow label-specified PPE guidelines and the product material safety data sheet.

General Ecotoxicity Profile

In general, a variety of acute and chronic studies conducted for vertebrates, invertebrates, and plant species have shown that lanthanum toxicity is generally very low. In fact, with many tests, due to the amount needed to cause toxic responses to test biota, many studies (as reported by SePro) did not test concentrations high enough to result in significant impacts, and thus toxicity endpoints are reported as simply greater than the highest concentration tested and does not necessarily indicate the actual lowest observed effect levels. Typical Phoslock® application rates are < 150 mg/L, with applications occurring either as a single event or over several days. Applications may also be split over a season or multiple seasons depending on the water body restoration and management objectives. Studies conducted to determine the toxicity of Phoslock® to aquatic biota are summarized below.

Fish Ecotoxicity

Several acute studies of Phoslock® have been performed on test fish species. No mortality or adverse impacts to fish have been observed in field applications in the United States or internationally (SePro, 2012). Based on data generated for several different fish species, there is minimal risk to fish expected with applications at standard dose rates in aquatic environments. Results of a crimson-spotted rainbowfish (*M. duboulayi*) acute 96-hour study yielded an LC₅₀ value of greater than 50,000 mg/L. Results of a rainbow trout (*O. mykiss*) acute study yielded a 96-hour LC₅₀ value of greater than 3,125 mg/L, and a 48-hour LC₅₀ value of greater than 13,000 mg/L. As noted above, due to the amount of Phoslock needed to cause toxic responses to test biota with many tests, some studies were not able to generate adequate responses to test appropriate endpoints, and results are reported as simply greater than the highest concentration tested. These test concentrations are likely considerably higher than any environmental concentrations of Phoslock expected to occur in association with or following treatments.

Avian Toxicity

No avian toxicity studies were identified as part of the literature review for aquatic birds likely to inhabit lakes potentially treated for lanthanum, but it is not likely to be bioavailable to birds in a form that could produce a toxic response, and it is highly unlikely that birds would be exposed to high enough concentrations of lanthanum or Phoslock® to experience acute or chronic toxicity.

Invertebrate Ecotoxicity

Regarding potential exposure to benthic macroinvertebrates inhabiting lake and pond bottom sediments, when lanthanum settles at the sediment-water interface it forms a thin layer that is neither reactive nor bioavailable to benthic organisms. Several acute studies of lanthanum have been performed on test aquatic invertebrate species. Results of several tests using the zooplankton invertebrate *C. dubia* yielded a 48-hour mortality LC₅₀ value of greater than 50 mg/L, and a comparable mortality test over 7 days yielded an LC₅₀ value of greater than 1 mg/L. Another mortality test using *C. dubia* in laboratory water yielded a 48-hour mortality LC₅₀ value of greater than 12,500 mg/L, and a similar study using the daphnid *D. magna* in laboratory water yielded a 48-hour mortality LC₅₀ value of greater than 50,000 mg/L. Results of a reproductive study *C. dubia* yielded a 48-hour mortality LC₅₀ value of greater than 1 mg/L.

In addition to the zooplankton data cited above, several other invertebrate toxicity tests have been conducted using midges, amphipods, mayfly larvae, and shrimp. Eight invertebrate studies studied a wide range of response variables, including lethality, emergence time, growth, and sex ratio produced at emergence. LOECs were calculated for each of these tests, and produced a range of LOEC values from 400 mg/L to 50,000 mg/L. These results uniformly demonstrated that no significant impacts or toxicity to these invertebrates occur at or even above anticipated use rates for lanthanum or Phoslock®. In addition, no field toxicity has been observed in invertebrate species. In fact, as noted above, due to the amount of material needed to cause toxic responses to test biota with many tests, some Phoslock® studies were not able to generate adequate responses to test appropriate endpoints, and results are reported as simply greater than the highest concentration tested, which does not necessarily indicate the actual lowest observed effect levels.

Phytotoxicity

Lanthanum is intended to deactivate phosphorus, which is an essential nutrient for plants, but no direct acute or chronic phytotoxicity test results were identified. It is not likely to be directly toxic to sensitive plant species, even at high concentrations. These test concentrations are likely considerably higher than any environmental concentrations of lanthanum or Phoslock® expected to occur in association with or following treatments.

4.9.2 Environmental and Human Health Impacts

4.9.2.1 Earth

Soil and Sediments

Lanthanum used for phosphorus inactivation is not likely to be directly toxic to plants or organisms in soils or sediments, and the resulting complexes (e.g. rhabdophane) will be non-toxic, and largely non-reactive, so would not be expected to cause or be associated with adverse effects to lake sediments or adjoining soils.

Agriculture

The type of application under consideration is in-water application for phosphorus inactivation, so no agricultural impacts are expected.

Terrestrial Land Use

The type of application under consideration is in-water application for phosphorus inactivation, so no terrestrial land use impacts are expected.

4.9.2.2 Water

Surface Water and Runoff

Lanthanum is a phosphorus deactivating formulation that has been specifically designed to decrease potential bioavailability and toxic exposure to aquatic biota. It therefore poses a negligible to very low risk to the aquatic environment, including both the water column and benthic environment, while providing a high affinity to bind and remove phosphorus that will benefit water quality, diminish the potential for eutrophication, and contribute to lake restoration.

Groundwater and Public Water Supplies

In-water treatments of lanthanum or Phoslock® to lakes or ponds are not expected to cause any effects to groundwater or to public water supplies. This is due to the fact that lanthanum and derivatives are largely non-toxic. Even drinking lanthanum-treated water directly after an application would pose negligible risk to human health.

Water and Shoreline Use

In-water treatments of lanthanum to lakes or ponds are not expected to cause any long-term effects to the water column of treated lakes or ponds, or to impact shoreline uses of these water bodies. Lanthanum is largely non-toxic in the aquatic environment (see discussion in Section 4.9.1.5), is not

prone to environmental transport, bioconcentration, or other properties that could impact water or shoreline use.

4.9.2.3 Human Health Hazards

As discussed above in Section 4.9.1.5 and elsewhere, there is very little for potential human exposure or risk to lanthanum in Phoslock® following treatment due to its low toxicity and minimal bioavailability. Even if a human exposure occurs, lanthanum is readily processed by the liver and excreted with no negative impacts observed. The discussion above regarding bioaccumulation of Phoslock® and lanthanum (Section 4.9.1.4) indicates minimal risk of bioaccumulation or toxicity accruing from exposure to contaminated fish tissues. Lanthanum is used in an FDA-approved prescription drug called Fosrenol® to decrease blood phosphate levels in humans (Persey *et al.*, 2006).

In case of lanthanum ingestion via drinking even a large volume of Phoslock®-treated reservoir water, there is negligible risk to human health. Applying the material to a reservoir at the dose rate of 50 mg/L (a typical dose rate in a waterbody with average concentrations of phosphorus and alkalinity), the person would need to drink 80 gallons of reservoir water per day to ingest the minimum dose that corresponds to the lowest Fosrenol® daily intake. Human health concerns via direct exposures such as direct contact or oral ingestion associated with swimming or other recreational uses are expected to be negligible.

4.9.2.4 Ecological Risk

As discussed above, lanthanum is not acutely or chronically toxic to a wide variety of test organisms, and as such is not expected to cause short- or long-term ecotoxicity in the receiving water environment. Typical application rates are < 150 mg/L. Lanthanum applications may occur as a single event or over several days and also may be split over a season or multiple seasons depending on the site and management objective.

4.9.2.5 Wetlands

If applied according to label specifications, lanthanum is not expected to cause short- or long-term ecotoxicity in the aquatic or within a wetlands environment. Environmental concentrations would be carefully considered as part of label-specified dose calculations performed by the permittee prior to the in-water treatments, and these concentrations would not be expected to contribute to or cause long-term adverse impacts to plants or animals within a wetland environment. Moreover, lanthanum binds irreversibly within the environment and is not reactive or bioavailable to receptor plants or organisms.

4.9.2.6 Plants

Higher Plants (Including Crops) and Algae

Target species for phosphorus deactivation treatments in eutrophic water bodies using lanthanum are aquatic algae and phytoplankton, and as such non-target algal species may be at risk. It is not believed to be directly phytotoxic, and therefore would not be expected to cause or contribute to short- or long-term adverse effects to vascular or higher aquatic plants.

4.9.2.7 Habitat

Phoslock® or lanthanum are not expected to cause short- or longer-term effects to aquatic habitats. In fact, administration of lanthanum to the aquatic lake or pond environment for the purpose of phosphorus deactivation is more likely to benefit and improve aquatic habitats and the aquatic environment overall. As discussed above, it will not cause long-term ecotoxicity in the aquatic environment, although temporary reductions in phytoplankton and/or zooplankton levels, which are important prey species for protected species such as salmonids, may temporarily occur following applications. In addition, Phoslock® and lanthanum complexes in sediment will be chemically stable and non-reactive complexes (e.g. rhabdophane), which will thus improve water quality. Environmental concentrations will be carefully calculated by the permittee as part of dose calculations prior to the in-water treatments, it does not readily bioconcentrate or bioaccumulate, post-treatment monitoring will be conducted as required by Ecology, and thus lanthanum residues over time are not expected to contribute to or cause long-term adverse impacts to aquatic habitats within these water bodies.

4.9.3 Mitigation

4.9.3.1 Use Restrictions

A major use restriction recommended for the in-water use of lanthanum will be to carefully control treatments according to label specifications to generate environmental concentrations that are effective in phosphorus inactivation, but not high enough to allow or cause ecotoxicity, even if effects are temporary in nature. It is recommended that pH, alkalinity, and other key water quality parameters be carefully monitored to ensure that Phoslock® and lanthanum will complex as anticipated, and will thus not be bioavailable within the aquatic environment.

4.9.3.2 Swimming and Skiing

Phoslock® and lanthanum are not directly toxic to humans, and are even used in edible products (see discussion above). So long as in-water treatments are administered in accordance with label specifications, no impacts to swimming or other recreational aquatic activities are expected. Based on available data, there are no restrictions on swimming or recreational activities associated with lanthanum-clay treatments.

4.9.3.3 Irrigation, Drinking and Domestic Uses

As noted above in Section 4.9.3.2, lanthanum is not expected to impact groundwater or drinking water supplies. In addition, there are no registered or anticipated residential applications for Phoslock, which further diminishes the likelihood of adverse exposures or the need for mitigation associated with drinking water.

4.9.3.4 Fisheries and Fish Consumption

The potential for toxicity to various life stages of fish is minimal due to the low ecotoxicity of lanthanum and derivatives. Before application the permittee must determine if compliance with appropriate WDFW timing windows to protect salmon, steelhead, and bull trout populations as well as priority habitats and species is required. WDFW may periodically update this table as new information becomes available or on request from Ecology. The timing table is available at:

http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/aquatic_plant_permit_index.html.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water treatments such as Phoslock to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations. Fish consumption of Phoslock- or lanthanum-contaminated tissue is not expected to be problematic or require any mitigation, because Phoslock does not bioaccumulate into edible fish tissue and would therefore not present any adverse exposures to fish consumers.

4.9.3.5 Endangered Species

There is no anticipated hazard from lanthanum or its derivatives to listed animal species of concern such as fish or mammals, and it is not anticipated that it could present a potential hazard to non-target endangered plant species. EPA may suggest mitigation measures as needed to eliminate or mitigate risks to non-target plants associated with lanthanum treatments.

Concerning additional requirements for discharges to water bodies where sensitive, threatened, or endangered plants could be present, before issuing permit coverage, Ecology will determine whether such plant species may be present in the proposed treatment area. If rare plants are potentially present, for aquatic plant control projects, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

4.9.3.6 Wetlands or Non-Target Plants

As discussed above, lanthanum would not be expected to cause or contribute to environmental problems in wetlands due to its low toxicity to animal species and the fact that it does not readily bioaccumulate within tissues or bioconcentrate within sediments (Section 4.9.2.4). As stipulated by Ecology for the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed above in Section 4.9.4.3.

4.9.3.7 Post-treatment Monitoring

Post-treatment monitoring for water quality, turbidity, pH, alkalinity, phosphorus and other water quality parameters is important in association with lanthanum treatment to ensure that the appropriate physical, chemical, and other processes occur as expected to enhance water quality and promote lake or pond restoration. Part of the rationale for both short- and long-term post-treatment monitoring would be to ensure that it inactivates phosphates and phosphorus over the longer term, and that treatments are effective.

EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from a phosphorus-deactivating agent such as lanthanum. For Ecology, this post-treatment monitoring would be required under the APAM and/or NPDES discharge permit, and would be a permit condition requiring monitoring to determine potential non-target impacts. These would be incorporated into the permit requirements as appropriate.

4.9.4 References

- Clayton, G, and F. Clayton. 1982. Patty's Industrial Hygiene and Toxicology; Volumes 2A, 2B, and 2C: Toxicology. 3rd edition, John Wiley & Sons, New York. [1]
- Cooke, G. 1993. Restoration and Management of Lakes and Reservoirs, Second Edition. Lewis Publishers. [1]
- Cooke, G. and R. Kennedy. 1981. Precipitation and Inactivation of Phosphorus as a Lake Restoration Technique. EPA-600/3-81-012. [1]
- Holdren, C., W. Jones and J. Taggart. 2001. Managing Lakes and Reservoirs. EPA, N. American Lake Mgt. Society and Terrene Institute. EPA 841-B-01-006. [1]
- Landman et al. 2007. Lake Okareka and Tikitapu Fish Health Monitoring, 2007. Report. [9]
- Lind, C. 1997. Phosphorus Inactivation: Chemical Precipitants and Strategies. North American Lake Management Society (NALMS) Annual Conference. [1]
- Persey et al. 2006. Lanthanum: A Safe Phosphate Binder. Seminars in Dialysis 19 (3): p. 195-9. [1]
- SePro Corp (SePro). 2012. Technical Bulletin: An overview of Phoslock and Use in the Aquatic Environment.
<http://www.sepro.com/documents/Phoslock/TechInfo/Phoslock%20Technical%20Bulletin.pdf>. [1]
- US Department of the Interior (DOI). US Geological Survey (USGS). 1984. Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States. [1]
- Wagner, K. 2001. Management Techniques within the Lake or Reservoir. Managing Lakes and Reservoirs. North American Lake Management Society, the Terrene Institute and US EPA. [1]
- Welch, E. and J. Jacoby. 2001. On Determining the Principal Source of Phosphorus Causing Summer Algal Blooms in Western Washington Lakes. Lake and Reservoir Management 17: p. 55-65. [1]

4.10 UPDATE OF CURRENTLY REGISTERED HERBICIDES AND ALGAEICIDES IN WASHINGTON STATE

In addition to the eight (8) proposed new herbicides and chemical agents evaluated as discussed above, there are currently 14 herbicides and algaecides registered for aquatic use in Washington State. These include: 1) 2,4-D (amine and ester); 2) bispyribac-sodium; 3) carfentrazone ethyl; 4) diquat; 5) endothall (dipotassium salt) used as an herbicide; 6) flumioxazin; 7) fluridone; 8) glyphosate; 9) imazapyr; 10) imazamox; 11) penoxsulam; 12) triclopyr (triethylamine salt); 13) endothall (mono salt) used as an algaecide; and 14) sodium carbonate peroxyhydrate.

Each of these currently registered aquatic herbicides or chemical agents were reviewed in a similar manner to the new or proposed chemical agent evaluation discussed above, except that generally speaking more environmental data and testing information (e.g. environmental fate and transport, acute and chronic toxicity, bioaccumulation, etc.) is already available for these currently registered materials, and as such the emphasis was on updating current information since the time of registration..

The intent of this section is to provide an update on the scientific literature, emphasizing non-target effects and hazards, labeling and registration updates, and other updated information not available or represented in Ecology's earlier SEIS (Ecology 2000). Similar to the impact evaluation of the new or proposed chemicals, at the conclusion of each individual evaluation a discussion is provided on potential ecological and human health impacts, proposed or possible mitigation requirements, and label restrictions needed to reduce or eliminate potential adverse effects to human health or the environment. Based on this evaluation, potentially applicable mitigation measures are discussed or proposed for each chemical agent. References cited and used to evaluate each of these chemical agents are listed at the end of each individual section.

4.10.1 Tank Mixes, Inerts and Surfactants

Surfactants, adjuvants, inerts, and other compounds used in manufactured formulated products may be toxicologically significant in some cases, as they may be toxic themselves or chemically interact with active ingredients in herbicidal or algaecidal formulations. Tank mixes may be used in the State of Washington for control of aquatic plants and weeds, when allowed by the FIFRA product label. As an example, the combination of the algaecide endothall mixed with copper sulfate for the control of algae in impounded golf course ponds appears to show more effective algal control than either of these compounds alone.

Not all formulations have similar toxicity on an acid equivalent basis. "Inert" materials within a formulation, for example, may interact with the technical active ingredient to cause antagonistic, additive, cumulative or synergistic effects against target plants and/or non-target fish and aquatic invertebrates. As an example, endothall acid is considerably more toxic to rainbow trout and bluegill sunfish when certain "inerts" are added, possibly due to a synergistic effect (Ecology, 2000). If surfactants are used, surfactants should be carefully selected. In Washington State, adjuvants and surfactants must be registered for aquatic use by WSDA prior to use in the aquatic environment. As an example, thickening agents such as Polysar® or Nalquatic® are used in other states (not registered in WA State) to control drift with liquid endothall applied to floating weeds and may also allow subsurface applications to sink more deeply into the water column where they can be more effective.

As another example of toxicity caused by surfactants, the surfactant MON 0818 used in some glyphosate formulations is acutely toxic to glochidia and juvenile mussels. MON 0818 has been shown to be the most toxic compound to freshwater mussels in this group of herbicides and related surfactants. Mon 0818 has also been shown to reduce growth of juvenile freshwater mussels. Application of MON 0818 containing compounds to water bodies at the maximum recommended application rates would result in concentrations of MON 0818 four times greater than its acute threshold of 0.05 mg/L (Bringolf *et al.* 2007a). MON 0818-containing formulations disrupt protein formation in adult mussels, which could affect mussel cell cytoskeletons, though these formulations are less acutely toxic to adult than to juveniles (Conners and Black 2004; Malécot *et al.* 2013). At least one herbicide compound containing glyphosate IPA salts but not MON 0818 was not shown to be acutely toxic to glochidia and also has little impact on juvenile mussel viability (Bringolf *et al.* 2007a). The surfactant MON 0818 is not approved for use in the aquatic environment in Washington State.

4.10.1.1 References

- Bringolf, R.B., W.G. Cope, S. Mosher, M.C. Barnhart, and D. Shea. 2007a. Acute and chronic toxicity of glyphosate compounds to glochidia and juveniles of *Lampsilis siliquoidea* (Unionidae). *Environmental Toxicology and Chemistry* 26(10): 2094-2100. [1]
- Conners, D.E. and M.C. Black. 2004. Evaluation of lethality and genotoxicity in the freshwater mussel *Utterbackia imbecillis* (Bivalvia: Unionidae) exposed singly and in combination to chemicals used in lawn care. *Archives of Environmental Contamination and Toxicology* 46: 362-371. [1]
- Malécot, M. B. Guével, C. Pineau, B.F. Holbech, M. Bormans, and C. Wiegand. 2013. Specific proteomic response of *Unio pictorum* mussel to a mixture of glyphosate and microcystin-LR. *Journal of Proteome Research* 12: 5281-5292. [1]
- Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]

4.10.2 2,4-D amine and ester

Two chemical forms of the active ingredient 2,4-dichlorophenoxy acetic acid (2,4-D), a selective post-emergent herbicide, have been approved by WSDA for control of aquatic macrophytes in lakes and ponds in Washington state. These include 2,4-D butoxyethyl ester (BEE) and 2,4-D amine or DMA (dimethylamine salt).

Key target species for 2,4-D include watermilfoil and water stargrass, and 2,4-D DMA is used for control of water hyacinth and brush along ditch and canal banks as well. The BEE and DMA forms have different labeling and permit restrictions and requirements. Two frequently used formulated products include Aqua-Kleen® and Navigate®.

Regarding mitigation of 2,4-D formulations, aquatic formulations of 2,4-D have not been evaluated for aerial applications in Washington State. Both Aqua-Kleen® and Navigate® applied at concentrations of 110 lb formulation/acre will control Eurasian watermilfoil and spare most non-target species of native aquatic vegetation.

Informational postings should be placed around the treatment area with an enforced 24-hour swimming restriction. Ecology requires that these postings go up within 400 ft of the treatment area that indicate the swimming restriction

(http://www.ecy.wa.gov/programs/wq/pesticides/final_pesticide_permits/aquatic_plants/permitdocs/R_eissue2016/DraftAPAMShorelinePostingTemplate.docx).

Current labels stipulate that 2,4-D may not be applied to waters used for irrigation, agricultural sprays, watering dairy animals, or domestic water supplies. The specimen label for Navigate® (Applied Biochemists 2002), a 2,4-D DMA aquatic formulation, specifies toxicity to both fish and non-target plants, and provides warnings and proposed mitigation for irrigation, potable water sources, and groundwater contamination issues. These warnings and mitigation measures are different than those specified by the Aqua-Kleen® label, and need to be considered when proposing either of these (or related) aquatic formulations for aquatic weed control in Washington.

Both 2,4-D DMA and BEE have shown acute toxicity to fish (CSI 2001). CSI (2001) reported such toxicity particularly to rainbow trout fry and fathead minnow fingerlings. When fish are actually exposed to 2,4-D BEE granules, fish show little impact due to the insolubility of the BEE formulation in water. Following label restrictions for oxygen ratios should help to minimize toxicity potential to fish (CSI, 2001). Extra precaution should be taken to avoid exposures to ESA-listed or sensitive fish species during each of their life stages. Following WDFW fish timing windows for application will be valuable in helping to avoid adverse exposures to these species. Label and permit restrictions on seasonal applications must be enforced to protect Chinook salmon and other salmonid smolts or juveniles from the toxic effects of 2,4-D BEE, DMA, and derivatives.

CSI (2001) performed a comprehensive environmental effects assessment under SEPA, including an assessment of toxicity on a wide variety of animal species, plant species, and endangered species as well as habitats. They concluded that the DMA formulation of 2,4-D is safe to use for control of nuisance aquatic vegetation at labeled use rates and provides a large safety factor for protection of fish and free-swimming aquatic biota from acute and chronic effects. However, although more sensitive species of

benthic invertebrates could be both acutely and chronically impacted based on laboratory toxicity data, field studies have shown that these invertebrate species should not be impacted by the use of 2,4-D DMA for the control of ditch bank weeds or aquatic weeds in ponds (CSI, 2001; Shearer and Halter, 1980).

Similarly, although 2,4-D BEE has the potential to harm fish and aquatic invertebrates based on risk assessments conducted using laboratory data, field studies have indicated that the use of 2,4-D BEE granular pellets has no direct impact on fish populations (Shearer and Halter, 1980), presumably due to the insolubility of these granular materials. Limited field data with benthic invertebrates indicates a similar lack of direct effects, but indirect effects such as decreased dissolved oxygen content can result in a shift in dominant organisms to those more tolerant of low dissolved oxygen content (Marshall and Rutschky, 1974). Low solubility of 2,4-D BEE and a rapid hydrolysis of 2,4-D BEE to 2,4-D acid also improves the safety of Aqua-Kleen® and Navigate® by decreasing contact time of 2,4-D BEE and increasing contact time to 2,4-D acid, which appears to cause little toxicity to aquatic biota. Thus, as long as label specifications are followed, field data have indicated that use of 2,4-D aquatic use products should be safe to aquatic biota at label-specified use rates.

Harnois (1999) reported that human health data are insufficient to justify classifying 2,4-D as a human carcinogen and that potential adverse health effects can be adequately addressed using well-documented non-carcinogenic toxicological endpoints as a basis for identifying protective exposure limits and assessing human health risks. In 2004, EPA (reported in EPA OPPTS, 2005) completed an evaluation of the potential for carcinogenicity of 2,4-D products, and concluded that 2,4-D is classified at Group D (not classifiable as to human carcinogenicity, and “the data are not sufficient to conclude that there is a cause and effect relationship between exposure to 2,4-D and non- Hodgkin's Lymphoma (NHL).” As an update from the International Agency for Research on Cancer (IARC), 2,4-D was classified in 2015 as “possibly carcinogenic to humans” based on inadequate evidence in humans and limited evidence in experimental animals. There is strong evidence that 2,4-D induces oxidative stress, a mechanism that also occurs in humans, and moderate evidence that 2,4-D causes immunosuppression, based on both *in vivo* and *in vitro* studies. However, epidemiological studies did not find consistent increases in risk of NHL or other cancers in relation to 2,4-D exposure (https://www.iarc.fr/en/media-centre/pr/2015/pdfs/pr236_E.pdf).

Concerning non-target ecotoxicity and eligibility for re-registration based on updated toxicological information, EPA (EPA OPPTS, 2005) reported that 2,4-D is not considered hazardous to beneficial insects due to its low insecticidal activity and an adequate safety margin when products containing 2,4-D are used at label-recommended levels. They also reported that LC50 values for 24-hour exposures in honey bees (*A. mellifera*) were estimated to be 104 and 115 µg per bee, which is consistent with earlier estimates, and signifies that 2,4-D is considered practically non-toxic to honey bees.

Relyea (2005) reported on a mesocosm study that indicated that an unspecified form of 2,4-D applied at typical labeled rate (0.117 mL/m²) had no negative effects on species richness, biomass, or survival on algae and 25 species of aquatic animals, including frog larvae, salamanders, snails, and a range of other invertebrates. EPA (EPA OPPTS, 2005) also reported that 96-hour LC50 concentrations for several species of amphibian larvae exceeded 100 mg/L for the amine salt (DMA) form, and that 2,4-D acid, 2,4-

D DMA, and other forms are considered practically non-toxic to amphibian larvae based on tests with the frog *R. pipiens*.

Parsons *et al.* (2001) performed another field investigation beginning in 1998 of 2,4-D for control of EWM in Loon Lake, WA, which appears to be consistent with the investigation summarized above (Relyea 2005). Plant biomass and frequency data were measured before treatment as well as 6 weeks and 1 year following treatment. EWM biomass and frequency significantly diminished following treatment, but no non-target plant species were significantly affected by the herbicide application. Aqueous concentrations of 2,4-D were measured at 1 to 2 mg/L within one day of treatment, and were below detection limits by one week after treatment.

Concerning toxicity to freshwater mussels, due to the persistence and mobility of 2,4-D, freshwater mussels are vulnerable to acute toxicity from 2,4-D. In addition to direct mortality, 2,4-D has been shown to cause demineralization in freshwater mussel shells (Alves and Oliveira 2014; Milam *et al.* 2005). 2,4-D also causes the loss of calcium and magnesium across the gills of *Anodonta californiensis*, and impacts the flux of primary amines (Swinehart and Cheney 1983). As reported by Alves and Oliveira (2014) and Milam *et al.* (2005), established criteria for environmental concentrations of 2,4-D may not adequately protect all species of freshwater mussels.

4.10.2.1 References

- Alves, M.G., and P.F. Oliveira. 2014. 2,4-Dichlorophenoxyacetic acid alters intracellular pH and ion transport in the outer mantle epithelium of the bivalve *Anodonta cygnea*. *Aquatic Toxicology* 154: 12-18. [1]
- Applied Biochemists. 2002. Specimen Label for Navigate® Selective Herbicide, 2p. http://www.aces.edu/dept/fisheries/rec_fishing/documents/navigate_label.pdf. [1]
- Compliance Services International, Inc. (CSI). 2001. Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides. Vol. 3: 2,4-D: 435 p. Ecology Report No. 00-10-043. [3]
- EPA. 1987. Health advisory for 2,4-D. USEPA, Washington DC. [1]
- Harnois, M. 1999. Toxicological Profile for 2,4-D. Office of Research and Standards, Mass. Department of Env. Protection, Boston MA. [1]
- Hazardous Substances Databank (HSDB). 2005. 2,4-D; U.S. Department of Health and Human Services, National Institutes of Health, National Library of Medicine. <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>, updated June 2005. [1]
- Jervais, G., B. Luukinen, K. Buhl, and D. Stone. 2008. 2,4-D Technical Fact Sheet. National Pesticide Information Center, Oregon State University Extension Svcs. <http://npic.orst.edu/factsheets/archive/2,4-DTech.html>. [1]
- Marshall, C. and C. Rutschky. 1974. Single Herbicide Treatment: Effect on the Diversity of Aquatic Insects in Stone Valley Lake, Huntingdon CO., PA. *Proc. PA. ACAD. SCI.* 48: p. 127-131. [9]

- Milam, C.D., J.L. Farris, F.J. Dwyer, and D.K. Hardesty. 2005. Acute toxicity of six freshwater mussel species (glochidia) to six chemicals: implications for daphnids and *Utterbackia imbecillis* as surrogates for protection of freshwater mussels (Unionidae). *Archives of Environmental Contamination and Toxicology* 48: 166-173. [1]
- Parsons, J., K. Hamel, J. Madsen, and K. Getsinger. 2001. The Use of 2,4-D for Selective Control of Eurasian Milfoil in Loon Lake, WA. *J Aquatic Plant Mgt.* 39: p. 117-125. [1]
- Relyea, R. A. 2005. The Impact of Insecticides and Herbicides on the Biodiversity and Productivity of Aquatic Communities. *Ecol. Applns.* 15 (2): p. 618-627. [1]
- Shearer, R., and M. Halter. 1980. Literature Review of Four Selected Herbicides: 2,4-D, Dichlobenil, Diquat and Endothall. Metro King County, Seattle WA. [4]
- Swinheart, J.H., and M.A. Cheney. 1983. 2,4-dichlorophenoxyacetic acid (2,4-D) and paranitrophenol (PNP) interactions with gills of *Anodonta californiensis* and *Mytilus californianus*: uptake and effects on membrane fluxes. *Pesticide Biochemistry and Physiology* 20: 49-56. [1]
- US Environmental Protection Agency (EPA). Office of Prevention, Pesticides, and Toxic Substances. (OPPTS). 2005. Reregistration Eligibility Decision 2,4-D. Washington, DC, 2005. EPA 738-R-05-002. [5]
- Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]

4.10.3 Bispyribac-sodium

Bispyribac-sodium is a narrow-spectrum, post-emergent herbicide that is useful for selective management of submersed, surface-dwelling, and emergent aquatic weeds in various water bodies such as lakes, wetlands, ponds, reservoirs, drainage ditches, and non-irrigation canals, for which Tradewind™ Aquatic Herbicide was registered by EPA in March 2011. WSDA has also registered Tradewind™ Aquatic Herbicide for aquatic use in Washington State. Its herbicidal mode of action is to inhibit ALS, which is a plant enzyme that regulates the production of essential amino acids in plants (valine, leucine, and isoleucine).

Non-target effects of bispyribac-sodium are expected to be largely non-problematic, and for that reason the mitigation measures recommended by Ecology (2012) are minimal. They specify simply to follow current label requirements (see Valent (2011) for Tradewind™ Aquatic Herbicide label requirements). For example, the label warns that as an ALS inhibitor, weed populations could contain or develop plants that are naturally resistant to bispyribac-sodium or other ALS inhibitor herbicides (e.g. penoxsulam, imazamox, imazapyr). The label recommends specific steps to delay the development of herbicide resistance.

Ecology also requires that only state-licensed applicators be used, that the material be applied in compliance with Ecology's water quality permits, that all permit provisions be followed, and that it not be applied in areas where rare non-target submersed or floating plant species occur unless Ecology agrees to a mitigation plan beforehand. There are no swimming restrictions for bispyribac-sodium label in Washington State. Given both the low use rates and low human and mammalian toxicity, Ecology does not implement a 24-hour swimming advisories after treatment. In fact, removal of aquatic vegetation from swimming areas will likely improve swimmers' safety.

EPA (2010) concluded that the use of bispyribac-sodium to control aquatic weeds has the potential for direct adverse effects on threatened or endangered aquatic plants. EPA does not anticipate any direct adverse effects to aquatic life (fish, aquatic amphibian or invertebrates due to very low toxicity), although they report a potential for indirect effects to listed aquatic animals, for example, through alteration in or effects to their habitats such as food or prey sources, cover or shelter, nesting areas, or other habitat features.

Regarding protection of listed or priority species in Washington State, Ecology mitigates indirect effects of herbicides by requiring timing or consultation with WDFW when applicators use herbicides in water bodies inhabited by priority species. Ecology's permit manager consults with the state Natural Heritage Program database for rare plants before issuing permit coverage. If applicable, Ecology coordinates mitigation efforts with the permittee, WDFW, and others as needed. Because of low toxicity and use rates bispyribac-sodium, Ecology does not plan to impose treatment timing requirements for salmon, bull trout, or steelhead in its water quality permits, but timing windows for other priority species will remain in effect.

Washington State has rare wetland and aquatic plant species that could be at risk in association with bispyribac-sodium treatments. To ensure adequate protections, the applicator may apply the material for in-water treatments only under water quality permit provisions designed by Ecology to protect rare

plants. If rare plants are present, Ecology's manager will work with the applicant to develop specific mitigation measures to protect the rare species in question.

Regarding updated toxicology research since the 2012 FEIS was published, Lajmanovich *et al.* (2013) tested a variety of commonly used soybean herbicides on a common toad (*R. arenarum*), including bispyribac-sodium, and found that both butyrylcholinesterase (BChE) and acetylcholinesterase (AChE) were significantly inhibited by this material. Bispyribac-sodium was also found to increase erythrocyte (red blood cell) abnormalities as part of this study. This study examined toxicity from both the individual herbicides and the mixtures of herbicides to determine the potential for interaction between these herbicides, and found synergistic effects on both mortality and neurotoxicity, and both synergistic and additive effects on genotoxicity in this test species.

4.10.3.1 References

- Lajmanovich, R., et al. 2013. Individual and Mixture Toxicity of Commercial Formulations Containing Glyphosate, Metsulfuron-methyl, Bispyribac-sodium, and Picloram on *Rhinella arenarum* Tadpoles. Doi:10.1007/211270-012-1404-1. Water, Air and Soil Pollution 224: p. 1404. [1]
- US Environmental Protection Agency (EPA). 2010. Ecological Risk Assessment for Bispyribac-sodium. Section 3: New Use as an Aquatic Herbicide. [1]
- Valent. 2011. Tradewind™ Aquatic Herbicide Specimen Label. [1]
- Washington Department of (Ecology). 2012. Environmental Impact Statement for Penoxsulam, Imazamox, Bispyribac-sodium, Flumioxazin, and Carfentrazone-ethyl. Addendum to the Final EIS for Freshwater Aquatic Plant Management. Pub. No. 00-10-040addendum1. [3]

4.10.4 Carfentrazone-ethyl

Carfentrazone-ethyl is a rapid-acting, photo-dependent, contact (i.e. non-systemic) herbicide that inhibits the plant enzyme protoporphyrinogen oxidase (commonly abbreviated as protox). In plants, inhibition of the protox enzyme induces the formation of peroxides that attack the lipids and proteins of the cell membrane. This disruption causes leakage of cell contents, resulting in drying and disintegration of terrestrial plants within 24 to 48 hours. The onset of plant response from carfentrazone-ethyl is slower on aquatic plants than terrestrial plants. Symptoms on susceptible aquatic plants include leaf discoloration and necrosis, with time to appearance of these symptoms varying by plant species, but are generally observed within two to five days. Rapid destruction of plant tissue results in self-limited translocation of the herbicide in the plant, and subsequently limits herbicide damage to the point of contact. Stingray™, a carfentrazone-ethyl formulation, exhibits selectivity to non-target grass species. Typical use rates for carfentrazone-ethyl are considered extremely low.

Stingray™ is a liquid formulation that is emulsifiable in water. The maximum label-specified application rate is 0.2 lb a.i. per acre for any single application, or 200 µg/L for submersed weeds (FMC, 2004a). State licensed applicators may use Stingray™ in ponds, lakes, reservoirs, marshes, wetlands, drainage ditches, canals (non-irrigation), streams, rivers, and other slow-moving or quiescent bodies of water. They may apply the product as a broadcast spray to floating or emergent vegetation (with a surfactant), or via subsurface injection for submersed species. The manufacturer claims that Stingray™ is resistant to being washed away by rain within one hour of application, although the label does warn applicators to avoid wash-off of the chemical by boaters or rain. When applying in flowing water, applicators should apply carfentrazone-ethyl when traveling upstream to prevent concentrations above label specification in the water column. Carfentrazone-ethyl requires light activation for herbicide symptoms to appear, which occur rapidly at the point of contact. Using muddy or turbid water when preparing spray solutions can reduce herbicidal activity. The Stingray™ label allows the applicator to treat up to a maximum of one-half of the water body at one time, with a minimum of 14 days before retreatment or treatment of the remaining half of the waterbody. It performs best when target plants are young and actively growing. Because carfentrazone-ethyl is a contact herbicide, rooted plants can regrow.

Carfentrazone-ethyl products were conditionally registered by EPA in 1998 under Section 3, for broadleaf weed control on cereal grain groups and soybeans. In 2004, EPA registered carfentrazone-ethyl as Stingray™ aquatic herbicide for use in freshwater bodies. EPA classified Stingray™ as a reduced risk pesticide. WSDA has registered Stingray™ for aquatic use in Washington.

EPA (2004b, 1998) reported that carfentrazone-ethyl breaks down rapidly in the environment, although its' degradates are more persistent in aquatic and terrestrial environments. Due to low application rates, EPA does not expect these residues to trigger acute or chronic risk to non-target plants or animals. A Canadian risk assessment of carfentrazone-ethyl (Health Canada, 2008) reported that although laboratory studies indicate that carfentrazone-ethyl and its metabolites may be mobile in soil, there is no field evidence that indicate the herbicide will result in groundwater contamination.

Concerning drinking water, there are potable water restrictions. Applicators cannot apply Stingray™ within a quarter mile of an active potable water intake unless the water intake is turned off prior to and for a minimum of 24 hours after application. Water users may turn the water intake on before 24 hours

if carfentrazone-ethyl and major degradate levels in the intake water are below 200 µg/L as determined by a laboratory. Ecology's water quality permits make special provision to protect municipal and community water intakes if an herbicide treatment could potentially affect large numbers of the public. In these cases, the potentially affected water right holder must agree to the treatment before Ecology will issue permit coverage.

There are no swimming or fishing restrictions, but there is one-day livestock watering restriction if 20 to 50% of the surface acreage of the water body is treated with Stingray™. Irrigation with treated water may result in injury to vegetation. The Stingray™ label prohibits the use of treated water in commercial nurseries or greenhouses. There is a one-day irrigation restriction for crops when the treatment is equal or less than 20 percent of the surface area of the water body and a 14-day irrigation restriction when the treated area is 20% or more of the surface area. However, irrigation can resume when testing by a laboratory determines that the concentration of carfentrazone-ethyl and its major degradates is less than 5 µg/L. Ecology's water quality permit mitigates for the possible loss of irrigation water rights by allowing project proponents to provide an alternative water supply to affected parties holding legal water rights while irrigation restrictions are imposed.

As would be expected for an herbicide, EPA (2008) found that carfentrazone-ethyl was toxic to both vascular and nonvascular aquatic plants. However, the Stingray™ label claims treatment efficacy for just a few species found in Washington State, including duckweed (*Lemna* spp.), mosquito fern (*A. caroliniana*), and watermeals (*Wolffia* spp.). Stingray™ does not claim any effectiveness for treating algae, but the (FMC, 2004a) label reports that the product is very toxic to certain species of algae. Ecology (2012) concluded that rare plant species were potentially at risk from the use of carfentrazone-ethyl.

Regarding protection of rare plant species potentially at risk from carfentrazone-ethyl, typically applicators may only apply carfentrazone-ethyl legally under water quality permits that make provision for mitigations for rare plants. Before issuing permit coverage, Ecology's permit manager consults the WDNR Natural Heritage Program database to determine the potential presence of any aquatic rare plants. If present, the applicant would presumably hire a botanist to survey the water body. The permit manager would consult with the Natural Heritage Program botanist, and the applicant to select appropriate mitigation measures to protect the rare plant populations. The permit manager may also request that Ecology's Aquatic Weeds Program botanist survey the lake before and after treatment. In some cases, carfentrazone-ethyl may not be an appropriate choice of herbicide.

Carfentrazone-ethyl is classified as moderately toxic to some fish and invertebrate species, but EPA determined that the acute risk for any group of non-endangered freshwater aquatic organisms was negligible, even if retreatment with carfentrazone-ethyl was made in shallow waters. However, the chronic risk to fish is exceeded for application of carfentrazone-ethyl to shallow waters. However, given the low use rates and the short half-life of carfentrazone-ethyl expected in Washington waters, EPA or Ecology do not expect to see chronic effects on fish in waters treated with this herbicide. In addition, carfentrazone-ethyl is practically non-toxic to birds and mammals. EPA (2004) concluded that environmental concentrations are low (maximum use rate of 200 µg/L), and therefore it expects minimal risk to animals from the use of carfentrazone-ethyl as an aquatic herbicide.

EPA determined that the acute and chronic level of concern for endangered freshwater fish inhabiting shallow waters is exceeded even with a single application of carfentrazone-ethyl. Ecology mitigates impacts to threatened and endangered animal species and WDFW priority species by requiring applicators to comply with timing windows. These windows allow treatment at times when the herbicide will not affect priority or listed species as well as its food and habitat. As a mitigation measure to protect Washington's priority animals, Ecology requires the applicators to follow WDFW timing windows for carfentrazone-ethyl treatments.

Regarding mitigation against potential adverse environmental or human health effects, it is recommended to follow current label requirements, to use state-licensed applicators, and where required, to apply carfentrazone-ethyl under Ecology water quality permits, following all permit provisions. The special conditions in the permit provide mitigations for herbicide use in general and Ecology sets out any specific provisions for each chemical in its permits. It is not recommended to use carfentrazone-ethyl in areas where rare submersed or floating plant species have been identified, unless Ecology agrees to the mitigation plan.

Ecology mitigates indirect effects of food and habitat loss through its permitting process by requiring work windows or consultation with WDFW when herbicides are used in water bodies with priority or listed species and habitats. Ecology's permit manager also consults the Department of Natural Resources (DNR) Natural Heritage Program database for rare plants before issuing permit coverage for in-water treatments. If applicable, Ecology coordinates mitigation efforts with the permit applicant, WDFW, the Natural Heritage Program and others, to ensure adequate protections to threatened and endangered species and state priority species and habitats from herbicide use such as carfentrazone-ethyl.

4.10.4.1 References

- California Environmental Protection Agency (CalEPA). Department of Pesticide Regulation (DPR). 2003. Public Report 203-6. Flumioxazin. Tracking ID No. 191861 N. [1]
- FMC. 2004a. Stingray™ Aquatic Herbicide Technical Guide and Label. [1]
- FMC. 2004b. Stingray™ Material Safety Data Sheet (MSDS). [1]
- Glomski, L., A. Poovey, and K. Getsinger. 2006. Effect of Carfentrazone-ethyl on Three Aquatic Macrophytes. *J. Aquat. Plant Manage.* 45: p. 43-46. [1]
- Gray, C., et al. 2007. Eurasian Watermilfoil and Parrotfeather Control Using Carfentrazone-ethyl. *J. Aquat. Plant Manage.* 45: p. 43-46. [1]
- Health Canada. 2008. Evaluation Report: Carfentrazone-ethyl. PMRA Document Number: 1591610. [9]
- Koschnick, T. J., W. T. Haller, A. W. Chen. 2004. Carfentrazone-ethyl Pond Dissipation and Efficacy on Floating Plant. *J. Aquat. Plant Manage.* 42: p. 103-108. [1]

- New York State Department of Environmental Conservation (NYSDEC). 1999. Application for Registration of a New Pesticide Product, AIM Herbicide (EPA Reg. No. 279-3194), Which Contains the New Active Ingredient Carfentrazone-ethyl. [5]
- Pesticide Action Network (PAN). Carfentrazone-ethyl: Identification, Toxicity Use, Water Pollution Potential, Ecological Toxicity and Regulatory Information.
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC39672. [1]
- Richardson, R., R. Roten, A. West, S. True, and A. Gardner. 2008. Response of Selected Aquatic Invasive Weeds to Flumioxazin and Carfentrazone-ethyl. J. Aquat. Plant Manage. 46:154-158. [1]
- Toxnet. 2012. Carfentrazone-ethyl. Hazardous Substance Data Base, National Library of Medicine.
<http://toxnet.nlm.nih.gov/cgibin/sis/search/a?dbs+hsdb:@term+@DOCNO+7253>. [1]
- US Environmental Protection Agency (EPA). 2004a. Carfentrazone-ethyl; Notice of Filing Pesticide Petitions to Establish a Tolerance for a Certain Pesticide Chemical in or on Food. Federal Register. Volume 69, Number 62. March. [5]
- EPA. 2004b. EFED New Use of Carfentrazone-ethyl as an Aquatic Herbicide. [1]
- EPA. 1998. Pesticide Fact Sheet for Carfentrazone-ethyl. [1]
- EPA. November 1998. Carfentrazone-ethyl Registration Approval. Federal Register. Volume 63, Number 224 (Notices). [5]
- EPA. June 1998. Carfentrazone-ethyl Pesticide Tolerance Petition Filing. Federal Register. Volume 63, Number 111 (Notices). [5]
- Fluoride Action Network Pesticide Project (FANPP). 2005. Carfentrazone-ethyl.
<http://www.fluoridealert.org/wp-content/pesticides/epage.carfentrazone-ethyl.htm>. [1]
- Washington Department of Ecology (Ecology). 2001. Herbicide Risk Assessment for the Aquatic Plant Management FEIS. Appendix D, Vol 2: Endothall. Publ. No. 00-10-044.
<https://fortress.wa.gov/ecy/publications/documents/0010044.pdf>. [3]
- Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]
- Wersal, R., et al. 2010. Comparison of Daytime and Night-time Applications of Diquat and Carfentrazone-ethyl for Control of Parrotfeather and Eurasian Watermilfoil. J. Aquat. Plant Manage. 48: p. 56-58. [1]

4.10.5 Diquat

Diquat® initially received EPA registration for control of submersed and floating aquatic weeds in 1962 and completed the Registration Eligibility Decision (RED) process in 2000. WSDA has registered diquat for use under several labels, but the only registered formulation for use in public waterways is Reward® Landscape and Aquatic Herbicide, containing 37.3% active ingredient diquat dibromide. There are a variety of diquat products registered by WSDA (except for Reward®) that are restricted in their use for application to ponds, lakes and drainage ditches where there is little or no outflow of water and which must remain under the control of the user. In addition to controlling watermilfoil, diquat is known to be particularly effective against water-lettuce (*P. stratiotes*), duckweed (*Lemna* spp.), cattails (*Typha* spp.), flowering rush (*B. umbellatus*) and other species. Very few aquatic herbicides are effective in controlling all of these species of aquatic macrophytes, which makes diquat particularly effective (Reward® LA label and ECOFacts, 2000).

Diquat dibromide is a water-soluble dipyridylum herbicide compound related to quaternary ammonium compounds. All diquat formulations are liquid bromine salts. Diquat is a broad-spectrum (non-selective), post-emergent contact herbicide that kills both submerged and emerged plants, but is used primarily for submerged weeds, including watermilfoil. The action of diquat depends on sunlight-inducing photolysis, so control of aquatic plants above water occurs more quickly than those below water. Its mode of action is to inhibit photosynthesis, rapidly inactivating cellular functions of target plants through the release of strong oxidants. Diquat is not typically used for algae control and most species of algae are not affected strongly by diquat. The current label claims no systemic action at current labeled use rates.

Paul *et al.* (1994) conducted toxicity testing for effects on early life stages of non-target aquatic game fish found in lakes undergoing treatment. Commercial formulations of diquat, endothall, and fluridone were selected for acute toxicity testing using early life stages of walleye (*S. vitreum*), largemouth bass (*M. salmoides*), and smallmouth bass (*M. dolomieu*). In addition, the rates of diquat photodegradation and uptake by sediment were determined, and used to predict diquat concentrations in lakes of various depths. The results of the toxicity tests were compared to the predicted concentrations. Diquat, with 96-h LC₅₀s of 0.74 to 4.9 mg/L, was considerably more toxic to these early life stages than endothall or fluridone, although expected exposure concentrations for the highest label-use rate is 0.37 mg/L, with a 24-hour dissipation level of 0.1 mg/L. This is below the range of LC₅₀ values cited above. As the measured LC₅₀ values for diquat were relatively close to the predicted concentration, the safety margin for the use of diquat is reportedly very small.

A review of the toxicity literature as reported by Paul *et al.* (1994) for diquat indicates that diquat is highly toxic to some aquatic animals. *H. azteca*, a benthic amphipod and important prey species for fish, is one of the most sensitive aquatic organisms tested with a very low 96-h LC₅₀ of 0.048 mg/L, indicating a high level of acute toxicity. A 96-hr LC₅₀ of 35 mg/L to bluegills (*L. macrochirus*) has been reported, as well as a 96-hr LC₅₀ of 289 mg/L to the mosquitofish (*G. affinis*). Numerous other aquatic organisms have been tested and found to fall between the range of 0.048 mg/L and 289 mg/L. Young walleyes have been among the most sensitive fish species tested, with a reported a 96-hr LC₅₀ of 1.2 mg/L for two month old walleyes, which is indicative of quite high acute toxicity. A reported 96-hr LC₅₀ of diquat to largemouth bass was 7.8 mg/L, which also shows considerable toxicity.

Paul *et al.* (1994) report that according to product literature, diquat has a “wide margin of safety between recommended dosages and rates necessary to cause signs of toxicity to fish species” as claimed by the registrant. If diquat is applied according to label specifications (2 gallons/acre to control certain plant species; Diquat Label EPA Reg. No. 239-1663-ZA- 59639), water concentrations of 1.5 mg/L in one foot and 0.75 mg/L in two feet of water will result. Both of these concentrations are greater than the reported 96-hr LC₅₀s for young walleyes and therefore do not provide a “wide margin of safety” as claimed by the registrant. If incomplete mixing occurs, some areas of a lake would have even higher concentrations of diquat.

During treatment, applicators dilute diquat and apply it with weighted hoses from boats to attain labeled concentrations. As noted above, the expected exposure concentration would be 0.37 mg/L for the highest label use-rate, and 0.1 mg/L as the 24-hour dissipation level. These methods of application are likely to produce regions of high herbicide concentration. Even spray applications can produce uneven diquat concentrations. Very little diquat was reported to be degraded by sunlight, as photodegradation is reportedly insignificant in the dissipation and removal of diquat from the water column. Therefore, the possibility for diquat to be present in potentially lethal concentrations to early life stages of several fish species does exist. For example, bass are known to be sensitive to diquat and it is recommended that where diquat is used, caution should be exercised. The safe use of diquat seems to depend upon the removal of the active ingredient through binding to sediment and/or plant material. Diquat was thought to bind quickly to clay particles in sediment, so that it would not be present in the water column for long. In the study conducted by Paul *et al.* (1994), it was found that 40% of the original concentration of diquat remained after 4 days with sediment present in the test system.

In an ecological risk assessment conducted for diquat, Emmett (2002) concluded that early life-stage striped bass, smallmouth bass, and similarly sensitive species may be at risk when exposed to diquat at labeled use rates. She also reported that impacts on salmonid life histories need to be evaluated. Aquatic invertebrates are at risk from acute and chronic effects of diquat treatment at concentrations ranging from 0.1 to 1.0 mg/L under whole pond treatment scenarios and reservoir spot treatments of 0.30 to 0.37 mg/L. Cladocerans (e.g. *D. magna* and *S. vetulus*) have been reduced in numbers for up to several months after application of 1.0 mg/L diquat. Furthermore, concentrations of 1.0 mg/L have been shown to sharply decrease the numbers of the benthic amphipod *H. azteca* and four genera of snails, although these effects were believed to be at least partially due to the destruction of plant species serving as habitat. In the field, one other species of aquatic invertebrate (water scorpion) was observed to cease reproduction after exposure to diquat at 1.0 mg/L.

Not all invertebrates respond negatively to treatment with diquat. For example, some invertebrates (e.g. *Simocephalus* spp.) were observed to increase in number after an algal bloom brought on by nutrient release from decaying aquatic macrophytes. Emmett reported that 85% of tested invertebrate species do not appear to be adversely impacted by diquat.

Concerning non-target species, use of diquat at labeled rates may adversely impact non-target algae and aquatic plants when they are located at or adjacent to the site of application.

Emmett (2002) also conducted a human health risk assessment for diquat bromide. Based on diquat’s chemical and environmental fate characteristics, label use rates, removal from the aquatic environment

by adsorption to particulates as well as vegetation and sediments, and acute and chronic toxicology studies. Based on this review and developed environmental exposure concentrations, it appears that the label-directed use of diquat for aquatic weed control would not be expected to result in any significant adverse health effects. The exposure evaluation of persons swimming in water containing 0.37 mg/L (highest label use-rate) and 0.1 mg/L (24-hour dissipation level) diquat does not indicate that significant adverse systemic or other health effects would occur. The only health-based screening level exceeded involved the six-year-old group swimming for three hours in water containing 0.37 mg/L diquat. Even though the health-based screening level was exceeded under this scenario, the potential diquat dose would reportedly be approximately 88 times less than the margin of safety (MOS) based on an animal systemic chronic toxicology NOAEL.

Risk levels were significantly exceeded in situations where the drinking water source had been treated with diquat 24 to 36 hours prior. Although the calculated diquat doses were elevated, they remained 13 - 76 times below the systemic animal chronic toxicology NOAEL. Again, it is important to follow the diquat product label, which recommends waiting three days before resuming use of treated water as a drinking water source. If label directions are followed, the results of diquat toxicology studies suggest that the aggregate or combined daily exposure to diquat from aquatic weed control would not pose a significant adverse health concern. As an example of additional toxicity testing conducted since the 2002 risk assessment summarized above, Ducrot *et al.* (2010) performed an investigation on diquat in an attempt to assess risk or hazard to non-target invertebrates in association with diquat exposures. Freshwater snails (*L. stagnalis*) were exposed to acute, environmentally representative concentrations of diquat from the embryo to the adult stage. Endpoints tested included hatching rate, embryonic development duration, juvenile mortality, feeding rate and age at first spawning. Results showed that all endpoints were significantly impaired at environmentally realistic concentrations.

King *et al.* (2016) examined the effects of three aquatic herbicides (diquat dibromide [Reward®]), fluridone, and triclopyr) on specific endpoints related to smoltification success in juvenile Pacific coho salmon (King *et al.* 2016) at label-specified rates in seawater for each of these compounds. Preliminary results suggested that, at the chemical concentrations in seawater exposures tested, effects were short-lived and these aquatic herbicides are unlikely to affect smoltification success. In a similar study, Curran *et al.* (2007) tested the aquatic herbicides DMA® (2,4-D), triclopyr, diquat (Reward®), and fluridone for effects to the olfactory ability of juvenile rainbow trout (*O. mykiss*) when exposed to the maximum application rates of these formulations for 96 hours, using static-renewal tests. Results showed that olfactory function of the juvenile rainbow trout were not affected by three of the compounds, with effects observed only following exposure to the maximum rates of Reward® (diquat).

Regarding label restrictions and mitigation, several beneficial uses of water are affected by treatment with diquat. The most current EPA/Syngenta Corp. label (2007) for Reward® aquatic herbicide notes toxicity to aquatic invertebrates, an irrigation restriction, restricted post-treatment work entry intervals of 24 hours, spray drift management guidance, and drinking water restrictions. It does not include a swimming or fishing restriction. In general, the nature and magnitude of residues of diquat measured in natural waters are highly variable and unpredictable.

As discussed above, there is a strong body of evidence showing ecotoxicity of diquat to an array of potentially vulnerable aquatic species, and there are concerns about potential indirect effects to the

food chain. For example, diquat is known to be embryotoxic to the clawed frog (ENSR, 2005). This raises concerns about potential direct effects to other amphibians, including the spotted frog and Northern leopard frog, both candidates for listing under the ESA, and both priority species under the WDFW priority habitats and species program. The discussion above documents that both fish and invertebrate species may experience toxicity at environmentally representative application rates, and diquat should only be used for aquatic applications in Washington State in strict compliance with label specifications and prescribed mitigation measures.

Parsons *et al.* (2007) conducted a recent field investigation in which diquat was used to control invasive Brazilian elodea (*E. densa*) in Battle Ground Lake, Washington. The purpose of this investigation was to monitor plant community changes and water quality before treatment and up to three years following treatment with this herbicide. Results showed a significant reduction in elodea frequency and biomass after the herbicide treatment. The diquat spread throughout the lake and persisted at low levels in the water column for at least two weeks after treatment. There was a slight decrease in surface water dissolved oxygen and water transparency after the herbicide treatment due to increased algae growth.

4.10.5.1 References

- Curran, C., J. Grassley, L. Conquest, and C. Grue. 2007. Olfactory performance in salmonids exposed to aquatic herbicides. Master's Thesis, University of Washington. [9]
- Ducrot, V., A. Pery, and L. Lagadic. 2010. Modelling effects of Diquat under realistic exposure patterns in genetically differentiated populations of the gastropod *L. stagnalis*. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 365 (1557): p. 3485-3494.
<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2981967/> [1]
- Emmett, K. 2002. Final Risk Assessment for Diquat Bromide. Ecology Water Quality Program. Publ. No. 02-10-046. November 2002. 411 p.
<https://fortress.wa.gov/ecy/publications/publications/0210046.pdf> [3]
- ENSR Corp. 2005. BLM Vegetation Treatments Using Herbicides: Ecological Risk Assessment for Diuron and Nine Other Herbicides. November: 118 p. [1]
- EPA/Syngenta Corp. 2007. Label for Reward® Herbicide.
https://www3.epa.gov/pesticides/chem_search/ppls/000100-01091-20070627.pdf [1]
- K. King, C. Grue, J. Grassley, C. Curran, W. Dickhoff, and J. Winton. 2016. Effects of Three Aquatic Herbicides on Smoltification in Juvenile Pacific Coho Salmon. In press. [9]
- Parsons, J. 2007. The Impact of Diquat on Macrophytes and Water Quality in Battle Ground Lake, WA. Journal of Aquatic Plant Mgt. 45: p.35-39. [1]
- Paul, E., et al. 1994. The Toxicity of Diquat, Endothall, and Fluridone to the Early Life Stages of Fish. J. Freshwater Ecology 9(3): p. 239-239. [1]
- REWARD® Landscape and Aquatic Herbicide, ECOfacts. 2000. Zeneca Professional Products. [1]

Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]

4.10.6 Endothall (dipotassium salt) Herbicide

Endothall is a contact herbicide that disrupts solute transport processes in plant cells. It is formulated in two active ingredient forms, which are the dipotassium salt and the dimethylalkylamine (mono) salt. The potassium salt formulation is used in both Aquathol® and Aquathol®K herbicides, and the amine salt is formulated as Hydrothol®191 aquatic algaecide and herbicide (the latter ingredient, the mono salt, is discussed as an algaecide in Section 4.10.14).

Endothall dipotassium salt is the active ingredient in both Aquathol® and Aquathol® K, containing 10.1% and 40.3% of the active ingredient, respectively. Aquathol® Granular Aquatic Herbicide and Aquathol® K Aquatic Herbicide have been approved by WSDA and Ecology for use in control of aquatic macrophytes in lakes and ponds, and Aquathol® K has also been approved for control of aquatic macrophytes in irrigation canals.

In addition to these products, Hydrothol® 191 liquid and Hydrothol®191 granular have received federal registration for control of both algae and aquatic macrophytes in canals, lakes and ponds, and have been registered by WSDA in Washington State for control of aquatic algae and plants (WSDA 2014; see Section 4.10.14).

Target plant species for Aquathol® include watermilfoil, pondweed, naiad, coontail, and hydrilla. Some plant species are known to be tolerant to Aquathol®, including American waterweed, cattails, spatterdock, and some water lilies. Aquathol® K is *not* an algaecide and is generally ineffective in controlling algal species. In fact, algal species may bloom following treatment with Aquathol®, as nutrients released when affected plants degrade may reach levels that can sustain algal growth.

Ecology (2000) identified data gaps relating to soil and sediment, nutrient data in water and dead or dying plants, and chronic toxicity studies for both plants and animals relating to Aquathol®, Aquathol®K, and Hydrothol®. Ecology (2001) recommended that early life stage studies should be conducted on all end-use formulations with standard test species rainbow trout, fathead minnow, and sheepshead minnow.

To that end, Courter *et al.* (2012) and Courter *et al.* (2016) performed ten-day seawater challenge experiments on anadromous juvenile fish (steelhead, coho, and Chinook salmon) to support definition of chemical toxicity levels associated with aquatic exposure to endothall using Cascade® herbicide, for which the dipotassium salt is the active ingredient. Results of this testing showed that steelhead showed a lower survival rate than coho and Chinook salmon, although no effects of endothall to any test animals were observed during the initial 96 hour freshwater toxicity phase of the exposure. Surviving fish did not experience significant changes in osmoregulatory performance (a sublethal endpoint reflective of the smoltification process) in comparison with control fish. LOECs were 9 mg/L a.e. for steelhead and 12 mg/L a.e. for coho and Chinook salmon. This compares with the Washington NPDES regulation set at 2.5 mg endothall/L a.e. Based on these results, no sublethal effects of Cascade on steelhead and salmon are anticipated when discharged at the labeled rate of 5 mg endothall/L a.e.

Paul *et al.* (1994) conducted toxicity testing for effects on early life stages of non-target aquatic game fish found in lakes undergoing treatment. Commercial formulations of diquat, endothall, and fluridone were selected for acute toxicity testing using early life stages of walleye (*S. vitreum*), largemouth bass

(*M. salmoides*), and smallmouth bass (*M. dolomieu*). Toxicity testing results were compared to predicted concentrations. Diquat, with 96-h LC₅₀s of 0.74-4.9 mg/L, was more toxic to these early life stages than endothall or fluridone, with 96-h LC₅₀s of 16-130 mg/L and 1.8-13 mg/L respectively. The LC₅₀ values for endothall was about one order of magnitude greater (i.e. less toxic) than label-specified concentrations. They concluded that endothall appears to have an adequate margin of safety between application rates used for aquatic macrophyte control and concentrations which are toxic to early life stages of fish. An earlier reported 96-hr LC₅₀ value for largemouth bass was 120 mg/L, which is consistent with the value of 131 mg/L determined by Paul *et al.* (1994). Young walleyes are much more sensitive (96-hr LC₅₀ value of 16 mg/L), but even this is three times the maximum labelled application rate of 5 mg/L (Aquathol®K label, EPA Reg. No. 4581-204).

Archambault *et al.* (2015) and Archambault and Pope (2016)) conducted two separate studies to investigate the effects of two currently registered herbicides commonly used to control *Hydrilla* and other aquatic weeds (endothall (dipotassium salt) and fluridone) on freshwater molluscs, including a rare freshwater snail (*S. virginicus*). Toxicological endpoints measured were adult survival and egg hatching success. Results showed that neither herbicide indicated effects to either survival or egg hatching success at concentrations typically prescribed (1 to 5 mg/L for endothall) for control of a target plant species such as *Hydrilla*. The early life stages of the mussel *L. siliquoidea* were exposed to a formulation of the dipotassium salt of endothall (Aquathol®K). The 24-h LC₅₀ for the juvenile mussels exposed to the dipotassium salt of endothall was 31.2 mg/L, and the 96-h LC₅₀ for juvenile mussels was consistent at 34.4 mg/L. Endothall concentrations typically recommended for hydrilla treatment (1 to 5 mg/L) were not acutely toxic to the molluscs tested, although this work indicated that some mortality of mussels could occur below established threshold values.

Regarding use restrictions and mitigation measures, all of Ecology's general mitigation posting requirements apply. The APAM permit requires shoreline sign postings within 48 hours of treatment. It is recommended that informational buoys should be placed around the treatment areas, and a 24-hour swimming advisory is recommended in treated areas for protection against mild eye irritation. A 24-hour boating advisory is recommended for boaters entering areas of treatment for protection against mild eye irritation due to aerial drift (e.g. spray from boat engines, propellers, etc.). Application of endothall is generally made directly to the water surface or by using weighted booms and tubes to discharge below the water surface to further reduce the possibility of aerial drift.

It is recommended that exposure of wild fisheries to endothall should be avoided, although toxicity testing have suggested that the most common forms of endothall, including the dipotassium and mono salts, will not cause acute or chronic harm to non-target aquatic animals when label specifications are followed.

Seasonal restrictions for endothall treatments may be warranted to protect sensitive salmon smolts from potentially adverse effects; similar restrictions may be advisable to protect both the fisheries and human health when recreational or commercial fishing seasons are active. Washington state does not require any restrictions for Aquathol®K or Aquathol® regarding consumption of fish from treated areas following treatment (WSU PICOL Database (2017)).

Parsons *et al.* (2004) conducted a field investigation in Kress Lake, WA, using low concentrations (1.5 mg/L active ingredient) of endothall (formulated as Aquathol® K) in 2000 to selectively control EWM. Aquatic plant biomass and frequency data were collected before treatment, ten weeks after treatment and during the growing season for 3 additional years. Macrophyte data were analyzed to assess the herbicide's impacts on the target species (EWM) as well as the rest of the aquatic plant community. Results showed a significant decrease in EWM biomass and frequency 10 weeks after treatment. EWM continued to be present, but at significantly reduced levels throughout the study (three years after treatment). Of the native plant species, large-leaf pondweed (*P. amplifolius*) frequency and biomass was significantly reduced after treatment. Common elodea (*E. canadensis*), muskgrass (*Chara* sp.) and bladderwort (*Utricularia* sp.) all increased significantly after treatment.

In 2005 additional plant frequency data were collected following the same methods used in the original study. Data showed no significant difference between the frequency of Eurasian milfoil in 2005 and 2000, so it returned to essentially pretreatment levels. However, the big leaf pondweed frequency was still at significantly reduced levels compared with before treatment. The other common native species, however, were all still found at significantly higher frequencies in 2005 than before treatment.

4.10.6.1 References

Archambault, J, and W. Cope. 2016. Life Stage Sensitivity of a Freshwater Snail to Herbicides Used In Invasive Aquatic Weed Control. *Freshwater Mollusk Biology and Conservation* 19: p. 69-79. [1]

Archambault, J., *et al.* 2015. Sensitivity of Freshwater Molluscs to Hydrilla-targeting Herbicides: Providing Context for Invasive Aquatic Weed Control in Diverse Ecosystems. *J. Freshwater Ecology* 30(3): p. 335-348. [1]

Courter, L., T. Garrison, and I. Courter. 2016. Latent toxicity of endothall to anadromous salmonids during seawater challenge. *Bulletin Environ. Contam. Toxicol.* 96 (5): p. 533-579. [1]

Courter, I., L. Courter, T. Garrison, D. Cramer, S. Duery, D. Child, T. Hanna and E. Buckner. 2012. Effects of the aquatic herbicide Cascade® on survival of salmon and steelhead smolts during seawater transition. Final Rep. submitted to WSWRA 2012. 46 p.
<http://www.ecy.wa.gov/programs/wq/pesticides/irrigation/docs/cascade.pdf> [9]

Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]

Parsons, J., K. Hamel, S. O'Neal, and A. Moore. 2004. The impact of endothall on the aquatic plant community of Kress Lake, WA. *Journal Aquatic Plant Mgt.* 42: 109-114. [1]

Paul, E., et al. 1994. The Toxicity of Diquat, Endothall, and Fluridone to the Early Life Stages of Fish. *J. Freshwater Ecology* 9(3): p. 239-239. [1]

Washington Department of Ecology (Ecology). 2001. Herbicide Risk Assessment for the Aquatic Plant Management FEIS, Appendix D, Vol 2: Endothall. Publ. No. 00-10-044.
<https://fortress.wa.gov/ecy/publications/documents/0010044.pdf>. [3]

Washington State Department of Agriculture (WSDA). 2014. Non-agricultural Pesticide Use in Puget Sound Counties. Publication No. AGR PUB 103-409: p. 76.

<http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx>. [1]

Washington State University. 2017. Pesticide Information Center Online – PICOL output.

<http://cru66.cahe.wsu.edu/labels/ViewLabels.php?radOutputType=standard&selFld1=none&selFld2=none&selFld3=none&selFld4=none&selFld5=none&selFld6=none&selFld7=none&selFld8=none&selFld9=none&view=View+Labels&SrchType=C>. [4]

4.10.7 Flumioxazin

Flumioxazin is a broad-spectrum contact herbicide and algaecide effective on filamentous green algae species (e.g. *Pithophora* and *Cladophora*). Flumioxazin is a light-dependent, peroxidizing herbicide that blocks chlorophyll biosynthesis through formation of peroxides, which create phytotoxic compounds in plant tissues. Peroxidation of membrane lipids leads to irreversible damage of membrane function and structure, and target plants become necrotic and die shortly after exposure to sunlight.

EPA conditionally registered a formulation of flumioxazin in 2001 for terrestrial weed control in crops (peanuts, soybeans, and others). Flumioxazin is active against certain grasses, broadleaf plants, and sedges. Another subsequent regulatory review was conducted in 2011 by EPA for control of various submerged, emergent and floating aquatic plants and filamentous green algae, and registered an aquatic formulation of flumioxazin called Clipper™ in 2011. Clipper™ is a water-dispersible granular product, intended for application by conventional spraying equipment after disintegration and dispersion in water. These water dispersible granules are essentially dustless. WSDA has registered Clipper™ for aquatic freshwater use in Washington.

In its aquatic review, EPA (2008, 2010b) concluded that flumioxazin is short-lived and its potential to contaminate the environment or cause non-target toxicity is relatively low. Applicators may use flumioxazin to manage aquatic plants in drainage ditches, freshwater ponds, lakes, marshes, and reservoirs as long as these water bodies have limited or no outflow at the time of treatment. Flumioxazin is fast-acting and applied subsurface to control submersed and floating vegetation at a use rate of 100 to 400 µg/L. Flumioxazin can also control floating and emergent plants growing on or above the water surface when applied directly onto target foliage. According to the Clipper™ label (Valent 2011), this product is most effective when applied to young, actively growing plants in waters with a pH of less than 8.5. At higher pH levels, Clipper™ breaks down very rapidly and loses its effectiveness. The manufacturer notes that flumioxazin is most efficacious applied earlier in the growing season when plants have limited biomass with relatively high light penetration into the water column. The Clipper™ label allows applicators to re-treat the same area up to six times per year, but only at 28-day intervals.

Repeated use of flumioxazin can lead to domination of a waterbody by a weed population that is resistant to this herbicide. To delay or prevent herbicide resistance, the manufacturer recommends avoiding consecutive use of Clipper™ or other herbicides with a similar mode of action, basing herbicide use on a comprehensive integrated pest management program, and monitoring treated plant populations for loss of efficacy to flumioxazin.

Contact herbicides such as flumioxazin tend to be more acutely toxic to aquatic organisms than systemic herbicides such as the ALS inhibitors penoxsulam, imazamox, and bispyribac-sodium. However, there are few effective algaecide alternatives that are less toxic and available to use in Washington State. Ecology considers algaecides such as copper sulfate and chelated copper complexes to be too persistent and toxic to fish and aquatic invertebrates to allow their use under its Aquatic Plant and Algae Management Permit. Ecology generally limits other algaecides to very low concentrations (e.g., the endothall formulation Hydrothol®191) to mitigate toxic impacts to fish. This restricts options for applicators managing algae problems in lakes. Flumioxazin provides a contact herbicide alternative with fewer non-target effects relative to other algaecides for the management of filamentous green algae.

Contact herbicides such as flumioxazin tend to have a much shorter half-life in the environment than do systemic (but often less toxic) herbicides. Little information is available about flumioxazin degradation by-products. When developing its risk assessments, EPA (2008) made an assumption that flumioxazin breakdown products were at least as toxic as the parent herbicide compound, flumioxazin, which was later shown to not be the case.

Both MDAR/MDEP (2013) and EPA (2008) conducted comprehensive human health and ecological risk assessments for flumioxazin, and concluded that it is probable that aggregate exposure to flumioxazin residues will result in no adverse effects to the general population, including infants or children. Results from MDAR/MDEP (2013) were consistent with EPA (2008) in its assessment of human health risks, but showed evidence of chronic and acute ecotoxicity and hazard to fish, and chronic toxicity to aquatic invertebrates. In addition, results indicated some evidence of risk to endangered fish and plant species. Part of this risk was attributed to use of highly conservative risk assessment assumptions, including maximum application rates and a simplifying assumption that flumioxazin degradates were of equal toxicity to the parent compound flumioxazin (more recent and specific investigations have shown that these degradates are not as toxic as the parent compound). A subsequent risk assessment based on exposure data from an Iowa pond study showed lower toxicity, but still indicated some evidence of chronic toxicity and risk, although risk was lower from flumioxazin degradates.

No risk assessment has been done for estuarine exposures to flumioxazin as it is not proposed for this use, but MDAR/MDEP (2013) reports that this compound is highly toxic to marine invertebrates. Flumioxazin is also phytotoxic, both to endangered and non-endangered non-target plant species, especially at maximum application rates. Toxicity data indicate that flumioxazin is not toxic to birds, mammals, or insects such as honey bees even at maximum application rates. CalEPA (CalEPA DPR, 2003) concluded that flumioxazin has low acute mammalian toxicity and is safer for pesticide applicators to handle than many other contact herbicides. Based on mammalian toxicity information, flumioxazin is less toxic than the other two contact aquatic algaecides used in Washington.

Umphres (2012) conducted a field study to investigate the effects of flumioxazin, on both phytoplankton and zooplankton species, and concluded that flumioxazin showed no significant or long-lasting effects due to high turbidity and low light penetration, which inhibits the light-sensitive mode of action of flumioxazin and highlights the need to apply the material when light can freely penetrate the water column. In conclusion, based on several risk assessments conducted for flumioxazin, it appears that flumioxazin applied at maximum application rates can cause a variety of non-target environmental effects, and precautions should be taken to limit these effects.

Regarding mitigation for potential non-target effects of flumioxazin to a variety of non-target species, it is recommended that the maximum labeled rate not be used unless necessary. At a minimum, the current label requirements should be followed, state-licensed applicators should be used exclusively and the material should be applied only during WDFW work windows for salmon-bearing waters. Where required, flumioxazin should be applied only under Ecology water quality permits and all permit provisions should be followed. It should not be used in areas where there are rare submersed or floating plant species, unless Ecology agrees to a mitigation plan in advance.

4.10.7.1 References

- California Environmental Protection Agency (CalEPA). Department of Pesticide Regulation (DPR). 2003a. Summary of Toxicology Data for Flumioxazin, Chemical Code # 5802, Tolerance # 52894, SB 950 # New A.I. Revised January 2003.
www.fluoridealert.org/pesticides/flumioxazin.ca.epa.jan.2003.pdf. [1]
- CalEPA. DPR. 2003b. Public Report 203-6. Tracking ID No. 191861 N. [9]
- Health Canada. 2010. Evaluation Report. Flumioxazin. ERC2010-05. [1]
- Material Safety Data Sheet for Clipper™ Herbicide. 2011. 68. [1]
- Massachusetts Departments Agricultural Research and Environmental Protection (MDAR/MDEP). 2013. Flumioxazin. p. 63. <http://www.mass.gov/eea/docs/agr/pesticides/aquatic/flumioxazin.pdf>. [1]
- Richardson, R. J., Roten, R.L., West, A.M., True, S. L. and Gardner, A. P. 2008. Response of Selected Aquatic Invasive Weeds to Flumioxazin and Carfentrazone-ethyl. J. Aquat. Plant Manage. 46: p. 154-158. [1]
- US Environmental Protection Agency (EPA). Office of Pesticide Program (OPP). 2011. Flumioxazin: Human Health Risk Scoping Document in Support of Registration Review. Memorandum by: D. Dotson et al., Health Effects Division. Available at: [regulations.gov](http://www.regulations.gov), docket ID: EPA-HQ-OPP-2011-0176 (<http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2011-0176-0003>). [1]
- EPA. 2001. Pesticide Fact Sheet for Flumioxazin. [1]
- EPA. Flumioxazin. Human Health Risk Assessment for a Proposed Aquatic Use. Docket No. EPA-HQ-OPP-2008-0781.
<https://yosemite.epa.gov/ee/epa/ria.nsf/EIO/215CDECEC982C54B852577D70071AA10>. [1]
- EPA. 2010a. Drinking Water Assessment for the Proposed Use of Flumioxazin as an Aquatic Herbicide. [1]
- EPA. 2010b. EFED Section 3 Registration for Flumioxazin to be Used for Control of Weeds in Bayous, Canals, and other Aquatic Areas. [5]
- Umphres, G. D., Roelke, D. L., Netherland, M. D. 2012. A chemical approach for the mitigation of *Prymnesium parvum* blooms. Toxicon. 60:7 pg. 1235-1244.
- Valent. 2010. New Chemistry for Aquatic Weed Management. Aquatic Herbicide White Paper. [9]
- Valent. 2011. Clipper™ Herbicide Specimen Label. [1]

Valent Canada. 2009. Flumioxazin Herbicide. Technical Brochure. [1]

Washington Department of Ecology (Ecology). 2012. Environmental Impact Statement for Penoxsulam, Imazamox, Bispyribac-sodium, Flumioxazin, and Carfentrazone-ethyl. Addendum to the FSEIS for Freshwater Aquatic Plant Management, Final. January. Publ. No. 00-10-040Addendum1. <https://fortress.wa.gov/ecy/publications/documents/0010040addendum1.pdf>. [3]

Washington Department of Transportation. (WDOT). 2006. Flumioxazin Roadside Vegetation Management Herbicide Fact Sheet. [1]

4.10.8 Fluridone

The SEIS Assessments of Aquatic Herbicides (Ecology, 2000) provided a detailed overview of the registration of fluridone, its chemical and environmental fate properties, potential environmental and human health impacts to water, plants, animals, and soils, and proposed mitigation measures for its application. Fluridone requires 30 to 90 days to kill or control target aquatic plants such as elodea, hydrilla, and Eurasian watermilfoil. A common aquatic formulation of fluridone is Sonar®, a systemic herbicide which is applied just before or after the target plants begin to grow. It is transported from submersed foliage to roots or immersed foliage. Its chemical mode of action is through interference with RNA and protein synthesis, as well as carotenoid pigments, which serves to inhibit photosynthesis. The label specifies that Sonar® should not be applied in situations where heavy rains may dilute treated water or where water is flowing rapidly.

Fluridone has been found to be non-teratogenic, mutagenic, or carcinogenic to humans (Ecology, 2000). Hamelink *et al.* (1986) reviewed ecological effects to non-target aquatic life, and concluded that fluridone is not expected to have adverse effects on a range of aquatic species tested or on similar non-target aquatic organisms. There are no label restrictions against drinking, swimming, or fishing in water treated with fluridone. The current label for Sonar®PR provides detailed guidance for treatment within a quarter mile of a functioning potable water intake. The sum of all applications cannot exceed 150 µg/L per annual growth cycle, with no single application exceeding 20 µg/L when within ¼ mile of an active potable water intake. The label gives further guidance on application rate calculations per treated acre for static and moving canals, rivers, or with a potable water intake. It further recommends a lower application rate for controlling EWM or curlyleaf pondweed where greater plant selectivity is desired. Major potential impacts, as reported by Ecology (2000), include some loss of target species, persistence in sediment, and water quality impacts associated with plant decomposition.

Archambault and Cope (2016) updated the toxicity data base for fluridone by examining the potential toxicity of two currently registered herbicides, endothall (dipotassium salt) and fluridone, on a rare freshwater snail (*S. virginicus*). Toxicological endpoints measured were adult survival and egg hatching success. Results showed that neither herbicide indicated effects to either survival or egg hatching success, at concentrations typically prescribed for control of a common target plant species (*Hydrilla* sp.)).

King *et al.* (2016) examined the effects of three aquatic herbicides (diquat dibromide), fluridone [Sonar®], and triclopyr on specific endpoints related to smoltification success in juvenile Pacific coho salmon (King *et al.* 2016) at label-specified rates in seawater for each of these compounds. Preliminary results suggested that, at the chemical concentrations in seawater exposures tested, effects were short-lived and these aquatic herbicides are unlikely to affect smoltification success. In a similar study, Curran *et al.* (2007) tested the aquatic herbicides DMA® (2,4-D), triclopyr, diquat, and Sonar® (fluridone) for effects to the olfactory ability of juvenile rainbow trout (*O. mykiss*) when exposed to the maximum application rates of these formulations for 96 hours, using static-renewal tests. Results showed that olfactory function of the juvenile rainbow trout were not affected by three of the compounds, with effects observed only following exposure to the maximum rates of Reward® (diquat).

Concerning toxicity to freshwater mussels, month-long toxicity tests showed that adult freshwater mussels exhibited no mortality after exposure to fluridone-containing herbicides. Juvenile mussels did, however, experience toxicity after exposure at concentration levels three times higher than the maximum application dosage to fluridone-containing herbicides (Archambault *et al.* 2015).

ENSR International (2005) conducted an ecological risk assessment for fluridone, including a variety of exposure scenarios such as ingestion, direct contact, off-site aerial drift, surface water runoff, and accidental spills. Results showed a potential for risk to some ecological receptors from exposure to fluridone under specific conditions. For direct spray, no risks are anticipated for terrestrial wildlife (i.e., insects, birds, or mammals). Risks to terrestrial plants could not be evaluated due to a lack of phytotoxicity information, although one ecological incident report suggested the potential for risk to some terrestrial plants. Some risk or toxicity to non-target aquatic plants are predicted when waterbodies are accidentally sprayed, and some risks to fish or aquatic invertebrates may occur when waterbodies are accidentally or intentionally sprayed (ENSR 2005). A scenario evaluating unintentional spill to ponds indicated a possible risk to fish, aquatic invertebrates, and non-target aquatic plants when fluridone is spilled directly into a pond. Regarding threatened and endangered species, the ecological risk assessment found that it is unlikely that these species would be harmed by label-specified use of fluridone.

Based on the findings of the ecological risk assessment, ENSR (2005) made several recommendations designed to reduce potential unintended environmental impacts from the application of fluridone:

- Select adjuvants carefully from those that are approved by WSDA for aquatic use and listed in Ecology's permit (none are currently ingredients in fluridone-containing Sonar® products) to prevent potential increased toxicity above that predicted for the active ingredient (a.i.);
- Review, understand, and conform to the "Environmental Hazards" section on the herbicide label. This section warns of known pesticide risks to wildlife receptors or to the environment and provides practical ways to avoid harm to organisms or the environment.
- Avoid accidental direct spray on streams or ponds to reduce the most significant potential impacts.
- Limit fluridone use in areas where threatened or endangered plant species occur near application areas. Avoid accidental direct spray and off-site drift to non-target plants to reduce potential impacts.
- Limit fluridone application in wind, and monitor effects on adjacent non-target vegetation.

A "special project" was conducted by Ecology featuring use of fluridone in 2002 to control EWM and Brazilian elodea (*E. densa*) in Washington State (reported at: <http://www.ecy.wa.gov/programs/eap/lakes/aquaticplants/index.html#specialprojects>). This treatment occurred in Loomis Lake, WA. Monitoring of the aquatic plant community was conducted by Ecology prior to treatment and for three years following treatment, with WDFW also monitoring the fish community during this same time period (Parsons, 2009). Monitoring consisted of aquatic plant frequency of occurrence and biomass before herbicide application (2002) and for 3 years after the treatment (2003 to 2005). The fish population was assessed one year prior to herbicide treatment (2001) and three years post treatment (2005). Prior to domination by invasive macrophytes, the lake had a diverse native plant community with low-growing species in the deep

water providing open water. During that time the lake supported a stocked rainbow trout (*O. mykiss*) and warmwater fishery. As invasive macrophytes took over, the native plant richness decreased, the trout stocking program ceased, and small yellow perch (*P. flavescens*) dominated the fish community. The herbicide treatment resulted in a significant reduction in frequency and biomass for both *Egeria* and EWM for three years. The native submersed plant community was also significantly reduced for the study duration. This was attributed to fluridone use at a non-selective rate and poor light penetration caused by wind induced sediment entrainment. After treatment, the growth of largemouth bass (*M. salmoides*) and pumpkinseed sunfish (*L. gibbosus*) both increased. In addition, the abundance of small yellow perch decreased while abundance of larger pumpkinseed sunfish increased, suggesting that fluridone did not contribute to adverse effects to these fish species.

4.10.8.1 References

- Archambault, J.M., C.M. Bergeron, W.G. Cope, R.J. Richardson, M.A. Heilman, J.E. Corey III, M.D. Netherland, and R.J. Heise. 2015. Sensitivity of freshwater molluscs to hydrilla-targeting herbicides: providing context for invasive aquatic weed control in diverse ecosystems. *Journal of Freshwater Ecology* 30:335–348. [1]
- Archambault, J, and W. Cope. 2016. Life Stage Sensitivity of a Freshwater Snail to Herbicides Used in Invasive Aquatic Weed Control. *Freshwater Mollusk Biology and Conservation* 19: p. 69-79. [1]
- Curran, C., J. Grassley, L. Conquest, and C. Grue. 2007. Olfactory performance in salmonids exposed to aquatic herbicides. Master's Thesis, University of Washington. [9]
- ENSR International (ENSR). 2005. Fluridone Ecological Risk Assessment, Final Report. Prep. For Bureau of Land Management, Reno, NV: p. 92. <http://digitalcommons.usu.edu/govdocs/147>. [1]
- Hamelink, J., et al. 1986. Toxicity of Fluridone to Aquatic Invertebrates and Fish. *Environ. Toxicol. Chem.* 5: p. 87-94. [1]
- K. King, C. Grue, J. Grassley, C. Curran, W. Dickhoff, and J. Winton. 2016. Effects of Three Aquatic Herbicides on Smoltification in Juvenile Pacific Coho Salmon. In press. [9]
- Parsons, J. 2009. Effect of Fluridone on Macrophytes and Fish in a Coastal Washington Lake. *Journal of Aquatic Plant Mgt.* 47: p. 31-40. [1]
- SePro. (Undated). Sonar® PR Aquatic Herbicide Specimen Label. 6 pp. https://sepro.com/documents/SonarPR_Label.pdf [1]
- US Environmental Protection Agency (EPA). 1986. Pesticide Fact Sheet: Fluridone. No. 81: p. 5. [1]
- Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. Publication No. 00-10-040. [3]

4.10.9 Glyphosate

The SEIS Assessment of Aquatic Herbicides (Ecology, 2000) provided a detailed overview of the registration, chemical and environmental fate properties, environmental and human health impacts, to water, plants, animals, and soils, as well as proposed mitigation measures for application of this material. Glyphosate is formulated as Rodeo® or Pondmaster® for use in aquatic sites, and as Roundup® for terrestrial use. The former two formulations, used for in-water treatments, do not include a surfactant. For Ecology's two permits for which this SEIS provides support, glyphosate is only used for shoreline, emergent and floating leaf plant treatments. Glyphosate was evaluated for use in the Aquatic Plant Management Program as part of Ecology's 1980 FEIS, *Aquatic Plant Management through Herbicide Use*. Target aquatic plants for which glyphosate shows herbicidal action include purple loosestrife, cattails, and floating-leaved plants such as water lilies and duck weed. Glyphosate rapidly loses its effectiveness soon after contact with water; this loss is further heightened by suspended particulates in the water column. Rainfall, wind, and other factors may contribute to rapid attenuation of glyphosate in the aquatic environment within six hours following treatment.

Since 2000, numerous investigations have been conducted for glyphosate. For example, Oliveira *et al.* (2016) investigated the effects of glyphosate on macroalgae. They used technical grade glyphosate and aminomethylphosphonic acid, the main degradation product of glyphosate to conduct this investigation. They examined effects on photosynthetic rate, dark respiration rate, and chlorophyll a content of a widely spread and common species of algae (*Nitella microcarpa*). They found that glyphosate has a stronger inhibitory effect on photosynthetic rate when applied in association with a specific surfactant, although that surfactant is not registered for aquatic use in Washington by WSDA. Toxicity of various glyphosate formulations is known to vary widely (Henry *et al.* 1994, Cox 2001). From an ecological perspective, results suggest that the spatial distribution within the ecosystem of algal species can be modified or affected by glyphosate-based herbicides in streams.

Toxicity was shown to periphyton in association with glyphosate treatments (Vera *et al.* 2010), but cyanobacteria, on the other hand, reportedly increased in number following exposure to treated mesocosms. Cyanobacteria (e.g. *Microcystis aeruginosa*) are known to be resistant to stressed and extreme environments, and may be able to resist the toxicity of glyphosate. In fact, Forlani *et al.* (2008) and Lipok *et al.* (2007) both reported on the apparent ability of cyanobacteria to degrade glyphosate and use it as a phosphorus nutrient source, although little information is available to quantify the extent to which phosphorus specifically derived from glyphosate occurs.

Concerning ecotoxicity to freshwater mussels in various stages of their life history, technical-grade glyphosate on its own is not acutely toxic to glochidia, even at levels approaching the water-solubility concentration limits for glyphosate. While it does not have a large impact on juvenile mussel viability under limited-duration chronic tests, it has been shown to reduce growth of juvenile mussels (Bringolf *et al.* 2007b). Technical-grade glyphosate IPA salt is acutely toxic to both glochidia and juvenile mussels, as is IPA salt (Bringolf *et al.* 2007b).

Glyphosate itself has a high binding affinity to clay and soil products which can help reduce ecological effects, and it also may become sequestered in plant tissue and later released when the plant tissue decomposes (Lasier *et al.* 2016).

Vera *et al.* (2010), Hutchinson (1995), Cox (1995) and Austin *et al.* (1991) all report the possibility of the acceleration of the eutrophication process and its negative consequences for natural aquatic environments in association with glyphosate treatments. They report that following treatment eutrophication may increase, as measured by increases in algal species and oxygen decrease, and biodiversity may decrease, with the probable development of resistant species that could grow and increase rapidly. In addition, glyphosate is toxic to a number of non-target plant species, including potentially endangered plants (Hutchinson, 1995) and label restrictions must be followed to minimize these unintended effects in association with glyphosate applications.

As noted above, Forlani *et al.* (2008) have reported that cyanobacteria () is capable of using glyphosate as a phosphorus nutrient source. These cyanobacteria are not only not harmed by glyphosate, but their development is actually increased by the herbicide, thus impacting the overall ecological balance of the aquatic ecosystem. In conclusion, based on scientific evidence it appears that glyphosate may affect non-target organisms, the structure of plant communities, and water quality, thus altering the structure and functionality of aquatic ecosystems.

Solomon and Thompson (2003) conducted an ecological risk assessment for aquatic organisms following over-water applications of glyphosate, including a toxicity assessment of some recommended surfactants. They found that the surfactants LI-700® (the only aquatic surfactant registered for use with glyphosate in Washington State), X-77®, and Induce® showed insignificant risk to aquatic life. They also found that risks from glyphosate showed evidence of slightly greater ecological risk than the other herbicides tested, although over-water risks were still considered small.

Glyphosate shows relatively low toxicity to birds and mammals (Evans and Batty, 1986), but other studies show developmental and reproductive impacts to animals at the highest doses tested (Nature Conservancy, 2001). Glyphosate also shows moderate toxicity to fish (Neskovic, *et al.* 1996). The aquatic herbicide Rodeo® shows relatively low toxicity to aquatic species in general, and since Rodeo® includes no surfactant, it is registered by WSDA for aquatic use and supported by Ecology's permits. Glyphosate has an indirect effect on bird populations due to widespread toxicity to plants and birds depend on the plants for food, shelter, and nest support (Cox, 1995).

A number of studies have been done on surfactants used with glyphosate, and the surfactant X-77 Spreader® (not registered by WSDA) for aquatic applications is reportedly 100-fold more toxic to aquatic invertebrates than Rodeo® alone (Henry *et al.* 1994). However, Simenstad *et al.* (1996) found no significant differences between benthic communities of algae and invertebrates on untreated mudflats and those treated with Rodeo® and X-77 Spreader®. In conclusion, it appears that under most conditions rapid dissipation from aquatic environments of several glyphosate formulations prevent build-up of herbicide concentrations that would be lethal to most aquatic species.

IARC/WHO (2016), the preeminent agency on the potential carcinogenicity of glyphosate, recently reviewed the overall animal and human data for preponderance of evidence concerning human carcinogenicity associated with exposure to glyphosate. They concluded there is "sufficient evidence" in

experimental animals for the carcinogenicity of glyphosate, and they report a positive association with non-Hodgkin's lymphoma. Therefore glyphosate is classified as "probably carcinogenic" to humans by the IARC. The European Food Safety Authority (EFSA 2015) stated in their peer review of glyphosate that, "glyphosate is unlikely to pose a carcinogenic hazard to humans and the evidence does not support classification with regard to its carcinogenic potential." Additionally, the summary report from the May 2016 Joint FAO/WHO Meeting on Pesticide Residues, "concluded that glyphosate is unlikely to pose a carcinogenic risk to humans from exposure through the diet." Though glyphosate may pose a carcinogenicity risk in experimental animals, the levels of anticipated glyphosate exposure experienced by humans, through current use patterns, are not expected to be carcinogenic.

The current APAM permit notification requirements for aquatic application of glyphosate include contacting residents on lands adjoining lakes or ponds within a half-mile of the treatment area of the pending treatment. The applicator is required to post the shoreline with signage notifying that the herbicide is intended to be used as well as appropriate label restrictions. As recommended by Simenstad *et al.* (1996), glyphosate should only be used to treat one-third to one-half the water body at any one time to prevent fish kills caused by oxygen depletion.

4.10.9.1 Using Glyphosate to control *Spartina* in estuarine habitats

Glyphosate has been used widely to control the estuarine cordgrass *Spartina* spp. Both glyphosate and imazapyr can be effective at *Spartina* control and both are essentially safe for terrestrial and aquatic animals if used in accordance with manufacturer's recommendations and with adequate dry-time. However, WSDA (2003) reported that the use of imazapyr improves the margin of safety relative to potentially toxic environmental concentrations by three to four orders of magnitude relative to the use of glyphosate. This improvement is due to the lower toxicity of imazapyr, lower active ingredient concentration needed for *Spartina* control, lower spray volumes required for effective treatment, and the ability to use crop-oil based surfactants, which are themselves one to two orders of magnitude less toxic than those surfactants required for glyphosate use.

4.10.9.2 References

- Austin, A., et al. 1991. Impact of an Organophosphate Herbicide (Glyphosate) on Periphyton Communities Developed in Experimental Streams. *Bull. Environ. Contam. Toxicol.* 47: p. 29-35. [1]
- Bringolf, R.B., W.G. Cope, S. Mosher, M.C. Barnhart, and D. Shea. 2007a. Acute and chronic toxicity of glyphosate compounds to glochidia and juveniles of *Lampsilis siliquoidea* (Unionidae). *Environmental Toxicology and Chemistry* 26(10): 2094-2100. [1]
- Connors, D.E. and M.C. Black. 2004. Evaluation of lethality and genotoxicity in the freshwater mussel *Utterbackia imbecillis* (Bivalvia: Unionidae) exposed singly and in combination to chemicals used in lawn care. *Archives of Environmental Contamination and Toxicology* 46: 362-371. [1]
- Cox, C. 1995. Glyphosate: human exposure and ecological effects. *J. Pesticide Reform* 15(4): p. 1-16. [1]

- European Food Safety Authority. 2015. Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate. EFSA Journal. 13(11):4302. [1]
- Evans, D. and M. Batty. 1986. Effects of high dietary concentrations of Glyphosate on a species of bird, marsupial and rodent indigenous to Australia. Environ. Toxicol. Chem. 5: p. 399-401. [1]
- Food and Agriculture Organization of the United Nations (FAO) Panel of Experts on Pesticide Residues in Food and the Environment and the World Health Organization (WHO). 2016. Summary Report from the May 2016 Joint FAO/WHO Meeting on Pesticide Residues (JMPR). <http://www.who.int/foodsafety/jmprsummary2016.pdf>. [11]
- Forlani, G., et al. 2008. Biochemical Bases for a Widespread Tolerance of Cyanobacteria to the Phosphonate Herbicide Glyphosate. Plant Cell Physiol. 49: p. 443-456. [1]
- Henry, C., K. Higgins and K. Buhl. 1994. Acute toxicity and hazard assessment of Rodeo®, X-77 Spreader®, and Chem-Trol® to aquatic invertebrates. Archive Environ. Contam. Toxicol. 27: p. 392-399. [1]
- Hutchinson, G. 1995. Nitrogen cycle interactions with global change processes. In Nierenberg, W. (ed), Encyclopedia of Environmental Biology. Vol 2, San Diego CA, Academic Press, p. 557-563. [1]
- International Agency for Research on Cancer/World Health Organization (IARC/WHO). 2016. IARC WHO Monographs: Glyphosate. 92 p. <http://monographs.iarc.fr/ENG/Monographs/vol112/mono112-10.pdf> [1]
- Lasier, P.J., M.L. Urich, S.M. Hassan, W.N. Jacobs, R.B. Bringolf, and K.M. Owens. 2016. Changing agricultural practices: potential consequences to aquatic organisms. Environmental Monitoring and Assessment 188: 672. [1]
- Lipok, J., et al. 2007. Phosphorus NMR as a Tool to Study Mineralization of Organophosphonates: The Ability of Spirulina Spp. to Degrade Glyphosate. Enzyme Micro. Technol. 41: p. 286-291. [1]
- Malécot, M. B. Guével, C. Pineau, B.F. Holbech, M. Bormans, and C. Wiegand. 2013. Specific proteomic response of Unio pictorum mussel to a mixture of glyphosate and microcystin-LR. Journal of Proteome Research 12: 5281-5292. [1]
- Oliveira, R., et al. 2016. Assessment of the Potential Toxicity of Glyphosate-based Herbicides on the Photosynthesis of Nitella Microcarpa. Phycologia 55(5): p. 577-584. <http://www.phycologia.org/doi/pdf/10.2216/16-12.1> [1]
- Nature Conservancy. 2001. Weed Control Methods Handbook. 10 p. <https://www.invasive.org/gist/products/handbook/methods-handbook.pdf> [1]
- Neskovic, N., et al. 1996. Biochemical and histopathological effects of Glyphosate on carp (*C. carpio*). Bulletin Environ. Contam. Toxicol. 56: p. 295-302. [1]

- Simenstad, S., et al. 1996. Use of Rodeo® and X-77 Spreader® to control smooth cordgrass (*S. alterniflora*) in a southwest Washington estuary. 2: Effects on benthic microflora and invertebrates. *Environ. Toxicol. Chem.* 15(6): p. 969-978. [1]
- Solomon, K., and D. Thompson. 2003. Ecological Risk Assessment for Aquatic Organisms for Over-water Uses of Glyphosate. *J. of Toxicol. Environ. Health, Part B.* 6(3): p. 289-324. [1]
- Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July 2000. Publication No. 00-10-040. [3]
- Washington State Department of Agriculture (WSDA). 2003. Ecological Risk Assessment of the Proposed Use of the Herbicide Imazapyr to Control Invasive Cordgrass (*Spartina Spp*) in Estuarine Habitat of Washington State. Prep. By Entrix Inc., October 2003, for WSDA: p. 160. [1]
- Vera, M., et al. 2010 New Evidence of Roundup® Impact on the Periphyton Community and the Water Quality of Freshwater Ecosystems. *Ecotoxicology* 19: 710-721. DOI 10.1007/s10646-009-0446-7. [1]

4.10.10 Imazamox

Imazamox is an imidazolinone herbicide that inhibits the acetolactate synthase (ALS) enzyme which is essential for the synthesis in plants of three branched chain amino acids isoleucine, leucine, and valine. The lack of ALS biochemical pathways in animals likely contributes to the low toxicity of imazamox in mammals and other animal taxa. Currently Ecology allows the use of another imidazolinone herbicide, imazapyr, for use in freshwater and marine environments, although unlike imazamox, imazapyr does not demonstrate any in-water herbicidal activity.

The aquatic formulation, Clearcast® is a selective, fast-acting, systemic herbicide that may be applied subsurface into a waterbody for the control of submersed vegetation, or sprayed directly onto target emergent plants. However, application to emergent plants requires the use of an adjuvant, only some of which are approved for aquatic use by Ecology in its water quality permits. Aquatic sites labeled for treatment include estuarine and marine sites, ponds, lakes, reservoirs, streams/rivers, wetlands, ditches, canals, and other slow-moving bodies of water.

The maximum label concentration is 500 µg/L for in-water applications, but in-water use rates are expected to be lower, typically between 50 and 200 µg/L depending on the target species. The label allows multiple applications during the annual growth season, but does not specify retreatment intervals or the maximum amount of active ingredient that can be applied each growing season. Because imazamox is fast-acting, there is no need to maintain concentrations in the water column for an extended period to achieve good control of submersed species. For drawdown applications, the label specifies that applications should be made when the water has receded and the exposed soil is moist to dry. Imazamox is rapidly absorbed into foliage and translocated throughout the plant via phloem and xylem tissues, concentrating in the actively growing portions of roots and shoots.

Imazamox inhibits plant growth within the first 24 hours after application, but visual symptoms appear about one week after treatment, with symptoms evident first on new growth. Susceptible plants develop a yellow or discolored appearance and eventually die or suffer severe growth inhibition. For emergent applications, the registrant (BASF 2016) claims that Clearcast® is does not get washed away by rainfall within one hour of application. Weed populations may contain or develop plants naturally resistant to ALS inhibitor herbicides (e.g., penoxsulam, imazamox, imazapyr). Applicators can take the following steps to delay or avoid herbicide resistance: use alternate herbicides for aquatic weed control; base herbicide use on a comprehensive integrated pest management (IPM) program; and monitor treated weed populations for loss of efficacy to ALS herbicides.

EPA first granted a conditional registration for imazamox in 1997 and an unconditional registration Section 3 label in 2001. In 2003, imazamox received an exemption for tolerance designation from EPA. This exemption waives all food residue tolerance requirements for potential food or feed uses of imazamox, including fish, shellfish, and irrigated crops. Imazamox is the first and only organic pesticide to receive such a tolerance exemption (Ecology, 2012). EPA considers imazamox to be a reduced risk pesticide for both terrestrial and aquatic uses. Clearcast®, the aquatic and non-crop liquid formulation of imazamox, received full registration from EPA in 2008. Ecology (2014) completed an EIS addressing imazamox treatments of non-native seagrass (*Z japonica*). WSDA has registered Clearcast® for aquatic use in Washington.

Extensive toxicity testing (as summarized by Durkin (2010), Schumacher (2014), and Ecology (2012)) show that imazamox is practically non-toxic to fish, birds, mammals, and invertebrates, including insects such as honey bees. Perhaps the most serious environmental impact from the aquatic use of imazamox could occur to rare floating or submersed plant species.

Prior to issuing permit coverage for discharges to water bodies where sensitive, threatened, or endangered plants could be present, Ecology will determine whether such plant species may be present in the proposed treatment area. For aquatic plant control projects where rare plants are potentially present, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

Regarding mitigation of potential environmental or non-target effects of imazamox, all current label requirements (see BASF Clearcast® specimen label www.cdms.net/LDat/ld7J8007.pdf) must be followed. Only state-licensed applicators should be used to apply imazamox. Imazamox must be applied in accordance with Ecology water quality permits, and all permit provisions should be followed. It should not be used in areas where there are rare submersed or floating plant species, unless Ecology agrees to a mitigation plan in advance.

As long as in-water treatments of imazamox are administered in accordance with label specifications, no impacts to swimming or other recreational aquatic activities are expected, and therefore swimming and other recreational activities should be able to continue unimpeded. Moreover, Ecology prohibits treatments with pesticides that have water use restrictions on the FIFRA label that would restrict public water use during the opening week of fishing season or during tribal fisheries, WDFW Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. Ecology further requires that permittees must minimize treatments that restrict public water use during weekends.

The potential for toxicity to various life stages of fish and aquatic life is minimal due to the low ecotoxicity of imazamox and derivatives, and therefore fish are not an issue for imazamox nor a reason provided in Ecology's permit to implement WDFW timing windows.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water treatments such as imazamox to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations. Fish consumption of imazamox-contaminated tissue is not expected to be problematic or require any mitigation (note the discussion on exemption from tolerance requirements above), because the material does not bioaccumulate into edible fish tissue. Because of possible sublethal effects to juvenile salmon due to critical habitat modifications, Ecology imposes timing restrictions on the use of some chemicals, and this could include imazamox.

There is no anticipated hazard from imazamox or its derivatives to listed animal species of concern such as fish or mammals, although it could present a potential hazard to non-target endangered plant species. EPA's Endangered Species and Spray Drift Task Forces will suggest and implement mitigation measures as needed to eliminate or mitigate risks to non-target plants associated with such treatments.

Concerning additional requirements for discharges to water bodies where sensitive, threatened, or endangered plants could be present, before issuing permit coverage, Ecology will determine whether such plant species are present in the proposed treatment area. If present, for aquatic plant control projects, the permittee must submit a detailed plant survey and implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

Imazamox would not be expected to cause or contribute to environmental problems in wetlands due to its low toxicity to animal species and the fact that it does not readily bioaccumulate within tissues or bioconcentrate within sediments. As stipulated by Ecology for the aquatic plant and algae management (APAM) permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation.

Post-treatment monitoring for water quality may be important in association with imazamox treatment to ensure that water quality is protected and lake or pond restoration promoted. . Ecology doesn't generally require efficacy monitoring as part of these two permits, and the use of imazamox no longer requires residue monitoring in the Aquatic Noxious Weed Control permit as it has consistently been measured at either a non-detect or very close to non-detect levels.

The potential for groundwater contamination should be monitored when using imazamox in turbid or deep lakes where the chemical may not degrade quickly and could infiltrate into groundwater (Ecology 2014). EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, to evaluate non-target effects from an ALS-inhibiting herbicide such as imazamox. For Ecology, this post-treatment monitoring would be required under NPDES discharge permits, and would be a permit condition requiring monitoring to determine potential non-target impacts. These requirements may be incorporated into both label and permit requirements, as appropriate, in conjunction with pesticide registration and permit requirements prior to application.

4.10.10.1 References

- AECOM. 2009. Use of Aquatic Herbicide imazamox Clearcast® in the State of New York. Supplemental Environmental Statement. Final. Document No.: 00760-245-310. [1]
- BASF. 2016. Clearcast® Specimen label <http://www.cdms.net/LDat/ld7J8007.pdf>. [1]
- Burns, B. 2009. Clearcast® Herbicide Technical Information. PowerPoint presentation <http://www.seepc.org/2009/pres/ClearcastHerbicides.pdf>. [9]
- Durkin, Patrick R. 2010. Imazamox Human Health and Ecological Risk Assessment. Syracuse Environmental Research Associates, Inc. Submitted to USDA/Forest Service, Southern Region. [1]

- European Commission (EC). Health and Consumer Protection Directorate-General. (HCPDG). 2002. Review Report for the Active Substance Imazamox.
<http://ec.europa.eu/food/plant/protection/evaluation/newactive/imazamox.pdf>. [1]
- Madsen, J. D., R. M. Wersal, and C. McLaurin. 2011. Sensitivity of Native Aquatic Plant Species to Imazamox (Clearcast™) and Penoxsulam (Galleon™). Abstract from the 30th Annual Western Aquatic Plant Management Society Annual Conference. Westminster, Colorado. [4]
- Netherland, Michael D., C.A. Lembi, and L.M. Glomski. 2009. Potential for Selective Activity of the ALS inhibitors Penoxsulam, Bispyribac-sodium, and Imazamox on Algae Responsible for Harmful Blooms. *J. Aquat. Plant Manage.* 47: p. 147-150. [1]
- New York State Department of Environmental Conservation (NYSDEC), BASF Corporation. 2009. Approving the Registration of Clearcast® Herbicide (EPA Reg. No. 241-437). Letter [10]
- Nissen, S. J., J. D. Vassios, and G. Brunk. 2007. Eurasian Watermilfoil and Sago Pondweed Response to Imazamox. Abstract from the 26th Annual Western Aquatic Plant Management Society Annual Conference. Coeur d'Alene, Idaho. [4]
- Schumacher, D., and D. McGregor. 2014. Imazamox. World Health Organization. JMPR 209-239, 2014. [1]
- Schuler, S., M. Heilman, S. Hyde, and D. Blodget. 2011. Emerging Use Patterns for Clearcast® Aquatic Herbicide in the Western US. Abstract from the 30th Annual Western Aquatic Plant Management Society Annual Conference. Westminster, CO. [4]
- Syracuse Environmental Research Associates, Inc. 2010. Imazamox Human Health and Ecological Risk Assessment, Final Report. Prepared for USDA Forest Service.
www.fs.fed.us/foresthealth/pesticide/pdfs/052-24-02a_Imazamox.pdf. [1]
- Thurston County Health Department. 2011. Review of Imazamox. [1]
- US Environmental Protection Agency (EPA). 1997. Pesticide Fact Sheet for Imazamox (Raptor Herbicide).
www.epa.gov/opprd001/factsheets/imazamox.pdf. [1]
- EPA. 2008. Environmental Fate and Ecological Risk Assessment – Registration of New Use Imazamox for the Proposed New Use for the Control of Vegetation in and around Aquatic and Noncropland Sites. USEPA PC Code: 129171. [5]
- Vassops, Joseph D. 2010. Evaluation of Herbicides for Control of Eurasian Watermilfoil and Sago Pondweed. Master's Thesis. Colorado State University. [9]
- Vollmer, J. 2007. Clearcast® (Imazamox) Western Aquatic EUP Update. Abstract from the 26th Annual Western Aquatic Plant Management Society Annual Conference. Coeur d'Alene, Idaho. [4]

Washington Department of Ecology (Ecology). 2014. Management of *Zostera Japonica* on Commercial Clam Beds in Willapa Bay, WA. FEIS March. Publ. No. 14-10-050: p. 153.

<https://fortress.wa.gov/ecy/publications/SummaryPages/1410050.html>. [3]

Washington Department of Ecology (Ecology). 2012. Environmental Impact Statement for Penoxsulam, Imazamox, Bispyribac-sodium, Flumioxazin, and Carfentrazone-ethyl. Addendum to the FSEIS for Freshwater Aquatic Plant Management. Final, January. Publ. No. 00-10-040Addendum1.

<https://fortress.wa.gov/ecy/publications/documents/0010040addendum1.pdf>. [3]

Wersal, Ryan M, and J. D. Madsen. Comparison of Imazapyr and Imazamox for Control of Parrotfeather (*Myriophyllum aquaticum* (Vell.) Verdc.). J. Aquat. Plant Manage. 45: p. 132-136. [1]

4.10.11 Imazapyr

Imazapyr is a highly mobile broad-spectrum aquatic herbicide, and is generally persistent in soils, although photolysis in soils may be extremely rapid. Although risks to animals from imazapyr use appear to be insignificant, its use can cause significant impacts to non-target vegetation if inappropriately applied. Imazapyr is used to control a variety of grassy species, broadleaf weeds, vines, and brushy species, including for transportation right-of-way maintenance.

The Washington State Department of Agriculture has proposed the use of imazapyr formulations for weed control along freshwater riparian corridors in the State. To support this application they conducted a human health and ecological risk assessment (WSDA 2009) to assess the environmental consequences of using imazapyr to control weedy vegetation along riparian corridors. The mechanism for phytotoxicity, interruption of plant protein synthesis used by this herbicide, is generally not relevant or harmful to animal species such as birds, mammals, fish, or invertebrates.

Results of the WSDA (2009) human health risk assessment showed that under prescribed conditions, neither workers nor the general public would be exposed to concentrations of imazapyr that exceed levels of concern at the typical application rate of 0.26 lb acid equivalents (ae)/acre. Regarding ecological risk, WSDA (2009) evaluated exposure scenarios conducted for terrestrial animals, terrestrial plants, and aquatic animals (fish and invertebrates). These included exposure scenarios for terrestrial plants at a typical application rate of 0.26 lb ae/acre. Exposure scenarios for terrestrial animals included direct application and ingestion of contaminated water and prey species, and exposure scenarios for terrestrial plants included both surface water runoff and spray drift. Aquatic animal and plant species were evaluated via modeled spill and surface water runoff exposure scenarios. Results indicated that both terrestrial and aquatic species are not likely to be adversely affected by imazapyr under prescribed conditions. This is supported by the preponderance of toxicological data that no adverse effects are likely in mammals, birds, fish, and terrestrial or aquatic invertebrates.

Off-site movement of imazapyr could affect non-target sensitive plant species via drift or surface water runoff, depending on site-specific conditions. Exposure scenarios developed by WSDA (2009) showed that runoff appears to pose a greater potential ecological hazard than aerial drift. Residual soil contamination with imazapyr could persist under some scenarios, up to months or years, which could be harmful for some sensitive plant species. Given that the ecological risk assessment as reported by WSDA (2009) address the potential risk to ecological receptors potentially exposed to imazapyr throughout Washington State, characterizing risk to plants exposed to residual soil concentrations of imazapyr is very general, as the actual degree of risk is site-specific and depending on numerous risk factors such as precipitation, temperature, pH, soil types, and other factors.

WSDA (2009) also concluded that aquatic macrophytes are more sensitive to imazapyr than unicellular algae; modeled peak exposure concentrations of imazapyr in surface water could adversely affect some aquatic macrophytes. In addition, imazapyr could have indirect effects on sensitive or ESA-list animal and plant species, particularly through habitat alteration. Although the ecological risk assessment concluded that there is low risk to terrestrial and aquatic animal species due to direct toxicity, the herbicide could potentially cause habitat alterations that could ultimately affect sensitive species. For example native vegetation in riparian areas fulfills important ecological functions, such as providing both

terrestrial and aquatic habitat, stabilizing stream banks, providing shade to streams, regulating water temperature, and providing large wood debris to increase the complexity of in-stream habitat.

Yahnke *et al.* (2013) recently examined the effects of label-specified rates for imazapyr on juvenile Oregon spotted frogs (*R. pretiosa*), a state-endangered species in Washington. Endpoints evaluated include feeding behavior, growth, and body and liver condition indices. They reported no mortalities or significant differences for any endpoint between the herbicide-exposed and control frogs. These results suggest that imazapyr use in wetland restoration poses a low risk of direct toxic effects on juvenile Oregon spotted frogs. Technical-grade imazapyr as tested on mice, flies, and pulmonate freshwater snails was not found to be significantly toxic (Grisolia *et al.* 2004).

4.10.11.1 Estuarine applications of imazapyr

In addition to the freshwater applications of imazapyr discussed above, imazapyr is and has been used to control cordgrass (*Spartina* spp.) with some success in Washington State. *Spartina* is an estuarine, highly invasive weed spreading throughout many of Washington's estuarine and intertidal tide flats, and is listed as a class A noxious weed. Within the estuarine environments of Washington's only one herbicide, glyphosate (as Rodeo™), was originally authorized by WSDA for *Spartina* control. Glyphosate is relatively non-toxic to animals and is effective on a wide range of plant species, but its use to control cordgrass was hindered by drying times that limit its efficacy under the tidal conditions inherent to estuaries. Glyphosate requires higher application rates than imazapyr (i.e. as Arsenal™). The ecological risk assessment (WSDA, 2009) characterized the toxicity and risk of imazapyr to both target plants and non-target plants and animals, estimated potential exposures to ecological receptors relevant to the aquatic (estuarine) environments where the herbicide may be applied, and characterized risks from that exposure to individual species and ecosystems where *Spartina* is distributed. They concluded that these risks were relatively low and acceptable. Under EPA's pesticide registration guidelines for imazapyr use in estuaries, applications would be made directly to target plants during low tide, and it is this scenario for which ecological risks were evaluated and found to be acceptable (WSDA 2009).

Non-native *Spartina* has been a significant problem in Washington's estuarine and intertidal waters, most notably in Willapa Bay, impacting critical habitat for shorebirds, juvenile salmonids and other fish, and shellfish. However, WSDA's integrated pest management (IPM) program in addition to including chemical (e.g. glyphosate and imazapyr), mechanical, and biological control methods, has experienced ongoing success in this continuing effort. In fact, as of 2015, the total number of previously infested sites in Washington state from which *Spartina* has been eradicated is up to 43, mostly in the areas of the straits of Juan de Fuca and the Puget Sound (WSDA 2015). *Spartina* is now largely under control in Washington state, the extent of its infestation is small compared to past years, and it is no longer spreading at up to 20% per year as it once did. The use of imazapyr for control of *Spartina* has been generally successful in Washington State.

Representative imazapyr exposure scenarios in estuary settings were defined, and results showed that chemical control of *Spartina* using imazapyr did not produce aquatic concentrations or terrestrial doses that would pose significant risks to aquatic or terrestrial wildlife, even under the improbable "upper limit" conditions modeled. Only for spill scenarios where it was assumed that avian and mammalian wildlife could ingest undiluted spray solution was there the potential for significant risk identified, but wildlife behavioral mechanisms make this risk scenario highly unlikely.

As noted in Section 4.10.9 on glyphosate, both imazapyr and glyphosate can be effective for controlling *Spartina* and both are essentially safe for terrestrial and aquatic animals if used in accordance with manufacturers' recommendations with adequate dry-time. WSDA primarily uses imazapyr for *Spartina* control, although a glyphosate-imazapyr tank mix is sometimes used for this purpose.

However, the use of imazapyr improves the margin of safety relative to potentially toxic environmental concentrations by three to four orders of magnitude relative to existing applications using glyphosate (WSDA, 2003, 2009). This improvement is due to the lower toxicity of imazapyr, lower active ingredient concentration needed for *Spartina* control, lower spray volumes of the herbicide/surfactant solution required for effective treatment, and the ability to use crop-oil based surfactants which are themselves one to two orders of magnitude less toxic than the surfactants required for glyphosate use. Although risks to animals from imazapyr are largely insignificant, its use can cause significant impacts to non-target vegetation if inappropriately applied.

Toxicity is particularly acute for vascular plants such as *Spartina* (the target species), although risks to non-target algal species appear to be significantly less. In sediment, imazapyr is significantly less persistent than in soils, but it can still be expected to be detectable for several weeks after treatment. It should therefore be applied only to target species, avoiding drift or seepage to non-target species and sediment, and avoiding heavy rains or high winds (a 10 mph wind limit has been defined in RCW 90.48.445).

Imazapyr should be used primarily in areas where total vegetation control or eradication is desired, or in isolated spot applications due to reports of its potential to "leak" out of target plant roots into soil that contains non-target plants. Hand spray applications should be used on the periphery of *Spartina* "meadows" to minimize spraying of non-target plants and poor canopy interception. Broadcast system spraying can be conducted in or near the center of *Spartina* meadows with minimal risk of drift and maximum efficacy for control. In the tidally influenced habitats where *Spartina* is found, dilution and dissipation is rapid due to the frequency of tidal exchange. For example, in Willapa Bay, one of the primary areas where *Spartina* occurs, potentially toxic concentrations to aquatic life are unlikely to occur under the range of application rates and exposure scenarios considered in the risk assessment (WSDA, 2009). The overall weight of evidence from this analysis suggests that imazapyr can be a safe, highly effective treatment for *Spartina* control and possible eradication in estuarine settings, and offers a significantly improved risk scenario relative to alternative chemical treatment regimes.

4.10.11.2 Potential toxicity of imazapyr surfactants

Grisolia *et al.* (2004) conducted a comparative study of a formulated herbicide (Arsenal 250 NA™), its technical-grade active ingredient imazapyr, and the surfactant nonylphenol ethoxylate (NP). These compounds were evaluated using genotoxicity and ecotoxicity studies in different organisms, including species of freshwater snail, fruit fly, mice, and onion. A comparative study of these three compounds was tested on these organisms to assess whether the addition of the surfactant would pose the higher toxicological risk to the overall herbicide formulation. They reported that Arsenal, imazapyr, and NP showed no evidence of genotoxicity in either the onion or the mice. However, toxicological evaluations showed that NP was the most toxic of the three compounds to the mice, onion, fruit fly, and snail. This study appeared to demonstrate that adverse effects were produced by the surfactant additive used to

produce the end-use pesticide formulation. NP is not allowed by WSDA as a surfactant in the state of Washington, but this investigation illustrates the potential for such surfactants to contribute toxicity to the overall formulated product for an herbicide such as imazapyr.

4.10.11.3 References

- Grisolia, C., et al. 2004. A Comparative Toxicologic and Genotoxic Study of the Herbicide Arsenal, its Active Ingredient Imazapyr, and the Surfactant Nonylphenol Ethoxylate. *Ecotoxicol and Env. Safety* 59(1): p. 123-126. [1]
- Washington State Department of Agriculture (WSDA). 2009. Human Health and Ecological Effects Risk Assessment, Imazapyr. Prep. By AMEC Geomatrix for WSDA: p. 308.
http://www.ecy.wa.gov/programs/wq/pesticides/enviroReview/riskAssess/HHRA&ERA_063009.pdf. [1]
- WSDA. 2015. *Spartina* eradication program report. AGR PUB 809-505 (N/2/16). 40 p.
<http://agr.wa.gov/FP/Pubs/docs/pp/505-SpartinaReportFinal2015.pdf>. [4]
- WSDA. 2003. Ecological Risk Assessment Of The Proposed Use of the Herbicide Imazapyr to Control Invasive Cordgrass (*Spartina Spp*) in Estuarine Habitat of Washington State. Prep. By Entrix Inc., October 2003, for WSDA: p. 160. [1]
- Yahnke, A, C. Grue, M. Hayes, and A. Troiano. 2013. Effects of the herbicide Imazapyr on juvenile Oregon spotted frogs. *Environ. Toxicol. Chem.* 32: p. 228–235. [1]

4.10.12 Penoxsulam

Penoxsulam is a broad spectrum, systemic herbicide active ingredient used for both terrestrial and aquatic plant (e.g. hydrilla) control. Like imazamox and bispyribac-sodium, penoxsulam is an acetolactate synthase (ALS) inhibitor, a plant enzyme that regulates the production of essential amino acids in plants (valine, leucine, and isoleucine). ALS inhibitors slowly starve plants of these amino acids and kill the plant by halting DNA synthesis. This biochemical pathway does not exist in animals, which would explain why ALS-inhibitor herbicides tend not to be toxic to animals.

Penoxsulam is absorbed via leaves, shoots, and roots, and translocated to meristematic tissues, causing cell division to stop, which in turn slows or stops subsequent growth in plants. Penoxsulam affects new plant growth more rapidly than older tissue, and is considered a slow acting herbicide because it can require 60 to 120 days for complete control of target plants, with its effectiveness highly dependent on both contact times and growing conditions. Cool weather or other conditions that affect plant growth can delay the herbicide response if the plants have reduced growth rates. Herbicide symptoms include immediate growth inhibition, chlorosis and tissue reddening, necrosis of the terminal bud after two or more weeks of exposure, and slow plant death over a period of 60-120 days. Penoxsulam is generally very effective for the control of broadleaf plants (dicots and broadleaf monocots) and sedges, and exhibits some selectivity.

Pest managers can use penoxsulam as both a pre-and a post-emergent herbicide. Typically, applicators may use penoxsulam to manage freshwater aquatic vegetation in ponds, lakes, reservoirs, wetlands, drainage ditches, non-irrigation canals, and other quiescent bodies of water. Penoxsulam can also be effective along shorelines and in riparian areas for the control of floating, submersed, and emergent aquatic plants. Application methods may include spraying aquatic formulations directly onto emergent plants, applying directly into water, or applying to dewatered plants/sediment. Applicators must use a surfactant for effective emergent and floating-leaved plant treatments (Ecology lists adjuvants approved for aquatic use in its water quality permits). The rate for foliar applications are subject to change, but at the time of this writing is listed as 2-5.6 fluid ounces per acre. For in-water treatments, applicators may need to apply split or multiple applications to maintain herbicide concentrations in the water at sufficient levels for optimum control. Typical application rates of penoxsulam are 10-20 µg/L water column concentrations in an initial treatment with additional “bump” applications of 5-10 µg/L to maintain water concentrations for 45 to 90 days. This treatment scenario is similar to the way that applicators currently apply fluridone products for Brazilian elodea (*E. densa*) or Eurasian watermilfoil (*M. spicatum*) management.

Penoxsulam is an EPA reduced risk pesticide. It was originally conditionally registered by EPA in 2004 for use in rice fields to control broadleaf weeds. EPA has since registered penoxsulam to manage aquatic plants (in-water treatments, foliar applications, and dewatered sediment treatments) and broadleaf weeds in turf (especially golf courses). An aquatic formulation sold as Galleon SC™ by SePRO Corporation received Section 3 federal registration for aquatic use in 2007. WSDA has registered penoxsulam for aquatic use in Washington. According to the EPA label, the in-water concentration of any single application or sum of all applications must not exceed 150 µg/L per annual growth cycle. There are no drinking water restrictions for humans, livestock, pets, or other animals and no swimming or fishing/fish consumption restrictions for penoxsulam.

Concerning the 13 known degradation products identified for penoxsulam, six are considered as being of some toxicological concern due to greater persistence than the parent compound, although none of these metabolites are believed to have higher potential toxicity than the parent compound penoxsulam. During a previous assessment for the use of penoxsulam on rice, EPA concluded that some of degradation products could cause phytotoxicity. To reduce this uncertainty, EPA required additional testing on vegetative vigor and seedling emergence for major degradates. This testing found that none of the metabolites caused any observable injury to pre-emergent seeds, while two of the eleven caused noticeable injury to seedlings, and these only at the highest application levels. Based on these results, EPA elected to require no further testing of these degradates for phytotoxicity.

EPA's Fact Sheet (2004) reported that there were no acute risks of concern from the use of penoxsulam, and EPA (2007a) reported that any risk due to exposure to residues in food or water were below EPA's level of concern for all population subgroups, including infants and children. Regarding carcinogenicity, EPA classified penoxsulam as suggestive evidence of carcinogenicity, but insufficient to assess human carcinogenic potential. This raises a concern, but is judged by EPA as not sufficient for a conclusion regarding its human carcinogenic potential.

Regarding ecotoxicity or ecological risk, EPA (2007a) conducted an ecological risk assessment and found that penoxsulam exhibited low toxicity to both warm and cold water fish species, including low bioaccumulation potential. Findings were similar for both aquatic invertebrates and terrestrial invertebrates such as honey bees. Regarding threatened or endangered animal species, EPA does not anticipate any direct impacts to these species, although there could be an indirect impact associated with removal of plants as food, cover, and habitat.

Given the potentially lengthy time period scenarios involved with penoxsulam treatments, people may be exposed to low concentrations of penoxsulam through recreational activities. However, due to its low acute and chronic toxicity as well as low application rates, Ecology (2012) reports that penoxsulam is unlikely to pose any risk to human health when used at label rates. Similarly, penoxsulam has no aquatic use restrictions and its application should not interfere with boating or navigation. Regarding swimming, Ecology does not believe it is necessary to impose a 24-hour swimming advisory after treatment with penoxsulam. Physical removal of treated aquatic vegetation, however, could improve swimmer safety and is recommended.

Penoxsulam has no fishing or fish consumption restrictions due to low toxicity and low bioaccumulation, and its use should have no adverse effects on fishing. However, physical removal of aquatic plants, particularly during any whole-lake treatments, may be advisable to benefit fishers and the fishing experience. Prey species (sunfish) lose refugia (hiding places) and are vulnerable to predator species such as bass. A loss of prey fish species (e.g. sunfish) may result in the loss of shelter or refugia due to vegetation removal associated with whole lake herbicide treatments for aquatic weed eradication.

Ecology's water quality permits limit the amount of littoral zone that applicators may treat for nuisance native plant removal. Those limits are expected to help with leaving untreated native plants as refugia for fish and wildlife. Regarding agriculture, irrigation using water treated with penoxsulam may result in injury to sensitive irrigated vegetation. The label prohibits irrigating greenhouse or nursery plants and

hydroponic farming. The label (SePro, 2012) prohibits the use of penoxsulam treated water to irrigate food crops other than rice until the water concentration is 1 µg/L or less.

Regarding mitigation against potential adverse environmental or human health effects, it is recommended to follow current label requirements, to use state-licensed applicators, and where required, to apply penoxsulam under Ecology water quality permits, following all permit provisions. The special conditions in the permit provide mitigations for herbicide use in general and Ecology sets out any specific provisions for each chemical in its permits. Ecology may require groundwater monitoring in areas of cracked basalt or with permeable soils in water bodies being treated with penoxsulam. It is not recommended to use penoxsulam in areas where rare submersed or floating plant species have been identified, unless Ecology agrees to the mitigation plan.

Ecology mitigates indirect effects of food and habitat loss through its permitting process by requiring work windows or consultation with the WDFW when herbicides are used in water bodies with priority or listed species and habitats. Ecology's permit manager also consults the Department of Natural Resources (DNR) Natural Heritage Program database for rare plants before issuing permit coverage for in-water treatments. If applicable, Ecology coordinates mitigation efforts with the permit applicant, WDFW, the Natural Heritage Program and others, to ensure adequate protections to threatened and endangered species and state priority species and habitats from herbicide use such as penoxsulam.

4.10.12.1 References

- California Environmental Protection Agency (CalEPA). Department of Pesticide Regulation (DPR). 2005. Summary of Toxicology Data: Penoxsulam. Document Processing Number 52967, revised March 17. [9]
- Cheshier, J., R. Wersal, and J. Madsen. 2011. The Susceptibility of Duckweed (*Lemna minor*) to Fluridone and Penoxsulam. *J. Aquat. Plant Manage.* 49: p. 50-52. [1]
- Dow AgroSciences (Dow). 2008. Penoxsulam – Broad Spectrum Herbicide for Turf – Global Technical Bulletin.
http://www.dowagro.com/PublishedLiterature/dh_0115/0901b8038011596a.pdf?filepath=science/pdfs/. [9]
- European Food Safety Authority (EFSA). 2009. Peer Review of the Pesticide Risk Assessment of the Active Substance Penoxsulam. Scientific Report 343, 1-90.
<http://www.efsa.europa.eu/en/efsajournal/doc/343r.pdf>. [1]
- SePro Corp (SePro). 2012. Galleon SC™ Material Safety Data Sheet.
http://www.sepro.com/documents/Galleon_MSDS.pdf. [1]
- Glomski, L. & M. Netherland. 2009. Efficacy of Fluridone, Penoxsulam, and Bispyribac-Sodium on Variable-Leaf Milfoil. *J. Aquat. Plant Manage.* 46: p. 193-196. [1]

- King County. 2004. Pipe and Lucerne Lakes Integrated Aquatic Vegetation Management Plan. King County Dept. of Natural Resources and Parks, Water & Land Resources Div., Lake Stewardship Program, 2004. [9]
- Koschnick, Tyler J., M. Netherland and W. Haller. 2007. Effects of Three ALS-inhibitors on Five Emergent Native Plant Species in Florida. *J. Aquat. Plant Manage.* 45: p. 47-51. [1]
- Madsen, J. & R. Wersal. 2008. Herbicide Formulations for Managing Free-floating Aquatic Plants. *Proceedings, Southern Weed Science Society*. Volume 61: p. 201. [1]
- Madsen, J., R. Wersal, and C. McLaurin. 2011. Sensitivity of Native Aquatic Plant Species to Imazamox (Clearcast®) and Penoxsulam (Galleon™). Abstract from the 30th Annual Western Aquatic Plant Management Society Annual Conference. Westminster, CO. [4]
- Murussi, C., et al. 2014. Toxic Effects of Penoxsulam Herbicide in Two Fish Species Reared in Brazil. *Bull. Environ. Contam. Toxicol.* 92(10): p. 81-84. [1]
- Netherland, M, C. Lembi, and L. Glomski. 2009. Potential for Selective Activity of the ALS Inhibitors Penoxsulam, Bispyribac-sodium, and Imazamox on Algae Responsible for Harmful Blooms. *J. Aquat. Plant Manage.* 47: p. 147-150. [1]
- Netherland, M., C. Lembi, and A. Poovey. 2009. Screening of Various Herbicide Modes of Action for Selective Control of Algae Responsible for Harmful Blooms. ERDC/TN ANSRP-09-2. [9]
- Pesticide Action Network (PAN). Penoxsulam: Identification, Toxicity Use, Water Pollution Potential, Ecological Toxicity and Regulatory Information.
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC39672. [1]
- Toxnet. 2012. Penoxsulam. Hazardous Substances Data Base, National Library of Medicine.
<https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7887>. [1]
- US Environmental Protection Agency (EPA). 2007a. EFED Ecological Risk Assessment for the Proposed New Uses of the Chemical Penoxsulam on Turf and Aquatic Weeds. [1]
- EPA. 2007b, Penoxsulam. Human Health Risk Assessment for Proposed Uses on Fish and Shellfish. PC Code: 119031, Petition No. 5F7012, DP Num: 325461 [1]
- EPA. 2007c. ECOTOX User Guide. ECOTOXicology Database System. Version 4.0. Available:
<http://www.epa.gov/ecotox/>. [1]
- EPA. 2004. Pesticide Fact Sheet for Penoxsulam
<https://www.epa.gov/opprd001/factsheets/penoxsulam.pdf>. [1]
- Washington Department of Ecology (Ecology). 2012. Environmental Impact Statement for Penoxsulam, Imazamox, Bispyribac-sodium, Flumioxazin, and Carfentrazone-ethyl. Addendum to the FSEIS for

Freshwater Aquatic Plant Management, Final. January. Publ. No. 00-10-040Addendum1.
<https://fortress.wa.gov/ecy/publications/documents/0010040addendum1.pdf>. [3]

4.10.13 Triclopyr TEA

Triclopyr triethylamine (TEA) salt is a systemic herbicide used for controlling a wide variety of terrestrial and aquatic plant species by using a plant hormone mimic, which causes toxicity and mortality in target plants. Triclopyr is formulated as a solution in water, to which “inert” ingredients such as TEA are added. It was first registered by Dow AgroSciences in 1979 as an herbicide on non-crop areas and in forestry use for the control of broadleaf weeds and woody plants, and was registered for use on turf sites in 1984. In 1995, triclopyr TEA was registered for use on rice to control many resilient broadleaf weed species. The formulation Garlon® 3A from Dow AgroScience is currently registered by the WSDA (2014) for the control of aquatic weeds in public waterways and annual and perennial broadleaf weeds and woody brush in wetlands. Triclopyr is effective against target aquatic plants such as Eurasian watermilfoil (*M. spicatum*), purple loosestrife (*L. salicaria*), water hyacinth (*E. crassipes*) and alligator weed (*A. philoxeroides*). However, pondweed species, rushes, cattails, duckweed, and various algae species are not typically controlled even at the maximum labeled concentration of 2.5 ppm acid equivalents (a.e.).

Triclopyr TEA is also effective in controlling wetland associated plants including many woody plants and annual or perennial broadleaf weeds. Wetland application sites could include flood plains, deltas, marshes, and transitional areas between upland and lowland sites. These wetland application sites may occur in forests, non-crop sites, wildlife habitat restoration and management areas and areas adjacent to or surrounding domestic water supply reservoirs, lakes and ponds. SePRO Corporation received Federal EPA registration in 1992 for triclopyr TEA salt under the trade name Renovate®. The label specifies selective control of many of the same nuisance and invasive aquatic plants listed above. DowElanco currently manufactures and distributes Garlon® 3A and SePRO Corporation markets and distribute Renovate® under a separate label. WSDOT (2006) also uses several formulations of triclopyr in Washington State along rights-of-way for control of brush and small trees.

Triclopyr has been well studied and documented. Animal and plant toxicology, environmental chemistry and fate characteristics, and other key information concerning triclopyr has been reviewed and summarized by a number of investigators (Durkin 2011, ENSR, 2007, CSI 2001, EPA OPP 1998, etc.). An overview of the toxicology information indicates that triclopyr shows only a low degree of systemic toxicity based on findings from a variety of acute, subchronic, and chronic toxicology studies. The main adverse health effect appears to be associated with eye contact with concentrated Renovate® which can result in severe eye irritation and damage. Studies of eye irritation to applicators caused by undiluted triclopyr place the chemical in the FIFRA toxicity category that signifies the potential for irreversible eye damage from topical exposure, although this exposure can be mitigated by using PPE as required on the label. Triclopyr is not considered to be a carcinogen, mutagen or to cause adverse reproductive effects or birth defects. A review of the scientific and medical literature indicates that there have been no investigations conducted to determine the potential of either triclopyr or its degradation products to interact or to synergize with other chemicals.

CSI (2001) performed a comprehensive literature review as well as a human health and ecological risk assessment of triclopyr and concluded that label-specified use of triclopyr for aquatic weed control purposes would not be expected to result in any systemic adverse human health effects. An evaluation of swimmers exposed to 2500 and 500 µg/L triclopyr did not indicate that any adverse systemic health

effects would occur based on the parameters used. Aside from 6-year old children drinking treated surface water as part of their daily diet, the only other risk assessment that was exceeded involved the same age group swimming for 2 and 3 hours in water containing 2500 µg/L triclopyr and drinking potable water containing 500 µg/L. Even though the risk assessment was exceeded for multiple exposure pathways, the potential daily triclopyr dose calculates to approximately 73-87 times less than the margin of safety based on the established animal chronic toxicology NOAEL of 3,000 µg/kg/day. Risk assessment levels were significantly exceeded in situations where the source of drinking water involved ingestion of triclopyr from treated water, suggesting that people should avoid drinking triclopyr-treated water. Although the calculated triclopyr daily doses were elevated, they remained 26-42 times below the animal chronic toxicology NOAEL, which constitutes a margin of safety for human exposure. In response to this finding, CSI (2001) suggested that it would be important to follow the triclopyr product label that required waiting 21 days before resuming use of treated water as a drinking water source to eliminate human exposure to triclopyr via this route. CSI (2001) also reported that based on the label use specifications and the results of triclopyr toxicology studies, the aggregate daily exposure to triclopyr from aquatic herbicidal weed control does not pose an adverse health concern.

Durkin (2011) also conducted a comprehensive human health and ecological risk assessment for triclopyr, including triclopyr TEA. He found that neither terrestrial nor aquatic applications of triclopyr TEA pose substantial risks to aquatic animals across the range of labeled application rates. The likelihood of acute risks to aquatic animals depends very much on site-specific conditions. In areas with low rates of rainfall, acute risks to aquatic animals would be negligible, so long as drift to surface water were minimal. In areas with high rates of rainfall such as the Northwest, surface water contamination is more likely.

Durkin (2011) also reported that both the human health and ecological risk assessments indicated potential hazards associated with consumption of triclopyr-contaminated vegetation. In addition, because triclopyr is an effective herbicide, damage to terrestrial vegetation is to be expected in the event of direct spray or aerial drift, or from substantial runoff from the application site. Surface water runoff from the treated site should be limited to reduce potential environmental transport following treatments. In addition, damage to non-target aquatic plants, particularly macrophytes, may result from both terrestrial and aquatic applications of triclopyr.

King *et al.* (2016) examined the effects of three aquatic herbicides (diquat dibromide), fluridone [Sonar®], and triclopyr) on specific endpoints related to smoltification success in juvenile Pacific coho salmon (King *et al.* 2016) at label-specified rates in seawater for each of these compounds. Preliminary results suggested that, at the chemical concentrations in seawater exposures tested, effects were short-lived and these aquatic herbicides are unlikely to affect smoltification success. In a similar study, Curran *et al.* (2007) tested the aquatic herbicides DMA® (2,4-D), triclopyr, diquat, and Sonar® (fluridone) for effects to the olfactory ability of juvenile rainbow trout (*O. mykiss*) when exposed to the maximum application rates of these formulations for 96 hours, using static-renewal tests. Results showed that olfactory function of the juvenile rainbow trout were not affected by three of the compounds, with effects observed only following exposure to the maximum rates of Reward® (diquat). Servizi *et al.* (1987) reports that salmon and *Daphnia* invertebrates are both vulnerable to acute toxicity associated with triclopyr-containing herbicides.

To avoid adverse effects to human health following aquatic treatments with triclopyr, it is important to follow the triclopyr product label requirements before resuming use of treated water as a drinking water source. In addition, setback distances from potable water intake sources are specified on the label (e.g. SePro specimen label for Renovate 3®). These setbacks are calculated for different concentrations of triclopyr TEA in water (expressed as mg/L a.e.), and vary based on the number of acres treated. Based on the toxicity literature, if label specifications are followed, aggregate daily exposures to triclopyr from aquatic herbicidal weed control should not pose a human health concern. Ecology should require groundwater or sediment monitoring prior to any third application of triclopyr on a previously treated site within a three-year period. Evidence of persistence of triclopyr or its derivatives in sediment or groundwater would constitute a basis for denial of such a proposed third application (CSI 2001).

Regarding wetlands, estuaries and marshes into which triclopyr-treated water could flow, Ecology (2004) recommended that the total application of these products should not exceed 2.5 ppm a.e. for the treatment area per annual growing season. The total application of these products to control floating and emerged weeds should not exceed 2 gallons formulation/acre per annual growing season. Regarding non-target plant species, including endangered plants, the total application of these products should not exceed 2.5 mg/L a.e. for the treatment area per annual growing season.

Mitigation of possible effects on listed sensitive or endangered species is best accomplished by contacting WDFW, either by Ecology or by the applicant, to ascertain the presence of any listed species and the potential for them to be affected by the application of the chemical to the water body in question. Ecology would mitigate direct effects or indirect effects to food sources or habitat loss by requiring work windows or consultation with the WDFW when herbicides are used in water bodies where priority or listed species and habitats occur. Ecology's permit manager also consults the Department of Natural Resources (DNR) Natural Heritage Program to identify rare plants before issuing permit coverage for in-water treatments. Ecology coordinates mitigation efforts among the permit applicant, WDFW, the Natural Heritage Program and others, to ensure adequate protections to threatened and endangered species and state priority species and habitats from herbicide use such as triclopyr TEA.

Regarding swimming, the Washington State Dept. of Health has recommended a 12-hour restriction for re-entry into triclopyr treated water to assure that the eye irritation potential and any other adverse effects will not occur. WDOH also recommends that those wanting to avoid even small exposures can wait 1-2 weeks following application, by which time triclopyr residues would have largely dissipated from the water and sediments (WDOH, 1999).

Regarding mitigation for aerial drift, irrigation, surface water, fish, and other wildlife, potable water, and fishing or consumption of fish or shellfish, Ecology (2004) stipulates that following label directions for triclopyr TEA should be adequate for avoiding adverse environmental impacts. If triclopyr TEA is treated as a restricted use herbicide, it should not cause adverse impact to invertebrate biota.

4.10.13.1 References

- Compliance Services International (CSI). 2001. SEIS of Aquatic Herbicides, Volume 5: Triclopyr. March. Ecology Publ. No. 04-10-015: p. 360. [3]
- Curran, C., J. Grassley, L. Conquest, and C. Grue. 2007. Olfactory performance in salmonids exposed to aquatic herbicides. Master's Thesis, University of Washington. [9]
- Durkin, P. 2011. Triclopyr – Human Health and Ecological Risk Assessment, Final Report. USDA/US Forest Service SERA TR-052-25-03a: p. 267. [1]
- ENSR Corporation (ENSR). 2007. Use of the Aquatic Herbicide Triclopyr Renovate in the State of New York: Supplemental Environmental Impact Statement. Report prepared for SePRO Corporation. Document No.: 10746-001-310 dated March. [1]
- K. King, C. Grue, J. Grassley, C. Curran, W. Dickhoff, and J. Winton. 2016. Effects of Three Aquatic Herbicides on Smoltification in Juvenile Pacific Coho Salmon. In press. [9]
- Perkins, P., H. Boermans, and G. Stephenson. 2000. Toxicity of Glyphosate and Triclopyr Using the Frog Embryo Teratogenesis Assay – Xenopus. Environ. Toxicol. Chem. 19(4): p. 940-945. [9]
- Petty, D., et al. 1998. Aquatic Dissipation of the Herbicide Triclopyr in Lake Minnetonka, Minnesota. Technical Report A-98-1. U.S. Army Corps of Engineers. [9]
- SePRO. (undated). Specimen label for Renovate 3® Specialty Herbicide. SePro Corp., Carmel, IN. 8 pp. http://www.sepro.com/documents/Renovate_Label.pdf. [1]
- Servizi, J.A., R.W. Gordon, and D.W. Martens. 1987. Acute toxicity of Garlon 4 and Roundup herbicides to Salmon, *Daphnia*, and Trout. Bulletin of Environmental Contamination and Toxicology 39:15-22. [1]
- US Environmental Protection Agency (EPA). Office of Pesticide Programs (OPP). 1998. Reregistration Eligibility Decision (RED): Triclopyr. Available at: http://www.epa.gov/pesticides/reregistration/status_page_t.htm. [SET00]. [1]
- Washington Department of Ecology (Ecology). 2004. Environmental Impact Statement (EIS) for Permitted Use of Triclopyr, Final. May. Publication Number 04-10-018 revised. Available at: <http://www.ecy.wa.gov/pubs/0410018.pdf>. [3]
- Washington Department of Health (WDOH). 1999. Review of Proposed Spot Treatment with Renovate Aquatic Herbicide. [1]
- Washington Department of Transportation (WSDOT). 2006. Triclopyr – Roadside Vegetation Management Herbicide Fact Sheet. p. 4. [1]

Washington State Department of Agriculture (WSDA). 2014. Non-agricultural Pesticide Use in Puget Sound Counties. Publication No. AGR PUB 103-409: p. 76.

<http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx> [1]

4.10.14 Endothall (mono salt) algaecide

As noted in Section 4.10.6, endothall is both an herbicide for control of aquatic macrophytes and an algaecide. This section discusses endothall mono salt as the active ingredient in algaecides. Hydrothol® 191 liquid and Hydrothol® 191 granular, for which endothall mono salt is the active, have received federal registration for control of both algae and aquatic macrophytes in canals, lakes and ponds, and have been registered by WSDA in Washington State for control of aquatic algae and plants (WSDA 2014).

Ecology (2000) identified data gaps relating to soil and sediment, nutrient data in water and dead or dying plants, and chronic toxicity studies for both plants and animals relating to both Aquathol®, Aquathol® K, and Hydrothol®. Ecology (2001) recommended that early life stage studies should be conducted on all end-use formulations with standard test species rainbow trout, fathead minnow, and sheepshead minnow. In addition, because coho and Chinook salmon are keystone species for the Northwest, both early life stage and further smoltification studies should also be conducted with these species.

To that end, Courter *et al.* (2012) and Courter *et al.* (2016) performed ten-day seawater challenge experiments on anadromous juvenile fish (steelhead, coho, and Chinook salmon) to support definition of chemical toxicity levels associated with aquatic exposure to endothall using Cascade® herbicide, for which the dipotassium salt is the active ingredient. Results of this testing showed that steelhead showed a lower survival rate than coho and Chinook salmon, although no effects of endothall to any test animals were observed during the initial 96 hour freshwater toxicity phase of the exposure. Surviving fish did not experience significant changes in osmoregulatory performance (a sublethal endpoint reflective of the smoltification process) in comparison with control fish. LOECs were 9 mg/L a.e. for steelhead and 12 mg/L a.e. for coho and Chinook salmon. This compares with the Washington NPDES regulation set at 2.5 mg endothall/L a.e. Based on these results, no sublethal effects of Cascade on steelhead and salmon are anticipated when discharged at the labeled rate of 5 mg endothall/L a.e.

Paul *et al.* (1994) conducted toxicity testing for effects on early life stages of non-target aquatic game fish found in lakes undergoing treatment. Commercial formulations of diquat, endothall, and fluridone were selected for acute toxicity testing using early life stages of walleye (*S. vitreum*), largemouth bass (*M. salmoides*), and smallmouth bass (*M. dolomieu*). Toxicity testing results were compared to predicted concentrations. Diquat, with 96-h LC₅₀s of 0.74-4.9 mg/L, was more toxic to these early life stages than endothall or fluridone, with 96-h LC₅₀s of 16-130 mg/L and 1.8-13 mg/L respectively. The LC₅₀ values for endothall was about one order of magnitude greater (i.e. less toxic) than label-specified concentrations. They concluded that endothall appears to have an adequate margin of safety between application rates used for aquatic macrophyte control and concentrations which are toxic to early life stages of fish. An earlier reported 96-hr LC₅₀ value for largemouth bass was 120 mg/L, which is consistent with the value of 131 mg/L determined by Paul *et al.* (1994). Young walleyes are much more sensitive (96-hr LC₅₀ value

of 16 mg/L), but even this is three times the maximum labelled application rate of 5 mg/L (Aquathol®K label).

As discussed in Section 4.10.6 (endothall dipotassium salt), several key toxicity studies were performed to provide context on the toxicity of the active ingredient endothall. Archambault *et al.* (2015) and Archambault and Pope (2016) conducted two separate studies to investigate the effects of two currently registered herbicides commonly used to control Hydrilla and other aquatic weeds (endothall (dipotassium salt) and fluridone) on freshwater molluscs, including a rare freshwater snail (*S. virginicus*). Toxicological endpoints measured were adult survival and egg hatching success. Results showed that neither herbicide indicated effects to either survival or egg hatching success at concentrations typically prescribed (1 to 5 mg/L for endothall) for control of a target plant species such as Hydrilla. The early life stages of the mussel *L. siliquoidea* were exposed to a formulation of the dipotassium salt of endothall (Aquathol®K). The 24-h LC50 for the juvenile mussels exposed to the dipotassium salt of endothall was 31.2 mg/L, and the 96-h LC50 for juvenile mussels was consistent at 34.4 mg/L. Endothall concentrations typically recommended for hydrilla treatment (1 to 5 mg/L) were not acutely toxic to the molluscs tested. This work indicates that some mortality of mussels could occur below established threshold values. In addition, toxicity testing from Keller (1993) indicate that the freshwater mussel *Anodonta imbecillis* is generally less sensitive to Hydrothol® exposure than other tested aquatic organisms.

All of Ecology's general mitigation posting requirements apply. Shoreline postings are required and should be placed around the treatment areas, and a 24-hour swimming advisory is recommended in treated areas for protection against mild eye irritation. A 24-hour boating advisory is also recommended for boaters entering areas of treatment for protection against mild eye irritation due to aerial drift or dust.

It is recommended that exposure of wild fisheries or listed fish species to endothall should be avoided, although toxicity testing have suggested that the most common forms of endothall, including the dipotassium and disodium salts, will not cause acute or chronic harm to non-target aquatic animals when label specifications are followed, consistent with current research on salmonid smoltification discussed above (Courter, 2012 and Courter, 2016).

In addition, field data indicated that Hydrothol®191 should not be used to control aquatic weeds at concentrations higher than 0.5 mg ae/L, which may cause a significant fish kill. Hydrothol®191 has been recommended for the control of toxic blue-green algae at concentrations that may not harm green algae. A safe treatment rate of higher than 0.2 mg ae/L cannot be recommended due to potential acute and chronic toxicity to fish. The exposure period should be as low as possible (accounting for higher flow rates in canals), and the minimum area possible should be treated. In addition, treatments should occur from the shoreline outward to allow for possible avoidance of Hydrothol® by free-swimming fish (Ecology 2001). It is noted that these toxicity levels for Hydrothol® or mono salt-based endothall applications are at or below toxicity thresholds discussed above for the dipotassium salt exposures to endothall, so they are regarded as applicable to understanding endothall ecotoxicity.

Seasonal restrictions for endothall treatments may be warranted to protect sensitive salmon smolts from potentially adverse effects; similar restrictions may be advisable to protect both the fisheries and

human health when recreational or commercial fishing seasons are active. Regarding consumption of potential endothall-contaminated fish tissue, Washington state does not regulate either Aquathol®K or Aquathol® with regard to restricting consumption of fish from treated areas for food or feed following treatment (WSU PICOL output 2017).

Parsons *et al.* (2004) conducted a field investigation in Kress Lake, WA using low concentrations (1.5 mg/L active ingredient) of endothall (formulated as Aquathol® K) in 2000 to selectively control EWM. Aquatic plant biomass and frequency data were collected before treatment, ten weeks after treatment and during the growing season for 3 additional years. Macrophyte data were analyzed to assess the herbicide's impacts on the target species (EWM) as well as the rest of the aquatic plant community. Results showed a significant decrease in EWM biomass and frequency 10 weeks after treatment. EWM continued to be present, but at significantly reduced levels throughout the study (three years after treatment). Of the native plant species, large-leaf pondweed (*P. amplifolius*) frequency and biomass was significantly reduced after treatment. Common elodea (*E. canadensis*), muskgrass (*Chara* sp.) and bladderwort (*Utricularia* sp.) all increased significantly after treatment.

In 2005 additional plant frequency data were collected following the same methods used in the original study. Data showed no significant difference between the frequency of EWM in 2005 and 2000, so it returned to essentially pretreatment levels. However, the big leaf pondweed frequency was still at significantly reduced levels compared with before treatment. The other common native species, however, were all still found at significantly higher frequencies in 2005 than before treatment.

4.10.14.1 References

- Archambault, J, and W. Cope. 2016. Life stage sensitivity of a freshwater snail to herbicides used in invasive aquatic weed control. *Freshwater Mollusk Biology and Conservation* 19: p. 69-79. [1]
- Archambault, J., et al. 2015. Sensitivity of freshwater molluscs to hydrilla-targeting herbicides: Providing context for invasive aquatic weed control in diverse ecosystems. *J. Freshwater Ecology* 30(3): p. 335-348. [1]
- Courter, L., T. Garrison, and I. Courter. 2016. Latent toxicity of endothall to anadromous salmonids during seawater challenge. *Bulletin Environ. Contam. Toxicol.* 96 (5): p. 533-579. [1]
- Courter, I., L. Courter, T. Garrison, D. Cramer, S. Duery, D. Child, T. Hanna and E. Buckner. 2012. Effects of the aquatic herbicide Cascade® on survival of salmon and steelhead smolts during seawater transition. Final Rep. submitted to WSWRA 2012. 46 p.
<http://www.ecy.wa.gov/programs/wq/pesticides/irrigation/docs/cascade.pdf> [1]
- Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]
- Ecology. 2001. Herbicide risk assessment for the aquatic plant management FEIS, Appendix D, Vol 2: Endothall. Publ. No. 00-10-044.
<https://fortress.wa.gov/ecy/publications/documents/0010044.pdf>. [3]

- Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides, WA Department of Ecology, July 2000. Publication No. 00-10-040. [2]
- Keller, A.E. 1993. Acute toxicity of several pesticides, organic compounds, and a wastewater effluent to the freshwater mussel, *Anodonta imbecilis*, *Ceriodaphnia dubia*, and *Pimephales promelas*. Bulletin of Environmental Contamination and Toxicology 51: 696-702.
- Parsons, J., K. Hamel, S. O'Neal, and A. Moore. 2004. The impact of endothall on the aquatic plant community of Kress Lake, WA. Journal Aquatic Plant Mgt. 42: p. 109-114. [1]
- Paul, E., H. Simonin, J. Symula, and R. Bauer. 1994. The toxicity of Diquat, Endothall, and Fluridone to the early life stages of fish. J. Freshwater Ecology 9(3): p. 239-239. [1]
- WSDA (WA State Department of Agriculture). 2014. Non-agricultural pesticide use in Puget Sound Counties. Publication No. AGR PUB 103-409. 76 p.
<http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx>. [1]
- Washington State University. 2017. Pesticide Information Center Online – PICOL output.
<http://cru66.cahe.wsu.edu/labels/ViewLabels.php?radOutputType=standard&selFld1=none&selFld2=none&selFld3=none&selFld4=none&selFld5=none&selFld6=none&selFld7=none&selFld8=none&selFld9=none&view=View+Labels&SrchType=C>. [1]

4.10.15 Sodium Carbonate Peroxyhydrate (sodium percarbonate)

Sodium carbonate peroxyhydrate (sodium percarbonate, SP) is registered by both EPA and WSDA in Washington State (WSDA 2014) as a fast-acting algaecide. This compound generates hydrogen peroxide which directly oxidizes cell structures in algae, thus inhibiting algal growth and preventing algal bloom formation. Lake managers apply these products to waterbodies to prevent algal blooms or to treat existing algae as an alternative to copper-based algaecides, which are no longer allowed in Washington water bodies under the APAM and Aquatic Noxious Weed Control permits. Copper-resistant algal strains have developed elsewhere, and this product provides an alternative to treat copper-resistant algae. EPA has registered SP products for use in ponds, lakes, reservoirs, and drinking water sources, as SP acts as an oxidizing or disinfecting agent to kill algae. When applied to water, granular products break down into constituent sodium carbonate and hydrogen peroxide. Some evidence suggests that sodium carbonate products are more effective when used to prevent the occurrence of algae blooms, and may successfully spot-treat filamentous algae. Several brands of SP products are commercially available as GreenClean™ and Pak 27™, with some brands advertised as selective to cyanobacteria (blue-green algae).

Application of these SP-containing algaecidal products can be made in several ways, depending on the formulation used. In general, they are most effective when application is made while algae are not yet well established and when growth first begins to appear. Both sunlight and higher temperatures enhance the effect so application early in the day under calm, sunny conditions is optimal (MDEP/MDAR 2010, BioSafe Systems 2006, 2008). In water bodies with floating mats of algae, the best results are obtained by breaking up the algal mats before or during product application. Dead and/or floating plant material should be removed before it sinks and decays, as accumulations of decaying matter provide additional nutrients to the water that will stimulate regrowth of algae and further blooms. These products may be applied via either a spot treatment or a whole-lake treatment. Methods of application vary with formulation and include, for liquid products, spot application directly over the infested area on the water surface from a boat or shore or injection via a piping system. For granular forms of the product (BioSafe Systems, 2006; BioSafe Systems, 2008), application may be broadcast by hand or via mechanical spreader, and the product may also be deployed in bags dragged behind a boat or even applied using conventional aerial application equipment.

Sodium percarbonate rapidly dissolves in water and dissociates into sodium, carbonate and hydrogen peroxide. Example acute ecotoxicity tests with fish and daphnid invertebrates indicated LC50 values of 71 and 4.9 mg/L, respectively, indicating moderate to high toxicity. Available data (HERA 2002) show that observed aquatic toxicity of SP can be explained by the formation of hydrogen peroxide, which is non-persistent and not expected to cause lasting environmental exposures to non-target species. Because the parent compound SP dissociates into sodium, carbonate, sodium carbonate (soda ash), and hydrogen peroxide, the ecological risk assessment conducted by HERA (2002) was based on assessing individual components of SP. Hydrogen peroxide will degrade in the aquatic environment, while carbonate will be neutralized over time to bicarbonate. Sodium is essentially non-toxic and is not expected to affect the aquatic organisms in the water body. Thus, based on available data, the use of sodium percarbonate in lake and pond disinfections is expected to have little to no adverse effect on the aquatic ecosystem.

Concerning phytotoxicity, several fumigation studies (as reported by HERA 2002 and MDEP/MDAR 2010) with hydrogen peroxide in plants (i.e., wheat, Norway spruce and red beech) indicated reversible effects on assimilation and photosynthesis in wheat plants. Effects on trees were more severe and included effects on internal needle and leaf structure. A study conducted with hydrogen peroxide and the algae *Chlorella vulgaris* indicated an EC50 of 2.5 mg/L and a NOEC of 0.1 mg/L, with another study conducted with sodium percarbonate in *C. vulgaris* yielding an EC50 of 7.7 mg/L and a NOEC of 0.3 mg/L, both signifying moderate to high phytotoxicity (both studies reported by HERA 2002). Given that herbicide products that contain these active ingredients are formulated to treat algae, the effect levels cited above are consistent within the range of application levels for these products. However, as discussed above, the hydrogen peroxide, carbonate, and sodium fractions are either non-persistent or non-toxic, and therefore it should be reasonably straightforward to follow label specifications to control or avoid non-target plant toxicity.

Sodium percarbonate show low acute toxicity to mammals as well via the oral and dermal route (LD50 > 1000 mg/kg body weight). Existing animal data on acute toxicity show that sodium percarbonate causes a localized, slightly irritating effect on skin, and was highly irritating to rabbit eyes in laboratory tests (HERA 2002). When people (e.g. workers) are exposed to sodium percarbonate, neither hydrogen peroxide nor sodium carbonate is systemically available due to effective detoxification (degradation and neutralization) in the body. Accordingly, it is to be expected that neither concentrations of hydrogen peroxide nor sodium in the blood will be increased (HERA 2002). Because these constituents are not systemically toxic, neither sodium percarbonate or its degradates (hydrogen peroxide, sodium or carbonate) will reach any organs, and therefore there would be no risk for systemic toxicity. With regard to genotoxicity and carcinogenicity, the properties of sodium percarbonate resemble those of hydrogen peroxide and it can be concluded that there is no concern for possible genotoxicity or carcinogenicity of sodium percarbonate.

The only critical endpoint for sodium percarbonate seems to be local irritation. Human exposure to sodium percarbonate can cause skin irritation from solutions containing sodium percarbonate. Accidental eye exposure to sodium percarbonate products could result in eye irritation if the sodium percarbonate concentration in the product or the solution is very high (> 25%). Irreversible eye damage could occur if the product is not immediately washed or rinsed from the eye.

4.10.15.1 Label restrictions and mitigation

Based on laboratory testing results, SP and its derivatives (e.g. hydrogen peroxide) are potentially acutely toxic to invertebrates (including insects), birds, and fish. As such it is important to administer label and permit restrictions when conducting algal control treatments. As noted above, several label restrictions have been added as part of EPA registration, for example, label restrictions specify that SP-containing effluent should not be discharged to waterbodies unless an NPDES permit is in force, which Ecology would routinely enforce as part of its permitting requirements. Other restrictions concern application to surface waterbodies as an algaecide, and include treating along shorelines and proceeding outward in ponds or lakes allow fish or other aquatic life to move into untreated areas. It is further recommended to not apply SP-containing algaecides directly to treated, finished drinking water reservoirs or other potable water sources (BioSafe Systems, Inc. 2006, 2008).

4.10.15.2 Swimming /Water Recreation

Concerning swimming and water recreation, as long as in-water SP treatments are administered in accordance with label specifications, and no recreational exposures are allowed immediately following treatments, impacts to swimming or other recreational aquatic activities are not expected. Moreover, Ecology prohibits treatments with pesticides that have water use restrictions on the FIFRA label that would restrict public water use during the opening week of fishing season or during tribal fisheries, WDFW Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. Ecology further requires that permittees must minimize treatments that restrict public water use during weekends. SP is not expected to impact groundwater or drinking water supplies. In addition, there are no registered or anticipated residential applications for these materials, which further diminishes the likelihood of adverse exposures or the need for mitigation associated with drinking water.

4.10.15.3 Fisheries/fish consumption

Concerning potential effects to fisheries and human fish consumption, the potential for toxicity to various life stages of fish is possible due to the relatively high acute ecotoxicity of SP and its derivatives, but this product does not require compliance with WDFW timing windows for fish.

Ecology also stipulates as part of its permitting process that the permittee must not conduct treatments that adversely affect salmon or steelhead in hatcheries when applying in-water algal treatments such as SP to areas upstream of a hatchery water intake. Ecology will coordinate with the permittee, WDFW, and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations. Fish consumption is not expected to be an issue with these compounds, or require any mitigation, because SP in any of its chemical forms do not bioaccumulate and would not be present in edible fish or shellfish tissue.

Concerning effects to ESA-listed species, the potential for toxicity to various life stages of fish, including protected salmonid species such as steelhead, salmon, and bull trout, is possible due to the relatively high acute ecotoxicity of SP and derivatives, but label restrictions, and other mitigation measures in the APAM permit will be implemented for protection of these fisheries as well as their critical habitats. EPA's Endangered Species and Spray Drift Task Forces or other entities may suggest and implement mitigation measures as needed to eliminate or mitigate risks to non-target plants associated with these algal control treatments.

Prior to issuing permit coverage for discharges to water bodies where sensitive, threatened, or endangered plants could be present, Ecology will determine whether such plant species may be present in the proposed treatment area. For aquatic plant control projects where rare plants are potentially present, the permittee must conduct a detailed plant survey and if rare plants are found, implement mitigation measures to Ecology according to Special Condition S.9 (Mitigation for Protection of Sensitive, Threatened, or Endangered Plants).

Concerning impacts to wetlands or critical habitat, there is a potential for short-term effects to occur to wetlands in association with SP algaecidal treatments. It is therefore important that label and permit specifications be carefully followed, and these effects would be expected to be limited and temporary in

nature. Environmental concentrations will be carefully considered as part of dose calculations prior to the in-water algal control treatments to further minimize these impacts. There is a possibility that SP could affect some non-target aquatic vascular plants, and it would be prudent to consider possible mitigation measures for protection of wetlands due to these potentially phytotoxic properties.

As stipulated by Ecology for the APAM permit, the permittee may treat only high use areas in or adjoining wetlands to provide for safe recreation (e.g., defined swimming corridors) and boating (e.g., defined navigation channels) in identified and/or emergent wetlands. The permittee must limit the treated area to protect native wetland vegetation. Mitigation measures for rare or endangered non-target plant species are discussed above.

Post-treatment monitoring in aquatic water bodies is important and is strongly recommended, and should be incorporated into both label and permit requirements in association with use of these algaecidal chemical formulations. EPA, Ecology, and other agencies routinely require post-treatment monitoring, both short- and long-term, for the purpose of evaluating non-target effects from algal control compounds such as SP. For Ecology, this post-treatment monitoring would be required under their NPDES discharge permits, and would be a permit condition requiring monitoring to determine potential non-target impacts, especially to non-target plant species.

4.10.15.4 References

- Bertsch-Frank B, A. Dorfer, G. Goor, and H. Süss (1995). Hydrogen Peroxide And Inorganic Peroxy Compounds. *Ind. Inorg. Chem.: Prod. Uses*: p. 175-198. [1]
- BioSafe Systems. GreenClean Liquid: Broad Spectrum Algaecide/Bactericide. Specimen Label. Connecticut. 2006. [1]
- BioSafe Systems. GreenClean Pro: Granular Algaecide/Fungicide. Specimen Label. Connecticut. 2008. [1]
- Chater, B. 1978. Sodium Percarbonate, Acute Oral Toxicity with Histology, Skin and Eye Irritation. ICI Report CTL/T/1151. [9]
- Clarke, C. 1991. The Anti-algal Activity Of Peroxygen Compounds. Thesis. [9]
- De Groot, W.A. et al. 2002. Addition of Sodium Carbonate to a Solution with Sodium Bicarbonate to a Fixed pH. *Solvay Pharmaceuticals Int. Doc. No. 8320/48/01*. [9]
- European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC). 1993. Joint Assessment of Commodity Chemicals No. 22 – Hydrogen peroxide. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium. [1]
- European Commission (EC). 2001. Risk Assessment: Hydrogen Peroxide, According to Regulation (EEC) 793/93 on the Evaluation and Control of the Risks of "Existing" Substances, Final Draft of April 2001. Available on website: <http://ecb.jrc.it/existing-chemicals/>. [1]

- Human and Environmental Risk Assessment (HERA). 2002. Human and Environmental Risk Assessment for European Household Cleaning Products: Sodium Percarbonate.
<http://www.heraproject.com/files/6-F-04-HERA%20percarbonate%20full%20web%20wd.pdf>. [1]
- Shangya Jiehua Chemical Co. 2009. Technical Data Sheet: Sodium Percarbonate. p. 3
<http://www.runyoutech.com/pdf/sodium-percarbonate-specifications.pdf>. [9]
- Toxnet. 2009. Hazardous Substances Data Bank. National Library of Medicine.
<http://toxnet.nlm.nih.gov/cgi-bin/sis/search>. [1]
- US Environmental Protection Agency (EPA). 2016. ECOTOX Database, <http://cfpub.epa.gov/ecotox/>. [1]
- EPA. 2002. 40 CFR part 180 [OPP–301217; FRL–6822–7], RIN 2070–AB78, Hydrogen Peroxide; An Amendment to an Exemption from the Requirement of a Tolerance, 9214 Federal Register / Vol. 67, No. 40 9214-9218. [5]
- EPA. Office of Pesticide Program (OPP). 2004. Registration Eligibility Decision (RED) PAKTM 27 (Sodium Carbonate Peroxyhydrate with Active Ingredient Hydrogen Peroxide), Human and Ecological Risk Assessment for Section 3 Registration of the End-use Product PAKTM 27 for Application to Lakes, Ponds, and Drinking Water Reservoirs. DP#301201, PC#000595, EPA File Symbol No. 68660-O. November. [1]
- Washington State Department of Agriculture (WSDA). 2014. Non-agricultural Pesticide Use in Puget Sound Counties. Publication No. AGR PUB 103-409: p. 76.
<http://agr.wa.gov/FP/Pubs/NaturalResourcesAssessmentPubs.aspx>. [1]

5.0 Alternative 4: Manual and Mechanical Control Methods

Manual methods of aquatic plant control and management are generally low-technology and include hand pulling, cutting, and raking. Mechanical methods include mechanical harvesting and cutting, weed rolling and rotovation. Bottom barriers and diver assisted suction harvesting (DASH) are also included in the mechanical alternative. WDFW has issued a pamphlet (WDFW, 2015) which serves as an HPA (i.e. state requirements at WAC 220-660290) for some types of aquatic weed or plant control, including physical and mechanical methods. This pamphlet does not address use of grass carp or herbicides for this type of plant management or removal.

Impacts associated with the exclusive use of mechanical and manual methods are usually short-term and relatively localized. Currently, many agency aquatic plant control programs process permits required for mechanical control, including general and individual Hydraulic Project Approvals (HPA) from Washington State Department of Fish and Wildlife (WDFW) and shoreline substantial development permits from local agencies. Under this alternative, Ecology would continue to administer funds for water quality improvements and aquatic plant control. Manual methods (with the exception of diver dredging) are generally more practical for small areas, such as those around docks, in swimming areas, and in areas containing obstructions. These methods are labor-intensive but do not require specialized skill, formal training, or equipment, and generally do not contribute to long-term adverse environmental impacts.

Environmental impacts associated with manual methods are expected to be minimal, however manual harvesting could result in short-term sediment disturbances and turbidity with potential short-term adverse impacts to water quality, to habitat, and potentially to biota such as prey species, including threatened or endangered species. Manual and mechanical control of aquatic plants can lead to fragmentation of the plants being controlled. Project proponents should ensure that plant fragments are collected and properly disposed of, so that they do not settle to the sediment and initiate a new infestation of the plant population. Manual and mechanical methods tend to be labor-intensive and localized. When the use of manual methods is confined to small areas, it is expected that impacts would be short-term and localized. However, aquatic plant/weed harvesting and rotovation are generally performed on a larger scale and have the potential for wider scale impacts.

5.1 POTENTIAL IMPACTS AND MITIGATION MEASURES

5.1.1 Bottom barriers

Impacts from bottom barriers on sediment, water quality, plants, including rare or endangered species, and animals should be minimal if used to cover a small or localized portion of the total bottom area of the water body. When there is a large standing crop of vegetation, bottom barriers should be placed in the spring before plants resume growth or in the fall when the plants have senesced. Cutting the plants prior to placement of the barrier will facilitate barrier installation, and with or without plant cutting gases may be produced which could cause the barrier to billow.

Important fish spawning areas could be impacted if covered by bottom barriers. To avoid such impacts, the area proposed for treatment should be evaluated to determine its importance to fisheries, and critical spawning areas should be avoided. Installation of bottom barriers in lakes where

sockeye salmon regularly spawn requires an individual HPA from WDFW. In any event, WDFW limits the area that can be covered by bottom barriers (see requirements provides in WDFW 2015). Larger applications of bottom barriers require individual HPAs. Impacts to federal or state listed sensitive, threatened, or endangered species (or species proposed for listing) could be reduced or prevented by excluding bottom barriers from these sensitive areas.

The proponent should determine whether such species occur in the proposed treatment area by requesting this information from the Washington Natural Heritage Information System (WSNHI, 2000). This system provides the location of known sensitive, threatened, and endangered species populations. The data base contains only known locations so it cannot be considered a comprehensive list of all locations of unique species in Washington. If the data system indicated that a "unique" species may exist in the project area, a survey should be conducted for field verification and the project redesigned to avoid impacts to any unique species observed.

5.1.2 Diver assisted suction harvesting

Diver assisted suction harvesting (DASH), similar to but meant to replace suction dredging, requires hydraulic approval that can be obtained free of charge from WDFW. DASH is an updated method that reduces turbidity in the water column by having divers manually insert harvested plants or plant fragments into a suction tube or hose that is then transported via suction to a boat and removed from there. Local agencies should be consulted to determine which local regulations apply, such as a shoreline substantial development permit.

Suction dredging resuspends bottom sediment into the water column, and mud or sediment is often discharged back to the water column when the aquatic plants are removed. Suction dredging should not be conducted in areas known or suspected to contain contaminated sediments. If contaminated sediments are suspected, sediment samples can be tested for chemical contamination or toxicity using standard sediment bioassays or other techniques before permits are issued for diver dredging projects.

Suspended sediments cause turbidity, but impacts are expected to be limited because the treatment area is generally small. If the water/sediment slurry is discharged back into the water body, the discharge area should be cordoned off using a silt curtain. This will further minimize turbidity impacts. Diver dredging can be tailored to localized areas and plant species, with an intent to avoid turbidity, as turbidity diminishes visibility and the ability to target specific plants, so dredging should be suspended if water becomes turbid in areas where certain unique, rare or listed plants are to be preserved. The DNR Natural Heritage Program (2000) should be consulted to ensure that no listed or rare plants occur within the proposed treatment areas. As with use of bottom barriers, suction dredging should not be conducted in critical spawning areas unless WDFW has granted permission to do so. Suction dredging in lakes where sockeye salmon regularly spawn requires an individual HPA from WDFW. In addition, recent work by the Pacific Northwest Native Freshwater Mussel Workgroup (PNWNFMW 2016) as well as Aldridge (2000) review concerns associated with use of suction dredging on lake bed habitat with regard to effects on freshwater mussels.

5.1.3 Manual methods

Hand-pulling, raking, and cutting (including battery-powered equipment) to remove aquatic plants requires an HPA from WDFW. Manual methods in lakes where sockeye salmon regularly spawn requires an individual HPA from WDFW. Manual techniques in other waters may be covered by the *Aquatic Plants*

and *Fish Pamphlet* produced by WDFW (2015). In any event, WDFW limits the area of aquatic plants that can be removed by manual methods; small-scale manual methods are expected to minimally impact the aquatic environment. Nevertheless, care should be taken to avoid unique plant species and critical fish spawning areas.

5.1.4 Rotovation

WDFW requires an individual HPA prior to rotovating and before deadheads or logs can be removed and in many cases will not allow woody debris to be removed from a waterbody. Counties and cities may also require a shoreline permit.

It is important to determine whether sediments potentially identified for rotovation are contaminated, and a review of past use of the proposed treatment area may be required to make this determination, or environmental data (e.g. bioassay testing) may be required to determine whether such sediments are contaminated. In addition, efforts in or near the waterway should be made to minimize streambed erosion, turbidity, or other water quality impacts. Maintenance and operation procedures performed on rotovation equipment could release petroleum products or other deleterious materials into surface waters. Thus, such procedures may be required to be conducted at upland locations to prevent entry of toxic substances into waters of the state.

Due to the high probability of hydraulic fluid or fuel leakage into state waters caused by equipment failure or poor maintenance, permitting agencies may require a detailed inspection plan complete with maintenance logs to be maintained and available for inspection. Additionally, operators may be required to complete inspections of all hydraulic equipment, fuel systems, and other systems that may cause petroleum products to be leaked or discharged to waters of the state. To minimize impacts of a potential spill, operators may be required to carry oil-spill materials with the rotovator at all times, including containment booms and absorption pads. They may also be required to develop a spill contingency plan. To avoid impacts associated with plant fragments, the applicant may be required to dispose of vegetation on land in such a manner that it cannot enter into the waterway or cause water quality degradation to state waters.

To avoid damage from rotovators to water intake pipes, individuals should be given adequate notice of the treatment, informed of the potential for damage to intake pipes, and asked to pull intakes from the water prior to treatment. Areas containing desirable species, such as emergent wetland species, should be avoided by rotovation if at all possible.

An evaluation of each proposed treatment site for rotovation should be performed to determine whether the site is used by fish for spawning, rearing, or other purposes. In addition, recent work by Mageroy *et al.* (2017) discussed environmental concerns associated with the effects of rotovation on a Northwest native species of freshwater mussel (*G. angulata*).

If the area does provide important habitat, the plan should be revised to avoid impacts, either by avoiding or limiting the treatment area, or scheduling treatment to avoid interference with critical uses. Turbidity and disturbance caused by rotovation may interfere with juvenile salmon or fish passage. Therefore, WDFW would impose timing restrictions or “work windows” for when rotovation may be allowed within each waterbody. Because timing restrictions have been severe in salmon-bearing waters and because rotovation is extremely expensive, it has not been a popular method of aquatic plant control in Washington State.

5.1.5 Mechanical Harvesters and Cutters

Harvesting aquatic plants in Washington State requires an HPA from WDFW. Some local agencies may require Shoreline Master Program permits for harvesting. To minimize sediment disruption, operators may be required to demonstrate that the depth of mechanical cutter blades and harvester wheels would not extend into sediment, and operators may be instructed to limit activities to surface waters of more than about five feet in depth. Operators may also be required to remove all cut plants from the water to avoid water quality impacts and public water supplies.

To avoid impacts related to loss of habitat, a survey of each area proposed for treatment may be required to determine habitat value of plant species, and the potential impact of plant removal. Survey results would dictate appropriate mitigation, which could include limiting the size or location of the harvest area, and/or extent of the harvest. Proponents may be required to design the project to avoid migration routes, critical habitats, including wintering, breeding, rearing, nesting, and feeding habitats. The duration of control may be lengthened by requiring harvest later in the season as well. To minimize fish losses, operators may be required to remove any fish as cut plants move up the harvester conveyor belt. Fish loss may also be reduced or prevented by altering the harvest schedule to accommodate fish spawning or rearing. For example, if fry use nearshore areas in early summer, harvesting of these areas could be delayed until the fry moved out of the treatment area. Appropriate mitigation may require assessment of species use and behavior in the specific proposed treatment area.

Areas should be set aside from mechanical harvesting if a biological control agent is active in controlling target aquatic vegetation. For example, if the milfoil-eating weevil *Euhrychiopsis lecontei* is present and active as a biological control agent for Eurasian watermilfoil (see discussion under Section 6.0 (Biological Control) below). These areas could include shoreline areas where there was no human activity or in shallow areas where harvesters could not effectively harvest the milfoil.

Impacts to listed species (or species proposed for listing) could be reduced or prevented by excluding them from the mechanical harvest area. However, in order to avoid unique species, the location of any populations in the treatment area must be identified. The applicant could be required search the Washington Natural Heritage Information System, which provides the location of known sensitive, threatened, and endangered species populations. If the data system indicated that a "unique" species may exist in the project area, a survey should be conducted for field verification, and the project redesigned to avoid any unique species observed. The proponent may also be required to establish setbacks from breeding sites, nests, and feeding or perching areas for listed species.

5.2 REFERENCES

- Aldridge, D. 2000. The impacts of dredging and weed cutting on a population of freshwater mussels. *Biological Conservation* 95: 247-257.
- Mageroy, J, R. Snook, L. Neild, and I. Walder. 2017. The impact of control methods for Eurasian watermilfoil on western ridged mussel (*G. angulata*): Does rotoation harm the mussel? *Northwest Science* 91: 186-197. [1]

PNWNFMW (Pacific Northwest Native Freshwater Mussel Workgroup). 2016. Effects of suction dredge mining on freshwater mussels. Submitted to the Oregon Chapter of the American Fisheries Society's 2017 White Paper: *Suction dredge mining impacts on Oregon fishes, aquatic habitats, and human health*.

6.0 Alternative 5: Biological Control Methods

Biological control (biocontrol) is a biologically-based pest management approach where pathogens and predators feed on or cause disease to a target pest species. The clear advantage of this approach is that no chemical side (non-target) effects can occur because no chemicals are used, and no labor-intensive mechanical or physical efforts are required, as the biological agents (i.e. pathogens and predators) feed on or cause disease to the target species, thus controlling the target plant species with minimal human intervention. Some biocontrol methods are target-plant specific such as precise plant pathogens (e.g. fungi), herbivorous insects, and plant growth regulators, while others are not target species-specific, including planting competitive plants, and introduction of sterile (i.e. triploid) grass carp. Many of these biocontrol agents are in the experimental stages and are not yet realistic IPM alternatives. Many of these biocontrol agents appear to be promising for aquatic plant control and will be carefully considered after undergoing further laboratory and field analysis. Biocontrol research and development in to specific agents or organisms can require ten or more years of experimentation before a potential agent can be effectively released into the environment for control of a target nuisance or noxious aquatic plant species.

Biocontrol may be effectively combined with other treatment techniques such as chemical herbicides, mechanical or physical methods. For example, areas are set aside from mechanical harvesting when the milfoil-eating weevil *Euhrychiopsis lecontei* is present and potentially used as a biocontrol agent for Eurasian watermilfoil. These areas could include shoreline areas where there was no human activity or in shallow areas where harvesters could not gain access to effectively cut or harvest the milfoil. As an example of a non-aquatic biocontrol approach for weed control, as reported by Boyette *et al.* (2008), the fungal pathogen *Myrothecium verrucaria* is combined with the herbicide glyphosate to effectively control weeds in glyphosate-resistant soy bean crops.

6.1 POTENTIAL IMPACTS AND MITIGATION MEASURES

6.1.1 Plant Pathogens

Preliminary research has indicated that plant pathogens (e.g. fungi, bacteria) may be useful in the future control of aquatic vegetation in general, with the most promising results for hydrilla and Eurasian watermilfoil (EWM) in particular. Ongoing issues include defining inoculation strategies, inoculum thresholds, and determining the most effective point in the target species life cycle for inoculation. Shearer (2008) reported that fungal pathogens show promise as biocontrol agents for aquatic noxious plants such as EWM and hydrilla. For example, Shearer *et al.* (2012) evaluated numerous fungal pathogens of EWM and identified five strains to be further examined as candidates for EWM management. Shearer (1998) also tested the endemic Hydrilla pathogen *Mycoleptodiscus terrestris* as a potential candidate for hydrilla control. Gunnar (1983, 1988) reported that use of plant pathogens in

conjunction with mechanical techniques or organisms that feed on and damage plant tissues to provide inoculation sites may be particularly effective (Gunnar, 1983). As noted above, recent research (e.g. Boyette *et al.* 2008) shows that using fungal pathogens in conjunction with low levels of aquatic herbicides may be particularly effective in managing target aquatic plants.

A survey of the continental US for pathogens of EWM was conducted on more than 50 waterbodies in 10 states (Zattau, 1988), and results showed that both bacterial and fungal isolates showed promise as biocontrol agents. As noted above, a particularly promising plant pathogen as a biocontrol agent for both EWM and hydrilla is the fungus *Mycoleptodiscus terrestris* (Winfield, 1988). Extensive research on this fungus has shown rapid and devastating responses in EWM by the fungus in association with bacteria.

6.1.2 Herbivorous Insects

Certain species of herbivorous insects have shown promise as well, and further laboratory and field research is under way to determine which species of insect could be used for aquatic vegetation control. Two of the key target species for which research is under way with herbivorous insects are hydrilla and EWM. This research will help to determine how to produce or sustain insect populations to attain effective control and to determine at which stage in the life history the target plant would be most vulnerable to predation. Development of techniques for adult mating and egg collection is a critical limitation to laboratory rearing for these insects. Numerous factors governing weevil effectiveness are still being refined, but this approach shows great promise as a biocontrol agent for EWM.

Sheldon (1990) conducted a study of aquatic caterpillars and an aquatic weevil used to control EWM populations in a Vermont pond, and found that these underwater insects were effective in reducing EWM populations. They reported that the goal of future work would be to evaluate the potential of one or more of these herbivorous insects to control watermilfoil in other lakes. A number of weevil augmentation experiments have been conducted where numbers of laboratory-reared weevils were introduced into lakes in Vermont and the Midwest. Results have been mixed, with declines in EWM populations in some waterbodies with no decline in others.

Ecology has helped to fund research at the University of Washington to evaluate whether the milfoil weevil could be a suitable control for EWM in Washington State. Unfortunately, densities of naturally occurring native weevils in Washington appear to be much lower than the natural densities seen in other states. In comparison to states where weevils have been observed causing declines, Washington has cooler summer water temperatures and therefore a shorter seasonal window in which to feed on and help to control EWM.

In Washington State, several insect species have been observed to damage Eurasian milfoil growth. The milfoil weevil (*Euhrychiopsis lecontei*) has received the most attention. This weevil is native to the northern US, including Washington (Tamayo and Grue, 1996). Although the weevil's native host species is native northern milfoil (*M. sibiricum*), it has been shown to adapt to EWM as a prey species and even prefer it over northern milfoil. The weevils spend their entire life cycle on milfoil; adults eat leaves on the growing tips, and larvae mine into the stem causing reduced plant buoyancy.

Parsons *et al.* (2011) reported a milfoil weevil augmentation project in Mattoon Lake in central Washington. They monitored aquatic plant growth, invertebrates associated with EWM, and the fish community. During the project Eurasian watermilfoil decreased significantly, while non-target aquatic plant species did not change or even increased. The milfoil weevil required five years to establish, during which time a midge population controlled EWM growth. Fish diet analysis indicated that fish predation impacted herbivorous invertebrate (e.g. insect) populations, supporting the theory that fish and herbivorous invertebrates influence lake food web interactions.

The leaf beetle (*G. calamariensis*) has been successfully used (Hight *et al.* 1995) as a classical biocontrol agent for control of purple loosestrife (*Lythrum salicaria*), a common aquatic plant species in Washington State. As another example of classic biological control using herbivorous insects, Arundo scale (*R. donacis*) is an insect that attacks the rhizomes and developing underground buds of giant reed (*Arundo donax*) within its native range. This insect is anticipated to become a valuable biocontrol agent sometime in the future for control of giant reed, and could be potentially used in Washington State in the event that it becomes problematic within the state.

Wood *et al.* (2016) conducted a global meta-analysis of plant–herbivore interaction studies using a large worldwide dataset from 163 studies in order to test whether greater negative changes in plant abundance would be associated with higher herbivore biomass densities. Results showed that plant abundance declined with increased herbivore density, with some plants eliminated at higher densities. Despite numerous studies on herbivore effects on aquatic plants, factors controlling regulation of vascular plants in aquatic ecosystems remain poorly understood, which in turn hinders the ability to understand the structure and function of aquatic ecosystems, and to manage nuisance aquatic plants within such ecosystems effectively. These findings highlight the need for biologists to more effectively incorporate plant–herbivore interactions into aquatic ecosystem structure and function. Currently, the failure to incorporate “top-down” effects within the food web continues to hinder our capacity to understand and manage the ecological dynamics of habitats containing pest aquatic plants.

Wood *et al.* (2016) demonstrated a positive relationship between herbivore species richness and change in plant abundance, with the strongest reductions in plant abundance reported for low herbivore species richness, suggesting that greater herbivore diversity may protect against large reductions in plant abundance. They also found that herbivore–plant “nativeness” (i.e. non-invasive) was a key factor affecting the magnitude of herbivore impacts on plant abundance across a wide range of biological communities. Communities comprised of invasive herbivores and native plants were associated with greater reductions in plant abundance compared with invasive herbivores and invasive plants, native herbivores and invasive plants, and native herbivores and plants. Communities comprised of native herbivores and invasive plants were associated with lower reductions in plant abundance compared with native herbivores and native plants. However, the effects of herbivore–plant nativeness on changes in plant abundance were reduced at high herbivore densities. These findings are valuable in that they shed light on specific factors and dynamics controlling herbivore–plant interactions and can be instructive in developing IPM strategies for biocontrol of target plants involving herbivory.

6.1.3 Competitive Plants

Interspecific plant competition has also been investigated as a potential aquatic plant control method. Further research is under way to determine specific conditions which enable native plant species to outcompete invasive species such as purple loosestrife or EWM. Past research on use of interspecific plant competition in the control of EWM has led to mixed results (Johnson and Blossey, 2002). In an example study performed for Ecology, Gibbons *et al.* (1987) investigated the possibility that spikerush (*E. coloradoensis*) could be established following chemical control using 2,4-D on watermilfoil with mixed results. Spikerush was successful in surviving and reproducing in shallow areas planted with large, densely populated strips of cut sod, but was not successful in areas planted with strips composed of small wet plugs. Wave and water circulation patterns were shown to have played a major role in transplant success.

6.1.4 Plant Growth Regulators

Another strategy for aquatic plant management involves the use of plant growth regulators. These compounds inhibit gibberellin synthesis, thereby inhibiting normal plant elongation in target plants such as hydrilla and EWM. Bioassay results suggest that gibberellin synthesis inhibitors were effective in reducing plant height in aquatic systems but would have minimal adverse impacts on plant health, and therefore be limited in effectiveness as a target aquatic plant control agent (Lembi *et al.*; Lembi and Netherland, 1990). Although these plant growth regulators are technically chemical control methods, they are included in the biocontrol evaluation section because they are natural rather than synthetic chemicals. Past research on plant growth regulators has not been promising (Johnson and Blossey, 2002) and would require further research before they would be regarded as strong candidate biocontrol agents for controlling aquatic plants or weeds.

6.1.5 Grass Carp

WDFW and Ecology have evaluated the use of sterilized (triploid) grass carp in Washington State for control of aquatic plants, as part of an IPM approach of the Aquatic Plant Management Program. All requests for grass carp stocking and planning permits are made to and granted by WDFW (Appendix E to 2000 Ecology SEIS). This species of carp feeds on aquatic plants, can grow to 100 pounds and live for more than 20 years. They have been used effectively as biocontrol agents to control aquatic plant growth, and in some situations sterilized grass carp may be introduced in Washington State waters, although in many cases grass carp are not an option.

With regard to permitting grass carp, for lakes, ponds, or reservoirs less than five acres and without public access, triploid grass carp may be planted at the expense of the property owner. In such cases, a list of all property owners adjacent to the water and their opinion of the proposed introduction must be provided to WDFW. Water bodies with public access may be stocked with grass carp if a professional lake restoration feasibility assessment or an integrated aquatic vegetation management plan is completed. Both types of planning efforts must include public involvement. WDFW has provided detailed guidelines and an application process to provide guidance on use of triploid grass carp potentially introduced after the required permits are in place (<http://wdfw.wa.gov/licensing/sepa/checklists/grasscarpchecklist.pdf>). These permits include approval from WDFW to plant the fish, a SEPA determination from Ecology, a lake restoration study if the lake or

pond is public, an HPA permit from WDFW if screening is required, and documentation from USFWS verifying the planted fish are certified to be disease-free triploid grass carp. A professional lake restoration feasibility assessment should be conducted to address cultural resources, water quality, restoration feasibility, and public involvement. Where shoreline permits, or other local permits are required, local government may be the lead agency.

The Department of Natural Resources Natural Heritage Program must also be contacted for assessment of potential threatened and endangered or other listed species before WDFW will permit the stocking of grass carp.

Potential impacts from grass carp may be assessed by Ecology, WDFW, or other oversight agencies. Such impacts could include changes to water chemistry, turbidity, increased phytoplankton densities resulting from an influx of grass carp feces, and loss of desirable or unique plant species and/or excessive loss of plant biomass. Because waterfowl depend on aquatic plants for food, loss of plant biomass may adversely affect waterfowl. Information regarding impacts to fish populations, wetlands, and emergent vegetation warrants additional investigation. As the lead permitting agency for stocking grass carp, WDFW has developed policies designed to reduce or prevent some potential impacts (Ecology 2000 SEIS Appendix E). Impacts from grass carp depend on characteristics of the waterbody to be stocked, the stocking rate, the plant community, plant density, and the knowledge of feeding preferences of grass carp. WDFW generally permits the introduction of grass carp mostly into small, private ponds. However, their policy does not include a waterbody size threshold and the agency has received permit applications for larger waterbodies. Limiting permits to small, privately-owned ponds tends to reduce the scope of impacts, as well as the seriousness of impacts such as potential cumulative effects on wildlife, particularly waterfowl. Impacts may be reduced by assessing habitat needs, surveying existing habitat in a general area, evaluating potential cumulative impacts of habitat reduction in waterbodies in that area, and preserving habitat adequate to meet the needs of waterfowl.

6.1.6 Investigations into Biocontrol of Flowering Rush

Flowering rush (*B. umbellatus*) is an aggressive freshwater invasive plant of increasing concern to the state, and was added to the class A noxious weed list in 2009. It rapidly colonizes wetlands, lakes, canals and irrigation ditches. Appropriate chemical and mechanical control methods have been thus far found to be relatively ineffective, creating concerns that the flowering rush populations will continue to expand and spread. Andreas (2016) reports that flowering rush could be a good candidate for biocontrol because it is the only genus and species within its family. This increases the probability of finding an acceptable host-specific biocontrol agent and likely reduces the number of test plant species required for host-specificity testing.

The literature indicates that two fungal pathogens and 18 insect species utilize flowering rush and are candidates for biological control. Only flowering rush was accepted by the weevil *B. nodulosus*, indicating it is highly host-specific. Given these encouraging results, further studies are ongoing to bring this weevil to an appropriate quarantine facility for eventual release for biocontrol purposes. Harms and Shearer (2015), in contrast, claim that levels of damage from herbivory or pathogens on flowering rush in the Pacific Northwest were reportedly minimal, not sufficient to provide population-level impacts,

and therefore a poor candidate for biocontrol. The lack of natural enemies is often cited as a chief reason why invasive species thrive and prove resistant to biocontrol techniques.

6.2 REFERENCES

- Andreas, J. 2016. Flowering Rush Biocontrol Update, December 2016. Washington State University Integrated Weed Control Project and Flowering Rush Biocontrol Consortium Lead. [9]
- Bottrell, D. 1979. Integrated Pest Management. Council on Environmental Quality. #041-011-00049-1, US Government Printing Office, Washington, D.C. 120 pp. [1]
- Boyette, C., R. Hoagland, M. Weaver, and K. Reddy. 2008. Redvine (*B. ovata*) and Trumpetcreeper (*C. radicans*) Controlled Under Field Conditions by a Synergistic Interaction of the bioherbicide *M. verrucaria*, With Glyphosate. *Weed Biology and Manage.* 8: p. 39-45. [1]
- Washington State Department of Ecology (Ecology). 2000a. Ecology Water Quality Program. April 2000. Washington's Water Quality Management Plan to Control Nonpoint Source Pollution, Publication No. 9926. <http://www.wa.gov/ecology/biblio/9926.html>. [2]
- Ecology 2000b. Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides. July 2000. Ecology Publication No. 00-10-040. [3]
- Ecology 2000c. Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides: Appendix E 1992 SEIS Appendices: Grass Carp Supplement, Copper Compounds, Fluridone Human Health Risk Assessment, Fluridone Aquatic Risk Assessment, Glyphosate Risk Assessment, 1992 SEIS Responsiveness Summary. <https://fortress.wa.gov/ecy/publications/publications/0010040.pdf>. [3]
- Gibbons, M., H. Gibbons, Jr., M. Sytsma. 1994. A Citizen's Manual for Developing Integrated Aquatic Vegetation Management Plans, WATER Environmental Services, Inc. Ecology Publication No. 93-93. <https://fortress.wa.gov/ecy/publications/documents/93093.pdf>. [2]
- Gibbons, M., H. Gibbons, and R. Pine. 1987. Lake Osoyoos Demonstration Project. Prepared for Washington Department of Ecology. [2]
- Gunnar, H. and P. Weilerstein. 1988. Field Evaluation of Microbiological Control Agents on Eurasian Watermilfoil. Technical Report A-88-1. US Army Engineer Waterways Experiment Station, Vicksburg, MS. [4]
- Gunnar, H. 1983. Biological Control of Eurasian Watermilfoil. Proceedings, 17th Annual Meeting, Aquatic Plant Control Research Program. Miscellaneous Paper A-83-3, US Army Engineer Waterways Experiment Station, Vicksburg, MS. [4]
- Harms, N, and J. Shearer. 2015. Apparent Herbivory and Indigenous Pathogens of Invasive Flowering Rush (*B. umbellatus*) in the Pacific Northwest. ERSC/TN APCRP-BC-35, June 2015. [9]

- Hight, S., B. Blossey, J. Laing and R. DeClerck-Floate. 1995. Establishment of insect biological control agents from Europe against purple loosestrife (*L. salicaria*) in North America. *Environ. Entom.* 24(4): p. 967-977. [1]
- Johnson, R., and B. Blossey. 2002. Eurasian Watermilfoil. In: Biological control of invasive plants in the eastern US. USDA Forest Service Publ. FHTET 2002-04, 413 p. [1]
- Lembi, C., T. Chand, and W. Reed. 1990. Plant Growth Regulators Effects on Submersed Aquatic Plants. Proceedings, 24th Annual Meeting, Aquatic Plant Control Research Program. Miscellaneous Paper A-90-3, US Army Engineer Waterways Experiment Station, Vicksburg, MS. [1]
- Lembi, C. and M. Netherland. 1990. Bioassay of Plant Growth Regulator Activity on Aquatic Plants. Technical Report A-90-7. US Army Engineer Waterways Experiment Station, Vicksburg, MS. 16 pp. [1]
- Parsons, J., G. Marx and M. Divens. 2011. A study of Eurasian watermilfoil, macroinvertebrates and fish in a Washington lake. *J. Aquatic Plant Mgt.* 49: p. 71-82. [1]
- Shearer, J., B. Durham and N. Harms. 2011. Screening of biological control pathogens isolated from Eurasian Watermilfoil. *J. Aquatic Plant Management* 49: p. 118-121. [1]
- Shearer, J. 2008. Is classical biological control using fungi a viable option for submersed aquatic plant management? *J. Aquatic Plant Management* 46: p. 202-205. [1]
- Shearer, J. 1998. Biological control of Hydrilla using an endemic fungal pathogen. *J. Aquatic Plant Management* 36: p. 54-56. [1]
- Sheldon, S. 1990. A Sudden Decline of A Eurasian Watermilfoil Population In Brownington Pond, Vermont. Proceedings, 24th Annual Meeting, Aquatic Plant Control Research Program. Miscellaneous Paper A-90-3, US Army Engineer Waterways Experiment Station, Vicksburg, MS. [9]
- Tamayo, M. and C. Grue. 1996. Evaluation of the native status in North America for the weevil *Euhrychiopsis lecontei*. University of Washington cooperative Fish and Wildlife Research Unit. Seattle, WA. [3]
- USDA (US Department of Agriculture). 2014. Field Guide for Managing Giant Reed in the Southwest. USDA Report TP-R3-16-11. September 2014, 12 p. [1]
- Washington State National Heritage Data System (WSNHDS). 2000: Washington State Department of Natural Resources, National Heritage Program: <http://www.wa.gov/dnr/base/cons-prot.html>). [3]
- WDFW (WA State Department of Fish and Wildlife). 2015. Aquatic Plants and Fish. Rules for Aquatic Plant Removal and Control. July 2015, 29 pp.
<http://wdfw.wa.gov/publications/01728/wdfw01728.pdf>. [5]

- Winfield, L. 1988. Biological Control of Eurasian Watermilfoil with *Mycoleptodiscus terrestris*. Proceedings, 22nd Annual Meeting, Aquatic Plant Control Research Program. Miscellaneous Paper A-89-1, US Army Engineer Waterways Experiment Station, Vicksburg, MS. [4]
- Wood, K., et al. 2016. Herbivore Regulation of Plant Abundance in Aquatic Ecosystems. *Biol. Reviews* – press. Doi: 10.1111/brv.12272. [1]

APPENDIX A – Responsiveness Summary

Non-Project Supplemental Environmental Impact Statement

Aquatic Plant and Algae Management NPDES General Permit and
Aquatic Noxious Weed Control NPDES General Permit

August 14, 2017

Introduction

The Washington State Department of Ecology (Ecology) issued the Supplemental Environmental Impact Statement (SEIS), in part, to satisfy the State Environmental Policy Act (SEPA) requirements for its action in developing and issuing the National Pollutant Discharge Elimination System (NPDES) Permits to allow the chemical treatment of aquatic plants, algae, and nutrient management. The SEIS will be used to determine whether it is appropriate to include the use of the reviewed chemicals in future issuances of the Aquatic Plant and Algae Management NPDES General Permit and the Aquatic Noxious Weed Control NPDES General Permit. The SEIS document analyzes reasonable alternatives to the chemical treatment of aquatic plants, algae, and nutrient management, the probable significant adverse and beneficial environmental impacts of these alternatives, and their relation to existing policies, rules and regulations. This SEIS analyzed five possible alternatives.

- 1) Use of an Integrated Pest Management (IPM) Approach
- 2) No Action
- 3) Use of Chemical Methods Only
- 4) Manual and Mechanical Methods Only
- 5) Biological Control Methods Only

The SEIS discusses the principal features and mitigation measures for each alternative. The recommended alternative is the use of an integrated pest management approach. Ecology encouraged the public to comment on the Draft SEIS. A comment period was open from May 8, 2017 through June 6, 2017. Comments are listed by number below in Table 1. Comment originators are listed in Table 1 with the coordinating comment numbers referenced. Comments have been summarized and the response to comments and any resulting changes to the draft follow each summarized comment. The original full text of the comments are available on Ecology's webpage at: http://www.ecy.wa.gov/programs/wq/pesticides/seis/risk_assess.html

Section 1: List of Commenters and Comment Numbers

Table 1: Commenters

Commenter Name	Affiliation	Comment Number
Don Russell	Interested Party	1
Steven Richmond	Garden Cycles	2
Kim Patten	Washington State University	3
Emilie Blevins	Xerces Society for Invertebrate Protection	4
Tom Warmuth	BioSafe Systems, LLC	5, 6, 7, 8, 9, 10
Russel MacRae	US Fish and Wildlife Service	11
Douglas Dorling	Northwest Aquatic EcoSystems	12
Dodie Needham	Interested Party	13, 14
Mark Heilman	SePRO Corporation	15, 16, 17, 18, 19, 20
West Bishop	SePRO Corporation	21, 22,23, 24, 25, 26, 27, 28, 29, 30, 31

Comments and Responses

Comment 1: My concern with both aluminum sulfate and iron sulfate and iron chloride salt solution applications in State waters is that all three of these salt solutions introduce copious quantities of sulfate, or in the case of iron salt solution treatments, sulfate or chloride ions into the water body so treated. Whereas soluble and toxic aluminum ions and nontoxic iron ions combine with hydroxyl (OH⁻) ions from disassociated water molecules to form insoluble and nontoxic aluminum hydroxide (alum) and ferric hydroxide which adsorbs and co precipitates phosphate ions, the soluble sulfate and chloride ions remain in solution in quantities that greatly exceed concentrations found in unpolluted fresh water bodies.

Chloride ions are corrosion promoting and aggressive chemical agents and do have adverse ecological effects that are not addressed in TRC's report. Sulfate ions can be reduced to form hydrogen sulfide and sulfur, both toxic materials, that can have adverse impacts on aquatic life as well as bind with iron to remove it as the natural (vs aluminum) deactivation agent for phosphorus. I find omission of discussion of the ecological impact (and fate) of sulfate ions and chloride ions unacceptable in a document that purports to discuss the environmental impact of aluminum sulfate and iron sulfate and iron chloride treatment of State waters.

What I have proposed is the application of finely granulated iron particles (zero valent iron). This application technique provides iron without attendant and polluting sulfate or chloride ions. The surface of the finely granulated zero valent iron (ZVI) particles are chemically reactive and thus combine with the phosphate ions in water to form an insoluble iron phosphate encapsulating surface on the iron particle and/or combine with hydroxyl ions from disassociated water molecules to form an iron hydroxide or iron oxyhydroxide floc which adsorbs phosphate ions thus removing phosphorus from solution.

I believe that the omission of zero valent iron (vs iron in a salt solution) and failure to address the fate of metal salt provided sulfate and chloride ions in any future update of Ecology's Aquatic Plant and Algae Management NPDES General Permit is an oversight that needs to be addressed in the DSEIS for the State of Washington Aquatic Plant and Algae Management.

Response: We agree that a discussion on the use of elemental iron (zero valent iron), chloride, and sulfate were missing from the Draft SEIS. Please see the following discussion on chloride and sulfate ions as well as the changes referenced below.

Chloride in surface waters can be toxic to many forms of aquatic life. Aquatic species of concern include fish, macroinvertebrates, insects, and amphibians. Elevated chloride levels can threaten the health of food sources and pose a risk to species survival, growth, and/or reproduction (New Hampshire Department of Environmental Services: <https://www.des.nh.gov/organization/divisions/water/wmb/was/salt-reduction-initiative/impacts.htm>). Numeric limits to the discharge of chloride ions are given in the Water Quality Standards for Surface Water: WAC 173-201A-240. Chloride has an aquatic life criteria of 860 mg/L for a 1 hour average not to be exceeded more than once

every three years and 230 mg/L for a 4 day average not to be exceeded more than once every three years. The current Aquatic Plant and Algae Management Permit, which allows for the use of chloride containing products for nutrient inactivation, does not allow the Permittee to violate Surface Water Quality Standards (Permit Special Condition S3.A.1). EPA sets a secondary drinking water standard, which is not health threatening, mandatory or enforceable, at 250 mg/L, due to salty taste.

Excessive amounts of sulfate ions in surface waters can have a negative impact to aquatic life. Water Quality Standards for Surface Water do not provide numeric water quality criteria for sulfate in Washington State. EPA sets a secondary drinking water standard for sulfate, which is not health threatening, mandatory or enforceable, at 250 mg/L, due to taste and odor.

The toxicity of sulfate ions has been shown to be linked to water hardness (Elphick et. al. 2011). They propose a tiered water quality guideline for sulfate, to protect aquatic life, based upon water hardness.

Water Hardness	Proposed Aquatic Life Guideline for Sulfate
Soft water (10–40 mg/L hardness)	129 mg/L sulfate
Moderately hard water (80–100 mg/L)	644 mg/L sulfate
Hard water conditions (150–250 mg/L)	725 mg/L sulfate

Data presented in this table are from: Elphick, J. R., Davies, M., Gilron, G., Canaria, E. C., Lo, B., and Bailey, H.C. 2011. *An Aquatic Toxicological Evaluation of Sulfate: The Case for Considering Hardness as a Modifying Factor in Setting Water Quality Guidelines*. Environmental Toxicology and Chemistry. Vol. 30, No. 1, pp. 247–253.

Please also see comment #26.

Change: Changes have been incorporated into Final SEIS section 4.8.2 to include elemental iron. Changes to include discussion on chloride have been incorporated into Final SEIS sections 4.8.2.1, 4.8.2.5 and 4.8.4.1. Changes to include a discussion on sulfate have been incorporated into Final SEIS sections 4.8.2.1, 4.8.2.5, 4.8.4.1, 4.6.2.4 and 4.6.4.1.

Comment 2: Permits are too little too late, ineffective at preventing pesticide pollution or balancing the costs and benefits, where in many cases pesticides can provide an environmental gain by reducing soil disturbance and associated runoff. Also, the penalty and enforcement culture is discriminating against workers required to obtain licenses, while over-the-counter products are far more prone to misuse, but without corresponding penalties to the consumer. I suggest a risk management approach that measures pollution and assesses a fee commensurate with health and environmental risks, where funds will be raised to mitigate excesses, thereby encouraging wiser use, as industry will be motivated to better educate their customers and prevent misuse. Product labels are rarely read, but price is one label the consumer is guaranteed to read.

Response: Thank you for your comment. The Draft SEIS that was available for public comment and review is neither a National Pollutant Discharge Elimination System (NPDES) discharge permit or a regulatory document, rather, it is meant to inform and guide future versions of the Aquatic Plant and Algae Management and Aquatic Noxious Weed Control NPDES General Permits.

The Environmental Protection Agency (EPA) delegated NPDES permitting authority in Washington State to the Department of Ecology (Ecology). NPDES permits are required to discharge pesticides to waters of the state to protect water quality. The Washington State Department of Agriculture (WSDA) also regulates the use of pesticides in Washington State through the Pesticide Control Act (Chapter 15.58 RCW) and the Pesticide Application Act (Chapter 17.21 RCW). Replacement of NPDES discharge permits with the fee structure suggested is out of the scope of Ecology's NPDES permitting authority.

Pesticide applicators conducting treatments that do not require a pesticide applicators license or NPDES permit must comply with the pesticide product Federal Insecticide, Fungicide and Rodenticide (FIFRA) label. WSDA may enforce on label violations under RCW 15.58.150(2)(c). Compliance with FIFRA label law is required for both licensed and unlicensed applicators. NPDES permits are required when a pesticide discharge will occur in or around waters of the state. Application of aquatic labeled pesticides under an NPDES permit requires a pesticide applicators license with aquatic endorsement.

Comment 3: The toxicity of tank mixes is almost entirely driven by the toxicity of the surfactant uses in the tank mix, not the herbicide. While the EIS touches on this subject, it is missing some of the data developed for the EIS for imazapyr, and some of the new data since then. Also it should refer to the approved WSDA aquatic surfactant list and the EIS should refer to surfactant toxicity component of any broadcast applied herbicide that uses a surfactant as part of its application.

Response: SEIS section 4.10.1 discusses tank mixes, inerts and surfactants as well as the approved WSDA aquatic adjuvant list. As a supplemental EIS, information covered in a previously developed EIS is not duplicated; this would include information from the EIS for imazapyr. Additionally, the SEIS sections reviewing glyphosate and imazapyr specifically address potential toxicity from the use of surfactants.

Comment 4: Native species of freshwater mussels are important members of the aquatic community in Washington State. They provide valuable ecosystem services; as filter-feeders, they can substantially improve water quality. Mussels also support and improve fish habitat and are a valuable food source for other species. Unfortunately, freshwater mussels are also among the most imperiled species globally. Recent research has shown that western species like the western pearlshell, western ridged mussel, and floaters are declining in distribution, one reason for the recognition of four species of mussels as Washington State Species of Greatest Conservation Need, and for state restrictions on collection and take.

Freshwater mussels are relatively long-lived and generally sessile, and activities that harm freshwater mussel beds or habitat (including most perennial aquatic ecosystems) may require multiple years for recovery or recolonization. The Xerces Society has recently conducted a literature review to identify management practices with the potential to negatively impact freshwater mussels, including methods and chemicals used in the control of vegetation.

Freshwater mussels are highly sensitive to a suite of chemicals because of their sessile nature and exposure to sediment and water. Other life history characteristics, including the parasitic larval stage and the benthic juvenile stage, may increase exposure risks during these more sensitive life stages. Activities that disturb sediment or other aquatic habitat also have the potential to impact freshwater mussels.

As part of our literature review, we identified several studies that discuss toxicological impacts of several of Washington's currently registered chemicals (attached). In some cases, freshwater mussels have been found to be many times more sensitive to chemicals than other tested invertebrates, and we highlight this research so that the effects of these chemicals can be more fully evaluated with regards to their effects on Washington state sensitive, declining invertebrates. It is also important to note that many herbicides have not been evaluated for their effects on aquatic invertebrates, mollusks, or specifically freshwater mussels. Where research has not been conducted on freshwater mussels or research suggests potential negative effects, recommendations for mitigation should explicitly discuss avoidance of use near mussel beds or populations.

Additionally, freshwater mussels are covered by the Hydraulic Project Approval permit. Although the current SEIS document mentions fish and wildlife when discussing the need for an HPA as part of any vegetation management activity, these sections should also explicitly mention freshwater mussels. Activities that require an HPA have the potential to impact freshwater mussels as much as or more than fish, given their sessile nature and sensitivity to disturbance. When discussing activities requiring an HPA, a discussion of the possible effects of such activities on freshwater mussels should be included. For example, suction harvest is discussed as a potential alternative method of vegetation management, but a recent white paper by the Pacific Northwest Native Freshwater Mussel Workgroup reviews concerns associated with use of suction dredge mining equipment. Although these activities differ, the impacts of alteration of stream or lakebed habitat and sensitivity of mussels to disturbance is relevant. A recent study by Mageroy et al. (2017) has also identified concerns associated with the effects of rotoation methods on a native species of freshwater mussel.

Management of vegetation has the potential to improve freshwater mussel habitat, but the effects of these and other vegetation control practices should be more fully evaluated for freshwater mussels in the draft SEIS. More generally, the document should discuss the need to avoid and mitigate these activities if they occur near freshwater mussel beds.

Please see the original full text of this comment for specific references given regarding effects of herbicides and adjuvants on freshwater mussels or related species.

Response: Thank you for your comment. Ecology agrees that more information could be provided regarding the impacts to freshwater mussels from the five alternatives and the herbicides, algaecides and nutrient inactivation products evaluated. Changes have been made to the sections indicated below, to incorporate the references provided in the comment.

Change:

- Endothall and derivatives – See sections 4.10.6, 4.10.8 and 4.10.14
- Glyphosate, glyphosate formulations, and commonly used adjuvants – See section 4.10.1 and 4.10.9
- Imazapyr, imazapyr formulations, and commonly used adjuvants – See section 4.10.10 and 4.10.11
- 2, 4-D – See section 4.10.2
- Fluridone-containing herbicides – See 4.10.8
- Triclopyr-containing herbicides – See 4.10.13
- Diver assisted suction harvesting- See 5.1.2
- Rotovation – See 5.1.4

Comment 5:

FROM SEIS – 4.5.2.1 – Environmental Characteristics: Product Use Pattern and Chemistry

“Although they are not persistent in the environment, while in concentrated form or in storage they are considered highly reactive and even explosive, and therefore are normally stored in diluted form to reduce these hazards. PAA and HP are freely soluble (1,000 g/kg), both are highly volatile, with a vapor pressure of 14.8 mm Hg at 25°C (PAA). PAA also has Kow of -0.9, which indicates that PAA is incapable of bioaccumulation or bioconcentration, HP also has no capacity for bioaccumulation or bioconcentration. A vapor pressure for HP was measured at 5 mm Hg at 30°C, which is comparable to the vapor pressure for PAA (ACGIH, 1991; NCBI, 2008, MDEP, 2010).”

COMMENT – Under DOT and GHS (see section 2 of the SDS) GreenClean Liquid 5.0 is classified as a Type-F organic peroxide. Meaning it meets the following criteria: Type-F. Organic peroxide Type-F is an organic peroxide which will not detonate in a cavitated state, does not deflagrate, shows only a low, or no, effect if heated when confined, and has low, or no, explosive power.

Response: We agree that product formulations containing PAA and hydrogen peroxide can have different reactivity characteristics than the technical grade product. The Final SEIS will be modified as indicated below.

Change: The information provided in the comment was added to section 4.5.2.1

Comment 6:

FROM SEIS – 4.5.2.3 Field Surveys and Investigations

“Several studies report on the efficacy and relatively low toxicity of HP (as summarized by MDEP 2010) when used at high concentrations to treat parasites in farmed or hatchery fish for very short time periods (i.e., typically 1 hour or less). Some studies found, however, that toxicity of HP appears to be temperature-related. For example, one study (Kierner and Black, 1997) concluded that HP at these high concentrations should not be applied to waters at water temperatures higher than about 14°C due to potentially much-increased toxicity; the cause of this disparity is unknown. They recommend that HP water treatments would best be conducted during winter for this reason, although lakes and ponds in the Northwest typically experience algal blooms during summer months when these waterbodies are much warmer, often exceeding temperatures of 21°C or more. Nonetheless, based on this finding it appears that application of high concentrations of hydrogen peroxide-based products during warmer weather may not be prudent, assuming the concentrations are comparable, even for short periods of time, due to this elevated temperature-related toxicity.”

COMMENT – Speaking for the use patterns observed throughout the rest of the country, most applications of this product are performed using low rates (3-7 gallons per acre foot on fractions of an entire waterbody, either as a surface treatment for algae/cyanobacteria (as planktonic “algae”) or along lake margins for filamentous algae/cyanobacteria or cyanobacterial scums. (where the max rate is 28.5 gallons per acre-foot are not utilized except for the case of small spot treatments of high density/biomass of algae). Toxicity from applications in warmer temperature waters have not been observed nor reported when the product has been used according to the label.

Response: We agree that use patterns can affect whether or not application of a pesticide has negative environmental impacts. Language will be included in this section describing the typical observed use pattern for this active ingredient.

Change: The information provided in the comment was added to section 4.5.2.3.

Comment 7:

FROM SEIS – 4.5.3.1 Earth

“Soil and Sediments PAA and HP are proposed for treatment to ponds, lakes, and other water bodies in Washington State for one-time “shock treatments” to remove algae from the water column, thus improving water quality. This material is highly soluble and not persistent in water soils, or sediments, or the water column. Accordingly, treatments using PAA and HP as algaecides would not be expected to cause or be associated with adverse effects to lake sediments.”

COMMENT – Per the labelling of GreenClean Liquid 5.0 – this product is labelled for treatment of algae, bacteria (including Cyanobacteria), and fungus. It has a 48-hour retreatment interval for general use. Most uses for this product will likely not be entire lake volume treatments. In many cases the product may be utilized for the treatment of the upper strata (or other) of the water

column for cyanobacteria. It may also be utilized for the repeat treatment of filamentous algae and cyanobacteria as surface floating mats or around a shoreline.

Response: We agree that this active ingredient has the potential to be applied to control algae and cyanobacteria more than one time per year.

Change: The reference to “one-time ‘shock treatments’” has been removed from section 4.5.3.1 – Soils and Sediments.

Comment 8:

FROM SEIS – 4.5.2.4 Toxicological Profile

Avian Toxicity - No avian toxicity tests were identified as part of the literature review, although the labels (BioSafe 2008, 2016) specify that PAA and HP products are toxic to birds.

COMMENT – To be clear – this statement “toxic to birds” is in reference to the product as a concentrate. EPA ecotoxicity testing of the product involves the exposure of birds to the concentrate and not the diluted product or the product as it is labeled for application to surface waters. When applied according to the label the product has little to no chance of harming birds.

Response: We agree that it is important to differentiate between toxicity of the concentrated product and the toxicity of the diluted product as it would be used in the environment. This clarification will be made in the section indicated below.

Change: Clarification was made to section 4.5.2.4 – Avian Toxicity

Comment 9:

FROM SEIS – 4.5.4.1 Use Restrictions

“It is further recommended to not apply PAA-containing algicides directly to treated, finished drinking water reservoirs or other sources (BioSafe, 2016)”

COMMENT – BioSafe Systems would like to assure that WA DOE is aware and adds to the statement that the products are NSF/ANSI 60 Certified for potable water reservoir treatment and to distinguish “Finished Drinking Water Reservoir” (water that has been treated and in storage), from a surface water reservoir/lake that contains water that will eventually be drawn into a potable water facility for treatment and processing.

Response: We agree it is an important distinction to make between a finished drinking water reservoir and a surface water reservoir used for potable water.

Change: The clarification was made to section 4.5.4.1.

Comment 10:

FROM SEIS – 4.5.4.2 Swimming and Skiing and 4.5.4.3 Irrigation, Drinking and Domestic Uses
“Swimming and Skiing- PAA and HP may be acutely toxic to humans either via oral or inhalation exposures (see above discussion regarding General Ecotoxicity Profile in Section

4.5.2.4), although these materials are widely used in the food production industry for a variety of purposes. Thus, as long as in-water treatments are administered in accordance with label specifications, and no recreational exposures are allowed immediately following treatments, impacts to swimming or other recreational aquatic activities are not expected. Moreover, Ecology prohibits treatments with pesticides that have water use restrictions on the FIFRA label that would restrict public water use during the opening week of fishing season or during tribal fisheries, WDFW Free Fishing Weekend, Memorial Day weekend, Independence Day weekend, and Labor Day weekend. Ecology further requires that permittees must minimize treatments that restrict public water use during weekends.”

“Irrigation, Drinking and Domestic Uses – As noted in above in the Section 4.5.3.2, there are no registered or anticipated residential applications for these materials, which further diminishes the likelihood of adverse exposures or the need for mitigation associated with drinking water.”

COMMENT – There are no EPA restrictions on the use of GreenClean Liquid 2.0/5.0 in water intended for potable water (drinking), irrigation, livestock watering, or recreational use.

Response: We agree that the current GreenClean Liquid 2.0/5.0 label, as of the time of this writing, does not indicate any water use restrictions for potable water (drinking), irrigation, livestock watering, or recreational use. However, we permit active ingredients rather than products, because we cannot ensure that a product formulation and label will remain the same through the course of the permit issuance. Because of this, we wrote the SEIS to evaluate the active ingredient and do not rely upon FIFRA label language when evaluating potential impacts.

Comment 11: A more thorough analysis of existing literature and potential adverse effects to Endangered Species Act listed species and other sensitive aquatic biota is needed. The Service only became aware of this SEIS recently, and would need more time to review and comment in more detail. Thus, at this point, we would support Alternative 2, No Action.

Response: This draft SEIS evaluates the potential risks from the use of herbicides, algaecides, and nutrient inactivation product to aid in determining whether they are appropriate for use under permit coverage. A determination of whether to add a specific herbicide, algaecide or nutrient inactivation product to either the Aquatic Plant and Algae Management or Aquatic Noxious Weed Control NPDES General Permits will be made at a later time. If Ecology determines that it is appropriate to add any of the reviewed chemicals to either of the two permits, it will be through a permit modification or reissuance process that will include an opportunity for the public to review and comment on the draft. Potential impacts to endangered species were covered in this draft SEIS. The comment received did not provide specifics on which sections or species the USFWS would like to see more information. As a Supplemental EIS, information provided in previous EIS’s is not duplicated, including analysis of impacts to endangered species.

The USFWS was sent a notification letter on May 8, 2017, which represented the beginning of the 30-day comment period, with information on the public review of draft for this SEIS. If you would like additional notice of when aquatic pesticide permits and related documents are available for draft review please sign up for the Aquatic Pesticide Permit Listserv at <http://listserv.wa.gov/cgi-bin/wa?A0=ECY-AQUATIC-PESTICIDE-PERMIT>.

All EIS are required to include the no-action alternative, however, this being a Supplemental EIS means that NPDES discharge permits are already in place that allow the use of aquatic pesticides for the management of aquatic plants and algae. Ecology does not have information that would give us cause to revoke either of these permits, which would be required to follow the no action alternative. Furthermore, if no action was taken to manage aquatic noxious weeds and toxic algae, there would be negative impacts to the environment, including potential impacts to endangered species.

Comment 12: The addition of Green Clean 5.0 to those products currently available for algae control in Washington State would provide an additional exceptional tool to control toxic algae blooms. Currently all of the peroxide based materials registered in WA are granular formulations that are cumbersome to use and difficult to apply within any specific area of the water column. This new liquid formulation promotes safer easier application, better delivery within the water column and most importantly far superior control than the granular formulations. Use of this product in Washington State would have provided the residents residing around Summit Lake a safe and easy solution to their ongoing total use water ban now exceeding over 30 days because of toxic lake conditions. All of these property owners concerns and devaluation in property values for not having a safe protected water supply could have been resolved quickly with the use of this product. Green Clean 5.0 supports no water use restrictions similar to the other peroxide based formulations, is active in the water column for only a few hours and breaks down to simply basic elements of life. Northwest Aquatic Ecosystems strongly recommends that the Department of Ecology approve statewide use of this product ASAP. Green Clean 5.0 is the first new algaecide formulation manufactured in many years. Regions throughout the United States already support and have approved this products use. Please approve Green Clean 5.0 for use in Washington State so that lake residents have another tool to fight toxic algae blooms and maintain safe recreational waters.

Response: This draft SEIS evaluates the potential risks from the use of herbicides, algaecides, and nutrient inactivation product to aid in determining whether they are appropriate for use under permit coverage. A determination of whether to add a specific herbicide, algaecide or nutrient inactivation product to either the Aquatic Plant and Algae Management or Aquatic Noxious Weed Control NPDES General Permits will be made at a later time. If Ecology determines that it is appropriate to add any of the reviewed chemicals to either of the two permits, it will be through a permit modification or reissuance process that will include an opportunity for the public to review and comment on the draft.

Comment 13: Notify landowners via email/text/written notification that includes pictures of noxious weeds so they can pull and destroy it themselves, maybe provide an incentive such as property tax reduction, or a check.

Response: Ecology does not direct noxious weed control efforts and as a result, coordinating noxious weed control work is outside of our authority. To learn more about noxious weed identification, control, and laws please visit the Washington State Noxious Weed Control Board's webpage (<http://www.nwcb.wa.gov/>).

Comment 14: Instead of paying someone to walk our waterways while carrying cancer causing herbicides and spraying and poisoning our water and environment, have them carry a basket and shovel and pull the weeds instead.

Response: The Draft SEIS that was available for public comment and review is neither a National Pollutant Discharge Elimination System (NPDES) discharge permit or a regulatory document, rather, it is meant to inform and guide future versions of the Aquatic Plant and Algae Management and Aquatic Noxious Weed Control NPDES General Permits. Neither this SEIS nor the Department of Ecology directs individuals or entities to use herbicides when managing aquatic plants and algae. This draft SEIS evaluates the potential risks from the use of herbicides, algaecides, and nutrient inactivation product to determine whether they are appropriate for use under permit coverage.

Comment 15: Suggest changing the nomenclature from Rinskor to common name of the active ingredient (florpyroxifen-benzyl) or to the tradename Procellacor.

Response: We agree that the use of the common name of the active ingredient, florpyroxifen-benzyl, is most appropriate.

Change: Throughout the document all references to Rinskor was changed to florpyroxifen-benzyl.

Comment 16: Suggest updating the anticipated timing for the publication of the EPA Risk Assessment for Procellacor and the anticipated EPA registration of Procellacor.

Response: Ecology agrees to update the expected timeframe for release of these two documents.

Change: Changes were made to section 4.3.1.

Comment 17: Incorporate the provided preliminary results from the University of Washington study on the toxicological properties of Procellacor when used in salmon bearing waters.

Response: Thank you for providing these preliminary results. Ecology will incorporate reference to these preliminary results in the FSEIS.

Change: Changes were made to section 4.3.2.5 – Fish Ecotoxicology.

Comment 18: Add the labelled rate for Oasis (topramezone).

Response: Ecology agrees to make the requested addition of information regarding the pesticide active ingredient topramezone, formulated as the product Oasis.

Change: Changes were made to section 4.4.2.1.

Comment 19: Include the fact that Oasis (topramezone) has shown activity on fluridone resistant biotypes of dioecious hydrilla in Florida.

Response: Ecology agrees to make the requested addition of information regarding the pesticide active ingredient topramezone, formulated as the product Oasis.

Change: Changes were made to section 4.4.2.1.

Comment 20: Clarify that Sonar (fluridone) label does not allow a single application to exceed 20 ppb when used within one quarter mile of an active potable water intake.

Response: Ecology agrees to make the requested addition of information.

Change: Changes were made to section 4.10.8.

Comment 21: The flocculant layer formed by alum creates a physical barrier that can have negative impacts to benthic organisms.

Response: Thank you for your comment. We were not able to identify research that looks at this specific concern. The comment did not provide a reference to support this assertion. The flocculant layer formed may act as a physical barrier to benthic organisms, but we were not able to locate information that documents those impacts. We would anticipate that the formation of a physical barrier from the flocculant layer, and any subsequent impacts, would result from treatment of alum, calcium hydroxide/carbonate, and lanthanum-clay.

Comment 22: The commenter recommends using a newer citation, provided, for alum and associated reports on Alzheimer's disease.

Response: The citation will be included.

Change: Changes were made to section 4.6.2.4.

Comment 23: The safe upper limit of alum in the water is given as 50 mg/L. Some of the LC₅₀ values given for fish are below the 50 mg/L mark.

Response: The units were mistakenly stated as mg Al/L rather than µg Al/L. Clarification was provided in this section.

Change: Changes were made to section 4.6.2.4.

Comment 24: The statement on alum's impacts to surface water does not seem in line with the results. The impacts described would be difficult to classify as minimal and rapidly recovered.

Response: This section indicates that as a result of alum application the recovery from the described impacts began within several days post treatment and by two months post treatment zooplankton levels were greater than they were pretreatment. This indicates that impacts were not so severe that they did not recover within a fairly short duration. We do understand that this description of the potential impacts may not match others interpretation of minimal impacts and rapid recovery.

Comment 25: The discussion on alum makes the product sound pesticidal, which should require a Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) product label and maximum use rates.

Response: Clarification to indicate that alum is not directly toxic but rather acts as a nutrient inactivation product was added to the sections indicated below.

Change: Changes were made to sections 4.6.3.4 and 4.6.3.6.

Comment 26: Address the addition of sulfate to the waterbody through alum treatments.

Response: Clarification that the use of alum may add excess sulfate to the waterbody was made to the section indicated below. Please also see comment #1.

Change: Changes were made to section 4.6.3.7.

Comment 27: Does alum have a FIFRA label specifying use restrictions.

Response: Alum is not a pesticide and therefor does not have a FIFRA product label associated with its use. Alum is a nutrient inactivation product that removes phosphorus from the water column similar to calcium hydroxide/carbonate, lanthanum-clay, and iron.

Comment 28: The reduction of zooplankton as a result of alum treatment should be addressed in the endangered species section along with the potential for fish toxicity.

Response: We agree that impacts to zooplankton should be mentioned in the section on fisheries since they are an important prey source for many fish. Clarification was provided in the section indicated below.

Change: Changes were made to section 4.6.4.4.

Comment 29: Why is it recommended that no swimming or primary contact recreation be allowed immediately following a Phoslock treatment.

Response: We agree that as long as the application follows the label instructions, based upon available data, there is no indication of a need to restrict swimming or primary contact recreation following a lanthanum-clay treatment.

Change: Changes were made to section 4.9.3.2.

Comment 30: In reference to Flumioxazin, information on chronic toxicity and endocrine disruption should be required for metabolites that have been found at greater than 10% of parent compound levels in both water and sediments over 182 days after treatment before being permitted.

Response: The reference provided with this comment assesses a terrestrial application scenario. The reference does indicate that there are metabolites found at greater than 10% of the parent compound levels in soils. However, the reference also states, "Due to the extensive metabolism of flumioxazin in plant and animal tissues, and as finite residues are not likely to be encountered when flumioxazin is used according to Good Agricultural Practice, it is appropriate to set the residue definition as the parent compound only: Flumioxazin." Based upon this statement and a review of the reference, it does not appear that the reference provided indicates a need to require chronic toxicity and endocrine disruption testing for metabolites found at greater than 10% of the parent compound level in water and sediments.

Reference: Australian Pesticides and Veterinary Medicines Authority. 2003. *Evaluation of the New Active Flumioxazin in the Product Pledge 500 WG Herbicide*. ISSN1443-1335.

The use pattern that the Aquatic Plant and Algae NPDES General Permit covers is the discharge, to surface water, of Flumioxazin to manage aquatic plants. Chronic exposure to Flumioxazin metabolites, and there for chronic toxicity, should not occur under this use pattern. The Clipper™ label allows applicators to retreat the same area up to six times in a year, but only at 28-day intervals. The label further recommends early season treatments for the best efficacy.

The following is from the 2012 SEIS for Flumioxazin: "EPA concluded that the combined short-term food, water, and residential exposures to flumioxazin can result in a MOE of 690 for adults and 470 for children (Flumioxazin Human Health Risk Assessment for a Proposed Aquatic Use). Because EPA's level of concern for flumioxazin is a MOE of 100 or below, these MOEs are not of concern. EPA concluded that intermediate aggregate risks are identical to the short-term aggregate risks, since endpoints for short-term and intermediate-term risk assessments are the same, and because residential exposure durations are expected to be short-term in nature. Based on

their risk assessments, EPA concluded that there is a reasonable certainty that no harm will result to the general population and to infants and children from aggregate exposure to flumioxazin residues.”

(<https://fortress.wa.gov/ecy/publications/documents/0010040addendum1.pdf>)

Comment 31: Flumioxazin is described as highly toxic to marine invertebrates. Studies of its impacts on marine invertebrates should be included unless it is restricted from use near marine sites.

Response: Flumioxazin is permitted for use under the Aquatic Plant and Algae Management NPDES General Permit, which only allows for discharge to freshwaters of the state of Washington. Additionally, the Clipper product label prohibits use in the intertidal or estuarine areas. Clarification that Flumioxazin is meant for application to freshwater only was made to the section indicated below.

Change: Changes were made to section 4.10.7.