# Final Environmental Impact Statement: Irrigation System Aquatic Weed Control

August 16, 2023

Water Quality Program
Washington State Department of Ecology
Olympia, Washington

# Cover Memo

July 12, 2023

## Irrigation System Aquatic Plant and Algae Control
## Final Environmental Impact Statement

### Environmental Review

The Washington Department of Ecology (Ecology) is issuing this Final Environmental Impact Statement (FEIS) for the reissuance of the Irrigation System and Aquatic Weed Control National Pollutant Discharge Elimination System (NPDES) general permit. The proposed action analyzed by this EIS is the discharge of aquatic herbicides and algaecides into irrigation systems for aquatic plant and algae control. By reference, this EIS incorporates other EIS documents that assess discharges of aquatic herbicides to bank areas where overspray and other incidental discharges will occur. The EIS analyzes the potential impacts of the proposed action and alternative management methods for controlling aquatic plants and algae in irrigation systems. Consistent with our Wasington State Environmental Policy Act (SEPA) Determination of Significance and Scoping from April 21, 2017 (SEPA Register number 201702057[1]), this FEIS has been prepared to satisfy SEPA.

### Washington Department of Ecology Action Required

The proposal requires coverage under a NPDES and State Waste Discharge permit. The Washington State Department of Ecology (Ecology) proposes to issue coverage under a general permit to Irrigation Districts and similar entities requesting coverage under the permit. The duration of the proposed NPDES general permit is 5 years.

### Other Permits and Approvals Required

Applicators are required to obtain a pesticide applicator's license with aquatic endorsement from the Washington State Department of Agriculture (WSDA) for the use of aquatic labeled herbicide and algaecide products. Authorization from the irrigation district board or rate payers may also be required.

### Public Review and Comment Opportunities

Ecology accepted written comments on the Draft EIS from ***Wednesday, January 18, 2023,* through *Monday, March 20, 2023,* at 11:59 pm.** The Draft EIS was available on Ecology's website[2] by end of day on Wednesday, January 18, 2023. Ecology also held two public workshops and hearings on February 21, 2023, and February 22, 2023. No oral testimony was given at these hearings.

The draft ISAWC permit was also available on the Ecology website for review and comments.

The final ISAWC permit can be found on the Ecology website by end of day on July 19, 2023.

The full text of the comment received for the Draft EIS is available on ecomments[3].

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[1] https://apps.ecology.wa.gov/separ/Main/SEPA/Record.aspx?SEPANumber=201702057

[2] https://ecology.wa.gov/Regulations-Permits/Permits-certifications/Aquatic-pesticide-permits/Irrigation-system-aquatic-weed-control

[3] https://wq.ecology.commentinput.com/comment/extra?id=caV6F

## The Proposal and Alternatives

The Washington Department of Ecology is reissuing the NPDES general permit for a period of 5 years to allow discharge of herbicides and algaecides for management of aquatic plants and algae in irrigation supply systems.

The Final EIS evaluates four alternatives for implementing the proposed action of controlling aquatic plants and algae in irrigation supply systems:

1. No Action
2. Physical, Mechanical, and Cultural Methods Only
3. Use of Chemical Methods Only
4. Use of an Integrated Pest Management (IPM) Approach

Alternative 4, IPM, is the preferred alternative, though Ecology does not have the authority to require implementation of IPM. Irrigation Districts would combine the use of chemical treatments with existing manual and mechanical methods to achieve the most efficacy while minimizing use of herbicides and algaecides in the aquatic environment.

## Key Environmental Issues

The Washington Department of Ecology (Ecology) Water Quality Program, and Shorelands and Environmental Assistance (SEA) Program administer the State's Water Pollution Control Act (Chapter 90.48 RCW). Under this authority, Ecology must balance competing designated beneficial uses of water, and avoid impairment of designated uses, or long-term alteration of the physical, chemical, or biological properties of waters of the state.

Vincent McGowan, P.E.
Water Quality Program Manager
Washington State Department of Ecology

**Table 1:EIS Summary Information**

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| Project Title: | Irrigation System Aquatic Weed Control General Permit |
| Project Description: | The proposed action is the issuance of a discharge permit to allow the use of herbicides and algaecides for control of aquatic plants and algae in irrigation supply systems. Issuance of a 5-year National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permit by the Washington Department of Ecology (Ecology) is required to authorize the use of herbicides and algaecides in waters of the state of Washington.<br>This is a non-project proposal under the Washington State Environmental Policy Act (SEPA) rules. The Environmental Impact Statement (EIS) will be integrated with on-going agency planning and permitting processes for aquatic herbicides and algaecides and inform permit development. |
| Purpose and Objectives: | Ecology assessed potential significant impacts from developing and reissuing a discharge permit conditionally authorizing herbicide and algaecide use to manage aquatic plants and algae in irrigation water supply systems. The objective of conditionally authorizing herbicide and algaecide discharge is to allow irrigation districts the use of a tool for effective plant and algae management and prevent unacceptable impacts to all designated beneficial uses of natural receiving waterbodies. |
| Alternatives Considered: | This EIS identifies and analyzes reasonable alternatives that could be implemented to achieve the objectives of the proposal, as follows:<br>1. No Action<br>2. Physical, Mechanical, and Cultural Methods Only<br>3. Use of Chemical Methods Only<br>4. Use of an Integrated Pest Management (IPM) Approach<br>Alternative 4, IPM, is the preferred alternative (though Ecology does not have authority to require IPM implementation) where Irrigation Districts would combine the use of chemical treatments with existing manual and mechanical methods to achieve the most efficacy while minimizing use of herbicides and algaecides in the aquatic environment. |

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| Project Proponent: | Washington State Department of Ecology<br>Water Quality Program<br>300 Desmond Drive<br>PO Box 47696<br>Olympia, WA 98504-7696 |
| Lead Agency: | Washington State Department of Ecology<br>Water Quality Program<br>300 Desmond Drive<br>PO Box 47696<br>Olympia, WA 98504-7696 |
| Ecology File No. | PUBLICATION NUMBER - 23-10-032 |
| SEPA Responsible Official: | Vincent McGowan, P.E.<br>Water Quality Program |
| Contact Person, and Person to Whom to Direct Comments: | Danielle Edelman<br>Water Quality Program<br>Phone: (360) 763-2597<br>Fax: 360-407-6426<br>danielle.edelman@ecy.wa.gov |
| Permits and Approvals Required: | The list below reflects State and local permits and licenses that may be required for the chemical control of aquatic plants and algae in irrigation supply systems. Requirements may change or may vary for a particular Irrigation District. Applicants should check with State resource agencies and local and Federal government agencies to determine actual permit requirements for their particular project.<br>• **Washington State Department of Ecology:** Coverage under a NPDES and State waste discharge general permit<br>• **Washington State Department of Agriculture:** Pesticide applicators license with aquatic endorsement for the application of aquatic labeled herbicide and algaecide products.<br>• **Local Governments (e.g. City, County):** Shoreline permit (possible in some locations with natural waterbodies converted to irrigation canals). |

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| EIS Authors and Principal Contributors: | Chris Dudenhoeffer, Danielle Edelman, Angela Zeigenfuse, Ecology Water Quality Program |
| Draft EIS Date of Issue: | January 18, 2023 |
| Final EIS Date of Issue: | August 16, 2023 |
| Draft EIS Comment Period: | January 18, 2023 through March 20, 2023 at 11:59 p.m. |
| Address Comments to: | Danielle Edelman<br>Washington State Department of Ecology<br>Water Quality Program<br>300 Desmond Drive<br>PO Box 47696<br>Olympia, WA 98504-7696<br>360-763-2597<br>danielle.edelman@ecy.wa.gov |
| Location of Reference Material : | Washington State Department of Ecology<br>Water Quality Program<br>300 Desmond Drive<br>Olympia, WA 98503 |
| Availability: | A digital version of this EIS is available on Ecology's Irrigation System Aquatic Weed Control General Permit webpage[4]. |
| Schedule for Implementation: | The objective is to have the reissued NPDES and State Waste Discharge General Permit in-place by Summer 2023. |

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[4] https://ecology.wa.gov/Regulations-Permits/Permits-certifications/Aquatic-pesticide-permits/Irrigation-system-aquatic-weed-control

Issuance of a general permit and supporting documentation such as this EIS is considered a significant agency action. Such actions have data quality standards. RCW 34.05.272[5] requires that Ecology identify and categorize sources of information used in developing the action (permit). The legislative intent is that:

"*(1) The legislature finds that it is critically important that scientific information used to inform public policy be of the highest quality and integrity. Furthermore, the legislature recognizes that a public benefit is derived from greater transparency as to what scientific information, data, or records are being used to inform public policy or relied upon in agency decision making.*"

Information in this EIS was drawn from a variety of sources and the citations provided come from research that was performed for various purposes that range from dissertations, to the advancement of the body of knowledge in scientific journals, to a response to Irrigation Districts concerns. Citations can be grouped into three categories reflecting various levels of scientific rigor:

1. Peer reviewed and published scientific journal articles.
2. Grey literature, which includes: Agency technical reports, consulting company white papers, websites, and unpublished study results.
3. Anecdotal observations and personal communications.

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[5] https://app.leg.wa.gov/RCW/default.aspx?cite=34.05.272

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# Summary

The Washington Department of Ecology (Ecology) is proposing to reissue a combined National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge (SWD) General Permit conditionally authorizing a list of herbicides and algaecides for the control of aquatic plants and algae in and around irrigation systems. This does not include homeowner irrigation of small gardens and lawns. The proposed permit would authorize activities that result in the discharge of the aquatic herbicides and algaecides to waters of the state.

Ecology issues general permits in place of a series of individual permits when the permitted activities are similar. All agencies, organizations, and individuals that receive coverage under the general permit must comply with the same terms and conditions.

As lead agency under the Washington State Environmental Policy Act (SEPA), Ecology has made the determination that issuance of a general permit conditionally authorizing use of herbicides and algaecides for management of aquatic plants and algae in irrigation systems may have probable significant environmental impacts to waters of the state. This determination requires that an Environmental Impact Statement (EIS) be prepared to assess the probable significant impacts.

The preferred alternative for managing aquatic plants and algae in irrigation systems is an Integrated Pest Management (IPM) approach that uses the most effective combination of physical and mechanical practices, chemical methods, and adaptive management elements. However, Ecology does not have authority to require implementation of IPM in a discharge permit. Discharge permits only regulate conditionally authorized discharges or activities that cause a discharge. Other alternatives analyzed include No Action, Physical, Mechanical, Biological, and Cultural Methods Only, and Chemical Methods Only. Several methods used to control aquatic plants and algae in irrigation systems were found to be impractical for the proposed action. These are described in Final EIS Proposed Action and Alternatives, and were eliminated from further consideration.

## Introduction and Problem Formulation

### Irrigation Systems

The purpose of the irrigation systems assessed in this EIS is to transport water from a source waterbody (surface or groundwater) to a location where the water will be used to provide water to agricultural crops. This does not include small gardens, or ornamental lawns (house yards, building lawns), that are not supplied water by an irrigation district.

Operation of an irrigation system begins with water withdrawal from a natural surface or ground water. For surface waters, there is an intake structure which diverts water flow. For ground water, a well, or series of wells, is pumped to pull water to the surface. Once water is diverted from the natural waterbody, a series of, usually open-topped, canals and channels, and pipes is used to transport water from the diversion point to the location where the water is used (agricultural crop fields). After the water is used on an agricultural field, the return flow, or tailwater, is recaptured is and collected. Collected water is transported back, and released into, a surface waterbody.

**Irrigation Districts**

There are several types of special purposed districts that may be created via provisions of State law such as lake management districts, mosquito control districts, and irrigation districts. Such districts are created to serve a specific purpose, and may have special authorities, for example taxing authority to provide funding for the purpose of the district. Chapter 87 RCW describes the creation, powers, and duties, of irrigation districts. RCW 87.03.010 states:

"*An irrigation district may be organized or maintained for any or all the following purposes:*

*(1) The construction or purchase of works, or parts of same, for the irrigation of lands within the operation of the district.*

*(2) The reconstruction, repair or improvement of existing irrigation works.*

*(3) The operation or maintenance of existing irrigation works.*

*(4) The construction, reconstruction, repair or maintenance of a system of diverting conduits from a natural source of water supply to the point of individual distribution for irrigation purposes.*

*(5) The execution and performance of any contract authorized by law with any department of the federal government or of the state of Washington, for reclamation and irrigation purposes.*

*(6) The performance of all things necessary to enable the district to exercise the powers herein granted.*"

## Purpose and Need to Which the Proposal is Responding

Irrigation districts are created to transport and deliver water for agricultural crop use. Crop product depends on delivery of a consistent flow of water. When water flow is inhibited or impeded, the irrigation district must perform maintenance on the canal system to restore the full flow of transported water. Aquatic and riparian plants, and algae that grow in irrigation canals can greatly impede the flow of water. The plants and algae must be removed to restore water flow.

Irrigation districts need methods to remove aquatic plants and algae from canal systems to restore water flow. One method, which is the method Ecology has the authority to regulate under discharge permit, is the use of herbicides and algaecides.

## Description of the Proposed Action

The Washington Department of Ecology proposes to reissue a combined NPDES and SWD general permit for a period of 5 years to conditionally authorize the discharge of herbicides and algaecides to irrigation systems. The herbicide and algaecide products used under permit must have a Product Label that allows aquatic use within an irrigation system.

The general permit will help Ecology to:

- Mitigate and condition the aquatic use of herbicides and algaecides,
- Monitor for impacts to natural receiving waters,
- Record herbicide and algaecide use rates and locations,
- Ensure that notifications and postings occur in areas where the public or local residents may access the treated areas.

## Summary of Alternatives Considered

This Final Environmental Impact Statement (FEIS) identifies and analyzes probable significant environmental impacts, alternatives to herbicide and algaecide use for management of aquatic plants and algae, and potential mitigation measures for each alternative. The potential significant environmental impacts and mitigation measures for each alternative are described in Proposed Action and Alternatives. The information provided in this FEIS will be used by Ecology to assess reasonable alternatives and identify appropriate mitigation requirements for the proposed chemical applications for potential inclusion in the general permit. The alternatives evaluated include:

1. No Action
2. Physical, Mechanical, and Cultural Control Methods Only
3. Herbicide and Algaecide Use Only
4. Integrated Pest Management

This FEIS also describes other alternatives considered and eliminated from detailed evaluation (see Proposed Action and Alternatives).

### Alternative 1: No Action

Under this alternative, no actions would be taken to manage aquatic plants or algae in irrigation systems. All current methods of control would cease. Logically, if a human made structure is not maintained, it begins to degrade and eventually fail. Loss of the use of the structure as well as the degradation and failure may have significant environmental impacts.

### Alternative 2: Physical, Mechanical, and Cultural Control Methods Only

Under this alternative, only physical, mechanical, or cultural methods of aquatic plant and algae management would continue. Practices may include:

- Harvesting/removal with excavator
- Chaining
- Dredging
- Drawdowns
- Physical bottom barriers (e.g. replacement of earthen canals with concrete lined canals or with a pipe system)

In natural surface waterbodies, use of physical or mechanical control methods are habitat modification which is generally regulated by WDFW through a Hydraulic Project Approval (HPA).

2004 Triclopyr EIS[6], starting page 26.

The 2017 supplemental EIS for aquatic plant and algae management using herbicides, algaecides, and phosphorus sequestration products[7] has some information on physical, mechanical, and cultural management methods. See section 5.0-5.2. Information from this

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[6] https://fortress.wa.gov/ecy/publications/documents/0410018.pdf

[7] https://fortress.wa.gov/ecy/publications/documents/1710020.pdf

section is drawn upon for potential significant adverse impacts and mitigations where the method is appropriate for use in an irrigation system.

Some information may be out of date, but physical, mechanical and cultural management methods and their impacts and mitigation are also discussed in the 2000 supplemental EIS[8] in Section V. Some methods are not appropriate for use in irrigation systems such as diver dredging or using bottom barriers made of textile materials.

In summary, physical, mechanical, and cultural methods of management options remove the plant or algae mass from the irrigation system, or provide a barrier to the target organism growing successfully. Manual methods such as hand pulling and weed rakes are not considered here because these techniques are only feasible on small areas, such around a homeowner dock.

### Bottom Barriers

This method is efficient for small areas of control. There is difficulty installing and maintaining these barriers in a still water system. This method may not be appropriate for a flowing water system. Flowing water may add significant difficulty to keeping the barrier in place. Loose liners may cause blockages of canal infrastructure and additional maintenance and repair. Lining a canal with concrete or piping the canal may be more appropriate.

### Diver Dredging

Divers equipped with SCUBA equipment use a boat mounted suction dredge to remove aquatic plants. Labor and Industries (L&I) rules require that divers have a tender boat available. Dredged material must be appropriately disposed of if it contains noxious weeds. This is a slow process to perform on larger areas, therefore is likely inappropriate for use in an irrigation canal system.

### Mechanical Cutting and Harvesting

This method uses specially designed machinery to cut plant mass off below the surface of the water near the roots. Because the aquatic plant mass is essentially being mowed, regrowth will occur within a short amount of time. Plant fragments can move downstream and re-root or plug flow control structures causing the need for additional maintenance. Some additional turbidity in the waterbody is expected. Material removed from the canal must be appropriately disposed of if it contains noxious weeds.

### Rotovation

This method uses specially designed underwater rototiller systems that are used to uproot aquatic vegetation. This is not a suitable method of algae control. These systems have limited reach and may not reach the distance required to cover an entire canal. Rotovation will increase turbidity in the system. Plant fragments and algae that are uprooted during the operation will move downstream unless removed from the canal system. Some plant fragments have the ability to re-root if not removed. If material is removed from the canal after rotovation, it must be appropriately disposed of if it contains noxious weeds.

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[8] https://fortress.wa.gov/ecy/publications/documents/0010040.pdf

### Alternative 3: Use of Biological Control Agents Only

According to the United States Department of Agriculture (USDA) National Institute of Food and Agriculture[9] a biological control program is: "*Biological control can be defined as the deliberate use of natural enemies - predators, parasites, pathogens, and competitors to suppress and maintain populations of a target pest species (insects, mites, weeds, plant pathogens, and other pest organisms)*."

The USDA Animal and Plant Health Inspection Service[10] has a similar definition: "*Biological control (biocontrol) involves the reduction of pest populations through the use of natural enemies such as parasitoids, predators, pathogens, antagonists, or competitors to suppress pest populations*."

This alternative requires the use of biological control agents only. Biological control agents (e.g. predator or parasitic species) that target pest plant species, and only those species, with minimal/incidental harm to non-target species would be identified, bred, and deployed (released) into irrigation canal systems. Once released, natural predator/prey cycles would balance biological control agent and pest species populations. Additional releases of biological control agents (augmentation) could be made to supplement naturally reproducing populations.

One challenge in using this method is identifying an appropriate species to control the target plant. This could be an issue in canals where many types of plants grow. Another challenge is the limited ability to use supplemental chemical treatments while control species are present in the canal. Many of the chemicals approved under the Irrigation System Aquatic Weed Control General Permit are harmful to aquatic life when applied at effective concentrations.

If there are no previously identified predator species for a target plant or algae, the process to develop an appropriate control species in a lab is lengthy.

### Alternative 4: Use of Herbicides and Algaecides Only

Under this alternative, only herbicides and algaecides would be used to manage aquatic plants and algae. Herbicides would be used within the canal to target submersed and floating plants, and would also be used to manage vegetation growing on canal dykes where overspray or other incidental discharges occur.

The following herbicides and algaecides have been identified as being proposed for use by irrigation districts under this alternative: diquat dibromide, glyphosate, 2,4-D, imazamox, Flumioxazin, copper sulfate, chelated copper, acrolein, dipotassium salt of endothall, mono salt of endothall, xylene, sodium carbonate peroxyhydrate, fluridone, and imazapyr.

In response to comments on the draft Irrigation Permit, the following herbicides and algaecides will not be authorized in the final Permit: 2,4-D, diquat dibromide, flumioxaxin, glyphosate, and imazamox. They are included in the Final EIS as they were still considered as potential chemical treatment methods in the draft Permit, and Ecology may consider including them in a future reissuance of the Irrigation Permit.

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[9] https://nifa.usda.gov/program/biological-control-program

[10] https://www.aphis.usda.gov/aphis/ourfocus/planthealth/plant-pest-and-disease-programs/biological-control-program/ct_biological_control_program

Irrigation districts currently use four primary active ingredients for control of aquatic plants and algae that are assessed in this FEIS: acrolein, copper sulfate, chelated copper complexes, and xylene. Endothall is also used in limited circumstances and was assessed in a previous SEPA document[11] that is incorporated into this FEIS by reference. Additionally, irrigation districts may undertake some ditch-bank weed control similar to noxious weed control (next to water where overspray or dripping into water occurs) and potentially use the same active ingredients as conditionally authorized by the Aquatic Noxious Weed Control General Permit (NOX permit). Active ingredients conditionally authorized for use in the NOX permit were assessed in a previous Supplemental EIS[12], which this FEIS adopts by reference.

All products that include the active ingredients assessed in this and other two EIS documents adopted by reference above that are allowed for use in Washington waters must also have an appropriate aquatic Product Label and be applied by a Washington State Department of Agriculture (WSDA) licensed pesticide applicator with aquatic endorsement. An appropriate Product Label is one that includes the irrigation system use pattern as an allowed use on the label.

### Alternative 5: Integrated Pest Management (IPM)

The IPM Institute of North America[13] defines integrated pest management (IPM) as:

"*. . . a science-based, decision-making process that identifies and reduces risks from pests and pest management related strategies. IPM coordinates the use of pest biology, environmental information, and available technology to prevent unacceptable levels of pest damage by the most economical means, while minimizing risk to people, property, resources, and the environment. IPM provides an effective strategy for managing pests in all arenas from developed agricultural, residential, and public lands to natural and wilderness areas. IPM provides an effective, all encompassing, low-risk approach to protect resources and people from pests*." (quoted from IPM's Frequently Asked Questions webpage[14]).

IPM does not mean only using herbicides and algaecides. It also does not mean using no herbicides and algaecides. IPM focuses on using available information and pest monitoring to determine the most efficacious method, or combination of methods, of pest control at the time, balancing risks/rewards and cost of various pest control methods. This alternative is a combination of alternatives 1 through 4 (no action, physical, mechanical, and cultural practices, biological control agents, and herbicide and algaecide use). Each management method has a place in controlling a target pest.

IPM is considered the preferred alternative for pest management because all pest control methods are considered and used as appropriate. However, Ecology does not have the authority to require IPM in discharge permits. Discharge permits regulate discharges of pollutants which can also translate to regulating activities that generate pollutants. Activities that do not generate discharge of pollutants are not within the scope of regulation under a discharge permit. Any permit Ecology issues conditionally authorizing herbicide and algaecide use in water could be accounted for as part of a larger IPM program.

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[11] https://apps.ecology.wa.gov/publications/documents/0010044.pdf

[12] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

[13] https://ipminstitute.org/

[14] https://ipminstitute.org/faq/

## Summary of Impacts and Mitigation Measures from Alternatives Considered

### Alternative 1: No Action

The 2017 supplemental EIS for aquatic plant and algae management using herbicides, algaecides, and phosphorus sequestration products[15] has some on no action alternatives. Information from this section is drawn upon for potential significant adverse impacts and mitigations where the method is appropriate for use in an irrigation system.

Some information may be out of date, but physical, mechanical and cultural management methods and their impacts and mitigation are also discussed in the 2000 supplemental EIS[16] in Section V. Some methods are not appropriate for use in irrigation systems such as diver dredging or using bottom barriers made of textile materials.

Utilizing only the No Action option for managing algae and plants in irrigation systems potentially leads to the following impacts based on the diminished flow of water, or uncontrolled alterations to irrigation systems from water flow:

- Loss of farmable land due to lack of available surface water flow.
- Loss of water rights/claims by right holders due to inability to access water granted by right or claim.
- Flooding canals and other nearby structures (e.g. homes, roadways).
- Physical damage to, or failure of, canal structures.
- Increased groundwater withdrawal to supplement diminished surface water supplies.

Alternatively, no-action potentially leads to elimination of:

- Herbicides and algaecides directly applied to water for aquatic plant and algae control in the irrigation system.
- Discharges of sediment to natural receiving waterbodies from physical/mechanical methods of aquatic plant and algae management.

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[15] https://fortress.wa.gov/ecy/publications/documents/1710020.pdf

[16] https://fortress.wa.gov/ecy/publications/documents/0010040.pdf

### Alternative 2: Physical, Mechanical, and Cultural Control Methods Only

The 2017 supplemental EIS for aquatic plant and algae management using herbicides, algaecides, and phosphorus sequestration products[17] has some information on physical, mechanical, and cultural management methods. See section 5.0-5.2. Information from this section is drawn upon for potential significant adverse impacts and mitigations where the method is appropriate for use in an irrigation system.

Some information may be out of date, but physical, mechanical and cultural management methods and their impacts and mitigation are also discussed in the 2000 supplemental EIS[18] in Section V. Some methods are not appropriate for use in irrigation systems such as diver dredging or using bottom barriers made of textile materials.

In summary, physical, mechanical, and cultural methods of management options remove the plant or algae mass from the irrigation system, or provide a barrier to the target organism growing successfully. Manual methods such as hand pulling and weed rakes are not considered here because these techniques are only feasible on small areas, such around a homeowner dock.

#### Bottom Barriers

Efficient for small areas of control. Difficulty installing and maintaining in a still water system. May not be appropriate for a flowing water system. Flowing water may add significant difficulty to keeping the barrier in place. Loose liners may cause blockage of canal infrastructure and additional maintenance and repair. Lining a canal with concrete or piping the canal may be more appropriate.

#### Diver Dredging

Divers equipped with SCUBA equipment use a boat mounted suction dredge to remove aquatic plants. Labor and Industries (L&I) rules require that divers have a tender boat. Dredged material must be appropriately disposed of if it contains noxious weeds. This is a slow process to perform on larger areas, therefore is likely inappropriate for use in an irrigation canal system. Material removed from the canal must be appropriately disposed of if it contains noxious weeds.

#### Mechanical Cutting and Harvesting

Use of specially designed machinery to cut plant mass off below the surface of the water near the roots. Similar to how a lawnmower works. Because the aquatic plant mass is essentially being mowed, regrowth will occur within a short amount of time. Plant fragments can move downstream and re-root or plug flow control structures causing the need for additional maintenance. Some addition turbidity in the waterbody is expected. Material removed from the canal must be appropriately disposed of if it contains noxious weeds.

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[17] https://fortress.wa.gov/ecy/publications/documents/1710020.pdf

[18] https://fortress.wa.gov/ecy/publications/documents/0010040.pdf

### Rotovation

The use of specially designed underwater rototiller systems that are used to uproot aquatic vegetation. Not a suitable method of algae control. Limited reach may not reach the distance required to cover and entire canal. Rotovation will increase turbidity in the system. Plant fragments and algae that are uprooted during the operation will move downstream unless removed from the canal system. Some plant fragments have the ability to re-root if not removed. If material is removed from the canal after rotovation, it must be appropriately disposed of if it contains noxious weeds.

**Alternative 3: Use of Biological Control Agents Only**

- Some information may be out of date, but biological control is also discussed in the 2000 Supplemental EIS[19] in Section VI.
- See also:
  - 2004 Triclopyr SEIS[20], page 49.
  - 2017 SEIS[21], page 177.

Release of biological control agents has the possibility of unintended consequences if the agent is not thoroughly assessed prior to release for target pest specificity. Classically used examples of such releases without thorough assessment, with unintended consequences are the Cane Toad (*Rhinella marina*, previously *Bufo marinus*) and mongoose on the Hawaiian Islands. Released to control sugar cane pests, these species have major impacts on non-target native species. While true biological control agents are thoroughly assessed for non-target impacts and tightly regulated, the possibility exists for unintended impacts, but is not considered a probable significant impact for this EIS.

Some target pest species are likely to be non-native and therefore have no natural predators or parasites in the area they become established. In such a case, the impact of relying completely on biological control agents is that no control of the target pest actually occurs. Or the control is minimal and incidental due to native predator or parasite species using the pest species as a target of opportunity rather than as a preferred host. If no approved biological control agents are available for the target pest species then relying only on biological control is the equivalent of the No Action alternative and would have the same probable significant impacts.

The Pacific Northwest Pest Management Handbooks maintains a list of current biological control agents that potentially may be used in Washington[22]. Because biological control agents are very host specific, the list of target species is narrow. This list does not include many plants that are potential pests in irrigation canals (e.g. cattails, grasses, reeds), or algae species. Due to the need of irrigation systems to remove most, or all, plants and algae from the canal systems, use of biological control for all species present is likely impractical and would not achieve the necessary level of control.

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[19] https://fortress.wa.gov/ecy/publications/documents/0010040.pdf
[20] https://fortress.wa.gov/ecy/publications/documents/0410018.pdf
[21] https://fortress.wa.gov/ecy/publications/documents/1710020.pdf
[22] https://pnwhandbooks.org/weed/biological-control/agents-their-roles

### Alternative 4: Use of Herbicides and Algaecides Only

This EIS references previous EIS documents for many of the active ingredients considered in the draft Irrigation System Aquatic Weed Control General Permit. The impacts and mitigation measures for diquat dibromide, glyphosate, 2,4-D, imazamox, Flumioxazin, dipotassium salt of endothall, mono salt of endothall, sodium carbonate peroxyhydrate, fluridone, and imazapyr are referenced from previous assessments. The impacts and mitigation measures for chelated copper, copper sulfate, and xylene are new to this document.

See section 4.0 in the 2017 SEIS[23]:

Acrolein

Chelated Copper Complexes

Copper Sulfate

Xylene

Active Ingredients Assessed in Other EIS Documents (starting with 2,4-D in this document).

Choosing only this method may lead to an increase in herbicide and algaecide use within irrigation systems. In absence of physical, mechanical, or biological control methods, more chemicals may be required to control the growth of plants and algae in canals.

Entities and individuals that use water from irrigation canals are at risk of possible exposure. Permittees are required to maintain strict compliance with water quality standards before water is discharged from the canal into waters of the state, and they are required to post notice of treatments to both water users and the public (in the form of warning signs).

Irrigation systems are private property, and security of the canals and barriers to unlawful entrance are the responsibility of the permittee. Barriers to trespass which may lead to excessive exposure to herbicides and algaecides are not in the scope of the permit.

Irrigation districts coordinate the use of herbicide and algaecide treatments with ratepayers and water users. Water users are notified when treatments occur to avoid harmful exposure and potential damage to crops and landscaping.

Salmonids and other species of concern may be impacted by the active ingredients approved for use under the permit, including residues from treatments. Permittees are required to meet water quality standards and effluent limits at the point of compliance before treated water exits the canal. Permittees must comply with Washington State Department of Fish and Wildlife (WDFW) treatment timing windows when applicable to avoid harming salmonids and other sensitive or endangered species.

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[23] https://fortress.wa.gov/ecy/publications/documents/1710020.pdf

### Mitigation

Irrigation systems are private property. Non-irrigation district individuals who use the system without district authorization are trespassing. The unauthorized use is often unknown to the district, and direct action against trespassing is outside the scope of the permit. For these reasons, mitigation opportunities are limited to permit conditions which encourage permittees to reduce the use of pesticides when possible and maintain strict compliance with Product Labels, treatment timing windows, and water quality standards. Human health and property impacts are mitigated through the notification of treatments to water users and the public.

#### Alternative 5: Integrated Pest Management (IPM) – Preferred Alternative

The 2017 update to the environmental impact statement for aquatic plant and algae management using herbicides, algaecides, and phosphorus sequestration products[24] has a detailed discussion of integrated pest management (IPM). See section 2.0-2.2. Information from this section is drawn upon for potential significant adverse impacts and mitigations where the method is appropriate for use in an irrigation system.

Some information may be out of date, but IPM is also discussed in the 2000 Supplemental EIS[25] in Section III.

The discussion of IPM in the 2017 EIS update applies to the irrigation systems as well. In summary, IPM has to potential to cause any of the impacts summarized in Alternatives 1 through 4 depending on the management option chosen. Because IPM considers the use of all management Alternatives, impacts are varied. The probable adverse environmental impacts that are significant from implementing an IPM strategy will be a mix of impacts from Alternatives 1-4 and the mitigation strategies for the impacts will also be a mix of strategies from the Alternatives. IPM itself is a mitigation strategy because the intent of IPM is to pick the most effective management option, or set of options, for a particular situation that also considers risks to human health and the environment.

However, Ecology cannot require the implementation of IPM through a discharge permit. Permits may regulate the discharge of a pollutant. Therefore, the conditions in a permit must be related to controlling pollutant discharges. Many strategies included in IPM, while encouraged, are not related to discharge of pollutant and therefore not included in a permit or regulated under discharge permit.

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[24] https://fortress.wa.gov/ecy/publications/documents/1710020.pdf

[25] https://fortress.wa.gov/ecy/publications/documents/0010040.pdf

## References

1. Washington State Department of Ecology. *Environmental Impact Statement for Permitted Use of Triclopyr* (Publication No. 04-10-018 revised). May 2004. https://fortress.wa.gov/ecy/publications/documents/0410018.pdf.
2. Washington State Department of Ecology. *Final* Supplemental *Environmental Impact Statement for State of Washington Aquatic Plant and Algae Management* (Publication No. 17-10-020). August 14, 2017. https://fortress.wa.gov/ecy/publications/documents/1710020.pdf.
3. Washington State Department of Ecology. *Draft Supplemental Environmental Impact Assessments of Aquatic Herbicides* (Publication No. 00-10-040). July 2000. https://apps.ecology.wa.gov/publications/documents/0010040.pdf.
4. Washington State Department of Ecology. *Herbicide Risk Assessment for the Aquatic Plant Management Final Supplemental Environmental Impact Statement, Appendix D, Volume 2: Endothall.* (Publication No. 00-10-044). February 2001. https://apps.ecology.wa.gov/publications/documents/0010044.pdf.
5. National Institute of Food and Agriculture. Biological Control Program. Accessed January 2023: https://www.nifa.usda.gov/grants/programs/biological-control-program.
6. U.S. Department of Agriculture. Biological control program. Accessed January 2023. https://www.aphis.usda.gov/aphis/ourfocus/planthealth/plant-pest-and-disease-programs/biological-control-program/ct_biological_control_program.
7. IPM Institute of North America. Accessed January 2023. https://ipminstitute.org/.
8. U.S Department of the Interior, Bureau of Reclamation. *Reclamation, Managing Water in the West, Canal Operation and Maintenance: Vegetation.* November 2017. https://www.usbr.gov/assetmanagement/docs/Canal_Vegetation.pdf.
9. Hawaii Invasive Species Council. *Mongoose*. Accessed January 2023. https://dlnr.hawaii.gov/hisc/info/invasive-species-profiles/mongoose/.
10. Pacific Northwest Pest Management Handbooks. *Biological Control Agents and Their Roles.* March 2022. https://pnwhandbooks.org/weed/biological-control/agents-their-roles.

# 1. Description of the Proposal and Alternatives

## Project Proponent

The Washington Department of Ecology (Ecology) is proposing to reissue a general permit under the National Pollutant Discharge Elimination System (NPDES) for the control of aquatic plants and algae in irrigation supply systems and noxious weeds on irrigation canal banks. This permit will authorize aquatic plant and algae control activities that result in the discharge of aquatic herbicides and algaecides directly into waters of the state of Washington as well as indirect discharges from overspray during application. This general permit is issued at the request of Irrigation Districts in order to authorize the discharge of herbicides and algaecides into a water of the state. Ecology issues general permits in place of a series of individual permits when the permitted activities are the same or similar. Irrigation districts that receive coverage under the general permit must comply with the terms and conditions of the permit. Irrigation districts that do not obtain permit coverage are not allowed to discharge any herbicides directly or indirectly to waters of the State.

## Purpose and Objectives of the Proposal

Ecology is reissuing the Irrigation System Aquatic Plant and Algae Management NPDES general permit for the purpose of allowing chemical use tomanage aquatic plants and algae in irrigation systems. Irrigation systems are waters of the State of Washington. The objectives of the proposal are to:

- Issue a general permit that complies with federal and state laws allowing for aquatic plant and algae management using aquatic labeled herbicide and algaecides.
- Facilitate the delivery of irrigation water to ratepayers.
- Provide an option for maintaining beneficial use of State waters (water supply) as defined in the Surface water Quality Standards (Chapter 173-201A-200(3)) and set-up through the creation of an irrigation district (RCW 87.03.010).

## Location

The proposed action would cover irrigation supply systems located statewide. There are 34 irrigation districts that are members of the Washington State Water Resources Association (WSWRA) based on their member listing. However there are potentially many other districts in Washington that could be considered irrigation districts for the purpose of reissuing the Irrigation System Aquatic Weed Management General Permit. These include Boards of Joint Control (Chapter 87.80 RCW), Diking, Drainage, and Irrigation Improvement Districts (Chapter 85.22 RCW), Irrigations Districts (Chapter 87.03 RCW), Irrigation and Rehabilitation Districts (Chapter 87.84 RCW), and Reclamation and Irrigation Districts in Reclamation Areas (Chapter 89.12 RCW). A 2012 review by the Municipal Research and Services Center (MRSC) of Washington lists a total of 95 irrigation type districts operating under various statutes. This appears to be the most recent assessment of the number of special purpose districts that includes irrigation type districts as of the drafting of this EIS.

The 34 WSWRA member districts cover at least 1.1 million irrigated acres of farm land. Based upon the membership address of WSWRA members, irrigation districts are located primarily east of the crest of the Cascade Mountains in central and eastern Washington. The one exception is an irrigation company in Sequim, WA on the Olympic Peninsula. Historically 18 Irrigation Districts have held coverage under the Irrigation System Aquatic Weed Control NPDES General Permit.

## Description of Irrigation Supply System Operations

Irrigation systems are necessary for the agricultural operations east of the Cascade Mountains, as well as some parts of Western Washington during the summer months (WSU). Irrigation systems in Washington typically draw from the Columbia, Yakima, and Snake River watersheds, all of which converge in and flow out of the Columbia River. Irrigation systems are complex and are made up of multiple components to bring water from the source, transport it to water users, and finally release it to the receiving waters.

### Parts of an Irrigation Supply System

**Headworks:** The location where water enters the irrigation system, through gravity flow or pumping.

**Ditches:** Open channels used to carry irrigation water to the point of use. They may be unlined (earthen) or lined with concrete, asphalt, or other materials.

**Pipeline:** A closed conduit system of moving water in place of ditches.

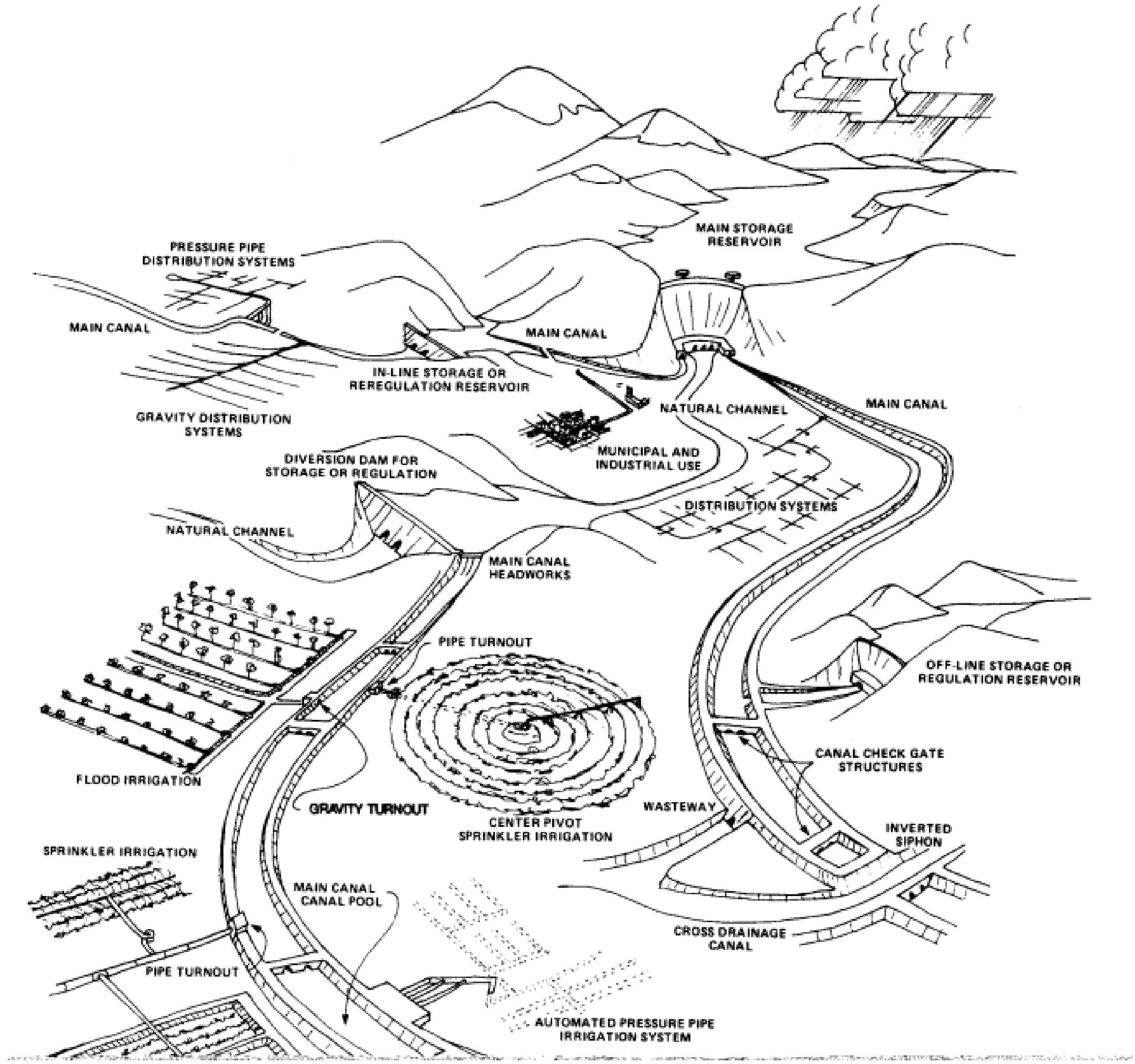
**Canal:** A large permanent ditch that carries water to multiple water users.

**Lateral:** A ditch or pipe used to carry water for a specific water-user on their farm land.

**Flume:** An artificial channel carrying water across areas where ditches are not practical. For example ravines, steep hillsides, swales, or draws.

**Flow Control Structures:** Devices that control the speed or volume of flowing water within an irrigation system such as checks, diversion gates, drops, chutes, turn-outs, grade control, road crossing, or inverted siphons.

**Figure 1: An illustration of an example irrigation system**



This example shows water traveling from a storage reservoir along a natural water source through a main canal. The main canal has multiple gates, pipes, and lateral channels that direct, hold, and release water to desired locations and water users. Excess water may return from water users back to the irrigation system canals to be used by other customers of the irrigation district or released into the receiving waters (Bureau of Reclamation).

## Socioeconomics

There are over 1.8 milliion irrigated acres in Washington State. This includes private residences, municipalities, farms, and other water users. 75% of water used in irrigation is from surface water resources (WSU). These are primarily the Columbia, Yakima, and Snake River watersheds. The agricultural industry in Central and Eastern Washington, and to a lesser extent parts of Western Washington, depend on the timely and efficient delivery of water through irrigation systems. If irrigation systems were to be disrupted through the mismanagement or neglect of aquatic plants and algae in irrigation canals, it would threaten crops and livelihoods throughout the state. Poor irrigation timing or delay may lead to lost yield or poor quality crops or landscaping.

### Regulatory Status and Regulatory Control

#### Regulatory Requirements for Irrigation Districts

Under Section 402 of the CWA, an activity involving a discharge into waters of the U.S. authorized by a Federal permit (such as an NPDES permit) must receive water quality certification (WQC) from the appropriate certifying agency or Tribe. The Washington Department of Ecology (Ecology) is authorized by the U.S. Environmental Protection Agency (EPA) to make Section 401 certification decisions for activities on non-Tribal and non-federal lands within the State.Regulatory requirements for irrigation districts depend on the enabling statute under which the district was created. These include:

- Chapter 87.80 RCW: Boards of Joint Control
- Chapter 85.22 RCW: Diking, Drainage, and Irrigation Improvement Districts
- Chapter 87.03 RCW: Irrigations Districts
- Chapter 87.84 RCW: Irrigation and Rehabilitation Districts
- Chapter 89.12 RCW: Reclamation and Irrigation Districts in Reclamation Areas

Generally, each RCW imposes restrictions and regulations on how irrigation districts are formed, managed, or designed.

In addition, where discharges of waste materials occur to waters of the State, a waste discharge permit is required from Ecology. The proposed Irrigation System Aquatic Weed Control General Permit is a combined NPDES and State Waste Discharge General Permit.

Other relevant regulations for the use of aquatic pesticides and discharges of treated water to waters of the state include:

- Washington State Water Quality Standards (Chapter 173-201A).
- Washington State Groundwater Quality Standards (Chapter 173-200 WAC).
- Sediment Management Standards (Chapter 173-204 WAC).
- Human Health-Based Criteria in the National Toxics Rule (40 ***Code of Federal Regulation*** (CFR) 131.36).
- The Washington Pesticide Control Act and rules adopted thereunder (RCW 15.58).
- The Washington Pesticide Application Act and rules adopted thereunder (RCW 17.21).
- The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).
- The pesticide, adjuvant, and other product labels (referred to collectively as Product Labels or Labels in this permit) currently registered and approved for use in Washington State, which may or may not be identical to the FIFRA label for registered pesticides.

WDFW Treatment Timing Windows and SOPs.Regulatory Requirements for Physical, Mechanical, and Cultural Management Methods*Washington State Department of Ecology (Ecology)*. Ecology's Shorelands and Environmental Assistance (SEA) Program administers the Washington Shoreline Management Act (Chapter 90.58 RCW) in partnership with local governments. Local shoreline master programs must protect shoreline ecological functions, provide for public enjoyment of public shores and waters, and plan for and foster all reasonable and appropriate uses. Local programs must be approved by Ecology and consistent with the Shoreline Management Act and its regulations.

Ecology's Water Quality and SEA Programs also administer the State Water Pollution Control Act (Chapter 90.48 RCW). Under this authority, Ecology must balance competing beneficial uses including aquatic life use, shellfish harvesting, recreation, wildlife habitat and harvesting, commerce and navigation, boating, and aesthetics.

### Local Regulatory Requirements

Each local government has adopted local implementing regulations for shoreline management. These vary somewhat from one another. If a Shoreline Conditional Use permit or variance is required, Ecology must review and approve these local permit decisions.

### Irrigaton District Rules

Each irrigation district is subject to the rules and bylaws enacted by the district or its governing body.

### Federal Regulatory Requirements

Irrigation Districts who intend to use physical or mechanical control methods may require Federal permits and/or Federal environmental review if this activity is proposed on Federal lands or would receive Federal funding. Federal permits and environmental reviews may include:

- National Environmental Policy Act (NEPA) review. NEPA applies to all major Federal actions, any project requiring a Federal permit, receiving Federal funding, or proposed on Federal land. NEPA is similar to Washington's SEPA process.

- Endangered Species Act (ESA) Section 7 consultation with the U.S. Fish and Wildlife Service (USFWS) and/or National Oceanic and Atmospheric Administration (NOAA)/National Marine Fisheries Service (NMFS). The ESA lists many salmon, steelhead, and bull trout populations and other aquatic biota as threatened or endangered for special protection in Washington waters. Irrigation Districts may obtain information regarding potential listings of endangered species in particular water bodies from the local office of WDFW or on their website[26].

- U.S. Army Corps of Engineers Section 10 Rivers and Harbors Act permit for any structures or work in navigable waters of the United States.

## Regulatory Requirements for Chemical Management Methods

### Washington State Department of Ecology (Ecology) Requirements for Chemical Applications.

Since 2002, Ecology has regulated herbicide application under general NPDES/State Waste Discharge permits instead of site-specific administrative orders. The special condition section of Ecology's general pesticide permits contain mitigations for herbicide and algaecide use. Mitigations include such things as notifications, application timing windows, holding times to avoid non-target impacts, preparation of Best Management Practices, monitoring, and other special provisions to help protect the environment from the regulated action.

Under the proposed reissuance of the Irrigation System Aquatic Weed Control General Permit, Washington State has made a tentative decision to allow the use of herbicides and algaecides in irrigation supply systems for the purpose of controlling aquatic plants and algae for a period of 5 years. Ecology intends to issue coverage under this NPDES general permit to Irrigation Districts. The Irrigation District may hire or contract with a licensed applicator to apply pesticides or the applicator may be a staff member of the Irrigation District. Entities such as a consortium of Irrigation Districts cannot be sponsors under this permit.

### Washington State Department of Agriculture (WSDA) Requirements for Chemical Applications.

WSDA is Washington's lead agency for the regulation of pesticides, and issues private, commercial, and other licenses required for the application of pesticides.

WSDA classifies all aquatic herbicides as "restricted use." Only trained and certified applicators or people under their direct supervision can legally purchase and apply aquatic herbicides in Washington. Most aquatic pesticide treatments occur under joint NPDES and State Waste Discharge permits administered by Ecology.

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[26] http://wdfw.wa.gov/conservation/endangered

## Laws and Codes that Apply to Chemical Applications.

The Washington State Water Pollution Control Act (Chapter 90.48 RCW) states that issuance of permits for using herbicides and surfactants registered under State or Federal pesticide control laws to control aquatic noxious weeds "shall be subject only to compliance with: Federal and State pesticide label requirements; the requirements of the Federal Insecticide, Fungicide, and Rodenticide Act; the Washington Pesticide Control Act; the Washington Pesticide Application Act; and the State Environmental Policy Act," subject to several enumerated exceptions.

## Local Regulatory Requirements for Chemical Applications.

Some local jurisdictions (City or County governments) may require Shoreline Substantial Development permit, Shoreline Conditional Use permit, or variance for chemical applications in or near Shorelines of Statewide significance under the jurisdiction of the Shoreline Management Act (Chapter 173-27-WAC). Each local government has local implementing regulations that vary somewhat from one another.

## EPA Statutory Requirements for Pesticides

EPA regulates pesticides under four major statutes:

1. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. § 136 et seq.).
2. Federal Food, Drug, and Cosmetic Act (FFDCA) (21 U.S.C. Chapter 9).
3. Food Quality Protection Act (FQFA) (7 USC §136).
4. Clean Water Act (CWA) (33 U.S.C. 1251 et seq.).

    - **FIFRA** provides the basis for regulation, sale, distribution, and use of pesticides in the U.S. FIFRA authorizes EPA to review and register pesticides for specified uses. WSDA coordinates with EPA if an applicant applies for a EUP, Section 24(c) or a Section 18 emergency exemption.
    - **FFDCA** authorizes EPA to set tolerances, or maximum legal limits, for pesticide residues in food. Tolerance requirements apply equally to domestically-produced and imported food.
    - **FQFA** fundamentally changed the way that EPA regulates pesticides. Some of the major requirements include stricter safety standards, especially for infants and children, and a complete reassessment of all existing pesticide tolerances.
    - **CWA** (1972 and later modifications [1977, 1981, and 1987]) established water quality goals for navigable waters of the United States. A 2011 court ruling directed EPA to require National Pollutant Discharge Elimination System (NPDES) permits for aquatic pesticide applications under the CWA. EPA delegated responsibility for administering the NPDES permit program to the State of Washington based on Chapter 90.48 RCW. This statute defines Ecology's authority and obligations in administering the Wastewater Discharge Permit Program.

EPA requires extensive data as part of its registration review and approval process, requiring more than 120 studies before granting a registration for most pesticides used in food production. EPA tiers these study requirements to the intended use and certain properties of the pesticide. The studies allow EPA to assess risks to human health, domestic animals, wildlife, plants, surface and groundwater, beneficial insects, and other environmental effects. When new evidence arises to challenge the safety of a registered pesticide, EPA may take action to suspend or cancel its registration and revoke the associated tolerances.

### EPA Ecological Risk Assessments.

EPA conducts an Environmental Fate and Ecological Risk Assessment (EFED) for each active ingredient during the pesticide registration process. EPA used the most sensitive toxicity endpoints from surrogate test species to estimate treatment-related direct effects on acute mortality and chronic reproductive, growth, and survival endpoints. In general, categories of acute toxicity ranging from "practically nontoxic" to "very highly toxic" have been established for aquatic organisms based on lethal concentration (LC50) values, terrestrial mammals based on lethal dose (LD50) values, avian species based on LC50 values, and non-target insects based on LD50 values for honey bees.

### EPA Human Health Risk Assessments.

Federal law requires detailed evaluation of pesticides to protect human health[27]. In 1996, Congress made changes to strengthen pesticide laws through the Food Quality Protection Act (FQPA), which require EPA to consider:

- *A new safety standard*: FQPA strengthened the safety standard that pesticides must meet before EPA approves their use. EPA must ensure with a reasonable certainty that no harm will result from the legal uses of the pesticide.

- *Exposure from all sources*: In evaluating a pesticide, EPA must estimate the combined risk from that pesticide from all non-occupational sources such as:

–Food sources
–Drinking water sources
–Residential sources.

- *Cumulative risk*: EPA is required to evaluate pesticides in light of similar toxic effects that different pesticides may share, or a “common mechanism of toxicity.” EPA is developing a methodology for this type of assessment.

- *Special sensitivity of children to pesticides*: EPA must ascertain whether there is an increased susceptibility from exposure to the pesticide to infants and children. EPA must build into their risk assessment an additional 10-fold factor of safety to ensure the protection of infants and children, unless it is determined that a lesser margin of safety will be safe for infants and children. The use of the extra 10-fold factor of safety for children is in addition to the traditional 100-fold factor of safety for human health. To further increase protections for infants and children, EPA now requires registrants to conduct acute, sub-chronic, and developmental

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[27] www.epa.gov/pesticides/factsheets/riskassess.htm

neurotoxicity studies. EPA also updated the set of test guidelines for development of data on reproductive and developmental effects.

The FQPA requires EPA to set tolerances or grant exemptions for all the ingredients in a pesticide product that is used on food. A tolerance is the maximum amount of pesticide chemical residue that can be in or on a food product or feed commodity. EPA must determine that the levels of the chemical proposed in the tolerance are “safe.” Safe means a reasonable certainty of no harm to human health. An exemption from a tolerance is issued when EPA determines that the total quantity of the pesticide chemical in or on the food will present no hazard to public health. Generally, other ingredients in pesticide formulations are not pesticidally active themselves and are exempt from the need for a tolerance determination so long as they do not present a hazard to public health.

**References**

1. Washington State University (WSU). *Irrigation in the Pacific Northwest*. Accessed January 2023. http://irrigation.wsu.edu/Content/Washington-Irrigation.php
2. U.S. Department of the Interior, Bureau of Reclamation. *Canal Systems Automation Manual Volume 1*. 1991. https://www.usbr.gov/tsc/techreferences/mands/mands-pdfs/CanalSysAuto1.pdf.

# 2. Proposed Action and Alternatives

Ecology listed alternative methods for the control of aquatic plants and algae in irrigation supply systems in the Determination of Significance (DS) and Scoping Notice for this Environmental Impact Statement (EIS), dated April 21, 2017. Issuance by Ecology of an NPDES general permit to allow the application of herbicides and algaecides to irrigation supply systems is required to implement the preferred alternative for aquatic plant and algae management (an Integrated Pest Management approach), or the use of chemical methods only.

The action that triggered preparation of this EIS is the Ecology proposal to reissue a NPDES general permit for a term of 5 years for the chemical management of aquatic plants and algae in irrigation supply systems. Ecology determined that applications of herbicides and algaecides to manage aquatic plants and algae may result in significant environmental impacts, resulting in the requirement to evaluate the potential impacts of the proposed action in an EIS.

This EIS identifies and analyzes reasonable alternatives to chemical control, probable significant environmental impacts, and potential mitigation measures for each alternative, including chemical control methods. The Draft EIS was made available for public review and comment. These comments were taken into consideration by Ecology both during preparation of the Final EIS and in making the decision regarding the NPDES general permit for application of the reviewed herbicides and algaecides to irrigation supply systems statewide.

The first Irrigation System Aquatic Weed Control Permit (permit) was issued in 2002. Since then, the permit was reissued two more times with the most recent reissuance occurring in 2012. This EIS is being developed to support the proposed 2023 permit reissuance.The previous permit issuances relied upon the SEPA checklist to comply with SEPA requirements, and all had a Determination of Non-significance (DNS).

The potential impacts and mitigation measures for each alternative are described in this section. The information provided will be used by decision makers to assess reasonable alternatives and appropriate mitigating conditions to be required for the proposed chemical applications. The alternatives evaluated include:

1. The No action Alternative.
2. Use of Physical and Mechanical Methods Only.
3. Use of Chemical Methods Only.
4. Use of Integrated Pest Management (IPM) with Adaptive Management Approach (the preferred alternative).

The EIS also includes a section on Other Alternatives Considered and Eliminated from Detailed Evaluation.

## Elements of the Environment

The Washington Department of Ecology (Ecology) Water Quality Program and Shorelands and Environmental Assistance (SEA) Program administers the State's Water Pollution Control Act (Chapter 90.48 RCW). Under this authority, Ecology must balance competing beneficial uses, and avoid contamination or other alteration of the physical, chemical or biological properties of waters of the state. Alterations to be avoided include:

- Change in temperature, taste, color, turbidity, or odor.
- Discharges likely to create a nuisance or render such waters harmful, detrimental or injurious to public health, safety or welfare.
- Discharges likely to create a nuisance or render such waters harmful, detrimental or injurious to domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses.
- Discharges likely to create a nuisance or render such waters harmful, detrimental or injurious to livestock, wild animals, birds, fish or other aquatic life (RCW 90.48.020).

The proposed action and alternatives are evaluated in relation to the elements of the environment listed below in order to address the RCW 90.48 criteria, with the following exception:

- The irrigation system waters are not used as drinking water by humans or livestock.
- The irrigation system waters are not used as commercial or industrial process waters.

## Mitigation Defined

Mitigation is defined by the Washington State Environmental Policy Act (SEPA) in the following order of preference:

1. Avoiding the impact altogether by not taking a certain action or part of an action.
2. Minimizing impacts by limiting the degree or magnitude of the action and its implementation by using appropriate technology, or by taking affirmative steps to avoid or reduce impacts.
3. Rectifying the impact by repairing, rehabilitating, or restoring the affected environment.
4. Reducing or eliminating the impact over time by preservation and maintenance operations during the life of an action.
5. Compensation for the impact by replacing, enhancing, or providing substitute resources or environments.

General mitigation strategies to minimize potential impacts associated with the use of aquatic herbicides are included in the General Conditions of the proposed draft NPDES permit. The Special Conditions listed in the proposed draft NPDES permit provide specific mitigations to reduce the potential impacts of imazamox applications.

## Analysis and Comparison of Alternatives

### Washington State Environmental Policy Act

The SEPA Rules (Chapter 197-11 WAC) that implement the State Environmental Policy Act (Chapter 43.21C RCW) require an EIS to describe and present the proposal (or preferred alternative, if one exists) and alternative courses of action. Reasonable alternatives are actions that could feasibly attain or approximate the objectives of the proposal, but at a lower environmental cost or decreased level of environmental degradation. The word "reasonable" is intended to limit the number and range of alternatives, as well as the amount of detailed analysis for each alternative. The level of detail is to be tailored to the significance of environmental impacts, and one alternative may be used as a benchmark against which to compare the other alternatives. The EIS may indicate the main reasons for eliminating some alternatives from detailed study. The guidelines also require that the No Action Alternative shall be evaluated and compared to other alternatives (WAC 197-11-440[5]).

### Washington State Surface Water Quality Standards

Washington State surface water quality regulations and standards (RCW 90.48; Chapter 173-201A WAC) provide authority to Ecology to establish criteria for waters of the State and to regulate various activities. These standards protect public health and maintain the beneficial uses of surface waters, which include recreational activities such as swimming, SCUBA diving, water skiing, boating and fishing and aesthetic enjoyment; public water supply; stock watering; fish and shellfish rearing, spawning, and harvesting; wildlife habitat; and commerce and navigation.

Key to the analysis and comparison of alternative methods is the goal to maintain beneficial uses of State waters and protect the environment. Therefore, Ecology will analyze each alternative for:

- The extent to which the approach may detract from beneficial use of the natural receiving waters downstream of the point of compliance.
- The extent to which the approach may detract from the use of irrigation canals to convey water to rate payers and water users.
- Potential adverse environmental impacts.
- Potential adverse human health impacts, particularly for chemical control methods.
- The effectiveness of the method in controlling aquatic plants and algae.

### Alternative 1: No Action

Under the No Action Alternative, irrigation districts would continue to manage the growth of aquatic plants and algae through a combination of physical, mechanical, and biological methods, which do not require an NPDES permit. Without issuance of an NPDES general permit by Ecology authorizing the use of aquatic herbicides and algaecides in irrigation systems, irrigation districts would only be able to use chemical plant and algae control under very limited circumstances, and they could not let treated water be discharged into waters of the state.

### Alternative 2: Physical and Mechanical Methods Only

Physical and mechanical methods of removal are described in the Summary of Alternatives Considered and the Summary of Impacts and Mitigation Measures from Alternatives Considered. These include dredging, hand pulling, rotovation, and other non-chemical, non-biological methods. Under this alternative, only non-chemical and non-biological methods would be used to manage aquatic plants and algae in irrigation canals. These methods are often costly and time consuming, though they do not always require extensive training to complete. Not all of the methods are suitable for large-scale irrigation systems with many miles of canal. Additionally, some methods may not be suitable for either unlined earthen canals, canals lined with concrete or bottom barriers, or piped canals. The addition of barrier methods to mechanical and other physical methods of plant removal and eradication may reduce the amount of vegetation which needs to be managed each year.

Many physical methods, such as chaining and dredging, can be very disruptive to irrigation systems. They may introduce a large amount of biomass and turbidity into the canal, which may cause problems with water quality or equipment maintenance.

Irrigation districts must be careful to avoid fragmentation and properly dispose of all plant and algae material away from the canal to avoid spreading plant infestations. Fragments may flow out of the canal into the receiving waters and cause noxious weed infestations in the natural environment.

### Alternative 3: Chemical Management Methods Only

As stated earlier in this document, this FEIS only contains new analysis of acrolein, copper compounds, and xylene. The other chemical reviews are referenced from the previous 2017 SEIS[28].

#### Acrolein

Acrolein, also known as 2-propenal, acrylaldehyde, and allyl aldehyde, is used for a wide variety of applications, including pesticidal and industrial uses. Some direct industrial uses include cross-linking protein collagen in leather tanning, for tissue fixation in histological samples, and as intermediates in the chemical industry (EPA 2009). Acrolein is released into the environment from several sources, including as products of natural fermentation and incomplete combustion of organic matter (waste incinerators, furnaces, fireplaces, power plants, burning vegetation, combustion of polyethylene plastics, and the cooking of food) (WHO 2001, as cited in EPA 2009). Acrolein is extremely toxic, and is on the 40 CFR 355, Appendix A list of extremely hazardous substances with threshold reporting and community planning requirements, and is on EPA’s list of priority pollutants found in 40 CFR Part 423, Appendix A.

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[28] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

## Registration Status (FIFRA and WA Registration)

Acrolein was registered in 1975 as an herbicide with the United States Environmental Protection Agency (EPA) by Baker-Petrolite Corporation. This registration was for the Magnacide pesticide product. Acrolein was previously registered as a biocide in 1959 under the trade name Aqualin, produced by Shell Chemical Company, and that registration was cancelled in 1989. Current pesticidal uses of acrolein are for the control of aquatic weeds and algae in irrigation canals and as a biocide for oil well drilling equipment (Table 1; EPA, 2008). All older registrations for use of acrolein in rodent burrows and burrow entrances have been cancelled. (EPA 2008). Table 1 shows the current registered pesticidal products for acrolein.

**Table 1. Current registered pesticidal products for acrolein.**

| Summary Report of Registered Pesticide Products | | | | | |
|---|---|---|---|---|---|
| **Reg #** | **Use Type** | **Registration Type** | **Name** | **Registrant** | **% Acrolein** |
| 10707-9 | Herbicidal use for direct applications to water irrigation canal systems in the western U.S. | Sec. 3 FIFRA | MAGNACIDE H HERBICIDE | Baker Petrolite Corporation | 95 |
| 10707-10 | Biocide for oil well drilling equipment | | MAGNACIDE B MICROBIOCIDE | | 95 |
| CA780039 | Herbicidal | Special Local Need, Sec. 24(c) FIFRA | MAGNACIDE H HERBICIDE | | 95 |
| ID900005 | | | | | |
| NE030003 | | | | | |
| OR910018 | | | | | |
| UT030001 | | | | | |
| WA040017 | | | | | |

(After: EPA 2008)

## Regulatory levels for Acrolein

Acrolein is regulated under many different agencies and programs. Several of the current regulatory, guideline, and requirement levels for acrolein are listed in Table 2.

**Table 2. Some environmental regulatory, guideline, or requirement levels for acrolein.**

| Regulatory/guideline/requirement level | Value | Source |
|---|---|---|
| Washington State surface water quality criteria for human health | 1 ug/L (water + organism exposure)<br>1.1 ug/L (organism-only exposure) | WAC 173-201A-240 |
| EPA recommended national water quality criteria for human health | 3 ug/L (water + organism exposure)<br>400 ug/L (organism-only exposure) | EPA 2015. Update of Human Health Ambient Water Quality Criteria: Acrolein 107-02-8. EPA 820-R-15-003. June 2015. |
| EPA recommended national water quality criteria for aquatic life - freshwater | Acute (CMC): 3 ug/L, 1-hr average<br>Chronic (CCC): 3 ug/L, 4-day average<br>Allowed exceedances: Freshwater aquatic organisms and their uses should not be affected unacceptably if the CMC and CCC are not exceeded more than once every three years on the average. | EPA 2009. Ambient aquatic life water quality criteria for acrolein. (CAS Registry Number I 07-02-8). July 1, 2009. 49 pp. |
| EPA OPP Aquatic life benchmarks - freshwater | Fish acute: 7 ug/L<br>Fish chronic: 11.4 ug/L<br>Invertebrate acute: <15.5 ug/L<br>Invertebrate chronic: 7.1 ug/L<br>Nonvascular plants: 28 ug/L<br>Vascular plants: 72 ug/L<br>CMC: 3 ug/L<br>CCC: 3 ug/L | https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk accessed 7/26/2018. |
| EPA CERCLA Reportable Quantities | Persons in charge of vessels or facilities are required to notify the National Response Center (NRC) immediately, when there is a release of this | [40 CFR 302.4 (EPA); as cited in HSDB 2018. |

| | | |
|---|---|---|
| | designated hazardous substance, in an amount equal to or greater than its reportable quantity of 1 lb or 0.454 kg. The toll free number of the NRC is (800) 424-8802. The rule for determining when notification is required is stated in 40 CFR 302.4 (section IV. D.3.b). | |
| Ontario Ministry of the Environment and Energy Interim Provincial Water Quality Objective | 0.03 µg/L<br>For many substances of concern, there is insufficient toxicological information available to prepare a Provincial Water Quality Objective. In these cases, an Interim Provincial Water Quality Objective is established. | Ontario Ministry of the Environment and Energy, Water Management: Policies, Guidelines, Provincial Water Quality Objectives.<br>https://www.ontario.ca/page/water-management-policies-guidelines-provincial-water-quality-objectives#section-13 |
| CERCLA Reportable Quantities | Releases of CERCLA hazardous substances are subject to the release reporting requirement of CERCLA section 103, codified at 40 CFR part 302, in addition to the requirements of 40 CFR part 355. **Acrolein** is an extremely hazardous substance (EHS) subject to reporting requirements when stored in amounts in excess of its threshold planning quantity (TPQ) of 500 lbs. | [40 CFR 355 (EPA); as cited in HSDB 2018. |
| RCRA - freshwater | As stipulated in 40 CFR 261.33, when **acrolein**, as a commercial chemical product or manufacturing chemical intermediate or an off-specification commercial chemical product or a manufacturing chemical intermediate, becomes a waste, it must be managed according to federal and/or state hazardous waste regulations. Also defined as a hazardous waste is any container or inner liner used to hold this waste or any residue, contaminated soil, water, or other debris resulting | [40 CFR 261.33 (EPA) ; as cited in HSDB 2018. |

| | | |
|---|---|---|
| | from the cleanup of a spill, into water or on dry land, of this waste. Generators of small quantities of this waste may qualify for partial exclusion from hazardous waste regulations (40 CFR 261.5(e)). | |
| Clean Air Act, section 202(l)(2); | The specific standard relating to combustion products limits emissions from passenger vehicles during operation at cold temperatures. These finalized standards are projected to reduce acrolein as a Mobile Source Air Toxic by 317 tons in the year 2020 (US EPA, 2007). | 40 CFR Parts 59, 80, 85, and 86; [EPA-HQ-OAR-2005-0036; FRL-8278-4] "Control of Hazardous Air Pollutants From Mobile Sources" |
| Federal Emergency Planning and Notification requirements. | Reportable quantity: 1 pound.<br>Planning quantity: 500 pounds. | 40 CFR 355. Emergency Planning and Notification. See Appendix A. |
| OSHA (Occupational Safety and Health Standards) | Threshold quantity = 150 pounds. | 29 CFR. Toxic and reactive highly hazardous chemicals which present a potential for a catastrophic event at or above the threshold quantity. |

## Chemical-use Patterns

Acrolein is used in aquatic applications as an herbicide and a biocide (for slime producing organisms). Both products are packaged as liquids and stored under an inert gas blanket. Acrolein is applied through a closed system for all uses (EPA 2008). Certified applicators are only allowed to buy acrolein pesticides, and only certified applicators or persons under their direct supervision can apply the acrolein products (EPA 2008).

### *Herbicide use*

Acrolein is used in irrigation canals to control submerged and floating aquatic weeds. The acrolein formulation is directly applied to subsurface waters and forms a "plug" of treated water that moves through canals killing plants on contact. Application rates range from < 8ppm (to control low weed density), 8 ppm (typical rate) to 15 ppm (maximum single application), and can be applied up to 26x per year in some systems. The typical application rate is 6x per year. (EPA 2008). Acrolein is also registered in some states for use in irrigation reservoirs.

### *Biocide use*

Acrolein is applied to injection well waters that are associated with petroleum production at a maximum single application rate of 15 ppm. Applications can occur multiple times during a year. There is no release of fluids to above-ground environment with this use (EPA 2008).

EPA (2008) states listed usage as approximately one million pounds annually.

A National Pollutant Discharge Elimination Sytem (NPDES) permit is needed in the state of Washington for MAGNACIDE H Herbicide applications (Irrigation System Aquatic Weed Control NPDES General permit WA0991000 2012). The Washington Section 24c Special Local Need (SLN) registration (*MAGNACIDE H Herbicide (10707-9) Reduced Holding Time for Washington State Special Local Need Registration EPA SLN WA-040017)* provides specific information for NPDES permittees (NPDES Permit No. WA0991000 ) on calculating minimum holding times from the point of acrolein application on to the confluence of the acrolein-treated Irrigation District water and any natural waterbody, to ensure that appropriate degradation of acrolein will occur at specific application rates and dilutions in field situations (EPA 2008 (dated July 23, 2008)). The label for the Section 24c SLN registration for the use of Magnacide H Herbicide (Acrolein) for control of submersed and floating weeds and algae in irrigation canals in Washington was revised in April 2022.

The SLN specifies that in all cases, no application of acrolein can exceed a concentration of 8 ppm either by individual application or by stacking an acrolein application on top of a previous acrolein application made upstream, and the duration of each acrolein application must not exceed 8 hours. The SLN correction factors for holding times prior to discharge to a natural waterbody for use in Washington applications are in Table 3 below.

Table 3. Washington SLN correction factors.P

| Information from SLN WA-040017 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| App. Rate (ppm) | *Correction Factor (cubic feet per second (cfs) of the natural waterbody divided by cfs of Irrigation District water) | | | | | | | | | | |
| | 1 | 5 | 10 | 50 | 75 | 100 | 250 | 500 | 750 | 1000 | ≥1043 |
| | Minimum Holding Time (Hours) | | | | | | | | | | |
| 8.0 | 115 | 91 | 81 | 57 | 51 | 47 | 34 | 23 | 17 | 13 | 12 |
| 7.0 | 113 | 89 | 79 | 55 | 49 | 45 | 32 | 21 | 15 | 12 | 12 |
| 6.0 | 111 | 87 | 77 | 53 | 47 | 43 | 29 | 19 | 13 | 12 | 12 |
| 5.0 | 108 | 84 | 74 | 50 | 44 | 40 | 27 | 16 | 12 | 12 | 12 |
| 4.0 | 105 | 81 | 71 | 47 | 41 | 37 | 23 | 13 | 12 | 12 | 12 |
| 3.0 | 100 | 77 | 67 | 43 | 37 | 33 | 19 | 12 | 12 | 12 | 12 |
| 2.0 | 95 | 71 | 61 | 37 | 31 | 27 | 13 | 12 | 12 | 12 | 12 |
| 1.0 | 84 | 61 | 50 | 27 | 21 | 16 | 12 | 12 | 12 | 12 | 12 |

* Correction Factor is defined as the cfs (cubic feet per second) of the natural waterbody divided by the cfs of Irrigation District water. The cfs of the natural waterbody is defined as the cfs of the natural waterbody immediately downstream from the confluence of the natural waterbody and Irrigation District water. The cfs of the Irrigation District water is defined as the cfs of treated Irrigation District water just prior to entering the natural waterbody. By definition there cannot be a Correction Factor less than 1. Using the intersection of the target field application rate of acrolein in ppm and the appropriate Correction Factor, the minimum holding time in hours can be found in the body of the table. For example, a 5.0 ppm acrolein application with a Correction Factor of 100 would have a minimum holding time of 40 hours.

See SLN for examples of how to calculate minimum holding times.

Additional Restrictions/Precautions contained in the SLN include:

- All applications must be made during daylight hours.
- Maximum number of applications: 8 applications per year.
- Minimum retreatment interval: 2 weeks.
- This pesticide is extremely toxic to fish and wildlife. MAGNACIDE™ H HERBICIDE should not be used under this SLN label where impact on listed threatened or endangered species is likely. You may refer to the WSDA Endangered Species Program web site at http://agr.wa.gov/PestFert/NatResources/EndangSpecies.aspx, or contact the Washington Department of Fish & Wildlife, National Marine Fisheries Service (NOAA Fisheries) or US Fish & Wildlife Service for information regarding aquatic species listed as threatened or endangered. Consult the federal label for additional restrictions and precautions to protect aquatic organisms.

### Chemical Description

Acrolein is the simplest unsaturated aldehyde (PubChem 2022). Its extreme reactivity is due to the presence of a vinyl group (H2C=H-) and an aldehyde group on a small-sized molecule (Windholz 1976 as cited by EPA 2009). Acrolein forms several degradates (acrylic acid, allyl alcohol, propanol, propionic acid, oxalic acid, and ultimately carbon dioxide) in the environment (EPA 2008). Glycidol, a metabolite of acrolein, is considered a probable human carcinogen by the International Agency for Research on Cancer (part of the World Health Organization) and is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals by the National Toxicology Program (EPA 2008). The chemical structures and properties of acrolein and its metabolite (glycidol) are presented below.

The following chemical information (Tables 4 and 5) is from EPA 2008 unless otherwise indicated.

**Table 4**

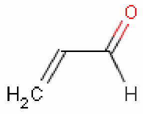
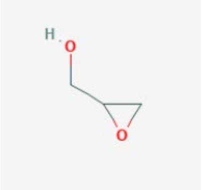
<table>
<tr><th colspan="2">Acrolein</th></tr>
<tr><td colspan="2">Chemical Structure<br></td></tr>
<tr><td>Common Name</td><td>Acrolein</td></tr>
<tr><td>Synonyms</td><td>2-propenal, acrylaldehyde, acrylic aldehyde, allyl aldehyde, propenal, trans acrolein, acquinite, aqualin, biocide, crolean, ethylene aldehyde, Magnicide, Magnicide H, NSC 8819, prop-2-en-1-al, 2-propene-1-one, slimicide, prop-2-enal</td></tr>
<tr><td>Molecular Formula</td><td>$C_3H_4O$</td></tr>
<tr><td>PC Code</td><td>000701</td></tr>
<tr><td>Name</td><td>2-propenal; Acrylaldehyde</td></tr>
<tr><td>CAS Registry Number</td><td>107-02-8</td></tr>
<tr><td>Melting Point/Range</td><td>-88 °C (-126 °F)</td></tr>
<tr><td>Boiling Point</td><td>53 °C (127 °F)</td></tr>
<tr><td>Molecular Weight</td><td>56.1 g/mol</td></tr>
<tr><td>Specific Gravity</td><td>0.0839</td></tr>
<tr><td>Vapor Density</td><td>1.94 (air = 1)</td></tr>
<tr><td>Solubility</td><td>208 g/L at 20 °C soluble in water, alcohol, ether, and acetone</td></tr>
<tr><td>Vapor Pressure</td><td>220 torr at 20 °C</td></tr>
<tr><td>Flashpoint</td><td>-15 °F (-26.1 °C)</td></tr>
<tr><td>Octanol Water Partition Coefficient (Log k)</td><td>0.98-1.10</td></tr>
<tr><td>Description</td><td>Clear, colorless to yellow liquid</td></tr>
</table>

**Table 5**

| **Glycidol** | |
|---|---|
| Chemical Structure |  (From https://pubchem.ncbi.nlm.nih.gov/compound/glycidol#section=Top |
| Molecular Formula | $C_3H_6O_2$ |
| IUPAC Name | Oxiranylmethanol |
| CAS Registry Number | 556-52-5 |
| Melting Point/Range | -54 °C |
| Boiling Point | 167 °C (decomposes) |
| Molecular Weight | 74.1 g/mol |
| Specific Gravity | 0.0839 |
| Vapor Density | 2.15 (air = 1) |

## Fate and transport in aquatic systems:

### *Sediment*

Acrolein has an estimated Koc =1.0, which indicates low expected absorbtion to sediments (Swann et al and EPA 2016, as cited in HSDB 2018). Swann et al (1983, as cited in ATSDR 2007) estimated a Koc of 24 from a calculated Kow (Lyman 1982, as cited in ATSDR 2007), suggesting that acrolein would not significantly absorb to suspended solids and sediments, and would have the potential to leach significantly. In sediment, both aerobic and anaerobic degradation appear to share hydrolysis as an early step (Shaner, 2014). Half-lives of 4.2 hours were observed in aerobic soil conditions, while 11 days was observed in anaerobic soil conditions (Shaner, 2014).

### *Volatilization from water*

Nordone et al ((Nordone et al. 1996a, 1996b)., as cited in ASTDR 2007) concluded that volatilization is a significant removal process for acrolein in surface waters. An estimated Henry's Law constant of 1.22X10-4 atm-cu m/mole indicates that acrolein will volatilize (Gaffney JS et al 1987, as cited in HSDB 2018). An estimated volatilization half-life for a river model is 7.6 hrs and for a lake model is 4.6 days (Lyman WJ et al DATE , as cited in HSDB 2018).

### *Degradation and dissipation of acrolein*

3- hydroxypropanol, acrylic acid, allyl alcohol, propanol, propionic acid and oxalic acid are all products of chemical degradation of acrolein (EPA 2009). In aqueous solutions acrolein goes into reversible equilibrium with a hydration product, 3-hydroxypropanal, and does not have full hydrolytic degradation. (EPA 2009). Figure X shows degradates of acrolein in water (from King 2016). Table 6 lists some degradation and dissipation half-lives reported for acrolein in water.

**Figure 2: Degradates of Acrolein in water (after King 2016)**

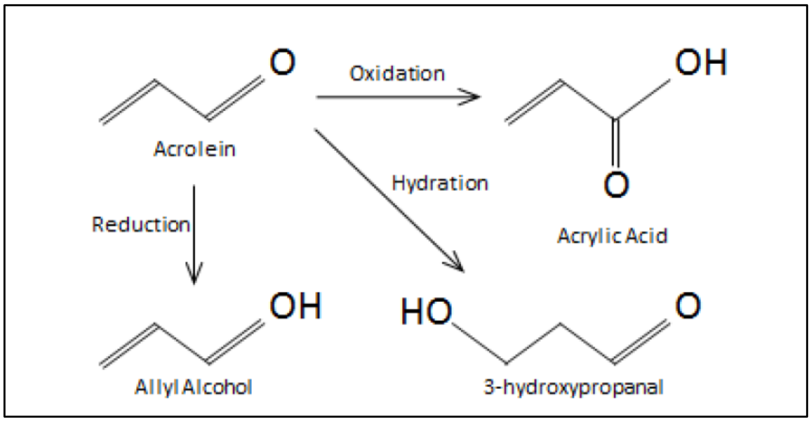


**Table 6. Some reported degradation/dissipation half-lives for acrolein.**

| Degradation/Dissipation information | Source |
|---|---|
| 150 hours at pH 5 | McBean 2010-2011, as cited in HSDB 2018 |
| 120-180 hours at pH 7 | |
| 5-40 hours at pH 9 | |
| 10.2 hours in weedy canals<br>(91.5% dissipated within 33.0 hours) | Nordone AJ et al 1996, as cited in HSDB 2018 |
| 7.3 hours in non-weedy canals<br>(48% dissipated within 7.9 hours) | |
| Buffered laboratory water: acrolein reached equilibrium with β-hydroxypropionaldehyde in approximately 300 hours (92% β-hydroxypropionaldehyde, 8% acrolein);<br>Irrigation channels: acrolein removal was complete. Half-lives were reportedly <1–3 days in surface water, combined effect of degradation and volatilization. | Bowmer and Higgins 1976; Bowmer et al. 1974, as cited in ATSDR 2007 |
| Irrigation canal and lateral: 2-hr 15 ppm exposure in weedy canal. Dissipation half-lives 275 minutes (main) and 64 minutes (lateral). No acrolein detected in either water at DL 0.01 ppm. No 3-hydroxypropanal detected in either water at DL 2.0 ppm (suggesting hydration may not be important in degradation). | Jacobson and Smith (1990), as cited in ATSDR 2007. |

Field monitoring programs and dissipation half-lives for Magnacide H use in Nebraska and Washington state are summarized below (Table 7). This information is taken from EPA 2008b. Data from field monitoring indicate that acrolein can be found at detectable concentrations >60 miles downstream from the application point, even 48 hours after the time of upstream application. In Washington a 48-hr holding time is required before the treated water is allowed to enter waters outside the irrigation systems (EPA 2008b).

Nebraska:

**Table 7. Acrolein movement in Nebraska irrigation canals. Canals marked with an asterisk had detectable concentrations at the drainage point from the canal.**

| Irrigation Canal | Nominal Application Concentration (μg/L) | Time for last Detection (hours) | Furthest Detected Distance from Application Site (mi) | Concentration at Furthest Detected Distance (μg/L) | Dissipation Half-life† (hours) |
|---|---|---|---|---|---|
| Red Willow* | 2400 | 23 | 15 | 410 | 9.8 |
| Meeker* | 2400 | 27 | 31 | 230 | ** |
| Franklin Main | 1900 | 12 | 16 | 700 | 2.8 |
| Farwell* | 4000 | 27 | 11 | 310 | 6.6 |
| Bone Lateral | 500 | 8 | 7.3 | 170 | 3.9 |
| Airport Lateral | 500 | 7 | 6.2 | 34 | 2.0 |
| 2165 Lateral* | 3200 | 8 | 6.5 | 54 | 3.8 |
| 2832 Lateral* | 4900 | 5 | 3 | 1150 | 5.2 |

* Sites marked with an asterisk had acrolein measured at the discharge point of the irrigation canal.

** Dissipation occurred but rate half-life could not be estimated.

† Dissipation half lives were estimated by using the peak concentrations and occurrence time at each sampling site as the pulse of acrolein moved downstream.

Table 7 after EPA 2008b.

Washington:

**Table 8. Acrolein movement in Washington irrigation canals. Canals marked with an asterisk had detectable concentrations at the drainage point from the canal.**

| **Irrigation Canal** | **Nominal Application Concentration (µg/L)** | **Time for last Detection (hours)** | **Furthest Detected Distance from Application Site (mi)** | **Concentration at Furthest Detected Distance (µg/L)** | **Dissipation Half-life† (hours)** |
|---|---|---|---|---|---|
| East Low* | 1500 | 23 | 61 | 50 † | 19.9 |
| Potholes East, 1st application* | 1500 | 26 | 35 | 410 †† | 12.2 |
| Potholes East, 2nd application* | 1600 | 5 | 21 | 280 †† | ** |
| Roza Main, app 1 * | app 1 *<br>770 | 27 | 64 | 80 | 13.6 |
| Roza Main, app 2* | app 2*<br>980 | 24 | 23 | 80 | *** |
| Roza Main, app 3* | 990 | 7 | 18 | 160 | ** |
| Town Ditch* | 3000 | 26 | 20 | 20 | ‡ |

*Sites marked with an asterisk had acrolein measured at the discharge point of the irrigation canal

** Dissipation occurred but rate half-life could be estimated from data set.

*** Application overlapped 1st application, and dissipation rate could not be estimated

† Concentration is the receiving water body just past the discharge from the canal.

†† Last measured values was in a stilling pond 1 mi downstream from the discharge of the canal into the PEC 66 Power Plant, just above the Columbia River.

‡ Dissipation estimate could not be made due to dilution from incoming return flow

Table 8 after EPA 2008b.

Nordone et al. in their paper entitled “The mobility and degradation of acrolein in agricultural canals treated with magnacide H herbicide,” found that the dissipation of Acrolein when applied according to the label at typical concentrations as high as 10.4 ppm and at various flow rates of 142, 283, and 453 L/sec did not result in the introduction of detectavle Acrolein 2.7 km downstream (Nordone et al. 1996).

## Biodegradation of acrolein:

Acrolein's reversible hydration to 3-hydroxypropanal allows acrolein to be available for removal by biotransformation (Ghilarducci and Tjeerdema, 1995). Biodegradation might be an important factor in reducing concentrations of acrolein in fresh waters. Low concentrations of acrolein may degrade in natural water by either aerobic biodegradation or reversible hydration to β-hydroxypropionaldehyde, which subsequently undergoes aerobic biodegradation (Bowmer and Higgins 1976; EPA 1979; Ghilarducci and Tjeerdema 1995; Tabak et al. 1981; as cited in ATSDR 2007). Acrolein degradation in supply water samples from an irrigation canal, unsterilized and sterilized (thymol-treated), produced half- lives of 29 and 43 hours, respectively, indicating a possible role of biodegradation in the unsterilized water (Bowmer et al 1976, as cited in Callahan et al 1980).

The Bowmer and Higgins (1976, as cited in ATSDR 2007) study suggests that the degradation of the hydration product of acrolein, 3-hydroxypropanal, occurs after the concentration of acrolein falls below 2–3 ppm. The degradation of 3-hydroxypropanal followed a 100-hour lag period, suggesting that biodegradation occurred via acclimated cultures (ATSDR 2007). Other biodegradation screening studies indicate that **acrolein** would be readily degraded by mixed microbial populations (Stover et al, 1983; Callahan et al 1979; Hultman 1982: all as cited in HSDB 2018). A loss of 100% was observed when 5 and 10 mg/L **acrolein** underwent a static incubation in the dark at 25 deg C with sewage inoculum for 7 days (Tabak 1981, as cited in HSDB 2018). Smith et al. (1995, as cited in EPA 2009) concluded that *"The presence of viable microbial populations also heavily influences the acrolein degradation rates in freshwater systems."* Conversely, EPA 2008 found that *"The Agency has no acceptable data to assess microbial degradation or photolysis. Therefore, it is unknown whether these pathways are significant routes of degradation in the environment."* Table 9 lists some studies that address biodegradation of acrolein.

**Table 9. Some reported biodegradation information for acrolein.**

| Biodegradation information | Source |
|---|---|
| Half-life of **acrolein** in natural unsterilized water was 29 hours.<br>Half-life of **acrolein** in natural unsterilized water 43 hours in sterilized (thymol-treated) water. | Bowmer and Higgins 1976, as cited in HSDB 2018 |
| 100% loss over 7 days of 5 and 10 mg/L acrolein, 25 degrees C incubation, sewage inoculum. | Tabak et al 1981, as cited in HSDB 2018 |
| Field study in irrigation canal. 100 hr lag in degradation of 3-hydroxypropanal, indicating possible acclimation followed by biodegradation | Bowmer and Higgins (1976), as cited in ATSDR 2007 |

## Fate and transport in air

Acrolein is expected to have limited transport in the atmosphere because of its relative instability (ATSDR 2007). Acrolein is not expected to partition from the vapor phase to particulates in the atmosphere (ATSDR 2007) because of its high vapor pressure (274 mm Hg at 25 °C (Daubert and Danner 1987, as cited in ATSDR 2007, Bidleman 1988 as cited in HSDB 2018). While in the vapor phase acrolein is degraded by reaction with hydroxyl radicals to end products which include formaldehyde, carbon dioxide, and glycoaldehyde. The periods of highest use of acrolein coincides with the yearly peak concentrations of the radicals (hydroxyl radicals) in the atmosphere that can lead to degradation (King 2016). Observed atmospheric half- lives range from 13.5 to 20 hours (Edney et al., 1981; Lyman *et al*., 1982, as cited in King 2016). This vapor phase reaction half-life is estimated to be 19 hours using the rate constant of $2.00 \times 10^{-11}$ cu cm/molecule-sec at 25 °C (Edney E et al 1983, as cited in HSDB 2018). Acrolein can also react with nitrogen oxides, producing compounds such as peroxynitrate, nitric acid, glycidaldehyde, malonaldehyde, and 3-hydroxypropanaldehyde (Edney et al. 1986, Grosjean 1990 and Liu et al. 1999b as cited in ATSDR 2007). Acrolein may be suspectible to degradation by photolysis as indicated by its absorption wavelength spectrum of >290 nm that overlaps with the ultraviolet light spectrum. (HSDB 2018). Acrolein has been detected in rainwater (WHO 2002 as cited in HSDB 2018) indicating wet deposition is another pathway for removal from the atmosphere.

## Fate and transport in soils

Acrolein’s Henry’s Law constant indicates that acrolein will volatilize from damp soil surfaces (Gaffney et al 1987 as cited in HSDB 2018) and its vapor pressure of 274 mm Hg indicates that it will also volatilize from dry soil surfaces (Daubert and Danner 1989 as cited in HSDB 2018). Acrolein’s estimated Koc = 1 (HSDB 2018) indicates that it is unlikely to bind to soils and instead is characterized by high mobility (HSDB 2018). Table 10 lists some dissipation rates from soils. Given these characteristics, acrolein is not expected to remain in soils and instead will move relatively quickly from soils to the vapor phase or be degraded.

**Table 10. Dissipation rates of acrolein from soils.**

| Dissipation/degradation Information | Source |
|---|---|
| Laboratory soil study, aerobic sandy loam:<br>Sterile soil, acrolein completely gone in 115 hrs.<br>Non-sterile soil, acrolein completely gone in 8 hrs.<br>Biotransformation half-life calculated at 4.2 hours. Four products/intermediates were identified: acrylic acid, 3-hydroxypropionic acid, 3-hydroxypropanal, and CO2.<br>Two transformation products (acrylic acid, 3-hydroxypropionic acid) were also biotransformed (half-life of 29 days) presumably converted to CO2. | ECHA as cited in HSDB 2018 |
| Easy metabolism in soils, with mineralization to CO2. | McBean 2010-2011 as cited in HSDB 2018 |
| Field dissipation studies with half-lives of 7.5 to 10.2 hours. | McBean 2010-2011 as cited in HSDB 2018 |

## Toxicological Profile

Acrolein is categorized as acutely toxic to mammals with a Toxicity Category I ranking for inhalation, oral, and dermal exposures. Acrolein is classified as a strong irritant to mucus membranes and skin. Symptoms of direct contact can include severe eye irritation,skin reddening, ulceration and necrosis. The primary route of inhilation toxicity observed in animal studies was the respiratory system. Symptoms of oral exposure to acrolein include: gastrointestinal distress, stomach ulceration and/or hemorrhage, and vomiting (EPA, 2008). Below in table 11 is a summary of the Acute Toxicity Profile for Acrolein as reported in the Reregistration Eligibility Decision (RED).

**Table 11. Acrolein Acute Toxicity Profile**

| Study Type | Results | Toxicity Category |
|---|---|---|
| Acute oral [rat] | $LD_{50}$ = 11 mg/kg | I |
| Acute dermal [rabbit] | $LD_{50}$ = 231 mg/kg | I |
| Acute inhalation [rat] | $LD_{50}$ = 0.019 mg/L | I |
| Primary eye irriation [rabbit] | Severely irritating | I |
| Acute Dermal Irritation [rabbit] | Severely irritating | I |
| Skin sensitization | Suggestive/ limited data | N/A |

Chronic toxicity to humans has been reported as rare, and no adverse effects have been reported from low concentration exposure to Acrolein. In addition, a review of the 2005 Agency for Toxic Substances Disease Registry (ATSDR), found that the central nervous system does not seem to be a target of Acrolein toxicity. Depression of the central nervous system was observed in some animal studies, but only at doses that would be lethal.

Table 12 summarizes the toxicological doses and endpoints used in the human health risk assessement of Acrolein included in the 2008 EPA RED:

**Table 12**

| C | | | |
|---|---|---|---|
| **Exposure Scenario** | **Dose Used in Risk Assessment** | **Uncertainty/Safety Factor** | **Study and Toxicological Effects** |
| Acute and Chronic Dietary –<br>(All populations) | Acute and chronic oral (dietary and drinking water) exposures to acrolein are not expected based on use patterns, physical-chemical properties, and plant metabolism data. Therefore, RfDs are not required and were not selected for this assessment. | | |
| Incidental Oral (all durations) | There are no residential uses for acrolein. Therefore, incidental oral exposure endpoints are not required and not selected for this assessment. | | |
| Dermal<br>(all durations) | Worker dermal exposures are not expected based on use patterns and personal protective equipment requirements. There are no residential uses for acrolein and dermal exposures to residential bystanders are not expected based on use patterns and physical-chemical properties. Therefore dermal exposure endpoints are not required and have not been selected for this assessment. | | |
| Short –Term Inhalation<br>(1-30 days) | LOAELs<br>0.09 ppm for eye irritation<br>0.3 ppm for nasal and throat irritation | Occupational LOC=30<br>Residential LOC=30<br>Eye irritation<br>$UF_H$ = 10x<br>3x lack of a NOAEL<br>Nasal and throat irritation<br>$UF_H$ = 10x<br>10x lack of a NOAEL | Human volunteers (healthy male and female college students) exposed by inhalation for 60 minutes (Weber-Tschopp et al. 1977) based on a minimal effect LOAEL of 0.09 ppm for eye irritation. The LOAEL of 0.3 ppm for nasal and throat irritation and decreased respiratory rate is also considered for endpoint selection. (MRID 47060601) |
| Cancer (oral, dermal and inhalation) | "The potential carcinogenicity of acrolein is inconclusive; however, exposure to parent acrolein is not expected.<br>Glycidol is a metabolite of acrolein in fish. Glycidol is anticipated to be a human carcinogen by NTP and IARC. To quantify the carcinogenic response of glycidol, a multistage model BMD analysis was performed to derive a cancer slope factor of 0.16 mg$^{-1}$kg$^{-1}$day$^{-1}$ at a 0.95 confidence level. | | |

(EPA, 2008)

## Occupational Exposure and Risk

Under the current use rates reported in EPA RED, occupational exposure to Acrolein handlers can occur. MAGNACIDE H is supplied in sealed pressured vessels for use with a metered device for direct injection below the surface of moving canal water. The application of MAGNACIDE H has stringent label requirements for PPE during both set up and breakdown of application equipment which is expected to effectively prevent dermal exposure. Inhilation exposure to MAGNACIDE H is possible since application times can vary considerably. EPA reported application times ranging from 30 min to 8 hours. Respiratory PPE is not required after set up and take down of the application equipment so exposure is possible following those activities. EPA's established inhalation risk of no concern is 3 ug/L . The target margin of exposure (MOE) for short-term inhalation exposure is 30 as reported in the table above. EPA considers an MOE of >30 to be of potential concern and found that MOE exceedences can occur during set up and breakdown of injection equipment as well as after disassembly is complete. Post application exposure to workers may occur and depends largely on the amount of time a worker remains on site after application. Respirator use is only required during application. Post-application MOEs for post application exposure may exceed EPA's level of concern (EPA, 2008).

## Non Occupational Exposure Risk

EPA reported that residential bystander exposure could occur if residential properties are located in the vicinity of treated water bodies. As reported in the chart above the target level of concern (LOC) for short term inhalation exposure is 30. This suggests that depending on how close the residential areas or bystanders are located to the treated canal, exposures may exceed the EPA established LOC of greater than 3 ug/L (EPA, 2008). However, due to the use conditions for Acrolein in Washington State under the Irrigation System Aquatic Weed Control NPDES General Permit (WA0991000), this is not expected to be a significant pathway for exposure.

### *Aquatic vertebrates and invertebrates*

In addition to toxicity to humans, toxicity testing indicates that acrolein is highly toxic to aquatic life and terrestrial vertebrates, invertebrates, and birds. Chronic toxicity tests indicate reduced growth and survival in fish and reduced survival in invertebrates. The main use of acrolein is herbicide applications to control aquatic plants in irrigation canals, resulting in the highest likelihood of exposures to aquatic biota and potentially for birds and mammals foraging or living in or proximate to the treated canals.

Several relatively recent comprehensive reviews of available aquatic toxicity information for acrolein have been conducted. In 2003 EPA's Office of Pesticide Programs developed a risk assessment for the use of acrolein as an aquatic herbicide, and its potential effects on the listed salmon and steelhead evolutionary significant units (ESUs) for California and a portion of southern Oregon (Turner and Erickson 2003). The assessment concluded that acrolein's use as an aquatic herbicide would either not adversely effect or would have no effect on the ESUs. EPA indicated they would produce an additional analysis for the listed salmon and steelhead ESUs in Oregon, Washington, and Idaho (Turner and Erickson 2003). These have not been published. EPA updated its national recommended aquatic life water quality criteria for acrolein in 2009

(EPA 2009). Much of the information in this discussion is from that review, as well as other review documents and databases as cited in the text. At this time there are no Biological Opinions of the new EPA criteria for acrolein by the services (NOAA and/or USFWS) for states in the Pacific Northwest.

The EPA reviewed the aquatic toxicity of acrolein in its 2009 update of its CWA §304(a) national recommended water quality criteria for acrolein (EPA 2009). That review included a comprehensive literature search conducted in June 2009 (EPA 2009). EPA's review of data for criteria development includes a rigorous process to determine suitable data (Stephan et al 1985). In the case of acrolein, data for 15 aquatic animal species covering 14 genera were found acceptable for water quality criteria development. From the toxicity tests for those 15 species, the species mean acute value for the most sensitive species was 7 ug/L for the African clawed frog, the next most sensitive species was the white sucker with a species mean acute value of 14 ug/L, and the least sensitive species was the insect *Peltoperia maria* with a species mean acute value of 5,920 ug/L. In general, insects were the least sensitive species. Acute toxicity values for salmonids ranged from 16 ug/L for adult rainbow trout to 68 ug/L for 12-17 month old Coho salmon. Following the guidelines (Stephan et al 1995) EPA developed a recommended freshwater national acute criterion of 3 ug/L, 1 hour average concentration. This criterion is calculated to protect both vertebrates and invertebrates. The species mean acute values from EPA 2009 are listed in Table 13.

Table 13. Aquatic toxicity data for vertebrates and invertebrates. Acceptable toxicity data used by EPA (2009; Table 1) in development of the freshwater aquatic life criteria for acrolein. This table was taken from EPA 2009. S = static; R = renewal; F = flow-through; M = measured; U = unmeasured. Each Species Mean Acute Value was calculated from the associated underlined number(s) in the preceding column based on recommendations in the Guidelines (e.g., a flow-through measured test value takes precedence over static tests).

## Table 13

| **Species** | **Method** | **Chemical** | **LCso or EC50 (ug/L)** | **Species Mean Acute Value (ug/L)** | **Reference (as cited in EPA 2009)** |
|---|---|---|---|---|---|
| **FRESHWATER SPECIES** | | | | | |
| Snail (adult), *Aplexa hypnorum* | F,M | - | >151 | >151 | Holcomb et al. 1987 |
| Snail Guvenile), *Physa heterostropha* | S, U | - | 368 | 368 | Horne and Oblad 1983 |
| Cladoceran, *Daphnia magna* | S, U | 99% | 57 | - | Macek et al. 1976 |
| Cladoceran, *Daphnia magna* | S, U | - | 80 | - | EPA 1978 |
| Cladoceran, *Daphnia magna* | S, U | - | 93 | - | Randall and Knopp 1980 |
| Cladoceran (<24-hr old), *Daphnia magna* | S, U | >=80% | 83 | - | LeBlanc 1980 |
| Cladoceran (<24-hr old), *Daphnia magna* | F,M | - | i1 | - | Holcomb et al. 1987 |
| Cladoceran, *Daphnia magna* | F,M | 96.4% | <31 | <39.76 | Blakemore 1990 |
| Scud (juvenile), *Gammarus minus* | S, U | - | 180 | 180 | Hrne and Oblad 1983 |
| Insect (juvenile), *Peltoperia maria* | S, U | - | 5,920 | 5,920 | Horne and Oblad 1983 |
| Midge (juvenile), *Chironomus riparius* | S, U | - | 510 | 510 | Horne and Oblad 1983 |
| Midge (3rd and 4th instar), *Tanytarsus dissimilis* | F,M | - | >151 | >151 | Holcomb et al. 1987 |
| Coho salmon (12-17 months old), *Oncorhynchus kisutch* | S, U | - | 68 | 68 | Lorz et al.1979 |
| Rainbow trout (45.7 mm), | S, U | - | 74 | - | Birge et al. 1982 |

| | | | | | |
|---|---|---|---|---|---|
| *Oncorhynchus mykiss* | | | | | |
| Rainbow trout (juvenile),<br>*Oncorhynchus mykiss* | S, U | - | 180 | - | Horne and Oblad 1983 |
| Rainbow trout (juvenile),<br>Oncorhynchus mykiss | R,M | - | 38 | - | Venturino et al. 2007 |
| Rainbow trout,<br>Oncorhynchus mykiss | F,M | 96.4% | <31 | - | Bowman 1990a |
| Rainbow trout (2.5 g),<br>*Oncorhynchus mykiss* | F,M | - | 16 | 16 | Holcomb et al. 1987 |
| Fathead minnow (adult),<br>Pimephales promelas | S, U | - | 320 | - | Union Carbide Corp. 1974 |
| Fathead minnow (43.2 mm),<br>Pimephales promelas | S,M | - | 45 | - | Birge et al. 1982 |
| Fathead minnow (42-46 day old),<br>Pimephales promelas | S, U | 99% | 14.0 | - | Geiger et al. 1986 |
| Fathead minnow (32-day old),<br>Pimephales promelas | R,M | 99% | 19.5 | - | Geiger et al. 1986 |
| Fathead minnow (43.2 mm),<br>*Pimephales promelas* | F,M | - | 61 | - | Birge et al. 1982 |
| Fathead minnow,<br>*Pimephales promelas* | F,M | - | 29.7 | - | Sabourin 1986 |
| Fathead minnow<br>(1-day old & 30-day old),<br>Pimephales promelas | F,M | 97% | 27 | - | Spehar 1989 |
| Fathead minnow (0.4 g),<br>Pimephales promelas | F,M | - | 14 | 28.77 | Holcomb et al. 1987 |
| White sucker (3.9 g),<br>Catostomus commersoni | F,M | - | 14 | 14 | Holcomb et al. 1987 |
| Flagfish (1-day old),<br>Jordanella jloridae | F,M | 97% | 60 | - | Spehar 1989 |
| Flagfish (30-day old),<br>Jordanella jloridae | F,M | 97% | i1 | 55.32 | Spehar 1989 |
| Bluegill (1.0 g),<br>Lepomis macrochirus | S, U | - | 100 | - | Louder and McCoy 1962 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Bluegill,<br>Lepomis macrochirus | S, U |  | 90 | - | EPA 1978 |
| Bluegill (young of year),<br>Lepomis macrochirus | S, U | >=80% | 90 | - | Buccafusco et al. 1981 |
| Bluegill,<br>Lepomis macrochirus | F,M | - | 33 | - | Holcomb et al. 1987 |
| Bluegill,<br>Lepomis macrochirus | F,M | 96.4% | 22.4 | 27.19 | Bowman 1990b |
| Largemouth bass (1.5 g),<br>Micropterus salmoides | S, U | - | 160 | 160 | Louder and McCoy 1962 |
| African clawed frog (tadpole),<br>Xenopus laevis | F,M | - | 1 | 7 | Holcomb et al. 1987 |

[Holcombe GW et al; Arch Environ Contam Toxicol 16: 697-710 (1987) Available from, as of August 31, 2016: https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&dirEntryId=37101&keyword=snail&actType=&TIMSType=+&TIMSSubTypeID=&DEID=&epaNumber=&ntisID=&archiveStatus=Both&ombCat=Any&dateBeginCreated=&dateEndCreated=&dateBeginPublishedPresented=&dateEndPublishedPresented=&dateBeginUpdated=&dateEndUpdated=&dateBeginCompleted=&dateEndCompleted=&personID=&role=Any&journalID=&publisherID=&sortBy=revisionDate&count=50&CFID=57441231&CFTOKEN=82641049

Acceptable chronic toxicity data were only found for 3 freshwater aquatic species. EPA used the acute and chronic data sets for each species to develop acute-to-chronic ratios (Table 14). EPA developed a chronic criterion of 3 ug/L, 4-day average concentration, based on an acute-to-chronic ratio, for protection of vertebrates and invertebrates.

**Table 14.**

| Acute-Chronic Ratios | | | | |
|---|---|---|---|---|
| **Seciies** | **Acute Value** | **Chronic Value** | **Ratio** | **Reference** |
| Cladoceran,<br>*Daphnia magna* | 57 | 23.83 | 2.392 | Macek et al. 1976 |
| Fathead minnow,<br>*Pimephales promelas* | 29.7 | 16.74 | 1.774 | Sabourin 1986, 1987 |
| Fathead minnow,<br>*Pimephales promelas* | 27 | 22.14 | 1.220 | Spehar 1989 |
| Flagfish,<br>*Jordanella jloridae* | 51 | 25.92 | 1.968 | Spehar 1989 |

Overall, acrolein has high toxicity to aquatic fish and invertebrates (fish and aquatic invertebrates). Canals where acrolein is applied according to label requirements are expected to incur impacts to these organisms in the treatment areas. Holding-time requirements as specified in the Washington SLN are expected to eliminate these effects where treated irrigation waters enter natural waters, although (as discussed above) acrolein has been detected at points of compliance and in downstream waters through NPDES monitoring requirements.

*Aquatic toxicity of inert ingredients in acrolein formulations.*

Acrolein formulations contain several ingredients that are considered inert. Hydroquinone is the only inert ingredient that is not an impurity in the manufacturing process (Turner and Erickson 2003). Toxicity testing of technical acrolein incorporates the toxic effects of these impurities. Hydroquinone is added at 0.25% to inhibit spontaneous reactivity of acrolein and is a “list one” ingredient, which means that it is of toxicological concern and is required to be listed on the label (and is therefore not “confidential”) (Turner and Erickson 2003). De Graeve et al. (1980) reported that the 96-hour LC50 for hydroquinone was 97 ug/L for rainbow trout and 44 ug/L for fathead minnows; the 48-hour LC50 for *Daphnia magna* was 162 ug/L . These were calculated values; the authors noted that 52% of the hydroquinone had hydrolyzed to *p*-benzoquinone in the high concentration. Thus the test incorporates the toxicity of both the hydroquinone and the degradate *p*-benzoquinone that formed during the test. The authors also noted, without providing quantitative data, that the *p*-benzoquinone apparently degrades rapidly to unidentified, less toxic compounds (Turner and Erickson 2003).

Based on these toxicity values hydroquinone is toxic to aquatic organisms. However, because it is present as a small percentage of the formulation relative to acrolein it is not expected to contribute significantly to toxicity in the use of the herbicide product.

### *Amphibian/Reptile*

EPA (2009) found that, from the toxicity tests for those 15 aquatic species found acceptable for criteria development, the African clawed frog species had the most sensitive mean acute value of 7 ug/L. Venturino et al (2009) tested *Bufo arenarum* larvae in 96-hr static renewal tests resulting in an LC50 of 23 ug/L acrolein. Canals where acrolein is applied according to label requirements are expected to incur impacts to amphibians in the treatment areas. Holding-time requirements as specified in the Washington SLN are expected to eliminate these effects where treated irrigation waters enter natural waters.

No information on acute or chronic effects of acrolein on North American reptiles were found. Reptiles could be exposed to acrolein if living or foraging in areas adjacent to treated canals, or if in agricultural fields where acrolein-treated irrigation water is sprayed.

### *Avian*

Available data indicate that acrolein is acutely toxic to birds. The toxicity test data for acrolein's effects on birds is limited. EPA (2008) concludes that acrolein is acutely toxic to birds via oral exposure, based on mallard duck (*Anas platyrhynchos*) single-dose studies. Effects accompanying the lowest LD50 of 9.1 mg/kg a.i. (6.32 – 13.1) included weakness, regurgitation, reluctance to leave the swimming pond, slow responses, wing tremors, geotaxia, withdrawal, muscular debility, and running and falling (USFWS 1984). Treatment levels as low as 3.33 mg/kg produced effects. Sublethal effects appeared as soon as 10 minutes after exposure, persisted up to 36 days after treatment. The first mortality occurred within 32 minutes of exposure while additional mortalities occurred several days after treatment (USFWS 1984). Inhalation data are not available. EPA (2008) calculated inhalation LD50s for mallard, ring-bill gull, and songbird (Table x) using estimated LD50s for gulls and songbirds and an adjusted rat inhalation LD50 (EPA 2008 July 23). The estimated LD50s for the gull and songbird indicate greater sensitivity of these birds compared to the mallard testing. No data on toxicity from dermal exposures were found. Chronic toxicity data are not available.

Based on avian toxicity data and acrolein's Henry's constant there is the possibility that birds foraging or nesting in the areas of the application could be exposed and affected via the inhalation and ingestion pathways. EPA (2008) found that application of acrolein to irrigation canals may result in sufficient acrolein in the air to cause acute mortality in both birds and mammals, however, concentrations of acrolein in air and water decrease with distance from the application site. No data on avian avoidance of volatilized acrolein were found.

EPA (2008) found that both birds and mammals foraging in areas where treated water is sprayed on fields for irrigation would exceed acute risk levels of concern (LOC) by factors as high as 28x (small birds) and 11x (small mammals). Inhalation and drinking water exposures could also are additional risk factors.

**The table below is taken from EPA 2008**

**Table 15: $LD_{50}$ for representative birds estimated from the acute oral $LD_{50}$ for mallard duck and the adjusted rat inhalation $LD_{50}$.**

| Species | Body weight (g) | Oral $LD_{50}$ ($mg \cdot kg^{-1}$) | Inhalation $LD_{50}$ ($mg \cdot kg^{-1}$) |
|---|---|---|---|
| Mallard | 1580 | 9.1 | 0.574[3] |
| Ring-bill gull | 350 | 7.25[1] | 0.458[2] |
| Songbird | 20 | 4.72[1] | 0.298[3] |

[1] oral $LD_{50(oral,\ A)} = LD_{50(oral,\ mallard)}(BW_A/BW_{mallard})^{(1.15-1)}$

[2] inhalation $LD_{50(inh,\ gull)} = LD_{50\ (or,\ gull)}/(LD_{50(or,\ rat)} * Fre / LD_{50(inh,rat)})$, Fre calculation is in text)

1. adjusted $LD_{50(inh)}$ for mallard and songbird: $LD_{50(inh,A)} = LD_{50(inh,\ gull)}(BW_A/BW_{gull})^{(1.15-1)}$

### *Bioconcentration and Bioaccumulation*

Barrows *et al* (1978) conducted a bioaccumulation study in bluegill (*Lepomis macrochiris*) exposed for 28 days and reported 13.1 ug/L acrolein in whole body measurements. The half-life in tissue was greater than seven days. The measured BCF was 344. EPA (2015) developed long-term average bioaccumulation potentials based on $K_{ow}$ of 1.0 kg/L for trophic levels 2 through 4. Because acrolein is in treated canals at high concentrations for short periods of time, and because the tendency of acrolein is to volatilize and break down in water, bioaccumulation of the compound at concentrations that do not result in lethality is expected to be extremely low.

### *Aquatic Phytotoxicity*

Peterson (1994) tested the effects of acrolein on four different algae and 6 species/strains of cyanobacteria at the single test concentration of 1,000 mg/L, a concentration expected to be reached with application for aquatic weed control. The 24-hr inhibition of C14 uptake was determined. Acrolein caused more than 90% mean inhibition in all algae and cyanobacteria that were tested, indicating a high level of phytotoxicity. Duckweed, an aquatic floating vascular plant, was also tested in the study at 1,000 mg/L. A 7-day mean growth inhibition of 73% was measured, indicating high aquatic toxicity of acrolein to this species of vascular plant.

#### *Aquatic Plants*

Acrolein kills plant cells through the destruction of cell membranes (Ashton and Crafts 1981 as cited in Ghilarducci and Tjeerdema 1995) and interruption of vital cell enzyme systems (WSSA 1983 as cited in Ghilarducci and Tjeerdema 1995 ). The action of acrolein is temperature dependent; photosynthesis stops in minutes in warm waters, but cessation occurs much more slowly in cooler water. To inhibit photosynthesis at a similar rate, twice as much acrolein is needed in 60 F as in 80 F water**.** (Ghilarducci and Tjeerdema 1995). Acrolein is expected to kill all vegetation growing in irrigation canals when used at the effective concentrations as specified on the label.

#### *Data Gaps*

EPA (2008) noted that there is currently no avian chronic toxicity data to evaluate the potential risk. Although this contributes to uncertainty when evaluating the risk to non-target species, EPA considers this uncertainty to be low as acrolein residues are expected to deter animals from ingesting treated water. Furthermore, EPA reported that field monitoring studies reported half lives of less than 1 day for treated water bodies which should reduce or prevent potential chronic exposures to non-target species such as birds.Therefore, both chronic exposure risk as well as subsequent chronic impacts are both considered to be low.

## Environmental and Human Health Impacts

### *Earth*

#### *Soil and Sediments*

Due to acrolein’s chemical characteristics, long term persistance in soil is not expected. No long term impacts to sediments themselves are expected from use of acrolein in irrigation canals. Any benthic biota in areas of treatment could be impacted due to the high acute toxicity of acrolein. Finally, no impacts to agricultural soil are expected from the use of acrolein in irrigation canals or from the use of treated water for irrigation. The required 48 hour hold time in combination with the vapor pressure and Koc of acrolein make it unlikely to persist after irrigation using treated water.

### *Water*

#### *Surface Water & Runoff*

The herbicide causes rapid disintegration of plant material into very small fragments that can effectively pass through pumps and irrigation equipment. The effects of the disintegration on water quality include potential increases of turbidity and nutrients downstream, with possible indirect effects on other water quality parameters (USFWS 1999). Nutrients traveling downstream can result in dissolved oxygen sags depending on other factors such as flow rates, dilution, and temperature. This circumstance could impact natural surface waters to which treated irrigation waters discharge, even if proper holding times are adhered to. Residential irrigation water withdrawal from irrigation canals could occur. If withdrawal of treated water occurs and is used for irrigation of other purposes impacts could occur. Recreational uses are prohibited in irrigation district canals and banks. However, if unauthorized uses occur in areas of treated water, and people or pets are exposed, then impacts could occur. The required holding time in Washington of 48 hours prior to discharge to natural waters should result in dissipation of acrolein prior to discharge. However, if treated waters are allowed to enter natural waters prior to full dissipation, then impacts to aquatic biota in natural waters would be expected.

#### *Groundwater*

Due to acrolein's reported Kow value and high volatilization rate, if acrolein is applied in way that is consistent with the pesticide label and Washington's *Irrigation System Aquatic Weed Control NPDES General Permit* (WA0991000), no impacts to groundwater are expected.

#### *Drinking Water/Public Water Supplies*

Withdrawing water from irrigation canals for drinking water purposes is prohibited. Canal banks are owned by the irrigation district and are private property. Use of the canals by non-irrigation district staff on district business is trespassing. If unauthorized withdrawal and ingestion of acrolein-treated water occurs, then impacts would be expected. Furthermore, acroleins use is restriced to managed irrigation networks and canals. If the label and general permit conditions are followed correctly, risk to drinking water and domestic water systems is low. In order to further mitigate risk to adjacent receiving waters including domestic water bodies, the use conditions require that treated water be held for a minimum of 48 hours before release to receiving water bodies.

#### *Air*

Because of acrolein's high propensity to volatilize, air adjacent to canals and over agricultural areas irrigated with treated water will contain some amount of acrolein. Acrolein is applied below the water surface, so at the site of highest concentration (application site) the acrolein will be subsurface and will subsequently mix with irrigation water. Humans and animals in areas where treated water travels or is sprayed could be exposed to acrolein. Additionally, direct contact with irrigation water could occur if persons or animals are directly sprayed with irrigation water.

#### *Plants and Algae*

Acrolein is a non-selective biocide and will treat a wide range of algae and aquatic plants including all target plants identified on the product label and EPA RED. As reported in the toxicological profile, acrolein is toxic to both non-vascular and vascular plants. Four algae were exposed to acrolein, green algae (*Pseudokirchneriella subcapitatum*), blue-green algae (*Anabaena flos-aquae*), freshwater diatom (*Navicula pelliculosa*) and marine diatom (*Skeletonema costatum*) for 72 hours to calculate $EC_{50}$ values. Of the four non-vascular plants, the marine diatom was found to be the most sensitive with a $EC_{50}$ value for reduction of cell density of 28 ug a.i. /L. Duckweed was used as a surrogate for vascular aquatic plants and had an $EC_{50}$ value of 72 ug a.i. /L. Acrolein's impact to terrestrial plants following pesticide application to irrigation water is not widely studied, and no toxicity data exists to assess risks to terrestrial plants (EPA 2008). EPA did note that there is an incident report noting some adverse effects to agricultural crops that were treated water was routinely applied. Although no data has been collected there is a hypothesis that the waxy cuticle of terrestrial plants may serve to protect plants from the toxic effects of acrolein. The Magnacide H product label allows treated water to be used for furrow, pasture or active crop irrigation with no restrictions on concentration or crop type (Magnacide H, 2022).

#### *Habitat and Wetlands*

Based on the available chemical information and toxicity data acrolein is not expected to cause chronic effects to aquatic habitats, but is acutely toxic to aquatic organisms. However, if acrolein is applied in the manner described on the product label, acute effects to non-target aquatic organisms would be contained to highly managed irrigation networks, and would not impact outside receiving waters. Highly managed irrigation ditches and canals are not expected to have large populations of sensitive aquatic organisms or be classified as critical habitat. Persistence and bioaccumulation in the environment is not expected due to the rapid volitilization of acrolein and reported degredation rates. The required holding time in Washington of 48 hours prior to discharge to natural waters should result in dissipation of acrolein prior to discharge and reduce the risk of acute toxicity to receiving water bodies.

If label directions or mitigation steps in the general permit are not followed, there is a potential risk for acute toxicity to organisms in receiving waters down stream of treated areas. Wetlands biota directly adjacent to treated canals could be impacted by volatized acrolein from treated canal water. Treated water should not enter wetlands directly as canals are designed to contain water for agricultural use only.

### Mitigation

#### *Use Restriction and Mitigation*

EPA-approved product labels list several precautions and restrictions when applying acrolein pesticides to aquatic environments. Some of the requirements include that: acrolein pesticides should not be applied through any type of irrigation system. Acrolein must be applied according to the Magnacide H Herbicide Application and Safety Manual by a certified on-site applicator. Acrolein should not be used where waters will flow into potential sources of drinking water. Acrolein treated water should only be used for agricultural irrigation. Acrolein should only be applied during daylight hours, a maximum of 8 applications per year, and with a minimum treatment interval of 2 weeks. In addition, the product label contains a requirement to post specific signage around the perimeter of the equipment area during the entire application period (Magnacide H, 2022). Specific pesticide labels should be consulted for a complete list of hazards, recommendations, and requirements. In addition, Ecology’s Irrigation System Aquatic Weed Control General Permit has additional use restrictions and conditions when applying acrolein pesticides in Washington State. Acrolein concentrations must not exceed a maximum instantaneous concentration (or highest allowable discharge), of 21 ug/l at the point of compliance and during the permit term, permittees must make a reasonable effort to reduce the use of acrolein in favor of more environmentally sensitive chemicals. This effort should be demonstrated in the discharge monitoring reports (Ecology, Permit Exp. 2019).

*Swimming and Skiing.*

Canal banks and irrigation canals are owned by the irrigation district and are private property. The use of canals by non-irrigation staff is trespassing on private property. As the application of acrolein is only registered for use in irrigation networks, no recreational impacts to swimming or skiing are expected. Trespassing on private agricultural waterways can and does occur. The label provides some mitigation measures for recreational risk by requiring that clear “No Swimming Allowed,” signs be placed at all access points to the treated waterway including roads and streets for the duration of the application period. Future versions of the permit should consider requiring appropriate notification signage to inform the public that a pesticide application has taken place and any potential impacts to uses of the waterbody.

*Irrigation and Potable (drinking and domestic) Uses*

The label for acrolein algaecides contains no restrictions for treated water when used for crop irrigation. Water treated with acrolein must be used for irrigation of fields (fallow, pasture, or crop bearing). Acrolein should not be used if treated waters will flow to potential sources of drinking water. The label also states that treated water should not be ingested by livestock such as dairy cows. The required signage and administrative controls contained in both the label and *Irrigation System Aquatic Weed Control General Permit* should be strictly adhered to in order to prohibit the incidental ingestion of treated water.

*Fisheries and Fish Consumption*

Acrolein is acutely toxic to aquatic organisms, and could impact local fish populations in receiving waters if acrolein treated water is prematurely released from irrigation networks before the minimum holding time of 48 hours. Care should be taken when applying acrolein, and the directions for use on the label should be strictly followed. Consumption of fish exposed to acrolein is not likely to be an issue as it’s not expected to bioaccumulate or bioconcentrate in fish or shellfish tissues. In addition, as previously stated acrolein is only registered for use in controlled irrigation networks where recreational fishing is not allowed. The label for Acrolein also requires that treated water applied to fields which is destined or will drain into fish bearing waters must be held for 6 days. Furthermore, Ecology’s current *Irrigation System Aquatic Weed Control General Permit* states, “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 Washington State Department of Fish and Wildlife (WDFW), and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations.” This permit condition should be carried forward in the next reissuance.

### *Wetlands and Non-target Species*

Acrolein, if used in a manner other than listed on the product label and general permit, has the potential to acutely affect wetlands and non-target plants and animals. Acrolein is a non-selective pesticide with known acute toxicity to both aquatic and terrestrial organisms. If used according to the product label, acrolein is not expected to affect adjacent wetlands. Acrolein is registered for use in managed irrigation networks only and should not be applied directly to wetland areas. Acrolein application requires a post application minimum hold time for treated water of 48 hours. This hold time allows acrolein concentrations to dissipate, mitigating potential acute or chronic toxicity to receiving waters containing non-target plants and animals. All plants and algae within a treated irrigation canal are considered to be target organisms since acrolein is a non-specific biocide.

### *ESA Listed Species*

Based on the available toxicity information, acrolein has the potential to be acutely toxic to ESA-listed species. Due to its propensity to volatilize rapidly and reported half life rates, acrolein is not predicted to cause chronic toxicity to ESA-listed animal species. Although there is a potential for toxicity to ESA-species from acute exposure, these species are not likely to inhabit managed irrigation networks where acrolein is permitted for use. The risk to endangered or vulnerable species is further mitigated through Ecology's permit process. The current *Irrigation System Aquatic Weed Control General Permit* (WA0991000) states,"Before issuing permit coverage, Ecology will determine whether sensitive, threatened, or endangered (rare) plants 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."Furthermore, "The Permittee must comply with WDFW timing windows referenced in Tables 3 and 4 to protect salmon, steelhead, and bull trout populations and WDFW priority habitats and species." In addition, acrolein application requires a post application minimum hold time for treated water of 48 hours. This hold time allows acrolein concentrations to dissipate, mitigating potential acute or chronic toxicity to receiving waters containing ESA listed plants and animals.

### *Roadsides or Utility Right-of-Way*

As acrolein is only approved for aquatic weed control in irrigation supply systems, its use is not expected to affect roadsides or utility easements. If the directions for use are followed, all access points should have appropriate signage detailing application information and swimming restrictions on roadsides and property adjacent to the treatment site.

### *Post-treatment Monitoring.*

The label acrolein contains no requirement for post-treatment monitoring following application. As part of Ecology's current permit requirements, short -term post-treatment monitoring is required. Ecology uses this monitoring to determine permit compliance and the potential for non-target impacts.

## References

1. MacBean C, ed; e-Pesticide Manual. 15th ed., ver. 5.1, Alton, UK: British Crop Protection Council. Acrolein (107-02-8) (2010-2011)
2. Bowmer KH, Higgins ML; Arch Environ Contam Toxicol 5: 87-96 (1976)
3. Tabak HH et al; J Water Pollut Control Fed 53: 1503-18 (1981)
4. Stover EL, Kincannon DF; J Water Poll Control Fed 55: 97-109 (1983) (6) Callahan MA et al; Water-Related Environmental Fate of 129 Priority Pollutants. EPA-440/4-79-029A pp. 20-1 to 20-11 (1979) (7) Hultman B; Water Sci Tech 14: 79-86 (1982)
5. ATSDR; Toxicological Profile for Acrolein. Atlanta, GA: Agency for Toxic Substances and Disease Registry, US Public Health Service (2007). Available from, as of Aug 11, 2016: http://www.atsdr.cdc.gov/toxprofiles/index.asp
6. Bidleman TF; Environ Sci Technol 22: 361-367 (1988)
   Edney E et al; Atmospheric Chemistry of Several Toxic Compounds. EPA-600/53-82-092 (1983)
7. Daubert TE, Danner RP; Data Compilation Tables of Properties of Pure Compounds. American Institute of Chemical Engineers (1989)
8. Edney, E.O., Mitchell, S., Bufalini, J.J. (1981). Atmospheric Chemistry of Several Toxic Compounds. Research Triangle Park, NC: Environmental Sciences Research Laboratory, US Environmental Protection Agency.
9. Lyman, W.J., Reehl, W.F., Rosenblatt, D.H. (1982). Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds. New York, NY: McGraw-Hill.
10. Grosjean D. 1990. Atmospheric chemistry of toxic contaminants. 3. Unsaturated aliphatics: Acrolein, acrylonitrile, maleic anhydride. J Air Waste Manage Assoc 40:1664-1668.
11. Liu X, Jeffries HE, Sexton KG. 1999b. Hydroxyl radical and ozone initiated photochemical reactions of 1,3-butadiene. Atmos Environ 33:3005-3022.
12. NIST; NIST Chemistry WebBook. Acrolein (107-02-8). NIST Gas Phase Kinetics Database No. 69, Feb 2015 Release. Washington, DC: US Sec Commerce. Available from, as of Aug 10, 2016: http://webbook.nist.gov
13. Edney E et al; Atmospheric Chemistry of Several Toxic Compounds. EPA-600/53-82-092 (1983)
14. WHO; Concise International Chemical Assessment Document 43. Acrolein. World Health Organization (2002). Available from, as of Aug 12, 2016: https://apps.who.int/iris/handle/10665/42490]
15. Gaffney JS et al; Environ Sci Technol 21: 519-23 (1987)
16. Daubert TE, Danner RP; Data Compilation Tables of Properties of Pure Compounds. American Institute of Chemical Engineers (1989)

17. ECHA; Search for Chemicals. Acrolein (CAS 107-02-8) Registered Substances Dossier. European Chemical Agency. Available from, as of August 12, 2016: https://echa.europa.eu/

18. Venturino A, Montagna CM and Pechen de D'Angelo AM, 2009. Risk Assessment of Magnacide H Herbicide at Rio Colorado Irrigation Channels (Argentina). Tier 3: Studies on Native Species, Environmental Toxicology and Chemistry, 26(1), 177-182

19. U.S. Department of the Interior, Fish and Wildlife Service. Handbook of Toxicity of Pesticides to Wildlife. Resource Publication 153. Washington, DC: U.S. Government Printing Office, 1984., p. 8] **PEER REVIEWED** /

20. [EPA; Office of Prevention, Pesticides and Toxic Substances; Reregistration Eligibility Decision (RED) for Acrolein p.25 EPA-HQ-OPP-2007-0588 (September 2008). Available from, as of August 23, 2016: chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://archive.epa.gov/pesticides/reregistration/web/pdf/acrolein_red.pdf] **PEER REVIEWED**

21. EPA 2015. Update of Human Health Ambient Water Quality Criteria: Acrolein 107-02-8. EPA 820-R-15-003. 24 pp. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0211

22. Barows,M.E., S.R. Peterson, H.G., C. Boutin, P.A. Martin, K.E. Freemark, N.J. Rueker, and M.J. Moody. 1994. Aquatic phyto-toxicity of 23 pesticides applied at Expeted Environmental Concentrations. Aquatic Toxicology 28, 275-292.

23. Ashton FM, Crafts AS (1981) Mode of Action of Herbicides, 2nd ed. Wiley, NewYork.

24. Weed Science Society of America (WSSA) (1983) Herhicide Handbook of the Weed Science Society of America, 5th ed. Weed Science Society of America, Champaign.Il.

25. 2015. A Synthesis of the Effects of Pesticides on Microbial Persistence in Aquatic Ecosystems

26. Zachery R. Staley, Valerie J. Harwood, and Jason R. Rohr*. HHS Author Manuscript at https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4750050/ . Final version at Crit Rev Toxicol. 2015 Nov; 45(10): 813–836.

27. Shaner, D. (2014). Herbicide Handbook. Lawrence, KS: Weed Science Society of America.

## Chelated Copper

### Registration Status (FIFRA and WA Registration)

Chelated copper pesticides are composed of elemental copper with an added chelating agent that enhances ion solubility. Chelation agents can vary, but they are usually organic compounds. Chelated copper herbicides typically use copper ethanolamine complexes or copper carbonate in their formulations and are designed to keep the active copper in solution for as long as possible. (SFEI, 2005). These products are registered for use as a fungicide, bactericide, algaecide, herbicide, insecticide, anti-fouling agent, and wood preservative. There are multiple trade names registered with the Environmental Protection Agency (EPA), as copper pesticide products. Some major trade names include Kocide, CuproFix, Basicop, K-tea, Captain, Cutrine, Captain, and Nautique. Copper pesticides are broad spectrum and are used to control a range of pests including, fungi, bacteria, aquatic weeds, algae, mollusks, and leeches (EPA, 2009). In the aquatic environment, copper is specifically registered for use as an algaecide, herbicide, molluscicide, and macro-invertebrate use. Copper applications for algae control include aquaculture facilities, drainage systems ponds, fountains, lakes, reservoirs, sewage lagoons, stocking and irrigation canals. For aquatic weed control, copper pesticide application includes aquaculture facilities, drainage systems, ponds, lakes, reservoirs, sewage lagoons, stocking and irrigation canals. Under the *Irrigation System Aquatic Weed Control,* general permit Washington State Department of Ecology currently allows the use of chelated copper for controlling a variety of floating and submerged aquatic vegetation (Ecology, 2012).

### Chemical-use Patterns

The registered herbicide label for SePRO brand Captain Liquid Copper Algaecide, describes chelated Copper as a non-selective herbicide that is effective in controlling a broad range of green and blue-green (cyanobacteria) algae, including filamentous, planktonic and macrophytic. Chelated copper is also effective on any aquatic weed species with susceptibility to copper. The label allows for use in a variety of still or flowing aquatic sites including: golf courses, irrigation and aquaculture ponds, fresh water lakes, ponds, fish hatcheries, potable water reservoirs, rivers, streams, saltwater environments and agricultural irrigation and drainage systems. For applications of liquid copper algaecide to water, the current label, at the time of this writing, allows for a variety of application methods and rates. Chelated copper can be applied by surface spray, subsurface injection, drip or metered pump and chemigation. The rate of application varies with type and density of algae. For aquatic weed control (including algae and vascular plants), a single application must not exceed a copper concentration of 1.0 ppm. Applications of chelated copper must be separated by a minimum of 14 days. When treating aquaculture ponds where fish are present, concentrations must not exceed 0.4 ppm during a single application when targeting algae. Applications to aquaculture ponds must be separated by a minimum of 10 days. Copper's use as an active ingredient in aquatic herbicides is listed in the Code of Federal Regulations (40 CFR 180.1021) as exempt from residue tolerance requirements if it is used as an aquatic pesticide (40 CFR 180.1021, 2018). However, there is a drinking water standard for copper of 1.3 ppm.

## Chemical Description

The active ingredient in chelated copper pesticides is elemental copper, a reddish metallic noble metal registered under the CAS Number 7440-50-8. It can exist in four oxidative states: Cu(0), Cu(I), Cu(II), and Cu(III). Cu(II) or cupric copper is the most important state of copper. Cu(II) is the most common form found in water and the common form of active copper released by copper pesticides. Complexes and compounds of cupric copper are typically blue or green in color and frequently soluble when added to water. (ATSDR, 2004). Copper pesticides can utilized various forms of copper such as those that use chelated copper. Regardless of the chelating agent used, chelated pesticides ultimately dissociate and release the cupric ion form of copper, which is the active component of concern (EPA, 2012).

Copper has a boiling point of 2,595°C a melting point of 1083°Cand a density of 8.96 g/cm3 (ATSDR, 2004). Given the Henry's Law constant of 0 atm/m^3 • mole and vapor pressure of 1 mm Hg at 1628 °C, indicating copper does not readily volatilize. Copper has a log octanol/water partition coefficient (log Kow) of -0.571 and a water solubility value of 0 mg/L, indicating that copper is insoluble in water. The environmental fate of metals such as copper are often complex.

## Fate and Transport

### *Water*

In water, chelated disassociates into dissolved elemental or cupric copper ($Cu^{2+}$ or Cu(II)) and the chelating agent. As free or ionic copper is already in the elemental form, it will not break down further into degradation products. However, copper is highly reactive in the aquatic environment, transitioning between free and bound states in varying proportions depending on the other chemical species present in the water (EPA, 2009).

In surface waters, copper is predominantly found in the cupric Cu(II) form. After copper is dissolved into a water body the cupric ions typically bind to ligands found in the water, soil, and sediments. Stable complexes typically include -Cl, -CO3 -$NH_2$, -SH, and -OH groups (Rader et. al., 2019).

The state in which copper exists is highly dependent on the reduction-oxidation (redox) conditions and pH of the solution. In conditions that favor redox reactions (many free electrons, based on pH) one chemical species (reducing agent) donates electrons to another chemical species (oxidizing agent) (University of Texas, Accessed: 2019). The pH represents the acidity of a solution, which is the concentration of hydrogen ions (H+). If a solution is more acidic, it has fewer free electrons to provide to redox reactions, while a more basic solution has more electrons to provide to redox reactions. Depending on the availability of free electrons, either copper or another chemical species will donate electrons based upon the redox conditions, which favors different copper species (Wright et. al., 2007).

### *Soil and Sediment*

In soil, copper's mobility and fate is determined by a range of chemical and physical interactions with soil constitutes (ATSDR, 2022). Copper fate in the terrestrial environment is driven largely by three main processes: transport to deeper soil levels through groundwater percolation, binding to soil constituents, and breakdown into metabolites (Siemering et al., 2005). Copper readily absorbs to organic matter, carbonates, clays, and metal oxides. In most temperate soils, the amount of organic matter, pH, metal oxyhydroxides and ionic strength of the soil solutions are the key factors affecting absorption (ATSDR, 2022). The distance copper will travel in soil is directly related to the absorption rates of the soil's constituents (Siemering et al., 2005). When soil has a high organic content copper will strongly bind to soil particles. When organic matter concentrations are low, the mineral content becomes more important in determining copper absorption rates (ATSDR, 2022). The strong binding properties of copper are important when considering fate, as transformations and fluxes of copper compounds may change the various locations copper is found in aquatic environments (Rader et. al., 2019). Microorganisms within the soil can also affect the absorption of copper via uptake and assimilation (ASTDR, 2022). A study looking at binding rates found that at a low pH of 3.9 only 30% of copper was bound to the soil and 99% of copper was bound at a pH of 6.6, suggesting that acidic soil can be a significant driver of binding rate (Temminghoff et. al., 1997). A study also found that copper more readily leaches from soils that are sandy or have high acidity (Flores-Vélez et. al. 1996). Copper complexes are inorganic compounds and thus not expected to photolysis in water, however these complexes are expected to readily solvate into copper ions. Post treatment copper bound in this way is unlikely to be re-suspended and released back into the water column at levels that would negatively affect free-swimming organisms (Ecology, 2001).

## Bioaccumulation

Bioconcentration factor (BCF) is the ratio of concentration of chemical in an organism divided by the ambient concentration of the chemical in the environment and is a measure of the readiness with which chemical sharing occurs (WAC 173-333, 2012). The BCF of copper in mollusks such as oysters and squid may reach as high as 30,000 and $2.1\text{x}10^{7}$ respectively, indicating high copper loading. As copper is often found in particulate form within the water column, filter feeding is likely the reason for higher BCF values. The BCF for copper obtained from fish through field studies ranges from 10-667 indicating a low potential for bioconcentration in aquatic organisms that do not filter feed. With a $K_{ow}$ value of less than 10, copper compounds have little to no likelihood of bioaccumulation (ATSDR, 2004).

## Volatilization from water

Copper complexes have low vapor pressures and Henry's Law constant indicating that copper complexes will not readily volatilize when introduced to water (USEPA, 2009) The Vapor Pressure at 20 degrees C was reported at $3.40 \text{ X } 10^{-10}$ indicating low volatility (IUPAC, 2022).

## Degradation and dissipation of chelated copper

The processes involved in the transport, partitioning and degradation of copper are not easy to separate. The transformation of a metal such as copper from one form to another can change the transport and partitioning properties within the environment. For example, complexation of copper with small organic compounds might result in enhanced mobility in soil or water. A chelated copper formation would decrease solubility and thus mobility in water or soil (ATSDR, 2022). Unlike organic pesticides, copper does not degrade. Instead, copper entering the environment enters a complex biogeochemical cycle. “In the water column, copper can exist bound to both organic and inorganic species and as free or hydrated copper ions. Water column chemistry affects copper speciation and bioavailability. In all water types (saltwater, brackish water, and freshwater), organic ligands in the water column can sequester the majority of free copper, and therefore, organic ligands play the largest role in copper bioavailability. In freshwater, however, the geochemistry of a particular location, including water column characteristics such as water hardness and pH, is a significant factor that can increase copper bioavailability and toxicity. In most cases, organic ligand concentrations greatly exceed copper ion concentrations in the water column and therefore provide a large buffering capacity” (Kiaune et al., 2011). Generally, much of the copper that is discharged into waterways is in the form of particulate matter that settles out. Both in the water column and in sediments copper readily absorbs to organic matter, hydrous metal oxides such as iron oxide, and clay (ATSDR, 2004).

## Field Surveys and Investigations

Several research, surveys, and laboratory investigations have been performed on chelated copper pesticide products in a range of environmental conditions. The San Francisco Estuary Institute’s (SFEI) Aquatic Pesticide Monitoring Program monitored the treatment of two irrigation canals using mixed copper ethanolamines with and without an emulsifier, Cutrine Plus and Clearigate, respectively. SFEI hypothesized that differences in chelating agent, inert ingredients, and adjuvants might alter behavior of chelated copper pesticides when applied to water bodies. SFEI found that both systems were similarly toxic following application regardless of the addition of emulsifiers, and therefore could not definitively conclude how different mixed copper ethanolamines may differ in toxicity to organisms within irrigation systems. Chelated copper products using the active ingredient copper carbonate were not monitored during this study. The study recommended further risk characterization of chelated copper pesticides for both water and sediment to better understand potential impacts (SFEI, 2005).

A study entitled *Algicidal Effectiveness of Clearigate, Cutrine-Plus, and Copper Sulfate and Margins of Safety Associated with Their Use*, by Murray-Gulde Et al., looked at the response of a variety of chelated copper pesticides to the green algae species Raphidocelis subcapitata in order to determine the potential contact time and critical burden of copper necessary to contain algal control. The study also explored changes in residence time of chelated copper pesticides in the water column under three different water characteristics. Finally, the study looked at the varying application rates necessary to control algae and compared them to nontarget species adverse thresholds to determine the relative safety margins from the three chelated products tested.

The study found that the critical burden or threshold concentration of copper that must be sorbed by Raphidocelis for control was 7.3 and 7.9 µg for Cutrine-Plus and Clearigate, respectively. Calculation of the critical burdens allows for an estimate of the maximum density of algae that can be treated using a given treatment. The study calculated that at the label rate for Clearigate of 1 mg Cu/L the maximum Raphidocelis density that could be controlled would be 3.7 x $10^6$ cells /ml. The half-life of copper was found to vary with water quality characteristics. The shortest half-life was found to be 2.6 days. The study concluded that chronic exposure data and risk characterizations for non-target species might not be appropriate given the relatively quick residence time copper has in the water column. Finally, the study compared the relative margin of safety for both Clearigate and Cutrine-Plus and found that toxic effects to non-target species is generally due to exposure within the first 24 h of application and not from cumulative exposure, with margins of safety increasing to around 200% by day 5 (Murray-Gulde, 2002).

### Toxicological Profile

Short-term inhalation exposures of copper have been associated with a range of symptoms in humans including but not limited to, respiratory, gastrointestinal, hematological, hepatic, endocrine and ocular effects. Symptoms from inhalation can vary with exposure level but can include symptoms such as headache, vertigo, drowsiness and eye irritation. Effects from oral exposure to copper are often gastrointestinal. The most prevalent symptoms from copper ingestion are nausea and vomiting. Other less typical symptoms can include abdominal pain and diarrhea. There are some reports that death can occur if very high levels of copper are ingested (ATSDR, 2004). The most common symptoms of acute dermal exposure to copper are skin dermatitis and eye irritation. The EPA has classified copper as Group D, or not enough available data to either support or refute human carcinogenicity (EPA, 2000). Under OSHA's toxicity category ranking system chelated copper algaecides ranged from II to IV depending on the route of exposure. $LD_{50}$ values for the Acute Oral Rat toxicity tests were reported between 590 and 1,312 mg/kg, a toxicity category of IV (slightly toxic to practically non-toxic). Acute dermal $LD_{50}$ values were all reported as >2000mg/kg and categorized chelated copper as category II, indicating the possibility of mild to severe skin and eye irritation. As the target medium for chelated copper application is water, toxicity to aquatic organisms is the highest concern when assessing environmental risk. The use pattern for copper as an aquatic herbicide indicates that it will remain in agricultural water bodies after treatment and a summary of aquatic toxicity studies indicate that chelated copper can be toxic to non-target aquatic species. Risk scenarios for humans include consumption of treated water and inhalation or skin contact with copper during application (Nautique, 2018). Based on the available data EPA concluded that there is no evidence that warrants calculating sub-chronic and chronic toxicity. Available short-term studies on mice and rats indicate decreased food and water intake as oral copper concentrations increase. Higher copper concentrations showed stomach irritation. At high levels of excess copper, some inhibition of immune response was noted, but is not unusual as other trace elements can show a similar response (EPA 2000).

## Mammalian, Avian, and Human Toxicity

In mammals and birds, copper is an essential trace element for maintaining mammalian and avian health. Copper is important for the function of many cellular enzymes due to its role as a catalyst in redox reactions (Tapiero, 2003). When ingested, copper is readily absorbed by both the stomach and intestine. After trace requirements in an organism have been met, species utilizing copper have multiple mechanisms that can regulate copper levels, helping to prevent copper toxicity. These regulatory pathways effectively reduce the risk of copper toxicity in the body following exposure to excessive copper levels. Copper homeostasis in the body is primarily driven through the binding protein metallothionein, which binds excess copper and allows for excretion from the body. Although these mechanisms help to prevent copper toxicity, high-level doses of copper can result in a number of adverse effects including anemia, liver and kidney damage, immunotoxicity, and developmental toxicity. Animal studies using orally exposed rats and mice have found no increased risk of cancer (ATSDR, 2004).

The EPA in its Reregistration Eligibility Decision for Coppers (RED) assessed the risk of oral ingestion and inhalation risk of copper-containing pesticides to birds, mammals, and other terrestrial animals. There are a variety of copper-based pesticides used in agriculture included in the RED. The risk assessment assumes instant disassociation of cupric ions from its ligand (binding molecule), which is a conservative estimate of bioavailability to exposed organisms. In order to estimate the potential risks to nontarget organisms, EPA calculated Estimated Environmental Concentrations (EECs), Risk Quotients (RQs), and Levels of Concern (LOCs) for different categories of organisms. EECs were derived from environmental fate, pesticide use, and soil and water chemistry data. RQs are a ratio of the calculated EEC to the most sensitive endpoint values of the organisms tested. Examples of these endpoints include lethal dose ($LD_{50}$) or median lethal concentration ($LC_{50}$). A comparison of RQ values to LOCs allows an estimate of risk to be made. If the RQ value exceeds the LOC for a category than there is a presumed potential risk to nontarget organisms. The table below displays the Risk Presumptions and LOCs EPA calculated for terrestrial animals and birds as part of the RED.

EPA’s LOCs and Risk Presumptions for Terrestrial Animals and Birds

| Risk Presumption | LOC |
|---|---|
| Acute Risk - there is potential for acute risk; regulatory action may be warranted. | 0.5 |
| Acute Endangered Species – there is potential for endangered species risk; regulatory action may be warranted. | 0.1 |
| Chronic Risk - there is potential for chronic risk; regulatory action may be warranted. | 1 |

The EPA’s ecological risk assessment suggests a potential risk to terrestrial animals exposed to copper resulting from use as an agricultural pesticide. RQs reflecting dietary exposure and toxicity to birds and mammals exceed both acute and chronic LOCs. The ecological risk assessment used both maximum labeled rates and average application rates to terrestrial crops (EPA, 2009).

### Occupational Exposure Risk

Workers are primarily exposed to copper pesticides through mixing, loading and/or application. Copper exposure can also occur when people re-enter treated sites. Exposure may also occur in home environments from the application of residential pesticide products. Exposure to copper may cause a range of effects in humans including acute dermal and eye irritation, abdominal pain, nausea, vomiting, or diarrhea. The EPA RED found that copper has low acute toxicity in humans, with the exception of acute inhalation of cuprous oxide, and no evidence that copper causes systemic toxicity or carcinogenicity in animals with copper homeostasis. As no systemic toxicity risk was established from reviewed materials, and there is no known upper limit toxicity level, EPA chose not to generate acute endpoints for dietary, dermal, oral, or inhalation exposure (EPA, 2009). Similarly, EPA reviewed available chronic toxicity data and found no evidence of an upper limit toxicity level that requires the development of chronic toxicity endpoints for, dietary, oral, dermal or inhalation exposures. The EPA noted that some studies have suggested chronic inhalation of copper sulfate and lime mixture in vineyard workers may be cancerous however; there is no information on the level of copper exposure experienced by the workers, or any additional substances that they may have been exposed to while working. Developmental and reproductive studies have shown a greater risk from copper deficiency than excess copper exposure when investigating potential reproductive and teratogenic effects. In summary, EPA found that all potential acute and chronic human health exposures to copper are below the established level of concern. The irritating effects of copper compounds are sufficiently addressed through appropriate product specific precautionary labeling language, handler Personal Protective Equipment (PPE), and workplace safety standards (EPA, 2009). Copper pesticide product labels include a Precautionary Statements section, which includes minimum requirements for Personal Protective Equipment (PPE) to mitigate risk from mixing, loading, and applying copper. Examples for meeting minimum requirements for applying chelated copper pesticides include coveralls, long sleeve shirt and pants, socks and chemical resistant shoes, chemical resistant gloves, protective eyewear, and a chemical resistant apron (SePRO, 2018).

### Non-Occupational Risk

The EPA *Coppers Facts* report found no aggregate risk from combined exposure to copper. EPA defines aggregate risk as the “combined risk from dietary (food and drinking water) and residential or other non-occupational exposures, Aggregate risk can result from one-time (acute), short-term or chronic exposures.” EPA concluded that due to the lack of systemic toxicity, the combined exposure concentrations from pesticide sources do not pose a health risk. Finally, due to the use restrictions for copper in Washington, non-occupational exposure is not expected to be a significant pathway for exposure.

## Aquatic Toxicity

Similar to mammals, many aquatic organisms also require small amounts of copper to maintain health; however, excessive copper exposure can result in significant toxicity. For organisms with gills, copper toxicity occurs when copper rapidly binds to gill membranes causing damage and interfering with osmoregulatory processes. Copper's toxicity threshold in aquatic organisms is dependent on the environmental water quality parameters. Some of the most important parameters to copper toxicity include, but are not limited to pH, alkalinity, and dissolved organic carbon. In the EPA RED, Copper toxicity is reported to be highest in water with low alkalinity and/or low dissolved organic carbon (EPA, 2009).

In evaluating risks to freshwater organisms, EPA employed the Biotic Ligand Model or BLM in addition to standard methods. The BLM is a metal bioavailability model that uses water body characteristics and monitoring data to generate site-specific water quality criteria. Some of the input data for the model include dissolved organic carbon, temperature, pH, major cations and anions, alkalinity, and sulfides. The BLM combines both speciation and toxicity and allows for the calculation of toxicity values. As the BLM covers only freshwater organisms, estuarine and marine animal RQs were calculated by EPA using estimates of total dissolved copper, a more conservative exposure value. EPA's site-specific pesticide transport models PRZM and EXAMS scenarios simulations were used to calculate copper inputs to the BLM. The EPA assessed water chemistry values at 811 sites representing median surface water quality conditions across the United States. All 811 sites were simulated using the BLM and calculated cupric ion concentrations were estimated at each site. $LC_{50}$s were calculated using the BLM for *Daphnia magna*, and *Pimephales* promelas (fathead minnow). Daphnia were found to be the most sensitive freshwater invertebrate. Salmonids of the genus Oncorhynchus were found to be the most sensitive fish, but at the time of the RED the BLM had not yet been implemented to calculate the $LC_{50}$ values for this genus. To account for the sensitivity to salmonids, the fathead minnow genus acute mean of 72.07 ug/L copper was adjusted using a factor derived from the ratios of the $LC_{50}$ values, which was calculated to be 0.404. The fathead minnow genus acute mean of 72.07 ug/L was multiplied by 0.404 to calculate the genus acute mean of 29.11 ug/L for salmonids. The adjustment factor was calculated to be 0.404. The Chronic toxicity values were derived from an acute-to-chronic ratio (ACR), as the BLM only estimates acute toxicity values. The ACR for chronic freshwater organisms was estimated to be 3.23 which was derived from a range of ACR's for freshwater species that had acute and chronic toxicity data. 3.23 represents the central value in this range. The ACR was then applied to the acute toxicity value of each of the 811 sites to calculate the chronic toxicity value. This chronic toxicity value was used for the Risk Quotient (RQ) when evaluating the EPA levels of concern (LOC's) for copper-based pesticides (EPA, 2009).

Use data for copper pesticides for algae and aquatic weed control indicated application rates of 0.1- 1ppm. EPA used the Exposure Analysis Modeling System (EXAMS) which is used to evaluate fate, transport, and exposure in aquatic ecosystem models and the BLM to produce RQs that were compared to EPA LOC values found in the table below. For other aquatic organism control, application rates can be higher (1-2.5 ppm).

EPA's LOCs and Risk Presumptions for Aquatic Animals

| Risk Presumption | LOC |
|---|---|
| Acute Risk - there is potential for acute risk; regulatory action may be warranted. | 0.5 |
| Acute Endangered Species – there is potential for endangered species risk; regulatory action may be warranted. | 0.05 |
| Chronic Risk - there is potential for chronic risk; regulatory action may be warranted. | 1 |

At these application rates, for invertebrates, fish, and aquatic plants, >99% of sites exceed the endangered species LOC and Acute LOC. The chronic risk for aquatic fish and invertebrates were exceeded at >96% of sites. Because of the large difference in waterbody chemistry, the models likely both over and under estimate risk, depending on the water body. Furthermore, when only portion of a water body is treated there is a range of exposure and resulting effects depending on an organisms distance from the treatment site and/or the ability of an organism to leave the treatment area. The EPA notes that for direct water applications of copper pesticides there are likely to be effects to invertebrates and a reduction in primary productivity (EPA, 2009).

Three studies (Mastin and Rodgers, 2000, Johnson et al, 2008, Murray-Gulde et al., 2002) derived laboratory copper LC50 values for a variety of aquatic organisms from various chelated copper compounds commonly used in aquatic plant management. The chelated copper herbicide values are summarized in the table below:

| OrganismCa | Algaecide | Test Duration | Concentration ug Cu/L |
|---|---|---|---|
| *C. dubia* | AlgimycinPWF | 96-h LC50 | 48 |
| | Cutrine-Plus | 96-h LC50 | 92 |
| | Clearigate | 96-h LC50 | 56 |
| *D. magna* | AlgimycinPWF | 96-h LC50 | 5 |
| | Cutrine-Plus | 48-h LC50 | 11 |
| | Clearigate | 48-h LC50 | 29 |
| *P. promelas* | AlgimycinPWF | 96-h LC50 | 250 |
| | Cutrine-Plus | 96-h LC50 | 1115 |
| | | 48-h LC50 | 255 |
| | Clearigate | 96-h LC50 | 481 |
| | | 48-h LC50 | 480 |
| *H. azteca* | AlgimycinPWF | 96-h LC50 | 390 |
| | Cutrine-Plus | 48-h LC50 | 248 |
| | Clearigate | 48-h LC50 | 158 |
| *L. macrochirus* | AlgimycinPWF | 96-h LC50 | 67,000 |

In general, the aquatic invertebrates *C. dubia and D. magna* were found to be the most sensitive in all studies referenced, while the fish *P. promelas* and *L. macrochirus* were found to be the most tolerant to copper exposure. It should be noted that the LC50 values reported here are likely a worst-case scenario when used to determine risk to the environment. When compared to field samples, laboratory values are often overly conservative. With manufacturer recommended application rates of chelated copper pesticides between 100- 1000 ug Cu/L depending on level of control needed, the margins for safety are minimal (Mastin and Rodgers, 2000). However, EPA considers canals to be part of highly managed agricultural systems that are frequently dry during the year, and as such, risk management is not warranted for aquatic organisms in canals (EPA, 2005b).

## Data Gaps

No data gaps have been identified for chelated copper as part of EPA's pesticide registration and reregistration process. Further toxicity studies on insect species would strengthen understanding of copper's ecotoxicological risk potential, and support existing label language.

## Environmental and Human Health Impacts

### *Earth*

### *Soil and Sediments*

Due to chelated copper's chemical characteristics long term persistence and impact in soil may occur. Van Zwieten et. al in a 2004 review of copper-based fungicides found that relatively low Cu concentrations can have impacts on several soil processes including microbial activity, earthworm activity and bioturbation. The review found that in most soils, copper residues from fungicide treatment are likely to remain indefinitely and will continue to impact soil health after application. An Australian study (Merrington et al., 2002), of soil biota health measured impacts using the difference in biomass carbon to total organic carbon at treated orchards and non-treated reference sites. The study found that significant reductions in biomass carbon occurred at treated sites compared to reference sites that had similar levels of total organic carbon indicating microbial stress. Furthermore, the study found significantly elevated soil respiration and significantly greater metabolic quotient (a measure of the capacity of microbes to use organic matter in soil), which are additional indicators of a stressed microbial community. Van Zweiten et. al also reviewed a 1996 copper avoidance study (Yeardley et al.) using earthworms. In the study dilutions of copper contaminated soil were used to better understand the concentration response of increasing copper concentrations on percent avoidance when earthworms. The results indicated that at copper residual levels of 4-34 mg/kg worms showed a significant response in copper soil avoidance. 90% earthworm avoidance was observed at 553 mg/kg copper. In addition, the review noted the results of a 2000 study by Helling et al. which found that earthworms showed chronic toxic responses at copper concentrations < 4-16 mg/kg. Van Zweiten concluded that orchard soil copper residue concentrations of 180-338 mg/kg resulted in the elimination of earthworms.

It is important to note that chelated copper labels for application to water bodies restrict metallic copper to < 1ppm (1 mg/kg) per treatment and Ecology's Irrigation System Aquatic Weed Control General Permit has additional use restrictions and conditions that dissolved copper concentrations must not exceed a maximum instantaneous concentration (or highest allowable discharge), of 25 ug/l (0.025 mg/kg) at the point of compliance (Ecology, Permit Exp. 2019). Under these use guidelines and because of the high reactivity and affinity for binding of copper, the actual concentration of copper applied to soil via irrigation is predicted to be much lower than the effects detailed in the review above.

Impacts to sediment from copper pesticide application are not as widely known as copper accumulation and bioavailability are greatly influenced by environmental conditions, but studies suggest copper is often not bioavailable and nontoxic to sediment species at use concentrations. Gallagher et al. in the 2005 study entitled "Responses of *Hyalella azteca* and *Ceriodaphnia dubia* to Reservoir Sediments Following Chelated Copper Herbicide Applications" looked at the toxicity of sediments treated with copper over approximately a decade of nuisance weed control. The focus of the study was on sediment copper residues and the ability for sediments to bind copper. The study used two species of invertebrates, *Hyalella azteca* and *Ceriodaphnia dubia*. Both field and lab amended sediments were used to measure any residual toxicity present. The results indicated that no toxicity was observed for either species or either site. Based on the binding capacity of the collected sediments concentrations of copper would have to increase from 16.3 to 180 mg Cu/kg before statistically significant toxic effects would be observed if no new binding material was added to the system. Results indicated a lack of bioavailable copper due to the strong binding capacity for copper at the sites studied. Huggett et. al. in the 1999 study “Copper bioavailability in Steilacoom Lake sediments,” also found a propensity of copper to bind and precipitate in sediments. Sediments from Steilacoom Lake in Washington State were amended with various concentrations of copper sulfate between 800 and 2000 mg Cu/kg to assess copper bioavailability and potential toxicity to three sediment associated species, *Hyalella azteca*, *Chironomus tentans*, *Ceriodaphnia dubia* and *H. azteca.* The most sensitive species after 10 days was *Ceriodaphnia dubia* with a no effect concentration (NOEC) of 906 mg Cu/kg and a lowest effect concentration (LOEC) of 1469 Cu/kg. Based on the experimental conditions, the study concluded that copper in the lake sediment collected was not bioavailable to the test organisms and toxicity would only occur at very high concentrations of copper.

At the copper pesticide label application rates of 1 mg/kg sediment toxicity to sediment dwelling organisms would be unlikely and copper accumulations would have to be exceptionally high before toxicity might occur. Furthermore, treatment in Washington is restricted to contained and highly managed irrigation networks and would have a low probability of negatively impacting sediments outside treatment areas. As the studies above suggest, copper used in irrigation networks is likely to quickly bind to particulate matter and sediments where it poses a very low risk of chronic toxicity. Highly managed irrigation ditches and canals are not expected to have large populations of sensitive sediment dwelling species or be classified as critical habitat for listed species.

#### *Agriculture*

At the use concentrations outlined on the product label, using agricultural water treated with copper is not expected to damage crops, or wild vegetation. Water may be used for livestock after treatment. The labels, at the time of this writing, do not contain any precautions or restrictions on irrigation or secondary use following product application. The labels do provide precautions against direct application of chelated copper pesticides at application rates to desirable plants or allowing concentrated chelated copper pesticides to contact any desirable plants (SePRO, 2018).

### *Water*

#### Surface water and Runoff

Though the half-life for chelated copper pesticides varies with water characteristics, the relatively short duration and pulsed nature of chelated copper treatment suggests that chronic exposure data is not as valuable when considering risk or safety margins (Murray-Gulde, 2002). The Environmental Hazards section of registered chelated copper products state that the pesticide is directly toxic to fish and invertebrates and treated water can be hazardous to aquatic life. In addition, treatment of aquatic plants can result in indirect hazards to aquatic species from oxygen loss due to the decomposition of plant material. Depletion of oxygen in a water body can cause suffocation for both invertebrate and vertebrate organisms (Nautique, 2018). Runoff of treated water is not expected to occur as chelated copper is only approved in Washington for use in highly managed agricultural water bodies. Furthermore, a 2009 study by Ecology entitled "Irrigation Canal Effects on Copper Levels in Water and Sediment of the Mid-Columbia and Wenatchee Rivers," investigated the copper concentrations from two irrigation project areas, Mid-Columbia and Wenatchee Reclamation that discharge into rivers. Surface water and sediment samples were collected before and after maximum copper use events to assess whether copper concentrations would exceed Washington State Water Quality Standards. The study results indicated that no surface water discharge sample exceeded the copper standard. Sediment concentrations were compared to a Canada interim standard and as Washington had no sediment standard at the time of the study and no concentration was found to be above these guidelines. The study concluded that based on the data collected, there is little potential for significant impacts to aquatic and sediment dwelling organisms in the receiving water areas studied.

#### Groundwater / public water supplies

Groundwater contamination potential for chelated copper under the use scenarios outlined in the product label is expected to be low, due primarily to its strong affinity for sediments and organic material. Similarly, the contamination potential to public water supplies is predicted to be low. Chelated copper algaecides are labeled for use in a variety of water body types including, potable water reservoirs. A permit may be required on a state-by-state basis.

### *Plants*

#### Higher Plants and Algae

Chelated copper is a non-selective biocide used to treat a wide range of submerged, floating, and emergent aquatic algae and weeds. Copper is highly toxic to algae. Copper increases cell membrane permeability and inhibits photosynthesis in both plants and algae. At high concentrations, copper interrupts electron transport in Photosystem II, the first stage of photosynthesis (Husak, 2015). EPA in its reregistration decision for coppers listed LC50's for the most sensitive both green algae *Selenastrum capricornutum*, (non-vascular aquatic plant), and Duckweed, *Lemna minot* (vascular aquatic plants). Selenastrum capricornutum had an LC50 = 3.1 ppb and a NOEC = 0.2 ppb. Duck weed was found to have a LC50 = 2.3 ppm and a NOEC = 0.1 ppm. EPA in its reregistration decision recommends that the potential risk to aquatic organisms should be considered in conjunction with the environmental benefits from intended use of copper algaecides. Copper can be effective at treating bot excessive algal growth as well as invasive plant infestations. Excessive algal growth can cause high oxygen demand in aquatic systems and eutrophication leading to deleterious water conditions for aquatic life. Invasive aquatic plans can outcompete native plants and negatively affect ecosystems and food availability (EPA 2006).

Based on available toxicity information chelated copper is not expected to cause long-term effects to higher plants but is acutely toxic to aquatic plants and algae. However, if chelated copper were applied in the manner described on the product label, acute effects to non-target aquatic plants would be contained to highly managed irrigation networks, and would not affect outside receiving waters. Highly managed irrigation ditches and canals are not expected to have large populations of sensitive aquatic plants or be classified as critical habitat for listed species.

Copper is used widely as a terrestrial pesticide and has a standing tolerance exemption for growing crops, as well as on meat, milk, poultry, eggs, fish, shellfish, and irrigated crops, suggesting that the total quantity of copper found in or on food presents no hazard to public health. Impacts to non-target vegetation are not expected due to the strictly aquatic application of chelated copper described on the product label (EPA, 2009).

## Mitigation

### *Use Restrictions*

EPA-approved product labels list several precautions and restrictions when applying chelated copper pesticides to aquatic environments. Specific precautions and restrictions listed include chelated copper pesticides should not be applied directly to desirable plants or crops, spray equipment should be thoroughly washed before and after application, treated waterbodies used as sources of drinking water should receive potable water treatment before use, and no applications of > 1.0 ppm metallic copper to any water (SePRO, 2018). None of the products have water use restrictions and water can be used immediately after application for swimming, domestic uses (drinking water), livestock watering and irrigation (CSI, 2001). When applied according to the product label, chelated copper does not require any other special mitigation measures. The product label contains no special cleanup procedures in the event of a spill (SePRO, 2018). Ecology's *Irrigation System Aquatic Weed Control General Permit* has additional use restrictions and conditions when applying copper pesticides in Washington State. Dissolved copper concentrations must not exceed a maximum instantaneous concentration (or highest allowable discharge), of 25 ug/l at the point of compliance (Ecology, Permit Exp. 2019).

### *Swimming and Skiing*

Canal banks and irrigation canals are owned by the irrigation district and are private property. The use of canals by non-irrigation staff is trespassing on private property. As the application of copper is registered for use in irrigation networks, no recreational impacts to swimming or skiing are expected. Trespassing on private agricultural waterways can and does occur. Furthermore, product labels state that chelated copper pesticides can be used in drinking water aquafers and swimming ponds with no additional application restriction language for these types of waterbodies, suggesting that application concentrations pose little to no human health risk from illicit swimming. Future versions of the permit should consider requiring appropriate notification signage to inform the public that a pesticide application has taken place to further decrease human health risks.

### *Irrigation, Drinking and Domestic Uses*

The label for chelated copper algaecides contains no restrictions for treated water used for crop irrigation. Some labels include a recommended 3 hour holding period before using water to ensure proper exposure rates to targeted plants and algae. If chelated copper pesticides are applied to potable water sources, the label states that, “sources treated with copper products may be used as drinking water only after proper additional potable water treatments.” There are no other listed restrictions for drinking water, but the label states that State or local agencies should be consulted to determine whether a permit is required. Using treated water for livestock watering is not addressed, but due to its omission from the list of uses, is not recommended (EPA, 2009).

### *Roadsides or Utility Rights-of-way*

As chelated copper pesticides are only approved for weed control in aquatic environments, its use is not expected to affect roadsides or utility easements. If the directions for use are followed, all access points should have appropriate signage detailing application information and swimming restrictions on roadsides and property adjacent to the treatment site.

### *Fisheries and Fish Consumption*

Copper is acutely toxic to aquatic organisms and could impact local fish populations in receiving waters if copper treated water is released from irrigation networks in exceedance of the maximum instantaneous concentration of 25 ug/L dissolved copper at the point of compliance as outlined in Ecology’s current (Expiration 2019) *Irrigation System Aquatic Weed Control* General Permit. Care should be taken when applying copper, and the directions for use on the label should be strictly followed. Consumption of fish exposed to copper is not likely to be an issue, as it is not expected to bioaccumulate or bioconcentrate in fish or shellfish tissues. Furthermore, the *Irrigation System Aquatic Weed Control* General Permit states, “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 Washington State Department of Fish and Wildlife (WDFW), and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations.” This permit condition should be carried forward in the next reissuance.

### *Wetlands or Non-Target Organisms*

Copper has the potential to acutely affect wetlands and non-target plants. Copper is a non-selective pesticide with known acute toxicity to aquatic fish and invertebrates. Treatment of aquatic weeds and algae with copper pesticides can lead to oxygen loss from the decomposition of dead plants because of treatment. Sufficient oxygen loss can cause fish and invertebrate mortality through suffocation. In order to minimize this hazard the label's state that chelated copper treatment should only be applied to ½ of the water body at a time with 10- 14 day wait period between treatments. Copper pesticide treatment should also begin along the shore and proceed outward in bands to allow for fish and other organisms to relocate to untreated areas. Furthermore, water conditions with low pH (<6.5), low dissolved organic carbon (3.0 mg/L or lower), and low alkalinity water (<50 mg/L). Copper pesticides should not be used in waters with trout or other fish species that are sensitive to copper. To further minimize the risk to non-target organisms, application of chelated copper pesticides should not exceed at concentration of 1.0 ppm during any single application. If treatment is conducted in aquaculture ponds with fish present, no single application should exceed 0.4 ppm and retreatments should be conducted after a minimum wait period of 10 days.

In the RED, the EPA also added a requirement that pesticide labels include language on reducing ecological effects on non-target organisms from potential spray drift during application. The Spray Drift Management section of the copper pesticide labels include a discussion on factors including weather conditions and application method (EPA, 2009). Copper pesticides must only be sprayed as a medium or coarse spray. If using a spinning atomizer mean spray should be 300 microns or greater. Application should not proceed if winds are greater than 15 mph. In winds between 3 to 10 mph the product should only be applied if it favors on-target application, and no sensitive areas are 250 feet downwind. In applications where the wind is less than 3 mph applicators must ensure that no temperature inversions or unstable atmospheric conditions exist. (SePRO, 2011).

Copper toxicity to nontarget insects was also included in the RED. The EPA included acute toxicity data on honeybees and found little to no toxicity with an acute $LD_{50}$ value of greater than 100 ug/bee. Although no other insect species exposure values were determined, and thus toxicity risk to other organisms is unknown, no additional mitigation measures were recommended (EPA 2009).

### *Endangered Species*

Based on the available toxicity information, chelated copper has the potential to be both acutely and chronically toxic to ESA-listed species. Although there is a potential for toxicity to ESA-species from exposure, these species are not likely to inhabit managed irrigation networks where chelated copper use is permitted. The EPA has established the Endangered Species Protection Program (ESPP), to evaluate pesticides for adverse impacts on federally listed species and develop or update appropriate mitigation measures. Using a variety of data including toxicity and exposure data, the ESPP will consider regulatory changes to pesticide registrations. The ESPP has yet to review whether listed species or critical habitat may be affected by copper use, and whether changes to the RED are needed, but the EPA states that mitigation measures currently set forth in the RED and subsequent labels will reduce the risk of copper exposure at levels of concern to listed species (EPA, 2009).

The risk to endangered or vulnerable species is further mitigated through Ecology's permit process. *The current Irrigation System Aquatic Weed Control* General Permit states, "Before issuing permit coverage, Ecology will determine whether sensitive, threatened, or endangered (rare) plants 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." Furthermore, "The Permittee must comply with WDFW timing windows referenced in Tables 3 and 4 to protect salmon, steelhead, and bull trout populations and WDFW priority habitats and species" (Ecology, Permit Exp. 2019).

### *Post-treatment Monitoring*

The labels for chelated copper contain no requirements for post-treatment monitoring following application. As part of Ecology's current permit requirements, short-term post-treatment monitoring is required. Ecology uses this monitoring to determine permit compliance and the potential for non-target impacts.

## References

1. 40 CFR 180.1021 – Copper; exemption from the requirement of a tolerance. | US Law | LII / Legal Information Institute. Available at: https://www.law.cornell.edu/cfr/text/40/180.1021. (Accessed: 27th December 2018)
2. *Appendix III-Copper 32 III.1 COPPER and COPPER COMPLEXES*.
3. *BIOACCUMULATION OF COPPER ALGAECIDES IN THE ENVIRONMENT*.
4. Weblet Importer. Available at: https://fortress.wa.gov/ecy/clarc/FocusSheets/Physical&ChemicalParameters.htm. (Accessed: 31st December 2018)
5. *Nautique ® Aquatic Herbicide*.
6. *Aquatic Herbicides: Overview of Usage, Fate and Transport, Potential Environmental Risk, and Future Recommendations for the Sacramento-San Joaquin Delta and Central Valley*.
7. Pesticides and Aquatic Animals: A Guide to Reducing Impacts on Aquatic Systems | VCE Publications | Virginia Tech. Available at: chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://vtechworks.lib.vt.edu/bitstream/handle/10919/48060/420-013_pdf.pdf. (Accessed: 18th December 2018)
8. copper chelate (Cutrine-Plus). Available at: http://www.cygnetenterprises.com/labels/Cutrine%20Plus%20Liquid.pdfAccessed: 1st August, 2023.)
9. CROPSTAR.
10. *Copper Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review*.
11. *Copper Compounds Chemical Fact Sheet*.
12. Atsdr. *TOXICOLOGICAL PROFILE FOR COPPER*. (2004).
13. Bishop, B. E., Willis, B. E. & Bishop, W. M. Understanding Fate and Effects of Copper Pesticides in Aquatic Systems. *J. Geosci. Environ. Prot.* **4**, 37–42 (2016).
14. Calomeni, A., Rodgers, J. H. & Kinley, C. M. Responses of Planktothrix agardhii and Pseudokirchneriella subcapitata to Copper Sulfate (CuSO4∈·∈5H2O) and a Chelated Copper Compound (Cutrine®-Ultra). *Water, Air, and Soil Pollution* **225**, (2014).
15. Christenson, T. A., Horton, M. E., Jackson, B. C., Smith, G. R. & Rettig, J. E. Effects of Cutrine-Plus® algaecide and predators on wood frog (Lithobates sylvaticus) tadpole survival and growth. *Environ. Sci. Pollut. Res.* **21**, 12472–12478 (2014).
16. Closson, K. R. & Paul, E. A. Comparison of the Toxicity of Two Chelated Copper Algaecides and Copper Sulfate to Non-Target Fish. *Bull. Environ. Contam. Toxicol.* **93**, 660–665 (2014).
17. Complexes, C. COPPER and COPPER COMPLEXES OH Cu OH. 32–42
18. Dameron, C. T. *et al. Copper*. (World Health Organization, 1998).

19. Department of Pesticide Regulation, C. *Copper Citrate Chelate and Copper Gluconate Chelate, Public Report 2007-7*. (2007).

20. Description, L. Supplemental Environment Impact Statement Assessments of Aquatic Herbicides : **6**,

21. DFWMR. *Recommendations Regarding the Use of Aquatic Herbicides in Fish-Bearing Waters of the State*. (2015).

22. Edta, C. & Solution, F. C. 6% Copper EDTA. 98903

23. Epa, U. & of Pesticide Programs, O. *US EPA – Pesticides – Amended Reregistration Eligibility Decision (RED) for Coppers*. (2009).

24. Epa, U. & of Pesticide Programs, O. *NOTICE OF PESTICIDE: X Registration X Reregistration Captain-Liquid Copper Algaecide*.

25. Fitzgerald, G. P. & Faust, S. L. Factors Affecting the Algicidal and Algistatic Properties of Copper. *J. Appl. Microbiol.* **11**, 345–351 (1963).

26. herbicide, A. *Other means of identification Emergency telephone number (with hours of operation) Section 1. Identification SAFETY DATA SHEET Komeen ® Crystal Aquatic Herbicide Aquatic Herbicide*.

27. Husak, V. COPPER AND COPPER-CONTAINING PESTICIDES: METABOLISM, TOXICITY AND OXIDATIVE STRESS. *J. Vasyl Stefanyk Precarpathian Natl. Univ.* **2**, (2015).

28. Johnson, B. M., Chao, M. M., Tedrow, O. R., Mcqueen, A. D. & Rodgers, J. H. *Plant Manage*. *J. Aquat. Plant Manage* **46**, (2008).

29. Kiaune, L. & Singhasemanon, N. Pesticidal Copper (I) Oxide: Environmental Fate and Aquatic Toxicity. In *Reviews of environmental contamination and toxicology* **213**, 1–26 (2011).

30. Leung, T. S., Naqvi, S. M. & Leblanc, C. Toxicities of two herbicides (Basagran, Diquat) and an algicide (Cutrine-plus) to mosquitofish Gambusia affinis. *Environ. Pollution. Ser. A, Ecol. Biol.* **30**, 153–160 (1983).

31. Mastin, B. J., Rodgers, J. H., Rodgers, J. H. & Rodgers, J. H. Toxicity and Bioavailability of Copper Herbicides (Clearigate, Cutrine-Plus, and Copper Sulfate) to Freshwater Animals. *Arch. Environ. Contam. Toxicol.* **39**, 445–451 (2000).

32. Masuda, K. & Boyd, C. E. Comparative evaluation of the solubility and algal toxicity of copper sulfate and chelated copper. *Aquaculture* **117**, 287–302 (1993).

33. Murray-Gulde, C. L. *et al.* Algicidal Effectiveness of Clearigate, Cutrine-Plus, and Copper Sulfate and Margins of Safety Associated with Their Use. *Arch. Environ. Contam. Toxicol.* **43**, 19–27 (2002).

34. of Ecology, D. Fact Sheet for the Draft Aquatic Invasive Species Management Npdes General Permit Department of Ecology. (2016).

35. Organisation, I. L., Wood, M., Kingdom, U., Programme, E. & Co-operation, E. http://www.inchem.org/documents/ehc/ehc/ehc200.htm 1/176. 1–176 (2018).

36. Ro, O. & Ob, A. *OVERVIEW OF COPPER TOXICITY TO AQUATIC LIFE*. *Report and Opinion* **4**, (2012).

37. Siemering, G. S., Hayworth, J. & Melwani, A. Aquatic Pesticide Monitoring Program Final Report. 57 (2005).

38. Siemering, G., David, N. & Franz, A. *Aquatic Pesticides Monitoring Program Literature Review Karl Malamud-Roam Contra Costa Mosquito Vec tor Control A P R I L 2 0 0 3*.

39. Siemering, G. S., Hayworth, J. & Melwani, A. *Aquatic Pesticide Monitoring Program Aquatic Pesticide Monitoring Program Final Report*. (2005).

40. Tapiero, H., Townsend, D. M. & Tew, K. D. Trace elements in human physiology and pathology. Copper. *Biomed. Pharmacother.* **57**, 386–98 (2003).

41. Wagner, J. L., Townsend, A. K., Velzis, A. E. & Paul, E. A. Temperature and toxicity of the copper herbicide (Nautique TM ) to freshwater fish in field and laboratory trials. *Cogent Environ. Sci.* **3**, 1339386 (2017).

42. Washington, S. *Final Supplemental Environmental Impact Statement for the State of Washington Aquatic Plant and Algae Management*. (2017).

43. Wersal, R. M. & Madsen, J. D. Effectiveness of a Chelated Copper Algicide on Algae Grown Under Differing Water Column Phosphorus Regimes A Summary Report Submitted to Diversified Waterscapes Incorporated Effectiveness of a Chelated Copper Algicide on Algae Grown Under Differing Water . (2007).

44. Williams, R. R., Hose, J. E. & Lightner, D. V. Toxicity and residue studies of cultured blue shrimp treated with the algicide Cutrine-Plus. *Progress. Fish-Culturist* **44**, 196–201 (1982).

45. Van Zwieten, L. & Merrington, Graham & Van-Zwieten, Melissa. (2004). Review of impacts on soil biota caused by copper residues from fungicide application.

46. Willis, Ben, "DETECTING COPPER RESIDUES IN SEDIMENTS FROM AQUATIC COPPER-BASED PESTICIDE APPLICATIONS" (2012). All Theses. 1527.

47. Hullebusch, E.V., Chatenet, P., Deluchat, V., Chazal, P.M., Froissard, D., Botineau, M., Ghestem, A., Baudu, M., 2003. Copper accumulation in a reservoir ecosystem following copper sulfate treatment (St. Germain Les Belles, France). Water, Air, and Soil Pollution 150: 3-22.

48. Gallagher, J., Duke, B., and Rodgers, J. 2005. Responses of Hyalella 85now85a and Ceriodaphnia to reservoir sediments following chelated copper herbicide applications. Journal of Aquatic Plant Management 43: 95-99.

49. Huggett, D.B., Gillespie, W.B., and Rodgers, J.H. Jr. 1999. Copper bioavailability in Steilacoom Lake sediments. Archives of Environmental Contamination and Toxicology 36: 120-123.

## Copper Sulfate

### Evaluation of Copper Sulfate

Copper Sulfate is used for a wide variety of applications including pesticide and industrial uses. Some direct industrial uses include copper plating and metal etching, as a drying agent, an activator in ore mining, and in anti-fouling paints as intermediates in the chemical industry (Copper.org). Ecology previously assessed the impacts from the use of copper compounds in aquatic environments in a Supplemental Environmental Impact Statement (SEIS) completed in 2000. This EIS adopts, by reference, the information in the *Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides, Appendix E* (Ecology Pub. No. 00-10-045 (Ecology, 2000)). This section updates the information from the 2000 SEIS to include recent scientific literature emphasizing non-target effects and hazards, labeling and registration updates, and other updated information not available during the previous assessment. References cited and used to evaluate copper sulfate are at the end of this section.

### Registration Status (FIFRA and WA Registration)

Copper-based pesticides are registered for use in Washington State for terrestrial and aquatic uses. The 27 copper-based products currently labeled for aquatic use in Washington only contain copper sulfate pentahydrate (CuSP) as the active ingredient (PICOL, September 2020).

Therefore this assessment excludes the other copper sulfate based active ingredients (e.g. basic copper sulfate, anhydrous copper sulfate) and copper-based active ingredients (e.g. elemental/metallic copper). In the United States copper sulfate was first used in the 1700's with the first EPA registration of copper in 1956 and the most recent reregistration completed in 2009 (USEPA 2009).

**Table 1.C Current registered pesticidal products for sulfates.**

| Case | Chemical Name | EPA PC Code | C.A.S. Number | Registrants |
|---|---|---|---|---|
| Copper Sulfates<br>#0636 | Basic Copper Sulfate | 008101 | 1344-73-6 | CSTF |
| | Copper Sulfate Pentahydrate | 024001 | 7758-99-8 | |
| | Copper Sulfate monohydrate | 024402 | 1332-14-5 | Cancelled |
| | Copper Sulfate Anhydrous | 024408 | 7758-98-7 | |

(After: USEPA 2009)

## Chemical-use Patterns

Copper-based pesticides have numerous registered uses such as a fungicide, bactericide, algaecide, herbicide, insecticide/molluscicide (snails, leechs), anti-fouling paint, mildewcide, or wood preservative (PICOL, September 2020). CuSP has agricultural, horticultural, aquacultural, homeowner, and commercial setting uses (EPA, 2008).

Application methods depend on the use, but general methods include direct application of Copper sulfate crystals/granules, liquid sprays via aerial or ground booms, chemigation, drenches, and paints (e.g. ship/boat bottom paint). In irrigation systems, Copper Sulfate treatment targets are algae and plant species that clog canals, reducing water flow.

The registered label for Triangle Brand Copper Sulfate Crystal, describes Copper sulfate pentahydrate as a non-selective herbicide that is effective in controlling a broad range algae, weeds, snails and microscopic organisms in impounded water bodies including: Tanks, Ponds, Raceways, Lakes and Reservoirs.

For applications of Copper Sulfate Crystal to impounded water, the current label at the time of this writing allows for a variety of application methods. Copper Sulfate Crystal can be applied by dragging it under water in burlap bags or baskets, spraying Copper Sulfate Crystal solution directly on water surface, directly injecting Copper Sulfate Crystal in the water, broadcasting dry Copper Sulfate Crystal into the water body and finally by spraying dry Copper Sulfate Crystal from aircraft. The rate of application varies with type and density of algae. For aquatic weed control (including algae and vascular plants), a single application must not exceed a Copper Sulfate Crystal concentration of 5.0 ppm (1.0 ppm metallic copper). Subsequent application must be separated by a minimum of 14 days and only half of the water body can be treated at a time. When treating water bodies where fish are present, concentrations must not exceed 0.4 ppm metallic copper or 1.6 ppm Copper Sulfate Crystal during a single application for algae control. Applications must be separated by a minimum of 7 to 14 days. Additional care should be taken when water temperature exceeds 85° F as this can cause the rapid decomposition of algae increasing oxygen depletion.

For applications of Copper Sulfate Crystal for the control of weeds and algae in flowing water such as irrigation conveyance systems, Copper Sulfate Crystal can be added by continuous addition or by “slug” method of addition. For continuous addition 0.1 to 0.2 pounds of Copper Sulfate Crystal is added per hour per cubic foot per second of flow for 12 hours during a 24-hour period. For weeds the rate is increased to 0.25 to 0.5 pounds per hour for each cubic foot. For “slug” method, Copper Sulfate Crystal is dumped into the irrigation ditch at ½ to 2 pounds per second of water per treatment. Applications should be separated by 14 days. Spacing of treatment is typically 5-30 miles depending on water chemistry and algae concentration. It’s important to note that as bicarbonate alkalinity increases Copper Sulfate Crystal becomes less effective with a significant reduction in toxicity when Calcium Carbonate is above 150 ppm. For both treatment types, 4 ppm Copper Sulfate Crystal (1.0 ppm metallic copper) should not be exceeded (Triangle Brand Cooper Sulfate Crystal, 2010).

Copper's use as an active ingredient in aquatic herbicides is listed in the Code of Federal Regulations (40 CFR 180.1021) as exempt from residue tolerance requirements if it is used as an aquatic pesticide (EPA, 2018). However, there is a drinking water standard for copper of 1.3 ppm.

## Chemical Description

Copper sulfate pentahydrate (CuSP) (CAS# 7758-99-8) is a hydrated metal salt with a chemical formula of: $Cu^{2+}SO_4 \bullet 5H_2O$. Copper sulfate is an odorless blue crystal in pure solid-form, or blue powder when processed. Copper sulfate pentahydrate has a molecular weight of 249.66 g/mol. CuSP is highly soluble in water with a solubility of: 31.6 g/100mL @ 0° C, 203.3 g/100ml @ 100° C. 148 g/kg @ 0 C, 230.5 g/kg @ 25 C, 335 g/kg @ 50 C, 736 g/kg@ 100 C, >= 100mg/ml @ 70 F CuSP has a vapor pressure of 7.3mm Hg @25° C. Due to the higher than atmosphere vapor pressure CUSP is efflorescent and will spontaneously lose water (hydrated salt) forming a layer of anhydrous copper sulfate (Pubchem, 2022). CuSP has a pH that ranges from 3.7 -4.5. CuSP has a melting/freezing point of 110° C and a boiling point of 150° C (Chemical book, 2020).

"*Copper sulfate.jpg*" by Von Stephanb – Eigenes Werk, used under CC BY-SA 3.0/Resized from original. No expressed or implied endorsement.

"Copper(II)-sulfate-pentahydrate-sample.jpg" by Benhjah-bmm27, used under CC BY 4.0/Resized from original. No expressed or implied endorsement.

The active ingredient in copper sulfate pesticides is elemental copper, a reddish metallic noble metal registered under the CAS Number 7440-50-8. It can exist in four oxidative states: Cu(0), Cu(I), Cu(II), and Cu(III). Cu(II) or cupric copper is the most important state of copper. Cu(II) is the most common form found in water and the common form of active copper released by copper pesticides. Complexes and compounds of cupric copper are typically blue or green in color and frequently soluble when added to water. (ATSDR, 2022). Copper pesticides can utilize various forms of copper. Regardless of the delivery agent used, copper sulfate pesticides ultimately dissociate and release the cupric ion form of copper, which is the active component of concern (EPA, 2009).

Elemental copper has a boiling point of 2,595°C a melting point of 1083°C and a density of 8.96 g/cm3 (ATSDR, 2022). Given the Henry's Law constant of 0 atm/m^3 • mole and vapor pressure of 1 mm Hg at 1628 °C, indicating copper does not readily volatilize. Copper has a log octanol/water partition coefficient (log 89now) of -0.571 and a water solubility value of 0 mg/L, indicating that copper is insoluble in water. The environmental fate of metals such as copper are often complex. The processes involved in the transport, partitioning and degradation of copper are not easy to separate. The transformation of a metal such as copper from one form to another can change the transport and partitioning properties within the environment. For example, complexation of copper with small organic compounds might result in enhanced mobility in soil or water. A copper sulfide formation would decrease solubility and thus mobility in water or soil (ATSDR, 2022). Unlike organic pesticides, copper does not degrade. Instead, copper entering the environment enters a complex biogeochemical cycle.

"In the water column, copper can exist bound to both organic and inorganic species and as free or hydrated copper ions. Water column chemistry affects copper speciation and bioavailability. In all water types (saltwater, brackish water, and freshwater), organic ligands in the water column can sequester the majority of free and ionic copper, and therefore, organic ligands play the largest role in copper bioavailability. In freshwater, however, the geochemistry of a particular location, including water column characteristics such as water hardness and pH, is a significant factor that can increase copper bioavailability and toxicity. In most cases, organic ligand concentrations greatly exceed copper ion concentrations in the water column and therefore provide a large buffering capacity" (Kiaune et al., 2011). Generally, much of the copper that is discharged into waterways is in the form of particulate matter that settles out. Both in the water column and in sediments copper readily absorbs to organic matter, hydrous metal oxides such as iron oxide, and clay (ATSDR, 2022).

## Fate and transport

### *Water*

In water, CuSP disassociates into dissolved elemental or cupric copper ($Cu^{2+}$ or Cu(II)) and sulfate ($SO_4^{2-}$). As free or ionic copper is already in the elemental form, it will not break down further into degradation products. However, copper is highly reactive in the aquatic environment, transitioning between free and bound states in varying proportions depending on the other chemical species present in the water (EPA, 2009).

In surface waters, copper is predominantly found in the cupric Cu(II) form. After copper is dissolved into a water body the cupric ions typically bind to ligands found in the water, soil, and sediments. Stable complexes typically include -Cl, -CO3 -$NH_2$, -SH, and -OH groups (Rader et. Al., 2019).

The state in which copper exists is highly dependent on the reduction-oxidation (redox) conditions and pH of the solution. In conditions that favor redox reactions (many free electrons, based on pH) one chemical species (reducing agent) donates electrons to another chemical species (oxidizing agent) (University of Texas, Accessed: 2019). The pH represents the acidity of a solution, which is the concentration of hydrogen ions (H+). If a solution is more acidic, it has fewer free electrons to provide to redox reactions, while a more basic solution has more electrons to provide to redox reactions. Depending on the availability of free electrons, either copper or another chemical species will donate electrons based upon the redox conditions, which favors different copper species (Wright et. al., 2007).

A 2003 study, *"*Copper accumulation in a reservoir ecosystem following copper sulfate treatment" by Hullebusch et al. looked at the fate and distribution of $CUSO_4$ treatment to a reservoir in France for phytoplankton control. Study results indicated that there was a rapid conversion of dissolved copper to particulate forms with a significant accumulation in the reservoir sediments. The study also found a significant amount of copper found in sediments was bound to organic material which may release copper back into the environment, but significant release would only occur under extreme changes to water chemistry. Using mass balance equations in conjunction with flow and known copper concentrations, the study also found that around 17% of the copper was exported from the reservoir over about 70 days with the majority most likely binding to sediments downstream.

### *Soil and Sediment*

In soil, copper's mobility and fate is determined by a range of chemical and physical interactions with soil constitutes (ATSDR, 2022). Copper fate in the terrestrial environment is driven largely by three main processes: transport to deeper soil levels through groundwater percolation, binding to soil constituents, and breakdown into metabolites (Siemering et al., 2005). Copper readily absorbs to organic matter, carbonates, clays, and metal oxides. In most temperate soils, the amount of organic matter, pH, metal oxyhydroxides and ionic strength of the soil solutions are the key factors affecting absorption (ATSDR, 2022). The distance copper will travel in soil is directly related to the absorption rates of the soil's constituents (Siemering et. al., 2005). When soil has a high organic content copper will strongly bind to soil particles. When organic matter concentrations are low, the mineral content becomes more important in determining copper absorption rates (ASTDR, 2022). The strong binding properties of copper are important when considering fate, as transformations and fluxes of copper compounds may change the various locations copper is found in aquatic environments (Rader et. al., 2019). Microorganisms within the soil can also affect the absorption of copper via uptake and assimilation (ASTDR, 2022).A study looking at binding rates found that at a low pH of 3.9 only 30% of copper was bound to the soil and 99% of copper was bound at a pH of 6.6, suggesting that acidic soil can be a significant driver of binding rate (Temminghoff et. al., 1997). A study also found that copper more readily leaches from soils that are sandy or have high acidity (Flores-Vélez et. al. 1996). Copper complexes are inorganic compounds and thus not expected to photolysis in water, however these complexes are expected to readily solvate into copper ions. Post treatment copper bound in this way is unlikely to be re-suspended and released back into the water column at levels that would negatively affect free-swimming organisms (Ecology, 2001). The International Union of Pure and Applied Chemistry (IUPAC) database reports the Koc of copper sulfate to be 9500 with other data sources reporting Koc values of 1000-18000 mL $g^{-1}$ suggesting that copper sulfate in non-mobile in soil (IUPAC, 2022).

### *Volatilization from water*

Copper complexes have low vapor pressures and Henry's Law constant indicating that copper complexes will not readily volatilize when introduced to water (USEPA, 2009) The Vapor Pressure at 20 degrees C was reported at $3.40 \times 10^{-10}$ indicating low volatility (IUPAC, 2022).

### *Degradation and dissipation of copper sulfate*

The processes involved in the transport, partitioning and degradation of copper are not easy to separate. The transformation of a metal such as copper from one form to another can change the transport and partitioning properties within the environment. For example, complexation of copper with small organic compounds might result in enhanced mobility in soil or water. A copper sulfide formation would decrease solubility and thus mobility in water or soil (ATSDR, 2022). Unlike organic pesticides, copper does not degrade. Instead, copper entering the environment enters a complex biogeochemical cycle. "Generally, much of the copper that is discharged into waterways is in the form of particulate matter that settles out.

Another consideration for metal toxicity is accumulation in tissues measured as a bioconcentration factor (BCF). A BCF is the ratio of concentration of chemical in an organism divided by the ambient concentration of the chemical in the environment and is a measure of the readiness with which chemical sharing occurs (WAC 173-333, 2012). IUPAC reports the Bioconcentration Factor value of copper sulfate as low risk based on a LogP value of <3 (IUPAC, 2022). The BCF of elemental copper in mollusks such as oysters and squid may reach as high as 30,000 and $2.1 \times 10^7$ respectively, indicating high copper loading. As copper is often found in particulate form within the water column, filter feeding is likely the reason for higher BCF values. The BCF for copper obtained from fish through field studies ranges from 10-667 indicating a low potential for bioconcentration in aquatic organisms that do not filter feed. With a $K_{ow}$ value of less than 10, copper compounds have little to no likelihood of bioaccumulation (ATSDR, 2022).

### *Field Surveys and Investigations*

A study entitled *Algicidal Effectiveness of Clearigate, Cutrine-Plus, and Copper Sulfate and Margins of Safety Associated with Their Use*, by Murray-Gulde et al., looked at the response of a variety of copper pesticides to the green algae species Raphidocelis subcapitata in order to determine the potential contact time and critical burden of copper necessary to contain algal control. The study also explored changes in residence time of copper pesticides in the water column under three different water characteristics. In low hardness and low alkalinity water copper sulfate had the shortest residence time in the water column of 3.5 days. Chelated copper products Clearigate and Cutrine-Plus had half-lives of 5.5 and 5.7 days, respectively. In moderately hard water, all three algicides showed similar half-lives of about 3 days. In high alkalinity waters copper sulfate fell between Cutrine-plus's half-life of 4.4 days and Clearigate's half-life of 2.6 days. All copper algicides achieved 100% control with a contact time of 3 days. Finally, the study looked at the varying application rates necessary to control algae and compared them to nontarget species adverse thresholds to determine the relative safety margins from the three products tested. The study found that the critical burden or threshold concentration of copper that must be sorbed by Raphidocelis for control was 7.3 (± 0.5) and 7.9 (± 0.5) µg for the chelated products Cutrine-Plus and Clearigate respectively, and 4.2 (± 0.2) µg for copper sulfate. Calculation of the critical burdens allows for an estimate of the maximum density of algae that can be treated using a given treatment. The study calculated that at the label rate for Clearigate of 1mg Cu/L the maximum Raphidocelis density that could be controlled would be 3.7 x $10^6$ cells /ml. The half-life of copper was found to vary with water quality characteristics. The shortest half-life was found to be 2.6 days. The study concluded that chronic exposure data and risk characterizations for non-target species might not be appropriate given the pulsed nature of discharge and relatively quick residence time copper has in the water column. Finally, the study compared the relative margin of safety for both Clearigate and Cutrine-Plus and found that toxic effects to non-target species is generally due to exposure within the first 24h of application and not from cumulative exposure, with margins of safety increasing to around 200% by day 5 (Murray-Gulde et. al., 2002).

## Toxicological Profile

Short-term inhalation exposures of copper have been associated with a range of symptoms in humans including but not limited to, respiratory, gastrointestinal, hematological, hepatic, endocrine and ocular effects. Symptoms from inhalation can vary with exposure level but can include symptoms such as headache, vertigo, drowsiness and eye irritation. Effects from oral exposure to copper are often gastrointestinal. The most prevalent symptoms from copper ingestion are nausea and vomiting. Other less typical symptoms can include abdominal pain and diarrhea. There are some reports that death can occur if very high levels of copper are ingested (ATSDR, 2022). The most common symptoms of acute dermal exposure to copper are skin dermatitis and eye irritation. The EPA has classified copper as Group D, or not enough available data to either support or refute human carcinogenicity (EPA, 2000). Under the acute toxicity category ranking system, copper sulfate pentahydrate ranged from I to IV depending on the route of exposure. Acute Oral $LD_{50}$ values were reported between 790 mg/kg for males and 2450 mg/kg for females, a toxicity category of II (moderately toxic and moderately irritating). Acute dermal irritation was found to be non-irritating and dermal $LD_{50}$ values were all reported as >2000mg/kg or category IV (practically non-toxic and not an irritant). Primary Eye irritation showed severe eye irritation day 1 to 21 and was classified as a Toxicity Category I (moderately toxic and moderately irritating). Finally, both acute inhalation and dermal sensitization had no available data and EPA reported no available data for basic copper sulfate and copper sulfate anhydrous copper types (EPA, 2000).

**Table 2C.Copper Sulfate Pentahydrate Acute Toxicity Profile summary**

| Study Type | Results | Toxicity Category |
|---|---|---|
| Acute oral | $LD_{50}$ M=790 F=450 mg/kg | II |
| Acute dermal | $LD_{50}$ = >2000 mg/kg | IV |
| Acute inhalation | None Available | N/A |
| Primary eye irritation | Severely irritating day 1-21 | I |
| Acute Dermal Irritation | Non-irritation | IV |
| Dermal sensitization | None available | N/A |

Based on the available data EPA concluded that there is no evidence that warrants calculating sub-chronic and chronic toxicity. Available short-term studies on mice and rats indicate decreased food and water intake as oral copper concentrations increase. Higher copper concentrations showed stomach irritation. At high levels of excess copper, some inhibition of immune response was noted, but is not unusual as other trace elements can show a similar response. There is some literature that shows chronic inhalation of Bordeaux mixture, a combination of copper sulfate and hydrated lime mixture may cause cancer; however, there is no information on the level of copper exposure experienced by the workers, or any additional substances that they may have been exposed to while working (EPA, 2000).

#### *Mammalian, Avian, and Human Toxicity*

In mammals and birds, copper is an essential trace element for maintaining mammalian and avian health. Copper is important for the function of many cellular enzymes due to its role as a catalyst in redox reactions (Tapiero, 2003). When ingested, copper is readily absorbed by both the stomach and intestine. After trace requirements in an organism have been met, species utilizing copper have multiple mechanisms that can regulate copper levels, helping to prevent copper toxicity. These regulatory pathways effectively reduce the risk of copper toxicity in the body following exposure to excessive copper levels. Copper homeostasis in the body is primarily driven through the binding protein metallothionein, which binds excess copper and allows for excretion from the body. Although these mechanisms help to prevent copper toxicity, high-level doses of copper can result in a number of adverse effects including anemia, liver and kidney damage, immunotoxicity, and developmental toxicity. Animal studies using orally exposed rats and mice have found no increased risk of cancer (ATSDR, 2022).

The EPA in its Reregistration Eligibility Decision for Coppers (RED) assessed the risk of oral ingestion and inhalation risk of copper-containing pesticides to birds, mammals, and other terrestrial animals. There are a variety of copper-based pesticides used in agriculture included in the RED. The risk assessment assumes instant disassociation of cupric ions from its ligand (binding molecule), which is a conservative estimate of bioavailability to exposed organisms. In order to estimate the potential risks to nontarget organisms, EPA calculated Estimated Environmental Concentrations (EECs), Risk Quotients (RQs), and Levels of Concern (LOCs) for different categories of organisms. EECs were derived from environmental fate, pesticide use, and soil and water chemistry data. RQs are a ratio of the calculated EEC to the most sensitive endpoint values of the organisms tested. Examples of these endpoints include lethal dose ($LD_{50}$) or median lethal concentration ($LC_{50}$). A comparison of RQ values to LOCs allows an estimate of risk to be made. If the RQ value exceeds the LOC for a category than there is a presumed potential risk to nontarget organisms. The table below displays the Risk Presumptions and LOCs EPA calculated for terrestrial animals and birds as part of the RED.

EPA's LOCs and Risk Presumptions for Terrestrial Animals and Birds

| Risk Presumption | LOC |
|---|---|
| Acute Risk - there is potential for acute risk; regulatory action may be warranted. | 0.5 |
| Acute Endangered Species – there is potential for endangered species risk; regulatory action may be warranted. | 0.1 |
| Chronic Risk - there is potential for chronic risk; regulatory action may be warranted. | 1 |

The EPA's ecological risk assessment suggests a potential risk to terrestrial animals exposed to copper resulting from use as an agricultural pesticide. RQs reflecting dietary exposure and toxicity to birds and mammals exceed both acute and chronic LOCs. The ecological risk assessment used both maximum labeled rates and average application rates to terrestrial crops (EPA, 2009).

Workers are primarily exposed to copper pesticides through mixing, loading and/or application. Copper exposure can also occur when people re-enter treated sites. Exposure may also occur in home environments from the application of residential pesticide products. Exposure to copper may cause a range of effects in humans including acute dermal and eye irritation, abdominal pain, nausea, vomiting, or diarrhea. The EPA RED found that copper has low acute toxicity in humans, with the exception of acute inhalation of cuprous oxide, and no evidence that copper causes systemic toxicity or carcinogenicity in animals with copper homeostasis. As no systemic toxicity risk was established from reviewed materials, and there is no known upper limit toxicity level, EPA chose not to generate acute endpoints for dietary, dermal, oral, or inhalation exposure (EPA, 2009). Similarly, EPA reviewed available chronic toxicity data and found no evidence of an upper limit toxicity level that requires the development of chronic toxicity endpoints for, dietary, oral, dermal or inhalation exposures. Developmental and reproductive studies have shown a greater risk from copper deficiency than excess copper exposure when investigating potential reproductive and teratogenic effects. In summary, EPA found that all potential acute and chronic human health exposures to copper are below the established level of concern. The irritating effects of copper compounds are sufficiently addressed through appropriate product specific precautionary labeling language, handler Personal Protective Equipment (PPE), and workplace safety standards (EPA, 2009). Copper pesticide product labels include a Precautionary Statements section, which includes minimum requirements for Personal Protective Equipment (PPE) to mitigate risk from mixing, loading, and applying copper. Examples for meeting minimum requirements for applying copper sulfate pesticides include coveralls, long sleeve shirt and pants, socks and chemical resistant shoes, chemical resistant gloves, protective eyewear, and a chemical resistant apron (Old Bridge Chemicals, 2019).

## Non-Occupational Exposure Risk

EPA's final rule; *Copper Sulfate Pentahydrate; Exemption from Requirement of Tolerance*, published in 2013 found that it was not necessary to conduct a quantitative analysis or assessment of non-occupational exposure after reviewing of the current toxicological effects of concern listed in EPA's databases (EPA, 2013). In addition, the EPA *Coppers Facts* report found no aggregate risk from combined exposure to copper. EPA defines aggregate risk as the "combined risk from dietary (food and drinking water) and residential or other non-occupational exposures, Aggregate risk can result from one-time (acute), short-term or chronic exposures." EPA concluded that due to the lack of systemic toxicity, the combined exposure concentrations from pesticide sources do not pose a health risk. Finally, due to the use restrictions for Copper Sulfate in Washington, non-occupational exposure is not expected to be a significant pathway for exposure.

### *Aquatic Vertebrates and Invertebrates*

As the target medium for copper sulfate application is water, toxicity to aquatic organisms is the highest concern when assessing environmental risk. The use pattern for copper as an aquatic herbicide indicates that it will remain in agricultural water bodies after treatment and a summary of aquatic toxicity studies indicate that copper sulfate can be toxic to non-target aquatic species.

Like mammals, many aquatic organisms also require small amounts of copper to maintain health; however, excessive copper exposure can result in significant toxicity. For organisms with gills, copper toxicity occurs when copper rapidly binds to gill membranes causing damage and interfering with osmoregulatory processes. Copper's toxicity threshold in aquatic organisms is dependent on the environmental water quality parameters. Some of the most important parameters to copper toxicity include, but are not limited to pH, alkalinity, and dissolved organic carbon. In the EPA RED, Copper toxicity is reported to be highest in water with low alkalinity and/or low dissolved organic carbon (EPA, 2009).

In evaluating risks to freshwater organisms, EPA employed the Biotic Ligand Model or BLM in addition to standard methods. The BLM is a metal bioavailability model that uses water body characteristics and monitoring data to generate site-specific water quality criteria. Some of the input data for the model include dissolved organic carbon, temperature, pH, major cations and anions, alkalinity, and sulfides. The BLM combines both speciation and toxicity and allows for the calculation of toxicity values. As the BLM covers only freshwater organisms, estuarine and marine animal RQs were calculated by EPA using estimates of total dissolved copper, a more conservative exposure value. EPA's site-specific pesticide transport models PRZM and EXAMS scenarios simulations were used to calculate copper inputs to the BLM. The EPA assessed water chemistry values at 811 sites representing median surface water quality conditions across the United States. All 811 sites were simulated using the BLM and calculated cupric ion concentrations were estimated at each site. $LC_{50}$s were calculated using the BLM for *Daphnia magna*, and *Pimephales* promelas (fathead minnow). Daphnia were found to be the most sensitive freshwater invertebrate. Salmonids of the genus Oncorhynchus were found to be the most sensitive fish, but at the time of the RED the BLM had not yet been implemented to calculate the $LC_{50}$ values for this genus. In order to account for the sensitivity to salmonids, the fathead minnow genus acute mean of 72.07 ug/L copper was adjusted using a factor derived from the ratios of the $LC_{50}$ values, which was calculated to be 0.404. The fathead minnow genus acute mean of 72.07 ug/L was multiplied by 0.404 to calculate the genus acute mean of 29.11 ug/L for salmonids. The adjustment factor was calculated to be 0.404. The Chronic toxicity values were derived from an acute-to-chronic ratio (ACR), as the BLM only estimates acute toxicity values. The ACR for chronic freshwater organisms was estimated to be 3.23 which was derived from a range of ACR's for freshwater species that had acute and chronic toxicity data. 3.23 represents the central value in this range. The ACR was then applied to the acute toxicity value of each of the 811 sites to calculate the chronic toxicity value. This chronic toxicity value was used for the Risk Quotient (RQ) when evaluating the EPA levels of concern (LOC's) for copper sulfate (EPA, 2009).

Use data for copper pesticides for algae and aquatic weed control indicated application rates of 0.1- 1ppm. EPA used the Exposure Analysis Modeling System (EXAMS) which is used to evaluate fate, transport, and exposure in aquatic ecosystem models and the BLM to produce RQs that were compared to EPA LOC values found in the table below. For other aquatic organism control, application rates can be higher (1-2.5 ppm).

EPA's LOCs and Risk Presumptions for Aquatic Animals

| Risk Presumption | LOC |
|---|---|
| Acute Risk - there is potential for acute risk; regulatory action may be warranted. | 0.5 |
| Acute Endangered Species – there is potential for endangered species risk; regulatory action may be warranted. | 0.05 |
| Chronic Risk - there is potential for chronic risk; regulatory action may be warranted. | 1 |

At the application rates for invertebrates, fish, and aquatic plants, >99% of sites exceed the endangered species LOC and Acute LOC. The chronic risk for aquatic fish and invertebrates were exceeded at >96% of sites. Because of the large difference in waterbody chemistry, the EXAMS and BLM models likely both over and underestimate risk, depending on the water body. Furthermore, when only a portion of a water body is treated there is a range of exposure and resulting effects depending on an organism's distance from the treatment site and/or the ability of an organism to leave the treatment area. The EPA notes that for direct water applications of copper pesticides there are likely to be effects to invertebrates and a reduction in primary productivity (EPA, 2009).

Three studies (Mastin and Rodgers, 2000, Johnson et al, 2008, Murray-Gulde et al., 2002) derived laboratory LC50 values for a variety of aquatic organisms using copper compounds commonly used in aquatic plant management. The copper herbicide LC50 values are summarized in the table below:

| OrganismFi | Algaecide | Test Duration | Concentration ug Cu/L |
|---|---|---|---|
| *C. dubia* | AlgimycinPWF | 96-h LC50 | 48 |
| | Cutrine-Plus | 96-h LC50 | 92 |
| | Clearigate | 96-h LC50 | 56 |
| | Copper Sulfate | | |
| *D. magna* | AlgimycinPWF | 96-h LC50 | 5 |
| | Cutrine-Plus | 48-h LC50 | 11.3 |
| | Clearigate | 48-h LC50 | 29.4 |
| | Copper Sulfate | 48-h LC50 | 18.9 |
| *P. promelas* | AlgimycinPWF | 96-h LC50 | 250 |
| | Cutrine-Plus | 96-h LC50 | 1115 |
| | | 48-h LC50 | 255 |
| | Clearigate | 96-h LC50 | 481 |
| | | 48-h LC50 | 480 |
| | Copper Sulfate | 48-h LC50 | 19.2 |
| *H. azteca* | AlgimycinPWF | 96-h LC50 | 390 |
| | Cutrine-Plus | 48-h LC50 | 248 |
| | Clearigate | 48-h LC50 | 158 |
| | Copper Sulfate | 48-h LC50 | 157.8 |
| *L. macrochirus* | AlgimycinPWF | 96-h LC50 | 67,000 |
| *C. tentans* | Cutrine-Plus | 48-h LC50 | 460.9 |
| | Clearigate | 48-h LC50 | 373.5 |
| | Copper Sulfate | 48-h LC50 | 1,136.5 |

In general, the aquatic invertebrates *C. dubia and D. magna* and the fish *P. promelas* were found to be the most sensitive to copper sulfate in all studies referenced while the *C. tentans* and *L. macrochirus* were found to be the most tolerant to copper exposure. Even though the study found that *P. promelas* or fathead minnow was the most sensitive, the study did not include toxicity data for Oncorhynchus salmonids. In comparing the reported $LC_{50}$ values from the EPA derived BLM data above to the $LC_{50}$ values reported in these 3 studies, salmonids were found to be the most sensitive aquatic vertebrate species.

Old Bridge Chemical's Copper Sulfate Pentahydrate pesticide Safety Data Sheet lists LC50 values for the species listed below:

| OrganismF | Test Duration | Concentration *ug* Cu/L |
|---|---|---|
| Lepomis macrochirus | 96-h LC50 semi-static | 0.66 – 1.15 |
|  | 96-h static | 0.96 – 1.8 |
| Oncorhynchus mykiss | 96-h flow-through | 0.1478 – 0.165 |
|  | 96-h static | 0.09 – 0.19 |
| Pimephales promelas | 96-h static | 0.6752 |
| Daphnia magna | 48-h static | 0.147-0.227 |

It should be noted that the LC50 values reported here are likely a worst-case scenario when used to determine risk to the environment. When compared to field samples, laboratory values are often overly conservative. With manufacturer recommended application rates of copper sulfate pesticides between 100- 500 micrograms Cu/L depending on level of control needed, the margins for safety are minimal (Mastin and Rodgers, 2000). However, EPA considers canals to be part of highly managed agricultural systems that are frequently dry during the year, and as such, risk management is not warranted for aquatic organisms in canals (EPA, 2005b).

## Data Gaps

No data gaps have been identified for copper sulfate as part of EPA's pesticide registration and reregistration process. Further toxicity studies on insect species would strengthen understanding of copper's ecotoxicological risk potential and support existing label language.

## Environmental and Human Health Impacts

### *Earth*

#### *Soil and Sediments*

Due to copper sulfates chemical characteristics long term persistence and impact in soil may occur. Van Zwieten et. al in a 2004 review of copper-based fungicides found that relatively low Cu concentrations can have impacts on several soil processes including microbial activity, earthworm activity and bioturbation. The review found that in most soils, copper residues from fungicide treatment are likely to remain indefinitely and will continue to impact soil health after application. An Australian study (Merrington et al., 2002), of soil biota health measured impacts using the difference in biomass carbon to total organic carbon at treated orchards and non-treated reference sites. The study found that significant reductions in biomass carbon occurred at treated sites compared to reference sites that had similar levels of total organic carbon indicating microbial stress. Furthermore, the study found significantly elevated soil respiration and significantly greater metabolic quotient (a measure of the capacity of microbes to use organic matter in soil), which are additional indicators of a stressed microbial community. Van Zweiten et. al also reviewed a 1996 copper avoidance study (Yeardley et al.) using earthworms. In the study dilutions of copper contaminated soil were used to better understand the concentration response of increasing copper concentrations on percent avoidance when earthworms. The results indicated that at copper residual levels of 4-34 mg/kg worms showed a significant response in copper soil avoidance. 90% earthworm avoidance was observed at 553 mg/kg copper. In addition, the review noted the results of a 2000 study by Helling et al. which found that earthworms showed chronic toxic responses at copper concentrations < 4-16 mg/kg. Van Zweiten concluded that orchard soil copper residue concentrations of 180-338 mg/kg resulted in the elimination of earthworms.

It is important to note that copper sulfate labels for application to water bodies restrict metallic copper to < 1ppm (1 mg/kg) per treatment and Ecology's Irrigation System Aquatic Weed Control General Permit has additional use restrictions and conditions that dissolved copper concentrations must not exceed a maximum instantaneous concentration (or highest allowable discharge), of 25 ug/l (0.025 mg/kg) at the point of compliance (Triangle, 2010) (Ecology, Permit Exp. 2019). Under these use guidelines and because of the high reactivity and affinity for binding of copper, the actual concentration of copper applied to soil via irrigation is predicted to be much lower than the effects detailed in the review above.

Impacts to sediment from copper pesticide application are not as widely known as copper accumulation and bioavailability are greatly influenced by environmental conditions, but studies suggest copper is often not bioavailable and nontoxic to sediment species at use concentrations. Gallagher et al. in the 2005 study entitled "Responses of *Hyalella azteca* and *Ceriodaphnia dubia* to Reservoir Sediments Following Chelated Copper Herbicide Applications" looked at the toxicity of sediments treated with copper over approximately a decade of nuisance weed control. The focus of the study was on sediment copper residues and the ability for sediments to bind copper. The study used two species of invertebrates, *Hyalella azteca* and *Ceriodaphnia dubia*. Both field and lab amended sediments were used to measure any residual toxicity present. The results indicated that no toxicity was observed for either species or either site. Based on the binding capacity of the collected sediments concentrations of copper would have to increase from 16.3 to 180 mg Cu/kg before statistically significant toxic effects would be observed if no new binding material was added to the system. Results indicated a lack of bioavailable copper due to the strong binding capacity for copper at the sites studied. Huggett et. al. in the 1999 study "Copper bioavailability in Steilacoom Lake sediments," also found a propensity of copper to bind and precipitate in sediments. Sediments from Steilacoom Lake in Washington State were amended with various concentrations of copper sulfate between 800 and 2000 mg Cu/kg to assess copper bioavailability and potential toxicity to three sediment associated species, *Hyalella azteca*, *Chironomus tentans*, *Ceriodaphnia dubia* and *H. azteca.* The most sensitive species after 10 days was *Ceriodaphnia dubia* with a no effect concentration (NOEC) of 906 mg Cu/kg and a lowest effect concentration (LOEC) of 1469 Cu/kg. Based on the experimental conditions, the study concluded that copper in the lake sediment collected was not bioavailable to the test organisms and toxicity would only occur at very high concentrations of copper.

At the copper pesticide label application rates of 1 mg/kg sediment toxicity to sediment dwelling organisms would be unlikely and copper accumulations would have to be exceptionally high before toxicity might occur. Furthermore, treatment in Washington is restricted to contained and highly managed irrigation networks and would have a low probability of negatively impacting sediments outside treatment areas. As the studies above suggest, copper used in irrigation networks is likely to quickly bind to particulate matter and sediments where it poses a very low risk of chronic toxicity. Highly managed irrigation ditches and canals are not expected to have large populations of sensitive sediment dwelling species or be classified as critical habitat for listed species.

### *Agriculture*

Copper sulfate use for irrigation diches and ponds is not expected to have significant impacts on nearby agriculture. Direct application of copper-based pesticides to agricultural crops is widely used. Copper is registered for use on virtually all food/feed crops in the United States. Major crops that either use the greatest volume of copper or are the most prevalent include but are not limited to tree nuts, citrus, grape, berries, peach, pepper and tomato.

Appendix A in EPA's Reregistration Eligibility Decision for Copper contains a list of crop types, their maximum single application and annual application rates of copper. At the use concentrations outlined on the product label and holding time requirements post treatment, using agricultural water treated with copper is not expected to damage crops, or wild vegetation. The registered labels, at the time of this writing, do not contain any precautions or restrictions on irrigation or secondary use following product application.

### *Water*

#### *Surface water and Runoff*

Though the half-life for copper pesticides varies with water characteristics, the relatively short duration and pulsed nature of copper treatment suggests that chronic exposure data is not as valuable when considering risk or safety margins (Murray-Gulde, 2002). The Environmental Hazards section of registered copper sulfate products state that the pesticide is toxic to fish and invertebrates and treated water may be hazardous to aquatic life. In addition, treatment of aquatic plants can result in indirect hazards to aquatic species from oxygen loss due to the decomposition of plant material. Depletion of oxygen in a water body can cause suffocation for both invertebrate and vertebrate organisms (Old Bridge, 2013). Runoff of treated water is not expected to occur as copper sulfate is only approved in Washington for use in highly managed agricultural water bodies. Furthermore, a 2009 study by Ecology entitled "Irrigation Canal Effects on Copper Levels in Water and Sediment of the Mid-Columbia and Wenatchee Rivers," investigated the copper concentrations from two irrigation project areas, Mid-Columbia and

Wenatchee Reclamation that discharge into rivers. Surface water and sediment samples were collected before and after maximum copper use events to assess whether copper concentrations would exceed Washington State Water Quality Standards. The study results indicated that no surface water discharge sample exceeded the copper standard. Sediment concentrations were compared to a Canada interim standard and as Washington had no sediment standard at the time of the study and no concentration was found to be above these guidelines. The study concluded that based on the data collected, there is little potential for significant impacts to aquatic and sediment dwelling organisms in the receiving water areas studied.

### *Groundwater / public water supplies*

Groundwater contamination potential for copper sulfate under the use scenarios outlined in the product label is expected to be low, due primarily to its strong affinity for sediments and organic material. Similarly, the contamination potential to public water supplies is predicted to be low. Copper sulfate algaecides are labeled for use in a variety of water body types including, potable water reservoirs. For applications of copper sulfate directly to water sources used as drinking water, those waters must have potable water treatment prior to use. Additionally, no more than 1.0 ppm as metallic copper should be applied in these water bodies. A permit may be required on a state-by-state basis.

### *Plants*

### *Higher Plants and Algae*

Copper sulfate is a non-selective biocide used to treat a wide range of submerged, floating, and emergent aquatic algae and weeds. Copper is highly toxic to algae. Copper increases cell membrane permeability and inhibits photosynthesis in both plants and algae. At high concentrations, copper interrupts electron transport in Photosystem II, the first stage of photosynthesis (Husak, 2015). In EPA's reregistration decision for coppers,the most sensitive plant was green algae *Selenastrum capricornutum* (non-vascular aquatic plant) and Duckweed, *Lemna minot* (vascular aquatic plants). Selenastrum capricornutum had an LC50 = 3.1 ppb and a NOEC = 0.2 ppb. Duck weed was found to have a LC50 = 2.3 ppm and a NOEC = 0.1 ppm. EPA in its reregistration eligibility decision recommends that the potential risk to aquatic organisms should be considered in conjunction with the environmental benefits from intended use of copper algaecides. Copper can be effective at treating both excessive algal growth as well as invasive plant infestations. Excessive algal growth can cause high oxygen demand in aquatic systems and eutrophication leading to deleterious water conditions for aquatic life. Invasive aquatic plans can outcompete native plants and negatively affect ecosystems and food availability (EPA 2006).

Based on available toxicity information copper sulfate is not expected to cause long-term effects to higher plants but is acutely toxic to aquatic plants and algae. However, if copper sulfate is applied in the manner described on the product label, acute effects to non-target aquatic plants would be contained to highly managed irrigation networks, and would not affect outside receiving waters. Highly managed irrigation ditches and canals are not expected to have large populations of sensitive aquatic plants or be classified as critical habitat for listed species.

Copper is widely used as a terrestrial pesticide and has a standing tolerance exemption for growing crops, as well as on meat, milk, poultry, eggs, fish, shellfish, and irrigated crops, suggesting that the total quantity of copper found in or on food presents no hazard to public health. Impacts to non-target vegetation is not expected due to the strict aquatic application of copper sulfate described on the product label (EPA, 2009).

## Mitigation

### *Use Restrictions*

EPA-approved product labels list several precautions and restrictions when applying copper sulfate pesticides to aquatic environments. Copper sulfate should not be applied where direct contact to workers, other persons or pets may occur. Treated waterbodies that are used as sources of drinking water should receive potable water treatment before use. Copper sulfate applications of > 1.0 ppm metallic copper should not be applied to any water body. Copper sulfate pesticides include requirements for spray drift management that must be evaluated prior to application. Finally, product labels contains no special cleanup procedures in the event of a spill (Triangle, 2010). Specific pesticide labels should be consulted for a complete list of hazards, recommendations, and requirements. In addition, Ecology's Irrigation System Aquatic Weed Control General Permit has additional use restrictions and conditions when applying copper pesticides in Washington State. Dissolved copper concentrations must not exceed a maximum instantaneous concentration (or highest allowable discharge), of 25 ug/l at the point of compliance (Ecology, Permit Exp. 2019).

### *Swimming and Skiing*

Canal banks and irrigation canals are owned by the irrigation district and are private property. The use of canals by non-irrigation staff is trespassing on private property. As the application of copper is registered for use in irrigation networks, no recreational impacts to swimming or skiing are expected. Trespassing on private agricultural waterways can and does occur. Furthermore, product labels contain no additional application restriction language for water used for skiing or swimming, suggesting that application concentrations pose little to no human health risk from illicit swimming. Future versions of the permit should consider requiring appropriate notification signage to inform the public that a pesticide application has taken place to further decrease human health risks.

### *Irrigation, Drinking and Domestic Uses*

The label for copper sulfate algaecides contains no restrictions for treated water used for crop irrigation. If copper sulfate pesticides are applied to potable water sources, label's state that, "For applications in waters destined for use as drinking water, those waters must receive additional and separate potable water treatment. Do not apply more than 1.0 ppm as metallic copper in these waters" (Triangle, 2010).There are no other listed restrictions for drinking water, but the label states that State or local agency's should be consulted to determine whether a permit is required. Using treated water for livestock watering is not addressed, but due to its omission from the list of uses, is not recommended.

### *Roadsides or Utility Rights-of-way*

As copper sulfate pesticides are only approved for weed control in aquatic environments, its use is not expected to affect roadsides or utility easements. If the directions for use are followed, all access points should have appropriate signage detailing application information and swimming restrictions on roadsides and property adjacent to the treatment site.

### *Fisheries and Fish Consumption*

Copper is acutely toxic to aquatic organisms and could impact local fish populations in receiving waters if copper treated water is released from irrigation networks in exceedance of the maximum instantaneous concentration of 25 *ug*/L dissolved copper at the point of compliance as outlined in Ecology's current (Expiration 2019) *Irrigation System Aquatic Weed Control* General Permit. Care should be taken when applying copper and the directions for use on the label should be strictly followed. Consumption of fish exposed to copper is not likely to be a risk, as it is not expected to bioaccumulate or bioconcentrate in fish or shellfish tissues. Furthermore, the *Irrigation System Aquatic Weed Control* General Permit states, "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 Washington State Department of Fish and Wildlife (WDFW), and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations." This permit condition should be carried forward in the next reissuance.

### *Wetlands or Non-Target Organisms*

Copper has the potential to acutely affect wetlands and non-target plants. Copper is a non-selective pesticide with known acute toxicity to aquatic fish and invertebrates. Treatment of aquatic weeds and algae with copper pesticides can lead to oxygen loss from the decomposition of dead plants because of treatment. Sufficient oxygen loss can cause fish and invertebrate mortality through suffocation. In order to minimize this hazard, the label's state that copper sulfate treatment should only be applied to ½ of the water body at a time with 10-14 day wait period between treatments. Copper pesticide treatment should also begin along the shore and proceed outward in bands to allow for fish and other organisms to relocate to untreated areas. Furthermore, water conditions with low pH (<6.5), low dissolved organic carbon (3.0 mg/L or lower), and low alkalinity water (<50 mg/L). Copper pesticides should not be used in waters with trout or other fish species that are sensitive to copper. To further minimize the risk to non-target organisms, application of copper sulfate pesticides should not exceed at concentration of 1.0 ppm metallic copper during any single application. If treatment is conducted in water bodies with fish present, no single application should exceed 0.4 ppm metallic copper (Triangle 2010).

In the Reregistration Eligibility Decision, EPA also added a requirement that pesticide labels include language on reducing ecological effects on non-target organisms from potential spray drift during application. The spray drift management section of the copper pesticide labels include a discussion on factors including weather conditions and application method. Copper pesticides must only be sprayed as a medium or coarse spray. If using a spinning atomizer, the mean spray droplet size should be 300 microns or greater. Application should not proceed if winds are greater than 15 mph. In winds between 3 to 10 mph the product should only be applied if it favors on-target application and no sensitive areas are 250 feet downwind. In applications where the wind is less than 3 mph, applicators must ensure that no temperature inversions or unstable atmospheric conditions exist. (Triangle, 2010) (EPA, 2009).

Copper toxicity to nontarget insects was also included in the RED. The EPA included acute toxicity data on honeybees and found little to no toxicity with an acute $LD_{50}$ value of greater than 100 *ug*/bee. Although no other insect species exposure values were determined, and thus toxicity risk to other organisms is unknown, no additional mitigation measures were recommended (EPA 2009).

### *Endangered Species*

Based on the available toxicity information, copper sulfate has the potential to be both acutely and chronically toxic to ESA-listed species. Although there is a potential for toxicity to ESA-species from exposure, these species are not likely to inhabit managed irrigation networks where copper sulfate use is permitted. The EPA has established the Endangered Species Protection Program (ESPP), to evaluate pesticides for adverse impacts on federally listed species and develop or update appropriate mitigation measures. Using a variety of data including toxicity and exposure data, the ESPP will consider regulatory changes to pesticide registrations. The ESPP has yet to review whether listed species or critical habitat may be affected by copper use, and whether changes to the RED are needed, but the EPA states that mitigation measures currently set forth in the RED and subsequent labels will reduce the risk of copper exposure at levels of concern to listed species (EPA, 2009).

The risk to endangered or vulnerable species is further mitigated through Ecology's permit process. The current *Irrigation System Aquatic Weed Control* General Permit states, "Before issuing permit coverage, Ecology will determine whether sensitive, threatened, or endangered (rare) plants 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." Furthermore, "The Permittee must comply with WDFW timing windows referenced in Tables 3 and 4 to protect salmon, steelhead, and bull trout populations and WDFW priority habitats and species" (Ecology, Permit Exp. 2019).

### *Post-treatment Monitoring*

The labels for copper sulfate contain no requirements for post-treatment monitoring following application. As part of Ecology's current permit requirements, short-term post-treatment monitoring is required. Ecology uses this monitoring to determine permit compliance and the potential for non-target impacts.

## References

1. Wright, B. W. G., Simon, W., Bove, D. J., Mast, M. A. & Leib, K. J. *Distribution of pH Values and Dissolved Trace-Metal Concentrations in Streams Mining in the Animas River Watershed , San Juan County , Colorado Professional Paper 1651*. *Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan County, Colorado* (2007).

2. Washington, S. *Final Supplemental Environmental Impact Statement for the State of Washington Aquatic Plant and Algae Management*. (2017).

3. Washington State University. Pesticide Information Center OnLine (PICOL) Database. Available at: https://picol.cahnrs.wsu.edu/.

4. University of Texas. Standard Reduction Potentials. Available at: http://ch302.cm.utexas.edu/echem/echem-cells/selector.php?name=std-red-potentials.

5. Temminghoff, E. J. M.; Van der Zee, S. E. A. T. M.; de Haan, F. A. M. Copper Mobility in a Copper-Contaminated Sandy Soil as Affected by pH and Solid and Dissolved Organic Matter. *Environ. Sci. Technol* **31**, 1109–1115 (1997).

6. Tapiero H, Townsend DM, T. K. Trace elements in human physiology and pathology. Copper. *Biomed Pharmacother* **57**, 386–98 (2003).

7. Siemering, G. S., Hayworth, J. & Melwani, A. *Aquatic Pesticide Monitoring Program Aquatic Pesticide Monitoring Program Final Report*. (2005).

8. Siemering, G., David, N. & Franz, A. *Aquatic Pesticides Monitoring Program Literature Review Karl Malamud-Roam Contra Costa Mosquito Vec tor Control A P R I L 2 0 0 3*.

9. Salam, D., El-Fadel, M. Mobility and Availability of Copper in Agricultural Soils Irrigated from Water Treated with Copper Sulfate Algaecide. *Water, Air, Soil Pollut. Vol.* **195**, 3–13 (2008).

10. Ro, O. & Ob, A. *OVERVIEW OF COPPER TOXICITY TO AQUATIC LIFE*. *Report and Opinion* **4**, (2012).

11. PubChem. Copper sulfate. Available at: https://pubchem.ncbi.nlm.nih.gov/compound/Copper-sulfate.

12. Paper, W., Work, P. C., Hay, J. & Estuar, F. Aquatic Herbicides : Overview of Usage , Fate and Transport , Potential Environmental Risk , and Future Recommendations for the Sacramento-San Joaquin Delta and Central Valley. *Work* (2005).

13. Murray-Gulde, C. L. *et al.* Algicidal Effectiveness of Clearigate, Cutrine-Plus, and Copper Sulfate and Margins of Safety Associated with Their Use. *Arch. Environ. Contam. Toxicol.* **43**, 19–27 (2002).

14. Masuda, K. & Boyd, C. E. Comparative evaluation of the solubility and algal toxicity of copper sulfate and chelated copper. *Aquaculture* **117**, 287–302 (1993).

15. Mastin, B. J., Rodgers, J. H., Rodgers, J. H. & Rodgers, J. H. Toxicity and Bioavailability of Copper Herbicides (Clearigate, Cutrine-Plus, and Copper Sulfate) to Freshwater Animals. *Arch. Environ. Contam. Toxicol.* **39**, 445–451 (2000).

16. Kiaune, L. & Singhasemanon, N. Pesticidal Copper (I) Oxide: Environmental Fate and Aquatic Toxicity. in *Reviews of environmental contamination and toxicology* **213**, 1–26 (2011).

17. Kevin J. Rader,Richard F. Carbonaro,Eric D. van Hullebusch,Stijn Baken, K. D. The Fate of Copper Added to Surface Water: Field, Laboratory, and Modeling Studies. *Environ. Toxicol. Chem.* **38**, (2019).

18. Johnson, B. M., Chao, M. M., Tedrow, O. R., Mcqueen, A. D. & Rodgers, J. H. *Plant Manage*. *J. Aquat. Plant Manage* **46**, (2008).

19. IUPAC. Copper sulphate. Available at: https://pubchem.ncbi.nlm.nih.gov/compound/Cupric-Sulfate#section=Structures.

20. Husak, V. COPPER AND COPPER-CONTAINING PESTICIDES: METABOLISM, TOXICITY AND OXIDATIVE STRESS. *J. Vasyl Stefanyk Precarpathian Natl. Univ.* **2**, (2015).

21. Fitzgerald, G. P. & Faust, S. L. Factors Affecting the Algicidal and Algistatic Properties of Copper. *J. Appl. Microbiol.* **11**, 345–351 (1963).

22. EPA, U. & of Pesticide Programs, O. *US EPA - Pesticides - Amended Reregistration Eligibility Decision (RED) for Coppers*. (2009).

23. EPA. *Coppers Fact Sheet*. (EPA, 2008).

24. EPA. 40 CFR 180.1021 - Copper; exemption from the requirement of a tolerance. | US Law | LII / Legal Information Institute. Available at: https://www.law.cornell.edu/cfr/text/40/180.1021. (Accessed: 27th December 2018)

25. Environmental, S. & Statement, I. Assessments of Aquatic Herbicides. (2000).

26. Ecology, W. D. of. *Supplemental Environment Impact Statement Assessments of Aquatic Herbicides :* **6**, (2001).

27. Dameron, C. T. *et al. Copper*. (World Health Organization, 1998).

28. Closson, K. R. & Paul, E. A. Comparison of the Toxicity of Two Chelated Copper Algaecides and Copper Sulfate to Non-Target Fish. *Bull. Environ. Contam. Toxicol.* **93**, 660–665 (2014).

29. Chemical Book. Copper(II) sulfate pentahydrate. Available at: https://www.chemicalbook.com/ChemicalProductProperty_EN_CB6705282.htm.

30. Calomeni, A., Rodgers, J. H. & Kinley, C. M. Responses of Planktothrix agardhii and Pseudokirchneriella subcapitata to Copper Sulfate (CuSO4∈·∈5H2O) and a Chelated Copper Compound (Cutrine®-Ultra). *Water, Air, and Soil Pollution* **225**, (2014).

31. Bishop, B. E., Willis, B. E. & Bishop, W. M. Understanding Fate and Effects of Copper Pesticides in Aquatic Systems. *J. Geosci. Environ. Prot.* **4**, 37–42 (2016).

32. Agency for Toxic Substances and Disease Registry (ATSDR). TOXICOLOGICAL PROFILE FOR COPPER. (2022). Available at: https://www.atsdr.cdc.gov/toxprofiles/tp132.pdf. (Accessed: 19th December 2019)

33. Uses of Copper Compounds: Copper Sulphate. Available at: https://www.copper.org/resources/properties/compounds/copper_sulfate01.html. (Accessed: 6th January 2022)

34. Copper Sulfate Crystal, Triangle Brand Pesticide Label.

35. *Old Bridge Copper Sulfate SDS*. Van Zwieten, L. & Merrington, Graham & Van-Zwieten, Melissa. (2004). Review of impacts on soil biota caused by copper residues from fungicide application.

36. Willis, Ben, "DETECTING COPPER RESIDUES IN SEDIMENTS FROM AQUATIC COPPER-BASED PESTICIDE APPLICATIONS" (2012). All Theses. 1527.

37. Hullebusch, E.V., Chatenet, P., Deluchat, V., Chazal, P.M., Froissard, D., Botineau, M., Ghestem, A., Baudu, M., 2003. Copper accumulation in a reservoir ecosystem following copper sulfate treatment (St. Germain Les Belles, France). Water, Air, and Soil Pollution 150: 3-22.

38. Gallagher, J., Duke, B., and Rodgers, J. 2005. Responses of Hyalella azteca and Ceriodaphnia to reservoir sediments following chelated copper herbicide applications. Journal of Aquatic Plant Management 43: 95-99.

39. Huggett, D.B., Gillespie, W.B., and Rodgers, J.H. Jr. 1999. Copper bioavailability in Steilacoom Lake sediments. Archives of Environmental Contamination and Toxicology 36: 120-123.

## Xylene

### Registration Status (FIFRA and WA Registration)

Xylene (1,2-, 1,3-, and 1,4-dimethyl benzene) is an aromatic solvent composed of three isomers.

A single product using xylene as the active ingredient currently registered with the EPA for use as an aquatic herbicide. The Thatcher Company currently produces the xylene herbicide under the trade name Aquatic Weed Killer® and uses 98% xylene (active ingredient) as mixed isomers. The U.S Department of Agriculture first registered Aquatic Weed Killer® in 1968, predating the creation of The EPA in 1970 (EPA, 2005b). The product label states that use is restricted to programs of the Bureau of Reclamation and Water User Organizations within registered states (AZ,CA,CO,ID,KS,MT,NE,NV,NM,ND,OR,SD,UT,WA, and WY). The use of xylene within these states is limited to highly managed irrigation canals and ditches. Washington State currently registers xylene for use by Irrigation Districts in managed irrigation systems for controlling a variety of floating and submerged aquatic vegetation (Thatcher, 2011). The Washington Department of Ecology currently administers its use in the *Irrigation System Aquatic Weed Control General Permit*.

### Chemical-use Patterns

Xylene is a non-selective herbicide used to control both algae and aquatic vegetation including but not limited to, filamentous algae, coontail moss, chara, horned pondweed, elodea, and various other pond and waterweeds (Thatcher, 2011). Xylene does not control emergent vegetation such as cattail (Sytsma & Parker 1999). For applications of liquid concentrate formulations of xylene to water, the current label, at the time of this writing, indicates that metered delivery through a high-pressure pump to a submerged weed sprayer is the preferred treatment method. Direct injection below the surface must be used. Ideally, application should occur when aquatic vegetation begins to interfere with water flow and delivery. To adequately treat longer stretches of water the label suggests two methods. The first involves adding Aquatic Weed Killer® at several locations 2-4 miles apart. In this scenario, 11 gallons of product are administered for each second-foot of water (cubic foot of water per second) over a period of 20-30 minutes. The second method of application involves adding 6 gallons of Aquatic Weed Killer® per second-foot over 20-30 minutes at stations spaced at approximately one-mile intervals. Following application, the label states that water treated with xylene must be held in an irrigation canal or ditch for a minimum of 96 hours before discharge into receiving waters outside of the irrigation network. If treated water is used to irrigate fields, the irrigated water must be held on the irrigation field until fully absorbed by the soil, or 96 hours has lapsed (Thatcher, 2011).

Xylene’s use as an active ingredient in aquatic herbicides is listed in the Code of Federal Regulations (40 CFR 180.1025) as exempt from pesticide residue tolerance requirements if its use meets several conditions (EPA, 2005b):

- Xylene's use is restricted to programs of the Bureau of Reclamation, U.S. Department of the Interior, and cooperating water use organizations.
- Xylene must be applied as an emulsion without exceeding initial concentrations of 750 ppm.
- Xylene should not be applied to waters containing a potable water system or where return, flows of treated water may enter receiving waters at concentrations greater than 10 ppm. And;
- Xylene when used as an aquatic herbicide must meet PAH limiting requirements outlined in CFR 172.250.

## Chemical Description

The pure form of the active ingredient Xylene (dimethyl-benzene or xylol) is a colorless, flammable, and sweet smelling aromatic hydrocarbon mixture composed of ortho (o-), meta (m-), and para (p-) xylene isomers under the collective CAS Number 1330-20-7. The three forms differ by the locations of methyl groups on the benzene ring. The individual CAS Numbers for o-, m-, and p-xylenes are; 95-47-6, 108-38-3, and 106-42-3 respectively. Mixed Isomers of xylene have a boiling point of 138.5$^{o}$ and a density of 0.864 gm/cm3 (ATSDR, 2007).

As noted in the EPA's Registration Eligibility Decision for xylene, given the Henry's Law constant of 6.4 x 10^-3 atm/m^3 • mole and vapor pressure of 5-9 mm Hg at 25$^{o}$C , volatilization is described as the most important fate property of xylene isomers applied to both aquatic and terrestrial systems. Due to xylene's rapid dissipation and low absorption of light at >290nm, abiotic degradation processes such as photolysis and hydrolysis are not expected to be important degradation factors. If environmental conditions exist where volatilization is hindered, biodegradation processes will play a more important role in degradation (ATSDR, 2007). If released in the air, the vapor pressure value of xylene suggests it will remain in the vapor phase and degrade rapidly with a half-life of 16-28 hours (HSDB, 2018). Xylene has a log octanol/water partition coefficient (log Kow) of 3.12- 3.20 and a water solubility value 130 - 190 mg/L, indicating that xylene does not easily mix with water (EPA, 2005b). The soil organic carbon sorption coefficient (Koc) values for mixed xylenes range from 25.4 to 540, indicating that there is high to moderate mobility when introduced to soil and will not absorb strongly to organic matter (ATSDR, 2007). Henry's Law constant values for Xylene of between 5.18 x 10-3 to 7.18 x 10-3 atm-cu m/mole indicate that volatilization from moist soil and water surfaces is likely a significant fate process. Estimated aquatic volatilization half-lives for xylene based on models for rivers and lakes were 3.1 hours and 4.1 days, respectively. For soil, complete degradation of Xylene in aerobic conditions ranges from 5-115 days with anaerobic degradation expected to be longer (HSBD, 2018). Bioconcentration factor is the ratio of concentration of chemical in an organism divided by the ambient concentration of the chemical in the environment and is a measure of the readiness with which chemical sharing occurs (WAC 173-333, 2012). The bioconcentration factor or BCF for Xylene ranges from 14-25.9 suggesting Xylene has a low potential for bioaccumulation in aquatic organisms (HSBD, 2018).

## Field Surveys and Investigations

The Bureau of Reclamation, Agricultural Research Service Cooperative Weed Control Program in Denver Colorado conducted several field studies on aromatic solvents including xylene starting in 1972. During the study, rainbow trout were exposed in artificial stream systems (flumes) to various concentrations of herbicide grade xylene. The study goal was to estimate LC50 values for rainbow trout from exposure to xylene, and document any observed non-lethal effects on the fish. The study design consisted of two time series; 56 day exposures at 0.36, 0.74 and 1.3 ppm and two hour exposures at 0.64, 3.6, 7.1, 16.1 and 25.6 ppm. Concentrations of 16.1 and 25.6 ppm resulted in 100% mortality after two hours resulting in an estimated $LC_{50}$ of 13.5 ppm. The study concluded that concentrations up to 7 - 10 ppm would likely cause no mortality, but concentrations exceeding this range may cause mortality, and should not be permitted to enter receiving waters (USBR, 1977).

Two-hour exposures of xylene at concentrations of 3.6 and 7.1 ppm resulted in no mortality, but did cause changes in behavior and symptoms similar to anesthesia. These physiological and behavioral changes were reversed after treated fish were placed in untreated water for 2-3 days. As a result of xylenes ability to inhibit behavior at non-lethal concentrations, the study suggested that treated water returning to fishery habitat should not be released if xylene concentrations are >1 ppm and exposures exceed two hours (USBR, 1977).

Furthermore, the study examined dissipation rates of xylene when introduced to irrigation systems at treatment use concentrations. After 10 miles of travel, Initial xylene concentrations of 548 - 760 ppm decreased to well below 100 ppm. After using the treated water for furrow irrigation, xylene concentration further decreased to < 0.2 ppm. The study concluded that xylene concentrations of < 0.2 ppm are inefficient to cause fish mortality or degrade water quality (USBR, 1977).

## Toxicological Profile

Short-term inhalation exposure of xylene has been associated with a range of symptoms in humans, including but not limited to, difficulty breathing, irritation of the eyes, nose and throat, gastrointestinal distress and short-term neurological impairment. The most common symptoms of acute dermal exposure to xylene is skin irritation, and dryness of the skin. Chronic symptoms from exposure to xylene are broad ranging and include, headaches, dizziness, fatigue, tremors, anxiety, impaired short term memory, labored breathing, impaired pulmonary function, heart palpitations, and severe chest pain. There is no reported information on carcinogenic effects of xylene; however, no studies have reported an increase in tumors in test animals. The EPA has classified xylenes as Group D, or not enough available data to either support or refute human carcinogenicity (EPA, 2000). Under EPA's toxicity category ranking system mixed isomer Xylene ranges from II to IV depending on the test endpoints and species used. $LD_{50}$ values for the Acute Oral Rat toxicity test range from 3523-8700 mg/kg, a Toxicity Category of III-IV (slightly toxic to practically non-toxic). Acute dermal $LD_{50}$ values categorized mixed Xylenes as III and Inhalation $LC_{50}$ values as IV. The highest classification (II-IV) was assigned to Dermal Irritation, indicating the possibility of mild to severe skin irritation from xylene exposure (EPA, 2005b).

As the target medium for xylene application is water, toxicity to aquatic organisms is the highest concern when assessing environmental risk. The use pattern for xylene as an aquatic herbicide indicates that xylene will be present in agricultural water bodies after treatment and a summary of aquatic toxicity studies indicate that xylene isomers are moderately to highly toxic to aquatic species (EPA, 2005). Risk scenarios for humans include consumption of treated water, inhalation of xylene during application, and from off gassing from treated water bodies (EPA, 2005b). Bioaccumulation of xylene is reported as low and is primarily limited by rapid metabolism and elimination in aquatic species. Bioconcentration is predicted to be low due to xylenes partition coefficient and rate of oxidation during metabolism. There is currently no data on the bioconcentration of xylenes in plants, which are a potential source of human exposure (ATSDR, 2007).

### *Mammalian, Avian, and Human Toxicity*

The EPA in its Reregistration Eligibility Decision assessed the risk for oral ingestion and inhalation risk of xylene-treated water to birds, mammals, and other terrestrial animals from several studies. For birds, the likely route of exposure is via food such as fish. A study using Japanese quail fed a xylene spiked diet for 5 -days reported NOEC values as high as 5000 mg/kg ($LC_{50}$ > 5000), with some $LC_{50}$'s exceeding 20,000 mg/kg. By multiplying the $LC_{50}$ (mg/kg) by body weight (kg) and dividing by food consumption (kg) a body weight $LC_{50}$ was calculated to be > 1746 mg/kg. This value was then used to calculate an estimated $LC_{50}$ for fish-eating birds (kingfisher weight) of >7990 mg/kg diet. A worst-case residue level was calculated to be 4.7 mg/kg by multiplying the highest water concentration of xylene reported by a predicted bioconcentration factor. A Toxicity exposure ratio of >1700 was then calculated by comparing the residual level of 4.7 mg/kg to the estimated $LC_{50}$. A value of >1700 is indicative of a very low risk to fish-eating birds. The assessment also reported that the Reportable Quantity (RQ) for mammals and birds from ingestion of xylene was below the acute endangered species Level of concern (LOC) of 0.1, indicating that there is little risk of deleterious exposure to terrestrial organisms from ingestion of treated water. Similarly, acute risk to terrestrial organisms from inhalation were found to have RQ values below acute LOCs (EPA, 2005b).

The Reregistration Decision also calculated quantitative risk to occupational handlers from dermal and inhalation exposure during the application process for xylene. Using the maximum xylene application rates, an average occupational workday of 8 hours and a calculated uncertainty factor, the EPA was able to derive a dermal Margin of Exposure (MOE) of 840 (EPA, 2005b). A MOE is the ratio of the toxic effect level to the estimated dose and is used to establish a margin of safety between a toxicity effect level dose and the predicted exposure dose. An acceptable MOE for a NOEC-based assessment is defined as 100 (EPA, 2005a). A dermal MOE of 840 is well below EPA's level of concern. For inhalation, the MOE was calculated to be 39,000, which is well below the level of concern. EPA found no worker risk concerns from handling or applying xylene when appropriate safety measures are used (EPA, 2005b). The product label's Precautionary Statements section includes minimum requirements for Personal Protective Equipment (PPE) to mitigate risk from mixing, loading, and applying xylene. These minimum requirements include, long sleeve shirt and pants, shoes and socks, chemical resistant gloves, protective eyewear, and a NIOSH approved half-face respirator with an organic-vapor removing cartridge (Thatcher, 2011). The EPA also considered the risk from post application exposure to treated canal water or water used to irrigate agricultural land. Though there is no uniform method to quantitatively assess risk potential, EPA assumes that these scenarios would not exceed the values derived from the dermal or inhalation assessment. Furthermore, due to xylene's propensity to volatilize it is not expected to remain in solution for long, thus further decreasing exposure risk. Dietary Exposure from the application of xylene treated irrigation water to crops was also considered. Due to xylenes vapor pressure of 5-9 mm Hg at 25° C and a Henry's Law Constant of $6.4 \times 10^{-3}$ atm/$m^3$ • mole, EPA determined that there is no risk for dietary exposure due to volatilization (EPA, 2005b). Furthermore, following the Reregistration Eligibility Decision, EPA exempted xylenes from the requirement of a tolerance for pesticide chemical residues in food when used as an aquatic herbicide (EPA, 2005a). No studies on terrestrial plants have been reported.

*Aquatic Organisms*

The EPA Reregistration Eligibility Decision for Xylene summarizes the acute toxicity values of several aquatic organisms as reported in the EFED Science Chapter as follows:

| Species | Endpoint | LC50 Value (mg/L) |
|---|---|---|
| freshwater fish: rainbow trout (*Salmo gairdneri*) | 96-hour $LC_{50}$ | 2.6 mg/L for p-xylene |
| freshwater invertebrates: water flea(*Daphnia magna*) | 24-hour $LC_{50}$ | 1.0 mg/L for m-xylene |
| estuarine/marine fish: striped bass*(Morone saxatilis)* | 24-hour $LC_{50}$ | 2.0 mg/L for p-xylene |
| estuarine/marine invertebrates: bay shrimp*(Crago francisocrum)* | 96-hour $LC_{50}$ | 1.3 mg/L for o-xylene |
| algae: green algae (*Selenastrum capricornutum*) | 72-hour $LC_{50}$ | 3.2 mg/L for p-xylene |

The EFED Science Chapter states that, "In general, results of acute toxicity studies indicate that mixed xylenes and xylene isomers are moderately to highly toxic to aquatic species (EPA, 2005b). Furthermore, EPA's ECOTOX Database provides amphibian LC50 values for Clawed Frog (*Xenopus sp.)*. Nine tests were reported with LC50 values ranging from 42 mg/L – 138 mg/L. The calculated average was 81 mg/L indicating a low risk of acute toxicity to amphibians (EPA ECOTOX, 2018). Due to xylenes rapid volatilization, chronic exposure to aquatic ecosystems is not expected and thus was not required during EPA's Reregistration Eligibility Decision. The acute LC50 values reported indicate a potential risk to aquatic organisms in canals treated with xylene. Studies conducted in 2004 by Parametrix for Ecology's *Irrigation System Aquatic Weed Control General Permit* showed an EC50 of 11.5 mg/l after 2 hours of exposure to xylene, and a 48-h LC-50 of 24.3 mg/l for xylene plus an emulsifier. The study also included the 48-h *Daphnia magna* test and found the LC50 to be 5.1 mg/L. The LC50 of 5.1 mg/L from the study was used to establish the General Permit instantaneous discharge limit of 5.1 mg/L for emulsified xylene (Ecology, 2012). Thatcher's product label indicates that the pesticide is extremely toxic to fish and other organisms treated with xylene (Thatcher, 2011). However, EPA considers canals to be part of highly managed agricultural systems that are frequently dry during the year, and as such risk management is not warranted for aquatic organisms in canals (EPA, 2005b).

EPA also evaluated the potential risk to aquatic organisms in water bodies receiving water treated with xylene. A "safe" concentration of 0.04 ppm was derived by the EPA using the most sensitive acute $LC_{50}$ reported (24-hour $LC_{50}$ value of 1.0 mg/L for m-xylene in water flea) and a Reportable Quantity for endangered species of 0.05. EPA flow models derived an acceptable discharge concentration of 1.0 ppm xylene into receiving waters considering xylenes rapid volatilization and the longer duration toxicity tests used to calculate the RQ estimates. The EPA label recommendation states, " Treated water must be either: (1) used to irrigate fields; or, (2) held in an irrigation ditch/canal until the xylene concentration has dropped to 1 ppm or below, as determined by and EPA approved method, before released from the irrigation network" (EPA, 2005b). The sole end-product label currently registered under Thatcher's Aquatic Weed Killer states, "Treated water must either be held on the irrigated field until absorbed by the soil or held in an irrigation canal/ditch for 96 hours prior to release from the irrigation network into receiving water bodies. Do not allow the treated water to enter any domestic water system. Treated water may be used for furrow or flood irrigation," (Thatcher, 2011). The label requirement to hold treated waters for 96 hours allows for the volatilization of xylene to occur before water exits the system. This holding time requirement is used to mitigate xylenes potential impact to receiving water at the treatment concentrations used.

### Data Gaps

No data gaps have been identified for xylene as part of EPA's pesticide registration and reregistration process. Further toxicity studies on terrestrial plant species would strengthen understanding of xylene's ecotoxicological risk potential, and support existing label language. Although oral ingestion of contaminated water by birds was assessed, toxicity data for acute exposure to volatilized xylene or combined exposure from volatized xylene and contaminated water could not be assessed due to lack of toxicity data (EPA 2005).

### Environmental and Human Health Impacts

#### *Earth*

#### *Soil and Sediments*

Mixed isomer xylene has a log octanol/water partition coefficient (log Kow) of 3.12- 3.20 and a water solubility value 130 - 190 mg/L, indicating low solubility (EPA, 2005a). Xylene isomer Koc values range from 129-331 indicating that there is high to moderate mobility when introduced to soil, and moderate affinity for sediment and particulate matter. Though xylene is mobile in soil and sediment, xylene readily biodegrades in both aerobic and anaerobic conditions. Complete biodegradation in aerobic soil conditions has been reported to be between 5-115 days, with anaerobic degradation predicted to be longer. Although some isomers take longer to biodegrade, a Japanese study using standard biodegradation tests classified xylenes as readily biodegradable with 100% theoretical BOD in active sludge. Furthermore, xylene's vapor pressure of 6.64-8.80 mm Hg and Henry's Law constant values of 5.18X10-3 to 7.18X10-3 atm-cu m/mole suggests that xylenes will readily volatilize in both wet and dry soils. Volatilization is expected to be a major fate process of xylene introduced to terrestrial environments (HSDB, 2018).

### *Agriculture*

At the use concentrations outlined on the product label, using agricultural water treated with xylene is not expected to damage crops, or wild vegetation. Water may be used for livestock immediately after treatment. The label, at the time of this writing, does not contain any precautions or restrictions on irrigation or secondary use following product application and holding period (Thatcher, 2011).

### *Water*

#### *Surface water and Runoff*

Xylene's primary route of degradation in water is volatilization. As noted in the chemical properties the Henry's Law constant of between 5.18x10-3 and 7.18x10-3 atm-cu m/mole and vapor pressure of 5-9 mm Hg at 25$^{o}$C suggest that volatilization from water is a significant fate process of xylene isomers applied to both aquatic and terrestrial systems. Estimated aquatic volatilization half-lives for xylene based on models for rivers and lakes were 3.1 hours and 4.1 days, respectively. As irrigation, canals often circulate water, when comparing volatilization rates are expected to be similar to river model rates. Due to xylene's rapid dissipation and low absorption of light at >290nm, abiotic degradation processes such as photolysis and hydrolysis are not expected to be important degradation factors (HSDB, 2018). As the application method for xylene is sub-surface direct injection, non-target plants outside the treatment zone are not expected to be harmed. Runoff of treated water is not expected to occur as xylene is only approved for use in highly managed agricultural water bodies.

#### *Groundwater / public water supplies*

Groundwater contamination potential for xylene under the use scenarios outlined in the product label is expected to be low, due to its high volatility, biodegradability in both aerobic and anaerobic conditions, and post application holding time requirements. Similarly, the contamination potential to public water supplies is predicted to be low. Thatcher's product label clearly states that the application of Aquatic Weed Killer is limited to irrigation and drainage canals managed be the Bureau of Reclamation and water use organizations in limited states. Furthermore, the label states that treated water must not be allowed to enter any domestic water system, and any treated water must be held for 96 hours prior to release from the irrigation network.

#### *Plants*

#### *<u>Higher Plants and Algae</u>*

Xylene is a non-selective biocide and will treat a wide range of algae and aquatic plants including all target plants identified on the product label. As reported in the toxicological profile above, xylene was tested with freshwater green algae (72-hour $LC_{50}$ value of 3.2 mg/L for p-xylene) indicating moderate to high toxicity to aquatic plants. Xylenes impact to terrestrial plants following pesticide application is not widely studied, but is expected to be minimal. Thatcher's product label allows treated water to be used for furrow or flood irrigation with no restrictions on concentration or crop type (Thatcher, 2011). Xylene's use as an active ingredient in aquatic herbicides is listed in the Code of Federal Regulations as exempt from pesticide residue tolerance requirements, suggesting that the total quantity of xylene found in or on food presents no hazard to public health. No impacts to non-target vegetation is expected due to the strictly aquatic application of xylene described on the product label.

#### *Habitat*

Based on available toxicity information xylene is not expected to cause long term effects to aquatic habitats but is acutely toxic to aquatic organisms. However, if xylene is applied in the manner described on the product label, acute effects to non-target aquatic organisms would be contained to highly managed irrigation networks and would not impact outside receiving waters. Highly managed irrigation ditches and canals are not expected to have large populations of sensitive aquatic organisms or be classified as critical habitat. Persistence and bioaccumulation in the environment is not expected due to the rapid oxidation of xylene into its corresponding metabolites. Xylene's oxidation rate is expected to prevent bioconcentration in animal tissue and therefore its ability to bioaccumulate up the food web (ATSDR, 2007). If label directions are not followed, there is a potential risk for acute toxicity to receiving waters down stream of treated areas.

## Mitigation

### Use Restrictions

Xylene is restricted for use in irrigation and drainage canals in programs of the Bureau of Reclamation and cooperating Water User Organizations in states listed on the product label. Furthermore, xylene can only be applied through direct injection below the surface of the water, and treated water must be held for a minimum of 96 hours after application. Treated

Water may be used for furrow or flood irrigation during the treatment period. When applied according to the product label, xylene does not require any other special mitigation measures. The product label contains no special cleanup procedures in the event of a spill (Thatcher, 2011). Ecology's *Irrigation System Aquatic Weed Control General Permit* has additional use restrictions and conditions when applying xylene as an aquatic weed killer in Washington State. Xylene must not exceed a maximum instantaneous concentration (or highest allowable discharge), of 5.1 mg/L at the point of compliance (Ecology, Permit Exp. 2019).

#### *Swimming and Skiing*

Canal banks and irrigation canals are owned by the irrigation district and are private property. The use of canals by non-irrigation staff is trespassing on private property. As the application of xylene is only registered for use in irrigation networks, no recreational impacts to swimming or skiing are expected. Trespassing on private agricultural waterways can and does occur. The label provides some mitigation measures for recreational risk by requiring that clear "No Swimming Allowed," signs be placed at all access points to the treated waterway including roads and streets for the duration of the application period. Future versions of the permit should consider requiring appropriate notification signage to inform the public that a pesticide application has taken place and any potential impacts to uses of the waterbody.

#### *Irrigation, Drinking and Domestic Uses*

The product label restricts xylene use to managed irrigation networks and canals. It explicitly states that xylene treated water must not be allowed to enter domestic water systems. If the label is correctly followed, risk to drinking water and domestic water systems is low. To further mitigate risk to adjacent receiving waters including domestic water bodies, the label requires that treated water be held for a minimum of 96 hours before release. Treated Water may be used within 96 hours for furrow or flood irrigation during the treatment period. Using treated water for livestock watering is not addressed, but due to its omission from the list of uses, is not recommended.

#### *Roadsides or Utility Rights-of-way*

As xylene is only approved for aquatic weed control in irrigation supply systems, its use is not expected to affect roadsides or utility easements. If the directions for use are followed, all access points should have appropriate signage detailing application information and swimming restrictions on roadsides and property adjacent to the treatment site.

#### *Fisheries and Fish Consumption*

Xylene is acutely toxic to aquatic organisms, and could impact local fish populations in receiving waters if xylene treated water is prematurely released from irrigation networks before the minimum holding time of 96 hours. Care should be taken when applying xylene, and the directions for use on the label should be strictly followed. Consumption of fish exposed to xylene is not likely to be an issue as it's not expected to bioaccumulate or bioconcentrate in fish or shellfish tissues. The Hazardous Substance Data Bank (HSDB) reported bioconcentration factors (BCF's) for xylene from two studies. A BCF of 14-15 was measured for goldfish exposed to 3 xylene isomers and a BCF of 25.9 was calculated from a 56-day flow through study using rainbow trout and emulsified xylene used for aquatic weed control. Using the Toxic Substances Control Act (TSCA) classifications a BCF value of less than 1000 is not bioacumulative. In addition, as previously stated xylene is only registered for use in controlled irrigation networks where recreational fishing is not allowed. Furthermore, Ecology's current (Expiration 2019) *Irrigation System Aquatic Weed Control* General Permit states, "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 Washington State Department of Fish and Wildlife (WDFW), and affected tribes to ensure treatments proposed upstream of a hatchery intake do not adversely affect hatchery fish or hatchery operations." This permit condition should be carried forward in the next reissuance.

#### *Wetlands or Non-Target Plants*

Xylene, if used in a manner other than listed on the product label, has the potential to acutely affect wetlands and non-target plants. Xylene is a non-selective pesticide with known acute toxicity to aquatic organisms. If used according to the product label xylene is not expected to affect non-target plants and wetlands. Xylene's is registered only for use in irrigation networks and should not be applied directly to wetland areas. Xylene application requires a post application minimum hold time for treated water of 96 hours. This hold time allows xylene concentrations to dissipate to levels that are not herbicidal, mitigating potential toxicity to receiving waters containing non-target plans and animals. All plants and algae within a treated irrigation canal are considered target organisms since xylene is a non-specific biocide.

#### *Endangered Species*

Based on the available toxicity information, xylene has the potential to be acutely toxic to ESA-listed species. Due to its propensity to volatilize rapidly, xylene is not predicted to cause chronic toxicity to ESA-listed animal species. Although there is a potential for toxicity to ESA-species from acute exposure, these species are not likely to inhabit managed irrigation networks where xylene use is permitted for use. The risk to endangered or vulnerable species is further mitigated through Ecology's permit process. *The current Irrigation System Aquatic Weed Control* General Permit states, "Before issuing permit coverage, Ecology will determine whether sensitive, threatened, or endangered (rare) plants 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." Furthermore, "The Permittee must comply with WDFW timing windows referenced in Tables 3 and 4 to protect salmon, steelhead, and bull trout populations and WDFW priority habitats and species" (Ecology, Permit Exp. 2019).

#### *Post-treatment Monitoring*

The label for Aquatic Weed Killer contains no requirement for post-treatment monitoring following application. As part of Ecology's current permit requirements, short -term post-treatment monitoring is required. Ecology uses this monitoring to determine permit compliance and the potential for non-target impacts.

## References

1. Andres S. Revilla, Cezar R. Pestana, Gilberto L. Pardo-Andreu, Antônio C. Santos, Sérgio A. Uyemura, María E. Gonzales, Carlos Curti. Potential toxicity of toluene and xylene evoked by mitochondrial uncoupling. Toxicology in Vitro, Volume 21, Issue 5, 2007. [1]
2. ATSDR (Agency for Toxic Substances and Disease Registry). 2007. Xylene. Accessed February 2018. Retrieved from: https://www.atsdr.cdc.gov/toxprofiles/tp71.pdf [1]
3. CITGO. 2015. Safety Data Sheet: Xylenes. Accessed: Feb 2018. Retrieved from: http://www.docs.citgo.com/msds_pi/07306.pdf [1]
4. Kandyala R, Raghavendra SPC, Rajasekharan ST. Xylene: An overview of its health hazards and preventive measures. Journal of Oral and Maxillofacial Pathology : JOMFP. 2010;14(1):1-5. doi:10.4103/0973-029X.64299. [1]
5. National Institute for Occupational Safety and Health (NIOSH). 2017. meta-Xylene International Chemical Safety Card. Accessed Feb 2018.Retrieved from: https://www.cdc.gov/niosh/topics/xylene/ [1]
6. National Park Service (NPS) National Park Service Water Resources Divisions. 1997. Environmental Contaminates Encyclopedia 0-Xylene Entry. [1]
7. Occupational Health and Safety Administration (OSHA). 2017. XYLENES (o-, m-, p-isomers) ETHYLBENZENE. Accessed: Feb 2018. Retrieved from: https://www.osha.gov/dts/sltc/methods/mdt/mdt1002/1002.pdf [1]
8. Skagit County. 2017. Tesoro Anacortes Clean Products Upgrade Project Environmental Impact Statement. Accessed February 2018. Retrieved From: https://tesoroanacorteseis.blob.core.windows.net/media/Default/Library/2017_07_10_Tesoro_Anacortes_CPUP_Final_EIS.pdf [4?]
9. Sytsma, M.D. & M. Parker. 1999. Aquatic Vegetation in Irrigation Canals – A Guide to Integrated Management. The Center for Lakes and Reservoirs, Portland State Univ, Portland, OR. [1]
10. Thatcher Company. 2011. Aquatic Weed Killer Product Label. EPA Reg. No. 9768-18. https://www.epa.gov/pesticides [1]
11. U.S. Bureau of Reclamation. 1977. Residues of Emulsified Xylene in Aquatic Weed Control and Their Impact on Rainbow Trout REC-ERC-76-11. Retrieved from: https://www.usbr.gov/tsc/techreferences/rec/REC-ERC-76-11.pdf [1]
12. U.S. Department of Health and Human Services. Hazardous Substances Data Bank (HSDB, online database). 2018. National Toxicology Information Program [1]
13. US Environmental Protection Agency (EPA), Office of Prevention, Pesticides and Toxic Substances. 2005a. Inert Reassessement - Xylene. [1]
14. US Environmental Protection Agency (EPA), Office of Prevention, Pesticides and Toxic Substances. 2005b. Reregistration Eligibility Decision for Xylene. [1]

15. US Environmental Protection Agency (EPA).ECOTOX Knowledgebase. Accessed 6/25/2018. Retrieved from: https://cfpub.epa.gov/ecotox/
16. US Environmental Protection Agency (EPA). 2000. Xylenes (A) (Mixed Isomers). Retrieved from: https://www.epa.gov/sites/production/files/2016-09/documents/xylenes.pdf [1]
17. Walsh, D.F., Armstrong, J.G., Bartley, T.R. Salman, H.A. and Frank, P.A., 1977. Residues of emulsified xylene in aquatic weed control and their impact on rainbow trout. Report#REC-ERC-76-11. US Bureau of Reclamation, Denver, CO. [1]
18. *Washington State Administrative Code (WAC) Chapter 173-333. 2006. "Persistent Bioaccumulative Toxins" [5]Washington State Department of Ecology. Irrigation System Aquatic Weed Control General Permit*

## 2,4-D

The following review is taken from the 2017 SEIS[29].

Two chemical forms of the active ingredient 2-4-dichlorophenoxy acetic acid (2,4-D), a selective postemergent 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. Because irrigation canals are private property, any swimming or wading in the canal is considered trespassing and no direct enforcement is required within the scope of the permit.

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.

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[29] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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 freeswimming aquatic biota from acute and chronic effects. However, although more sensitive species of Washington State Department of Ecology August 2017 SEIS for Aquatic Plant Management 116 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 welldocumented 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)[30], 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.

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[30] https://www.iarc.who.int/wp-content/uploads/2018/07/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- Washington State Department of Ecology August 2017 SEIS for Aquatic Plant Management 117 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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. 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]
2. Applied Biochemists. 2002. Specimen Label for Navigate® Selective Herbicide, 2p. http://www.aces.edu/dept/fisheries/rec_fishing/documents/navigate_label.pdf. [1]
3. 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]
4. EPA. 1987. Health advisory for 2,4-D. USEPA, Washington DC. [1]
5. Harnois, M. 1999. Toxicological Profile for 2,4-D. Office of Research and Standards, Mass. Department of Env. Protection, Boston MA. [1]
6. Hazardous Substances Databank (HSDB). 2005. 2,4-D; U.S. Department of Health and Human Services, National Institutes of Health, National Library of Medicine. https://www.nlm.nih.gov/toxnet/index.html, updated June 2005. [1]
7. 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]
8. 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] Washington State Department of Ecology August 2017 SEIS for Aquatic Plant Management 118
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]
10. 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]
11. 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]
12. 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]
13. 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]

14. 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]
15. Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]

### Diquat

The following review is taken from the 2017 SEIS[31].

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 dipyridylium herbicide compound related to quaternary ammonium compounds. All diquat formulations are liquid bromine salts. Diquat is a broad-spectrum (nonselective), 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 sunlightinducing 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

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[31] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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. Washington State Department of Ecology August 2017 SEIS for Aquatic Plant Management 126 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 Washington State Department of Ecology August 2017 SEIS for Aquatic Plant Management 127 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 shortlived 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 Washington State Department of Ecology August 2017 SEIS for Aquatic Plant Management 128 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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

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]
2. 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]
3. 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]
4. ENSR Corp. 2005. BLM Vegetation Treatments Using Herbicides: Ecological Risk Assessment for Diuron and Nine Other Herbicides. November: 118 p. [1]
5. EPA/Syngenta Corp. 2007. Label for Reward® Herbicide. https://www3.epa.gov/pesticides/chem_search/ppls/000100-01091-20070627.pdf [1]
6. 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]
7. 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]
8. 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]
9. REWARD® Landscape and Aquatic Herbicide, ECOfacts. 2000. Zeneca Professional Products. [1]
10. Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]

### Endothall (dipotassium salt)

The following review is taken from the 2017 SEIS[32].

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, spadderdock, 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

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[32] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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 proposed irrigation permit requires permittees to post warning signs along canals at points where the public may be able to access canals. However, irrigation systems are private property and it is not expected that the general public will come into contact with treated water.

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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

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]
2. 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]
3. 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]
4. 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. https://www.noaa.gov/sites/default/files/legacy/document/2020/Oct/07354626428.pdf [9]
5. Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]
6. 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]
7. 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]
8. 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]
9. Washington State Department of Agriculture (WSDA). 2014. Non-agricultural Pesticide Use in Puget Sound Counties. Publication No. AGR PUB 103-409: p. 76. https://cms.agr.wa.gov/WSDAKentico/Documents/DO/NRAS/103-409PSReportfinal2014.pdf. [1]
10. Washington State University. 2017. Pesticide Information Center Online – PICOL output. https://picol.cahnrs.wsu.edu/.

## Flumioxaxin

The following review is taken from the 2017 SEIS[33].

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.

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[33] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. 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. https://www.fluoridealert.org/wp-content/pesticides/flumioxazin.ca.epa.jan.2003.pdf.[1]
2. CalEPA. DPR. 2003b. Public Report 203-6. Tracking ID No. 191861 N. [9]
3. Health Canada. 2010. Evaluation Report. Flumioxazin. ERC2010-05. [1]
4. Material Safety Data Sheet for Clipper™ Herbicide. 2011. 68. [1]
5. Massachusetts Departments Agricultural Research and Environmental Protection (MDAR/MDEP). 2013. Flumioxazin. p. 63. https://www.mass.gov/doc/flumioxazin/download?_ga=2.57363106.982191718.1690928531-2014409489.1690928531. [1]
6. 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]
7. 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, docket ID: EPA-HQ-OPP2011-0176 (http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2011-0176-0003). [1]
8. EPA. 2001. Pesticide Fact Sheet for Flumioxazin. [1]
9. EPA. Flumioxazin. Human Health Risk Assessment for a Proposed Aquatic Use. Docket No. EPA-HQ-OPP2008-0781. https://www.govinfo.gov/content/pkg/FR-2010-11-10/html/2010-28132.htm. [1]
10. EPA. 2010a. Drinking Water Assessment for the Proposed Use of Flumioxazin as an Aquatic Herbicide. [1]
11. EPA. 2010b. EFED Section 3 Registration for Flumioxazin to be Used for Control of Weeds in Bayous, Canals, and other Aquatic Areas. [5]
12. 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.
13. Valent. 2010. New Chemistry for Aquatic Weed Management. Aquatic Herbicide White Paper. [9]
14. Valent. 2011. Clipper™ Herbicide Specimen Label. [1]
15. Valent Canada. 2009. Flumioxazin Herbicide. Technical Brochure. [1]

16. 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]
17. Washington Department of Transportation. (WDOT). 2006. Flumioxazin Roadside Vegetation Management Herbicide Fact Sheet. [1]

## Fluridone

The following review is taken from the 2017 SEIS[34].

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 nontarget 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 shortlived 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

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[34] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. Archambault, J.M., C.M. Bergeron, W.G. Cope, R.J. Richardson, M.A. Heilman, J.E. Corey III, M.D.
2. 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]
3. 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]
4. 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]
5. 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]
6. Hamelink, J., et al. 1986. Toxicity of Fluridone to Aquatic Invertebrates and Fish. Environ. Toxicol. Chem. 5: p. 87-94. [1]
7. 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]
8. 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]
9. SePro. (Undated). Sonar® PR Aquatic Herbicide Specimen Label. 6 pp. https://www.sepro.com/Documents/Sonar-PR_Label.pdf [1]
10. US Environmental Protection Agency (EPA). 1986. Pesticide Fact Sheet: Fluridone. No. 81: p. 5. [1]
11. Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. Publication No. 00-10-040. [3]

## Glyphosate

The following review is taken from the 2017 SEIS[35].

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.

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[35] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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 carcinogenity 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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. 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]
2. 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]
3. 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]
4. Cox, C. 1995. Glyphosate: human exposure and ecological effects. J. Pesticide Reform 15(4): p. 1-16. [1]
5. 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]
6. 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]
7. 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). https://www.who.int/publications/i/item/9789241655323 . [11]
8. 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]
9. 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]
10. 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](http://monographs.iarc.fr/ENG/Monographs/vol112/mono112-10.pdf) [1]
11. 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]
12. 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]

13. 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 Research12: 5281-5292. [1]

14. 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]

15. Nature Conservancy. 2001. Weed Control Methods Handbook. 10 p. https://www.invasive.org/gist/products/handbook/methods-handbook.pdf [1]

16. Neskovic, N., et al. 1996. Biochemical and histopathological effects of Glyphosate on carp (C. carpio). Bulletin Environ. Contam. Toxicol. 56: p. 295-302. [1]

17. 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]

18. 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]

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

20. 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]

21. 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]

## Imazamox

The following review is taken from the 2017 SEIS[36].

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.

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[36] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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 148quaticc 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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. AECOM. 2009. Use of Aquatic Herbicide imazamox Clearcast® in the State of New York. Supplemental Environmental Statement. Final. Document No.: 00760-245-310. [1]
2. BASF. 2016. Clearcast® Specimen label https://sepro.com/documents/clearcast_label.pdf. [1]
3. Burns, B. 2009. Clearcast® Herbicide Technical Information. PowerPoint presentation https://slideplayer.com/slide/4014310/. [9]
4. Durkin, Patrick R. 2010. Imazamox Human Health and Ecological Risk Assessment. Syracuse Environmental Research Associates, Inc. Submitted to USDA/Forest Service, Southern Region. [1]
5. 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]
6. 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]
7. 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]
8. New York State Department of Environmental Conservation (NYSDEC), BASF Corporation. 2009. Approving the Registration of Clearcast® Herbicide (EPA Reg. No. 241-437). Letter [10]
9. 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]
10. Schumacher, D., and D. McGregor. 2014. Imazamox. World Health Organization. JMPR 209-239, 2014. [1]
11. 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]
12. Syracuse Environmental Research Associates, Inc. 2010. Imazamox Human Health and Ecological Risk Assessment, Final Report. Prepared for USDA Forest Service. https://www.fs.usda.gov/foresthealth/pesticide/pdfs/052-24-02a_Imazamox.pdf. [1]
13. Thurston County Health Department. 2011. Review of Imazamox. [1]
14. US Environmental Protection Agency (EPA). 1997. Pesticide Fact Sheet for Imazamox (Raptor Herbicide).

https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_PC-129171_22-May-97.pdf. [1]

15. 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]
16. Vassops, Joseph D. 2010. Evaluation of Herbicides for Control of Eurasian Watermilfoil and Sago Pondweed. Master's Thesis. Colorado State University. [9]
17. 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]
18. 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]
19. 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]
20. 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]

## Imazapyr

The following review is taken from the 2017 SEIS[37].

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 precipitation, temperature, pH, soil types, and other factors.

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[37] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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).

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. 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]
2. Washington State Department of Agriculture (WSDA). 2009. Human Health and Ecological Effects Risk Assessment, Imazapyr. Prep. By AMEC Geomatrix for WSDA: p. 308. https://cms.agr.wa.gov/getmedia/c7759568-f7f2-41e3-91ab-7e3cf5395fba/2009AMECHumanHealthEcologicalEffectsRiskAssessmentImazapyr.pdf. [1]
3. WSDA. 2015. Spartina eradication program report. AGR PUB 809-505 (N/2/16). 40 p. https://cms.agr.wa.gov/WSDAKentico/Imported/505-SpartinaReportFinal2015.pdf?/505-SpartinaReportFinal2015.pdf. [4]
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]
5. 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]

### Endothall (mono salt)

The following review is taken from the 2017 SEIS[38].

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

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[38] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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. Warning signs are required at points where the general public may be able to access canals. However, irrigation canals are private property and the general public are not expected to contact treated water.

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 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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

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]
2. 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]
3. 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]
4. 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. https://www.noaa.gov/sites/default/files/legacy/document/2020/Oct/07354626428.pdf [1]
5. Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. July. Publication No. 00-10-040. [3]
6. 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]
7. Ecology. 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides, WA Department of Ecology, July 2000. Publication No. 00-10-040. [2]
8. 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.
9. 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]
10. 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]
11. WSDA (WA State Department of Agriculture). 2014. Non-agricultural pesticide use in Puget Sound Counties. Publication No. AGR PUB 103-409. 76 p. https://cms.agr.wa.gov/WSDAKentico/Documents/DO/NRAS/103-409PSReportfinal2014.pdf. [1]
12. Washington State University. 2017. Pesticide Information Center Online – PICOL output. https://picol.cahnrs.wsu.edu/. [1]

## Sodium Carbonate Peroxyhydrate (sodium percarbonate)

The following review is taken from the 2017 SEIS[39].

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

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[39] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

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.

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 SPcontaining 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).

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.

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.

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.

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.

It should be noted that the inside of irrigation canals within an irrigation system are not considered part of the natural environment. As treated water must meet water quality standards and effluent limits at the point of compliance before it can be released into the receiving waters, environmental impacts on plants, algae, and wildlife are not anticipated in the receiving waters.

## References

1. 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]
2. BioSafe Systems. GreenClean Liquid: Broad Spectrum Algaecide/Bactericide. Specimen Label. Connecticut. 2006. [1]
3. BioSafe Systems. GreenClean Pro: Granular Algaecide/Fungicide. Specimen Label. Connecticut. 2008. [1]
4. Chater, B. 1978. Sodium Percarbonate, Acute Oral Toxicity with Histology, Skin and Eye Irritation. ICI Report CTL/T/1151. [9]
5. Clarke, C. 1991. The Anti-algal Activity Of Peroxygen Compounds. Thesis. [9]
6. 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]
7. 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]
8. 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: https://publications.jrc.ec.europa.eu/repository/handle/JRC26024. [1]
9. 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]
10. Shangya Jiehua Chemical Co. 2009. Technical Data Sheet: Sodium Percarbonate. p. 3 http://www.runyoutech.com/pdf/sodium-percarbonate-specifications.pdf. [9]
11. Toxnet. 2009. Hazardous Substances Data Bank. National Library of Medicine. https://www.nlm.nih.gov/toxnet/index.html. [1]
12. US Environmental Protection Agency (EPA). 2016. ECOTOX Database, http://cfpub.epa.gov/ecotox/. [1]
13. 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]
14. 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]

15. Washington State Department of Agriculture (WSDA). 2014. Non-agricultural Pesticide Use in Puget Sound Counties. Publication No. AGR PUB 103-409: p. 76. https://cms.agr.wa.gov/WSDAKentico/Documents/DO/NRAS/103-409PSReportfinal2014.pdf. [1]

**Alternative 4: Integrated Pest Management (IPM) using Adaptive Management**
It is the preferred alternative to use an integrated pest management (IPM) approach for the management of aquatic plants and algae in irrigation systems. This approach would combine physical, mechanical, and biological methods with chemical applications of the herbicides and algaecides. The efficacy of herbicides and algaecides combined with physical and mechanical removal and general integrated pest management practices should reduce the interval at which herbicide applications will be necessary.The IPM approach relies on combined use of multiple methods to efficiently and effectively control the growth and spread of aquatic plants and algae in irrigation systems.

EPA defines integrated pest management (IPM)[40] as an effective and environmentally sensitive approach to pest management that relies on a combination of common-sense practices. IPM programs use current, comprehensive information on the life cycles of pests and their interaction with the environment. The information, in combination with available pest control methods, is used to manage pest damage by the most economical means with the least possible hazard to people, property, and the environment. IPM takes advantage of all appropriate pest management options, including, but not limited to the judicious use of pesticides.

Ecology's proposed NPDES general permit will require that applicants develop Integrated Vegetation Management Plans as well as pesticide application plans if they plan to use certain pesticides. Together, these plans serve as IPM within the scope of the permit.

## References

1. EPA. *Introduction to Integrated Pest Management.* June 28, 2002. https://www.epa.gov/ipm/introduction-integrated-pest-management.

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[40] https://www.epa.gov/ipm/introduction-integrated-pest-management

**Other Alternatives Considered**

Several alternative methods for freshwater weed management are described in Ecology's *Draft Supplemental EIS: Assessments of Aquatic Herbicides* (July 2000).

Information about these alternatives is referenced from the 2017 SEIS for Aquatic Plant and Algae Management[41].

### Manual Removal/Disposal to an Upland Site

Manual removal involves removing the entire plant or algae from the substrate by hand using tools such as shovels, rakes and knives to loosen the substrate and facilitate removal. This method is labor intensive but does not always require specialized skill or formal training. The plants would be disposed on an upland site, away from irrigation canals. Aquatic plants and algae ants are typically best removed when exposed by low water levels; otherwise, divers or snorkelers would have to be employed while water levels are high and plants are submerged. This would substantially increase the cost of removal. Workers may use bags, wheel barrows, hand carts, boats, barges, and/or motorized vehicles to transport plants away from removal sites. This work would generate turbidity, and would result in the removal of sediments that cling to the root/rhizome structure of aquatic plants.

Manual removal is generally only suitable for small populations (i.e., less than 0.05 acres) of mature plants. Seeds and recently sprouted plants are small and difficult to see and remove effectively. Manual removal of aquatic plants and algae is very labor-intensive, time consuming, and therefore expensive.

Manual control of extensive beds of aquatic plants and algae on a commercial scale of multiple miles of canal length is likely infeasible. Seeds, rhizomes, and fragments from unmanaged acreages can repopulate hand-pulled areas. Many species of aquatic plants and algae can regrow from settled fragments that are not captured or properly disposed of during hand pulling activities.

### Bottom Barriers/Covering

A bottom barrier, also called a benthic barrier or a bottom screen, would cover the sediment or substrate like a blanket. It would be analogous to using landscape fabric under bark chips to prevent weeds on an upland site. Barriers block light and limit water/oxygen circulation from plants and algae.

An ideal bottom barrier fabric is durable, heavier than water, reduces or blocks light, is easy to install and maintain, and readily allows decomposition gases to escape without billowing the barrier upwards into the water column. Many different materials have been used for bottom barriers, such as burlap, plastics, perforated black Mylar®, and woven synthetics. There are also some commercial bottom barrier products available; however, even the most porous materials can billow due to sediment gas buildup (Gunnison and Barko, 1989 and 1990).

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[41] https://apps.ecology.wa.gov/publications/documents/1710020.pdf

Fishing gear, anchors, vandalism, or storms can damage bottom barriers. Although fishing, swimming, and boating are not recognized uses of irrigation canals, trespassers may cause damage if they partake in these activities. Any tears in the fabric will reduce their efficacy.

Lining canals with hard barriers like concrete is typicallyl done to improve water efficiency of irrigation canals, but can also limit the growth of some aquatic plants. Fully encasing water delivery systems with pipes can limit light that allows for plant growth, but may not fully elimitate algae growth. These methods are expensive, and are often only implemented on sections of larger irrigation systems.

In practice, for logistical and economic reasons, bottom barriers would only be effective for aquatic plant and algae control where there are smaller sections of irrigation canal that need to be lined or piped for other reasons. Bottom barriers are one of the most expensive methods for aquatic vegetation control if used in a large-scale application. Cost estimates for bottom barrier material in freshwater applications range from $0.22 to $1.25 per square foot.

### Mechanized Cutting and Harvesting

Mechanical weed cutters cut aquatic plants several feet below the water surface. Plant roots and rhizomes are not removed by cutting and harvesting. Unlike mechanical harvesting, cut plants are not collected while the machinery operates. Cutting generates floating plants, seeds, and fragments. It would be nearly impossible to collect and remove aquatic plants, algae, seeds and fragments from the water to prevent them from drifting or re-rooting or seeding at new locations, with the result that this method may exacerbate the problem rather than contribute to the management of aquatic plants and algae.

Due to the low profile and flexible nature of some aquatic plants, it is unlikely that the mechanical cutters described above would be effective. It would be very difficult to consistently cut all aquatic plants close to the sediment/water interface. Due to the lack of control (i.e., removal) of the root and rhizome structure, plants would quickly re-sprout as cutting is similar to mowing a lawn; many subsequent cuttings are required during the growing season. Cutting at the sediment surface would also generate turbidity.

### Suction Dredging (Diver Dredging)

Diver dredging is a method whereby divers wearing Self Contained Underwater Breathing Apparatus (SCUBA) use hoses attached to small dredges to vacuum plant material out of the sediment. The purpose of diver dredging is to remove all parts of the aquatic plant, including the roots. The use of the suction dredge is slow, labor intensive, and expensive. Removal rates by an experienced diver vary from 0.25 acre per day to one acre per day (Washington Department of Ecology 2004).

Use of a suction dredge is practical and up to 90% effective for clearing plants from small areas and from areas containing obstructions. Removal can be very selective for an area and for a species; however, turbidity that occurs during the procedure tends to obscure visibility resulting in less effective removal.

Due to the high cost of suction dredging, this method is not considered a reasonable alternative to IPM or chemical methods of aquatic plant and algae management.

## Rotovation

Rotovation for the control of aquatic vegetation is performed using agricultural tilling machines. Rotating blades churn 7 to 9 inches deep into the bottom substrate to dislodge and damage plant foliage and roots. Rotovation appears to stimulate the growth of aquatic plants, so it would not be an effective tool to manage excessive growth of nuisance species (Washington Department of Ecology 2004). Due to an increase in plant biomass during summer months, plants must be cut by some other means before rotovation. Otherwise, long leaves and stems tend to wrap around the rototilling head.

The amount of area that could be rotovated per day can range from 2 acres to less than one acre depending on plant density, time of year, bottom obstructions, and weather conditions. Imprecise tracking of rotovated areas could result in incomplete removal of target plants, ultimately minimizing the effectiveness of this method and long-term control.

Rotovation would disrupt the bottom of earthen canals, which could lead to damage and reduced water carrying efficiency.

## Biological Control

Biological control (biocontrol) is the purposeful introduction of parasites, predators, and/or pathogenic microorganisms to reduce or suppress populations of plant or animal pests. Biocontrol agents must be living organisms so they can seek out the target pests. They may directly attack and kill the pest, or they may weaken the hosts so that they are unable to reproduce at their normal rate. Scientists conduct extensive research before releasing any biocontrol organisms to help ensure that these organisms are host-specific, thereby minimizing the chance that they may harm the environment in other ways.

Even when successful, a classical biocontrol agent generally does not eliminate all targeted individuals. A predator-prey cycle establishes where increasing predator populations will reduce the targeted individuals. In response, the predator species will decline. The pest species rebounds due to the decline of the predator species, and the cycle continues.

Biocontrol is most suited for non-native organisms not closely related to indigenous beneficial species. It is not suitable for organisms with many related members that are of economic or environmental importance, because the biocontrol agent may attack related species as well as the targeted pest. As the inside of irrigation canals within irrigation systems are not considered habitat for native species, this is not a strong concern. However, irrigation districts would need to be careful to not accidentally release biocontrol species into the source or receiving waters for the canals.

At this time, the primary biological control species used in irrigation canals is the sterile grass carp, which must be confined when not in use. Use of grass carp may be helpful in an IPM regime, but is not typically practical as a standalone option.

## References

1. University of Florida Center for Aquatic and Invasive Plants. *Plant Management in Florida Waters Section 2: Overview of Florida Waters.* October 27, 2020. https://plants.ifas.ufl.edu/manage/overview-of-florida-waters/waterbody-types/canals/.

## Cumulative Impacts

Cumulative impacts to be evaluated in environmental review documents prepared under the Washington State Environmental Policy Act (SEPA) are defined only in case law. The SEPA Rules limit the scope of environmental review to impacts that are probable (WAC 197-11-782) and significant (WAC 197-11-794), with attention to impacts that are likely, not merely speculative (WAC 197-11-060[4][a]). The SEPA Rules specifically define only direct and indirect impacts, as follows: those effects resulting from growth caused by a proposal (direct impacts), and the likelihood that the present proposal will serve as a precedent for future actions (indirect impacts) (WAC 197-11-060[4][d]). Recent court cases have indicated that cumulative impacts under SEPA are those impacts of the project that, when combined with the impacts of other projects that are dependent on the proposed project or upon which the proposed project depends, are significant. A cumulative impacts analysis is prospective only (i.e., it is required under SEPA only when it is probable that the project under review will facilitate future action that will result in additional impacts).

There is no information that indicates the proposed application of herbicides for use in irrigation applications is dependent upon any other proposed action. Nor is there any information that any other known proposed action is dependent upon the proposed application of herbicides used in irrigation systems. For these reasons there are, under SEPA, no cumulative impacts to evaluate related to the action that is the subject of this Environmental Impact Statement.

It is not necessary to review cumulative impacts within the irrigation canal system because the irrigation canals are permitted for herbicide use and water is tested at the point of compliance prior to discharge to waters of the state. Sometimes the canal water that has been treated with herbicides never reaches waters of the state because the water is completely used up onsite. If not all of the water is used up in the canal, it may be discharged once the pesticide concentrations meet water quality standards at the point of compliance. However, because the point of compliance is within each individual irrigation canal, any discharge of herbicide will be within the water quality standards for that herbicide before it is discharged to other waters of the state. Ecology does not anticipate direct toxic effects at the point of discharge to the natural receiving water.

Although we know that small quantities of herbicides may mix together in waters of the state after being discharged from individual irrigation canals, not much information exists about these specific herbicide mixtures in literature. However, since all herbicides must reach compliance prior to discharge to waters of the state where mixing may occur, any mixtures will be of small quantities of herbicides within water quality standards that are now diluted in a much larger body of water than their respective irrigation canals. Direct toxic effects on aquatic life is not expected due to this requirement. Receiving waters that have multiple outfalls from irrigation ditches have the highest potential for herbicide mixing. It should be noted that the discharges are intermittent, so even with multiple outfalls on the same receiving water, mixing might not occur due to timing. Herbicide-containing discharges from irrigation canals are not considered chronic impacts since the discharges are intermittent and there is typically only activity during the common growing months, not year-round. Also of note is that many herbicides volatilize or degrade faster when temperatures are high and that many herbicide treatments occur during the summer months when temperatures are higher, thus leading to faster volatilization or degradation and minimal or non-existent concentrations upon discharge from the canals. When herbicides have the ability to volatilize, this leaves the irrigation canals with even less of a concentration of such herbicides, so permittees may reach compliance quicker. Other factors influence toxicity of herbicides, including pH and hardness, among others, which should be taken into consideration when permittees are deciding which herbicide(s) to use.

### Mechanical and manual removal of noxious weeds

The additive effects of mechanical and manual removal*noxious weeds* combined with herbicide treatment is addressed by the discussion of Alternative 5, the integrated pest management option, in this FEIS.

### Actions Not Considered as Cumulative Impacts

There are limited studies on the effects of multiple herbicides tested at the same time, therefore, a synergistic effect between commonly used compounds and salmonids or other aquatic species could not be ruled out.

## References

1. 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.
2. 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.
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.
4. 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.
5. Hamelink, J., et al. 1986. Toxicity of Fluridone to Aquatic Invertebrates and Fish. Environ. Toxicol. Chem. 5: p. 87-94.
6. 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.
7. 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://www.sepro.com/Documents/Sonar-PR_Label.pdf
8. US Environmental Protection Agency (EPA). 1986. Pesticide Fact Sheet: Fluridone. No. 81: p. 5.
9. Washington Department of Ecology (Ecology). 2000. Supplemental Environmental Impact Statement of Aquatic Herbicides. Publication No. 00-10-040.

## Benefits and Disadvantages of Reserving the Proposed Action for Some Future Time

The herbicides covered under this permit are for use in irrigation ditches. The irrigation ditches are used to provide water to crops and the herbicides listed in this EIS are used to remove any plants that grow in these irrigation ditches. The presence of unwanted aquatic plants can decrease irrigation ditch volume. Some of the plants being treated may be noxious weeds identified for control in Washington State.

If reserved until a future time, irrigation ditches may become overrun by aquatic plants and the irrigation ditches may not be able to hold the water necessary to function appropriately to convey water to crops. Irrigation ditches may also have an increased incidence of flooding.

## Impacts to Irrigation Systems from Aquatic Plants and Algae

Selection of one or more of the alternatives described above is necessary to manage aquatic plant and algae growth in irrigation systems. The beneficial uses of irrigation canals depend on the free and efficient flow of water throughout the system. Overgrowth or mismanagement of aquatic plants and algae in irrigation systems can lead to blockages, damaged equipment and infrastructure.

# Appendix A: Response to Comments

The Washington State Department of Ecology (Ecology) received public comments on the draft Environmental Impact Statement for the Irrigation System Aquatic Weed Control General Permit that was released for public comment on January 18, 2023. Ecology also accepted oral testimony provided by participants at the two (2) workshops and hearings that were held virtually. No oral testimony was given at these hearings. One public comment was submitted prior to the close of the public comment period on March 20, 2023. Ecology has summarized this comment and identified specific topics to address. Ecology provided a written response to comments on the environmental impact statement (EIS) and indicated where revisions were made to the final EIS. Underlined language is used to indicate new final language compared to the draft EIS. Copies of all public comment letters are posted on ecomments[42].

The comment summaries and response to comment are in the separate Appendix A: Response to Comments on the permit webpage.

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[42] https://wq.ecology.commentinput.com/comment/extra?id=4GdZb