

Antifouling Paints in Washington State Report and Recommendations

Report to the Legislature Pursuant to SHB 2634 (2018)

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Report to the Legislature Pursuant to SHB 2634 (2018)

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Hazardous Waste and Toxics Reduction Program

Washington State Department of Ecology

Olympia, Washington

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Executive Summary

Boats kept in marinas, lakes, and other waterbodies are exposed to organisms such as bacteria or barnacles. When these organisms grow and colonize on the surface of vessels and structures, it is called "fouling" and can result in reduced performance and physical damage. To prevent these effects, boat owners often use hull paints that contain pesticides and other toxic chemicals. Copper-based hull paints have been the most popular antifouling choice since the 1980s. Although they are effective at discouraging organism growth, these paints also have toxic environmental impacts and can have significant negative effects on fish and other aquatic life.

In 2011, Washington enacted legislation to ban the use of copper-based antifouling paint starting in 2018. A 2017 follow-up investigation by Ecology showed that some non-copper alternatives might be more harmful to the environment than the copper-based paints they replaced. In 2018, the Legislature delayed the ban and directed Ecology to conduct additional research. Ecology was directed to review risk assessments, scientific studies, and other relevant analyses regarding the toxicity and environmental impacts of antifouling paints. Ecology was also directed to report back to the Legislature about those reviews, safer alternatives that might be available, and recommendations as to whether regulatory changes are needed.

This report summarizes the results of Ecology's review as directed by the Legislature. It addresses:

- Antifouling paints containing copper, Cybutryne/Irgarol, DCOIT/Sea-Nine, Tralopyril/Econea, and zinc pyrithione.
- Non-paint antifouling strategies, such as non-biocidal coatings, sonic antifouling systems, and dry dock-type fouling avoidance options.
- Ecology's scientific modeling of antifouling ingredients in Washington's marina waters.

Ecology's previous finding—that non-copper antifouling paints may pose a greater threat to the environment than copper-based paints—has not changed. Ecology continues to be concerned that non-copper antifouling alternatives may pose a threat to Washington's environment.

Ecology recommends that the Legislature:

- Delay the existing statutory ban on copper-based antifouling paints for an extended period, so as to allow more scientific information to be developed.
- Grant Ecology authority to require information from paint manufacturers regarding ingredients, leach rates, and other relevant data.
- Add a new section to Chapter 70.300 RCW banning the sale and application of antifouling paints containing Cybutryne/Irgarol for recreational vessels in Washington.

Antifouling Paints in Washington State

Background

Boats kept in marinas, lakes, and other waterbodies are exposed to organisms that live in those waters. These organisms range from single-celled bacteria and algae to larger mollusks like barnacles and mussels. When these organisms grow and colonize on the surfaces of vessels and structures, it is called "fouling" or "biofouling" and has challenged boat owners since at least 400 BCE.¹⁴¹ Fouling reduces performance by increasing drag (leading to higher fuel costs), impairs maneuverability, and can cause physical damage to vessels and structures.⁸⁶ 101 117 127

To prevent fouling, boat owners often use hull paints that contain pesticides and other toxic chemicals, commonly called "biocides." Copper-based hull paints have been the most popular antifouling choice since tributyltin (TBT) was banned internationally in the 1980s.⁷⁹ However, copper can have negative effects on aquatic life.¹⁵⁰

Types of antifouling paints

Antifouling products can be designed either to prevent fouling organisms from attaching, or to dislodge organisms that do try to attach. Some products use a biocide (like copper) to kill fouling organisms. Other products use techniques that are designed to be non-lethal. A summary of the different types of antifouling paints and coatings is provided in Tables 1 and 2 below.

Appendix A is a complete list of biocidal antifouling paints that are currently registered for sale in Washington State. This list was derived from Washington State University's Pesticide Information Center Online database.^A Information about paint leach rates was derived from California's Department of Pesticide Registration Product/Label database.^B

Non-paint alternatives also exist and are addressed later in this report.

^{*A*} Available at <u>http://cru66.cahe.wsu.edu/LabelTolerance.html</u>.

^{*B*} Available at <u>https://www.cdpr.ca.gov/docs/label/m4.htm</u>.

Table 1 Types of biocidal antifouling paints^c

Description	Action	Estimated Lifespan	Advantages	Disadvantages
Contact Leaching Coatings (aka "hard" coatings)	Continually release biocide through diffusion-controlled process that starts at a high level and slowly decreases	12–18 months	Resilient finish, does not require movement to work properly	Cannot be dry docked without repainting
Soluble/Sloughing Coatings	Paint releases biocide as the surface sloughs off in visible flakes as boat moves through the water	12–15 months	Least expensive, dries quickly	Short lifespan, needs movement in water to refresh surface, easily damaged
Controlled Depletion Polymer Coatings (a/k/a "ablative" coatings)	Paint surface slowly wears away, releasing biocide as vessel moves through the water	Up to 3 years	Effective against heavy fouling	Longevity based on thickness, needs movement in water to refresh surface, easily damaged
Self-polishing Copolymer Coatings	Acrylic ingredients react with saltwater to release biocide chemically instead of physically	Up to 5 years	Biocide release rate remains constant	Easily damaged, cannot be safely washed underwater

Table 2 Types of non-biocidal antifouling paints^D

Description	Action	Estimated Lifespan	Advantages	Disadvantages
Hard Surface Treated	Hard surface makes fouling	surface makes fouling		Requires frequent cleaning
Composite Coating	attachment difficult	Op to 2 years	fewer coats	to prevent fouling build-up
Biocide-free Self-Polishing Paints	Continuous hydrolysis reaction continually renews paint surface, releasing organisms	Unknown	Potentially no active ingredients	Not widespread in market

^C See <u>117</u> <u>148</u> <u>93</u> <u>86</u> <u>126</u> <u>154</u> <u>143</u> <u>147</u> ^D See <u>117</u> <u>142</u>

2011 Legislation

The Washington State Legislature passed Senate Bill 5436 (2011) that would have phased in a ban on the use of copper-based antifouling paints for small recreational vessels.¹⁵⁴ The bill restricted the use of copper-based paints (exceeding 0.5 percent copper) starting in 2018. It also directed Ecology to study antifouling paints and report back to the Legislature about its findings in late 2017.

The first stage of the copper restriction was scheduled to take effect January 1, 2018.

Ecology's report to the Legislature was completed in 2017. The report demonstrated that the alternative antifouling paints might actually pose a greater environmental threat than copperbased paints. It recommended the Legislature delay the ban on copper paints so Ecology could conduct additional research. A copy of the 2017 report is available at <u>https://fortress.wa.gov/ecy/publications/SummaryPages/1704039.html</u>.

2018 Legislation

In response to Ecology's 2017 report and recommendations, the Legislature passed Substitute House Bill 2634 (2018). The 2018 legislation allowed the use of copper-based paints on wood boats, delayed the restriction on copper-based paints for non-wood boats, directed Ecology to further study antifouling paints and their ingredients, and directed Ecology to report back to the Legislature about their review and recommendations for regulatory changes, if any.¹⁵⁵

Ecology has conducted an additional study and a review of recent applicable scientific publications. This report summarizes the highlights from that review, including scientific review of antifouling paint ingredients, non-paint antifouling strategies, and Ecology's scientific modeling of antifouling ingredients in Washington waters. It also references findings from earlier relevant studies, including Ecology's 2018 study of copper, zinc, and lead concentrations in five Washington State marinas.⁵⁸ This report also details Ecology's recommendations for future regulatory action.

Ecology's Scientific Information Review

Ecology's review of updated scientific information on biocides

Section 4(1) of SHB 2634 (2018) directed:

(1) By September 30, 2019, the department of ecology is directed to report to the legislature regarding the environmental impacts of antifouling paints and their ingredients, whether antifouling paints or their ingredients are causing environmental harm, safer alternatives to antifouling paints or ingredients found in antifouling paints, and recommendations as to whether changes to the existing regulation of antifouling paints are needed. The report may also include information about the advantages and disadvantages of using leaching rates as a regulatory standard. The department of ecology may include recommendations regarding the adoption of a leach rate standard but is not required to do so. The department of ecology shall specifically consider any new science with regard to the bioavailability and toxicity of antifouling ingredients, specifically including but not limited to copper and other biocides.

In order to prepare this report, the Legislature directed Ecology to review available scientific information and studies. Section 4(2) of the bill directed:

(2) In developing the report and recommendations in subsection (1) of this section, the department of ecology is directed to review risk assessments, scientific studies, and other relevant analyses regarding antifouling paints and coatings and their ingredients, including their environmental impacts and availability in Washington. The department of ecology shall consult with other affected state agencies and relevant stakeholders as appropriate.

As this is a follow-up report, whenever possible Ecology focused its review efforts on risk assessments, scientific studies, and other scientific analyses published since the completion of Ecology's 2017 report.⁹² Appendix B contains a list of the scientific studies, chemical assessments, government publications, and other documents Ecology reviewed or consulted in preparation of this report and development of Ecology's recommendations. That list also includes a statement about the peer review status of each source consulted (when applicable).

Ecology did not attempt to summarize the findings of every study or chemical assessment we reviewed. Instead, Ecology's comments are limited to those we determined were the most important or could possibly inform future regulatory action. Our efforts focused on copper and other biocidal antifouling ingredients as well as alternative antifouling methods.

Consultations with other affected state agencies and relevant stakeholders

As directed, Ecology consulted with a variety of stakeholders and requested their input during the preparation of this report. Ecology consulted with and received input from:

- American Chemet Corporation
- American Coatings Association
- National Marine Manufacturers Association
- Northwest Marine Trade Association
- Puget Soundkeeper Alliance
- Toxic-Free Future
- Washington Environmental Council
- Washington State Department of Agriculture
- Washington State Department of Fish and Wildlife
- Washington State Department of Natural Resources

Environmental Impacts and Harms

The 2018 legislation directed Ecology to provide an update about the environmental impacts of antifouling paints and their ingredients, and whether antifouling paints or their ingredients are causing environmental harm. In addition, the Legislature directed that Ecology "shall specifically consider any new science with regard to the bioavailability and toxicity of antifouling ingredients, specifically including but not limited to copper and other biocides."

Based on the scientific information reviewed to date, Ecology provides the following update about antifouling paints and their ingredients:

Copper

Copper is a naturally-occurring element that can be used as a broad-spectrum biocide, effective against a wide range of fouling species including bacteria, mollusks, and multiple types of fungus.²³ It is currently listed as a "Chemical of Concern" for Puget Sound.¹⁵⁰ Antifouling paints containing copper are regulated as pesticides by the Washington State Department of Agriculture and United States Environmental Protection Agency (USEPA) under authority from the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

Recent studies confirm Ecology's previous finding that the overwhelming majority of recreational vessel owners still use copper-based antifouling paints. These studies report that, "About 80% of boat owners use paint containing copper and/or zinc as an antifouling coating. This is a relevant source of emissions of toxic substances into the aquatic environment."¹¹⁷ 98

Copper-based paints sometimes use only copper as the active ingredient, and sometimes include other ingredients to improve the paint's effectiveness. Copper's effectiveness varies according to the type of fouling pest being controlled.²⁷

Bioavailability and toxicity

Our updated findings are consistent with our previous report: copper is toxic to some non-target species. As with other substances, copper's toxicity is a direct function of its bioavailability. A number of new studies addressed copper's toxicity to a variety of species and under a variety of environmental conditions. Two new studies addressed copper's potential to cause endocrine disruption. All of these topics should continue to receive scientific attention, but none of the underlying studies provided updated information about copper's effects in Washington's waters.

Are copper-based antifouling paints causing environmental harm?

Copper has the capacity to cause environmental harm and negatively affect some non-target species. A 2018 Washington State study of marinas reported copper-based antifouling paints significantly contribute to the amount of copper in Washington's marina waters.⁵⁸ However, this study also found that, of the five Washington marinas studied, only one marina had instances that potentially exceeded the state water quality criterion for copper (four water samples out of 14 total).⁵⁸

While it appears that copper could cause environmental harm in Washington State, Ecology believes additional, focused research is needed to answer whether that harm is attributable to copper-based antifouling paints. Ecology did not find sufficient new information to support this supposition, nor did we find sufficient new information to change our previous conclusion that copper-based paints may be safer than at least some of the alternative products.

Copper leach rates

A "leach rate" is the amount of biocide that leaches out of an antifouling paint into the surrounding water. A "leaching standard" refers to a regulatory standard based on a leach rate.

Ecology notes that the USEPA has begun the process to adopt a regulatory leaching standard for copper-based antifouling paints. The proposed limit for copper-based paints will be a maximum leach rate of 9.5 μ g/cm²/day, as calculated using an appropriate International Standards Organization (ISO) method. This is the same standard that California has already adopted.²³

Ecology was not able to find reliable public information about the leach rate of copper-based antifouling paints currently on the market in Washington State. This is a significant data gap and is one of the factors limiting our ability to determine whether copper is causing harm in Washington's environment.

Ecology obtained a list of paints currently sold in California. While this list identifies paints that meet the 9.5 μ g/cm²/day leaching standard, the list did not provide information about actual leach rates for these copper-based paints.

Paints currently sold in Washington that are not on the California list are presumed to leach more than the forthcoming USEPA leaching standard of 9.5 μ g/cm²/day, but Ecology cannot say for certain whether this is the case. A list of antifouling paints sold in Washington is provided in Appendix A to this document; copper-based paints with the notation "appears to meet 9.5 μ g/cm²/day leach rate" are those that also appear on California's list of approved paints.

Cybutryne/Irgarol

Cybutryne, commonly referred to as Irgarol 1051, is regulated as a pesticide by the Washington State Department of Agriculture and USEPA under authority from FIFRA. It is an algaecide that inhibits growth of target organisms by inhibiting carbohydrate production and reducing uptake of carbon dioxide.¹³

Bioavailability and toxicity

Ecology did not find any recent studies that provided new information about Cybutryne/Irgarol's bioavailability.

Cybutryne/Irgarol has been shown to be toxic (and therefore bioavailable) and persistent in the environment.¹³ It is also "the most widely detected booster biocide worldwide."⁷¹ meaning that it is frequently added to antifouling paints that contain copper or another chemical as a primary active ingredient in order to boost their performance. One 2019 study Ecology reviewed reported

toxic effects on some non-target species including starfish and sea squirts.⁸² Another 2019 study of the intertidal mud crab (*Macrophthalmus japonicas*) found that "crustacean embryogenesis and endocrine processes are impaired by the environmental pollutants DEHP, BPA, and Irgarol."⁹⁰ The European Chemicals Agency concluded, "There is insufficient evidence to identify Cybutryne as an endocrine disrupter, but the information available is considered sufficient to identify Cybutryne as a 'potential' endocrine disrupter."⁴

Are antifouling paints containing Cybutryne/Irgarol causing environmental harm?

In June 2015, the European Chemical Agency Biocidal Products Committee (ECHA BPC) adopted BPC Opinion ECHA/BPC/065/2015, not approving Cybutryne/Irgarol for antifouling purposes.¹³ This opinion was officially adopted by the Council of the European Union on June 29, 2018, resulting in a prohibition on the use or sale of Cybutryne/Irgarol paints due to adverse effects in marine environments and to human health.¹³⁰

In February 2019, the International Maritime Organization (IMO) determined Cybutryne/Irgarol is unacceptably dangerous to the environment and has agreed to ban the substance worldwide. Cybutryne/Irgarol will be added to the IMO's Antifouling Systems Convention, joining TBT as a prohibited antifouling substance. However, an effective date and specifics regarding sampling, certification, and inspection are yet to be agreed upon.¹³⁷ 138

While Ecology does not have sufficient information to conclude Cybutryne/Irgarol is actively causing environmental harm in Washington State at present, based on the information we reviewed, Ecology agrees with the IMO and European Chemical Agency that it has the significant potential to cause environmental harm.

DCOIT/Sea-Nine

DCOIT^{*E*}, commonly referred to as Sea-Nine, is a "broad spectrum biocide" that is intended to be used in antifouling paints along with another biocide (as a "co-biocide"). It is regulated as a pesticide by the Washington State Department of Agriculture and USEPA under authority from FIFRA. It is effective against algae, fungi, barnacles, and other fouling organisms.¹

Bioavailability and toxicity

Ecology did not find any recent studies that provided new information about DCOIT/Sea-Nine's bioavailability. It is considered acutely toxic and affects a variety of aquatic organisms.^{1 44} "The environmental occurrence, fate, and effects of Sea-Nine are consistently well-characterized, but there is still a lack of studies on its adverse effects on non-target animals."⁴⁹ New research detailed possible toxic effects (deformed fins and pericardial edema, for example) on non-target

^{*E*} Abbreviation for 4,5-Dichloro-2-octyl-2H-isothiazol-3-one.

organisms such as sea urchins, tilapia, killifish, flounder, polychaetes, marine mysids, and others. $\frac{44}{49}$ $\frac{49}{82}$ $\frac{111}{111}$

To date, DCOIT/Sea-Nine has been thought to produce overall low toxic effects in the environment despite its toxicity because it rapidly breaks down in both water and sediment, making it non-persistent. However, recent studies have reported environmental concentrations of DCOIT/Sea-Nine off the coasts of Spain, Korea, and Denmark.⁸²

Are antifouling paints containing DCOIT/Sea-Nine causing environmental harm?

Ecology does not have sufficient information to conclude DCOIT/Sea-Nine is actively causing environmental harm in Washington waters. However, based on the information we reviewed, Ecology believes that it has the potential to cause significant environmental harm and needs additional study, especially related to its effects on fish and its degradation process.

Tralopyril/Econea

Tralopyril, F commonly referred to as Econea, is an antifouling substance intended to combat barnacles, slimes, weeds, and other fouling species.¹⁸ It is regulated as a pesticide by the Washington State Department of Agriculture and USEPA under authority from FIFRA.

Bioavailability and toxicity

Ecology did not find any recent studies that provided new information about Tralopyril/Econea's bioavailability. Before Tralopyril/Econea breaks down, it is highly toxic. In the European Chemical Agency evaluation of Tralopyril/Econea, it was determined as being appropriate for professional application only, as it is very toxic to humans, including by inhalation.⁹ A 2019 study found it displayed "high toxicity" to sea urchin embryos.⁷⁵

Like DCOIT/Sea-Nine, Tralopyril/Econea's environmental effects are expected to be limited because it breaks down quickly.⁴⁵ One recent study reported that it breaks down more slowly in colder water.⁷⁵ However, at least one study found that Tralopyril/Econea "rapidly bioconcentrates in whole mussel tissue....We believe that [tralopyril] may be a risk to mussel populations residing in locations where a continuous exposure to this biocide is likely to occur (*e.g.* seawater marinas)."⁸⁸

Ecology has not found any studies indicating Tralopyril/Econea is an endocrine disruptor. It is on the European Commission for the Environment's 2016 "Chemical Substances Screened in the Context of the Impact Assessment on Criteria to Identify Endocrine Disruptors."²⁰ However, we note this is in contrast to the more recent 2019 assessment from ECHA that there is not currently evidence of any endocrine-disrupting properties associated with Tralopyril/Econea.⁹

^{*F*} Chemical name 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile.

Are antifouling paints containing Tralopyril/Econea causing environmental harm?

Ecology does not have sufficient information to conclude Tralopyril/Econea is actively causing environmental harm. However, based on the studies we reviewed, Ecology believes its toxicity and potential for bioaccumulation mean that it also has the potential to cause environmental harm. Considering the importance of Puget Sound's oyster and mussel production, the possibility of bioaccumulation in these species could be of significant concern in Washington State.

Zinc pyrithione

Zinc pyrithione is an antifouling ingredient that is effective against a variety of different bacteria, yeasts, and fungi.¹⁹ It is regulated as a pesticide by the Washington State Department of Agriculture and USEPA under authority from FIFRA.

Bioavailability and toxicity

Zinc pyrithione is "highly toxic to aquatic plants and animals."²⁹ It is not considered to be bioaccumulative and there is no indication it is an endocrine disruptor.

The European Chemicals Agency has identified zinc pyrithione as a reproductive toxicant Category 1B.¹³³ This means that the data is sufficient to presume it is toxic to reproduction in humans.¹⁹ This classification means that products containing zinc pyrithione will not be approved for use in antifouling paints by the European Chemicals Agency.¹³⁴

Are antifouling paints containing zinc pyrithione causing environmental harm?

Ecology does not have sufficient information to conclude zinc pyrithione is actively causing environmental harm. However, based on the information we reviewed, Ecology believes its toxicity (especially its potential reproductive toxicity) means that it also has the potential to cause significant environmental harm.

Additional Scientific Studies: Ecology's MAMPEC Modeling of Biocidal Antifouling Ingredients

In addition to reviewing existing scientific studies, the 2018 legislation directed Ecology to conduct additional research:

(3) In developing the report and recommendations in subsection (1) of this section, the department of ecology is directed to conduct performance testing, modeling, alternatives assessments, and other related scientific studies as needed or appropriate. This subsection specifically includes, but is not limited to, Washington specific studies to inform regulatory standards for antifouling paints and coatings and their ingredients, such as a leaching standard.

Due to the short deadline for providing this report, Ecology did not have sufficient time to conduct performance testing or prepare an alternatives assessment. However, Ecology's Environmental Assessment Program did conduct a modeling study using the Marine Antifoulant Model to Predict Environmental Concentrations, otherwise known as MAMPEC. This model allows researchers to estimate how antifouling ingredients might accumulate in the environment. It also allows researchers to estimate how much of an antifouling ingredient can be present in the environment before it starts to cause harm.

The modeling study looked at five different scenarios accounting for how often owners washed their boats in the water and whether they used best management practices when they did so. For each specific scenario, the MAMPEC model calculates the highest average leach rate that would be permissible while still meeting the chronic water quality criterion or "Predicted No Effect Concentration" (as applicable) in the marina's waters.

The toxicity of the biocides in antifouling paints affects the allowable leach rate. The MAMPEC calculations are the standard against which actual paint leach rates should be compared. Paints that have a leach rate higher than the MAMPEC results might result in marina waters exceeding the water quality criterion or "Predicted No Effect Concentration" for the biocide in question. At present, Ecology has very limited information about the leach rates of specific paints available for sale in Washington State.

MAMPEC results

A copy of the complete Technical Memo summarizing the modeling efforts and results is attached as Appendix C to this report. A summary of the results for each of the five substances modeled is as follows:

Copper

Ecology's modeling results used a target water concentration for copper of 3.1 parts per billion. This is the current marine chronic aquatic life water quality criterion for copper.^{*G*}

The MAMPEC modeling estimates that copper-based paint leach rates need to average between $6.3-15.4 \ \mu g/cm^2/day$ (using the mean figures), depending on how much in-water cleaning is assumed.^{*H*} Ecology notes the low (most conservative) end of this range matches reported calculations from similar USEPA modeling efforts. We also note these ranges are based on protecting more vulnerable, low-flushing marinas. If a high-flushing marina is incorporated into the calculations, the range of acceptable leach rates becomes $6.5-100 \ \mu g/cm^2/day$.

Cybutryne/Irgarol

Ecology's modeling results used a target water concentration for Cybutryne/Irgarol of 0.0058 parts per billion. This is the current "Predicted No Effect Concentration" for Cybutryne/Irgarol.^I

To achieve an acceptable level of Cybutryne/Irgarol in Washington's marine waters, the MAMPEC modeling estimates that Cybutryne/Irgarol-containing paint leach rates need to average between 0.024–0.86 μ g/cm²/day depending on how much in-water cleaning is assumed.

DCOIT/Sea-Nine

Ecology's modeling results used a target water concentration for DCOIT/Sea-Nine of 0.0068 parts per billion. This is the current "Predicted No Effect Concentration" for DCOIT/Sea-Nine.

To achieve an acceptable level of DCOIT/Sea-Nine in Washington's marine waters, the MAMPEC modeling estimates that DCOIT/Sea-Nine-containing paint leach rates need to average between $0.39-2.6 \,\mu g/cm^2/day$ depending on how much in-water cleaning is assumed.

Tralopyril/Econea

Ecology's modeling results used a target water concentration for Tralopyril/Econea of 0.0017 parts per billion. This is the current "Predicted No Effect Concentration" for Tralopyril/Econea.

To achieve an acceptable level of Tralopyril/Econea in Washington's marine waters, the MAMPEC modeling estimates that Tralopyril/Econea-containing paint leach rates need to average between 0.09–0.27 μ g/cm²/day depending on how much in-water cleaning is assumed.

Zinc pyrithione

Ecology's modeling results used a target water concentration for zinc pyrithione of 0.046 parts per billion. This is the current "Predicted No Effect Concentration" for zinc pyrithione.

^{*G*} As established at Chapter 173-201A WAC.

^{*H*} More detailed calculations, including ranges based on median figures, are available in Appendix C.

¹See Appendix C for more details about PNECs.

To achieve an acceptable level of zinc pyrithione in Washington's marine waters, the MAMPEC modeling estimates that zinc pyrithione-containing paint leach rates need to average between $0.48-8.1 \mu g/cm^2/day$ depending on how much in-water cleaning is assumed.

Biocide	Most conservative estimated maximum allowable leach rate	Least conservative estimated maximum allowable leach rate
Copper (low flushing marinas only)	6.3 μg/cm²/day	15.8 μg/cm²/day
Cybutryne/Irgarol	0.024 µg/cm²/day	0.86 µg/cm²/day
DCOIT/Sea-Nine	0.39 µg/cm²/day	2.6 µg/cm²/day
Tralopyril/Econea	0.09 µg/cm²/day	0.27 μg/cm²/day
Zinc pyrithione	0.48 µg/cm²/day	8.1 µg/cm²/day

Table 3 Estimated allowable leach rate comparison

Estimated allowable leach rate range comparison in μg/cm²/day



Figure 1 Chart comparing estimated allowable leach rate range in µg/cm²/day

Review of Antifouling Alternatives

The 2018 legislation directed Ecology to report about "safer alternatives to antifouling paints or ingredients found in antifouling paints..." Although released before Ecology's 2017 report, we believe the 2017 Washington State Antifouling Boat Paint Alternatives Assessment Report continues to be the most in-depth information available about alternatives.¹⁵⁰ It specifically addresses issues such as cost, performance, and comparative exposure.

The following summarizes our research on this topic and focuses on non-biocidal antifouling alternatives. However, it is important to note that even non-biocidal alternatives could still pose an environmental threat.

Non-biocidal antifouling paints and their ingredients

The Washington State Antifouling Boat Paint Alternatives Assessment Report classified nonbiocidal antifouling paints into five categories: "ceramic/quartz, silicone, wax-like polymers, photoactive, and epoxy based paints."¹⁵⁰ Other scientific studies Ecology reviewed instead focused on how the paints worked: those that cause fouling organisms to fall off and those that prevent them from attaching in the first place.^{93 86}

Recent scientific information about non-biocide coatings is focused primarily on silicone and fluorinated polymer coatings. These coatings are frequently described as an "ecofriendly alternative" to biocidal paints, but Ecology has not made a determination supporting that description.¹⁰⁴ Ecology did not review any recent reports or journal articles that focused on ceramic/quartz, photoactive, or epoxy-based non-biocidal paints.

Multiple studies reported that silicone-based coatings are the most promising alternative.²⁶ ¹⁰⁴ ⁸⁶ These coatings work by "releasing the attached organisms back to the sea without killing them."¹⁰⁴ One 2018 study alleged "Siloxane fouling release coatings are currently the only viable commercial non-toxic alternative...."²⁶

A 2017 study explained that, "Organo-silicone polymers, particularly polydimethylsiloxane (PDMS), are more efficient than fluoropolymers and thus are considered the most promising [foul-release] coating systems...."¹⁰⁴

However, multiple studies also reported silicone-based coatings have significant limitations: they only partially inhibit fouling, are easily damaged, and are difficult to apply which makes them unsuitable to "do it yourself" application.^{26 86} These coatings may also leach silicone-based fluids into the water.⁸⁶

The current alternative to silicone-based polymers is fluorine-based polymers. One substance recently reviewed in the literature is PTFE (more commonly known by the brand name Teflon). This substance can prevent fouling organisms from attaching to vessels and has "excellent resistivity towards pH, salinity, UV, temperature and some organic solvents. However, its

[inability to mix with] common organic solvents creates difficulties during processing and hence, limits its application on coatings."⁹³

One other option that received mention was polyethylene glycol. While this substance does not bioaccumulate (at least in humans), it is not stable long-term and gradually loses resistance to proteins associated with fouling.⁶⁷ Polyethylene glycol coatings are promoted as non-toxic with good performance but they oxidize quickly, causing them to decompose.¹⁰⁴ Nanoparticle versions of polyethylene glycol coatings may be able to overcome the oxidization problem.¹⁰⁴

Because each of these fouling release coatings rely on moving water to dislodge fouling organisms, boats that sit in the water unattended for extended periods may still experience fouling.

At present, there is limited information available about the environmental effects of these nonbiocidal antifouling coatings. Since silicone is a persistent chemical, this could create a new environmental problem, as mentioned in Ecology's 2017 report. However, none of the newer studies Ecology reviewed appeared to consider potential environmental problems from siloxane coatings nor did they provide updated information about the potential impacts on sediments or the organisms that live there.

Although it is well established that fluorinated compounds are persistent in the environment and can be bioaccumulative,¹⁵⁰ none of the four studies Ecology reviewed discussed these possible environmental effects. It appears this is an area that still needs additional study. Washington State is currently engaged in cleaning up poly- and perfluorinated alkyl substances (PFAS) in drinking water and studying alternatives to PFAS compounds in food packaging. Ecology does not believe it would be appropriate to assume antifouling coatings made from similar chemicals are safe for the environment without further research and information.^J

Non-coating antifouling alternatives

Trailers and lifts

Fouling occurs on boats left in the water. An option that many boat owners use is the most simple—removing their boat from the water. In some areas, using a boat lift is a popular choice. Many owners of smaller vessels also choose to store their boat on a trailer instead of a permanent mooring. This technique avoids the need for antifouling products of any kind.

^J For more information about Ecology's efforts on PFAS, visit <u>https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Addressing-priority-toxic-chemicals/PFAS</u>.



Figure 2 Picture of hydraulic boat lift^{κ}



Figure 3 Picture of boat on trailer^L

For boats left in the water, there are limited non-paint antifouling options that address multiple types of fouling. The four viable options currently are washing systems, liners, dry dock-like fouling avoidance products, and sonic-based systems.

Washing systems

One non-biocidal approach is to focus on cleaning. Boats can be painted with a hard, nonbiocidal paint than can stand up to multiple scrubbings. They can then be cleaned by divers, mechanical systems, or even a long-handled brush (if done often enough).

One newer development is the advent of a washing system that works like a car wash:

^{*K*} Photo from <u>https://www.shoremaster.com/lifts/lift-models/hydraulic-lifts/</u>. Used with permission.

^{*L*} Photo credit Department of Ecology Environmental Assessment Program.

The Swedish firm Drive-in Boatwash sells stationary and mobile washers. The stationary version cleans motorboats and sailing boats up to 16 m long and requires a dock space of about 7 to 8 m. The mobile version is mounted on a trailer and the boat is slid back and forth over rotating brushes.... Underwater cleaning can also be performed with cleaning robots.... These can be operated by remote control (no divers necessary). The brushes are adjustable, and so can be used for hard coatings and self-polishing paints. When cleaning painted boats underwater, there is a risk of removing paint, and debris needs to be collected carefully. It is possible to fit a vacuum cleaner bag to the robot, so that all debris, including pieces of old paint, is collected and does not enter the environment.¹¹⁷

Systems such as this are intended to be installed by a marina and made available to boaters, who pay a small fee to use the system.^M



Figure 4 Picture of drive-in boatwash station at Bosö Boat Club, Stockholm^{*N*}

There are also other mechanical systems that use robots to wash the hull of fouled vessels.¹³² In Washington, boat washing efforts must comply with Ecology's "Guidance on Hull Cleaning in Washington State Waters."¹⁵² O

Liners and in-water "dry docking"-like fouling avoidance

Liners protect boats from fouling organisms by preventing attachment. These covers can either be form-fitted to the boat (creating a temporary alternate skin that fouling organisms can attach

^M See, for example, https://driveinboatwash.com/discover-machines/.

^N Photo from <u>https://driveinboatwash.com/case-studies/boat-owners-care-about-environment/</u>. Used with permission.

^o Ecology also advises boat owners about restrictions on in-water cleaning of boats painted in ablative or other soft biocidal or other antifouling paints that could release toxic coatings into the water in the flyer located at <u>https://ecology.wa.gov/DOE/files/9f/9f9f5b86-865a-431c-9254-1216cf5bba49.pdf</u>.

to instead of the hull), or they can act as a "drive-in dry dock" (in essence, a floating garage as pictured below) that may involve either removing or chlorinating the water inside the liner.¹³³ 117</sup> Neither of these options requires the use of antifouling paints and both may be appropriate for recreational vessel of various sizes.



Figure 5 Picture of liner system^P

In addition to removing a boat from the water entirely using a lift or trailer, boat owners can also use a "floating dry dock" system that inflates to lift the boat out of the water.¹²⁵ There is also a floating system that uses buoyant cubes or platforms to lift the boat out of the water.¹³¹ Neither of these options would require antifouling paints. Both options would be inappropriate for boats painted with soft paints or siloxane coatings (due to the fragility of those coatings). These options would also be inappropriate for boats with hard biocidal paints, as these coatings oxidize and lose effectiveness when exposed to air.¹²⁶

^P Photo from <u>http://armoredhull.com/how-it-works/faqs/</u>. Used with permission.



Figure 6 Picture of inflatable system^Q



Figure 7 Picture of floating cube system^{*R*}

Sonic systems

Multiple recent studies discussed the use of sound for antifouling purposes—both audible frequencies and very high ones. "The amplified signals are fed into the projectors, directly emitting acoustic waves into the water that cause vibrations in the vessel hull. The methods can be classified into two types according to the frequency range of the signal: audible (20 Hz–20 kHz) and ultrasonic (>20 kHz)."⁸⁹ Some systems use sounds that are clearly within the audible range of non-target species, including marine mammals like orcas. There is limited information about whether these systems can or do interfere with orca and other marine mammal

^Q Picture taken from <u>https://fabdock.com/</u>. Used with permission.

^{*R*} Picture taken from <u>http://www.cubedocks.com/jetslide.html</u>. Used with permission.

communication and echolocation. One study suggested that when considering whales and other cetacean species, boat owners could use the system "only while in port" to help mitigate impact. It also expressed concerns about the effects on non-target species:

The impact of introducing acoustic energy into the marine environment is a concern as it may potentially produce a negative effect on marine life. Noise may cause stress to animals and interfere with sound-based orientation and communication systems. Furthermore, high intensity sound may create a risk of mortality by unbalancing the predator-prey interaction or by damaging auditory tissues.⁸⁹

Sonic approaches have met with limited success. They appear to be effective against organisms like snails but not against smaller organisms like slime.⁸⁹ There is inconsistent scientific information about their reliability.¹¹⁷ ¹⁵⁰ Ultrasound systems cannot be used on wood boats.¹¹⁷

Other alternatives

The literature Ecology reviewed also mentioned other non-toxic approaches, such as chemical reactions to create hypochlorous acid, ozone bubbles, hydrogen peroxide, or bromine through electrolysis of seawater.⁹³ However, electrolysis is a method used by commercial vessels. Ecology was unable to find these types of systems that are intended for small recreational vessels (the subject of the underlying legislation).

Another method mentioned was an air curtain method. "In this method, a copious flow of compressed air is continuously distributed around the wetted surface to prevent biofouling."⁸⁹ However, this is also a method intended for large ships, not small recreational vessels.

Environmental effects of non-coating alternatives

Storing boats out of the water, whether on a trailer or using a floating system, is not an option for all boats and all owners but it is the method that has no environmental impact from antifouling efforts.

One study used Life Cycle Analysis to determine the most environmentally friendly in-water option and determined that, "[u]sing a hull cover was the best-performing [lowest total toxic emissions] method analyzed here and emissions originate from production of the hull cover."³²

In-water boat washing can be an environmentally-friendly option for boats with non-biocidal paints or hard, resistant biocidal paints. Washing boats that are painted with ablative or other soft biocidal or other antifouling paints can release toxic ingredients into the water.¹⁵² For these types of paints (which include the most common options), this is not an environmentally-friendly choice.

The effects of sonic antifouling systems are unclear. The Antifouling Paint Alternatives Assessment concluded:

No clear studies rule out the impact of these devices on aquatic life, and none consider the combined effect of adoption by numerous vessels. However, it is likely that the ultrasonic frequencies do not travel far from the hull, reducing the chance of impact. More research is necessary to fully understand potential impacts, or the lack there-of.¹⁵⁰

Given Washington State's current efforts to reduce noise in Puget Sound,¹⁴⁸ Ecology does not recommend sonic systems at this time.

Emerging technologies

There are a variety of new technologies being developed to replace antifouling paints. The ones mentioned in recent studies include:

- Biocides developed from natural sources, including papain (papaya enzyme), butenolide (produced by fungi), cardenolides (plant steroids), capsaicin (from peppers)^S, juglone (from the family including Black Walnut), mango extracts, and various extracts from plants in the Brazilian *Fabaceae* family.^{50 105 100 114 24} There are limitations on development of these alternatives, including problems with production, paint compatibility issues, and costs.⁵⁰
- 2. Micropattern surfaces imitating naturally fouling-resistant surfaces, such as sharkskin, whale skin, pearlwort leaves, and clover leaves.⁵³ ⁹⁴ Each of these approaches has demonstrated promise as a possible non-toxic antifouling option.
- 3. Natural greases and oils may have antifouling potential. One study reports that some greases are marketed as antifouling alternatives and that "udder cream" is a topic of discussion in internet forums.¹¹⁷ Tea tree oil is also being evaluated as a possible base of a biodegradable antifouling film.⁶⁶
- 4. Chitosan is a derivative of a chemical found in crustacean shells. Coatings made from a combination of chitosan and nanoparticles of zinc oxide have been tested successfully against biofilm-causing marine bacteria.²⁸ Another combination of chitosan and nanoparticles of titanium dioxide was effective in combating algae.⁸⁵
- 5. Ultraviolet light has been used to deter fouling on large vessels without much success due to the uneven nature of dispersing the light. A new technique investigated by the Australian Department of Defense embeds small LEDs into "thin, flexible, coating-like structures," diffusing ultraviolet light uniformly around the hull.¹⁴⁶ The UV-emitting layer is intended to make it impossible for fouling organisms to attach to the hull. "This pilot study showed that UV LED technology can effectively prevent the accumulation of biofouling under high fouling pressure conditions."¹⁴⁶

^S One capsaicin-based product is currently on the market and is available in Washington State. However, it is not a paint, it is a wax-based substance that is rubbed onto boat or propeller surfaces. It is effective against barnacles and mussels.

- 6. Electrospun nanofiber mats could be used as a self-cleaning hull surface. "Compared to other materials, the electrospun nanofiber mats exhibit unrivaled properties, including a high surface to volume ratio, which leads to a high permeability and porosity. The electrospun nanofiber mats that are either functionalized or incorporate alternative (*i.e.*, 'greener') antibacterial agents could serve as conformal surface coatings that eliminate the spread of detrimental microorganisms."⁶⁷
- One study reported success in containing traditional biocides (in this case, DCOIT/Sea-Nine) inside a nanoparticle-sized shell of silicone dioxide. Their test showed that the encapsulated biocide released more gradually, increasing effectiveness.²⁵
- 8. Development of highly non-stick surfaces continues on a number of fronts, including using nanoparticles and graphene-related materials.¹⁰⁴

Safer alternatives to biocidal antifouling paints

At present, Ecology believes the safer alternatives include the use of boat lifts, liners, trailers, and other "dry dock"-like fouling avoidance options because they do not have the direct chemical effect on water quality and wildlife that toxic options produce. Also preferable is painting boats with non-biocidal paints and using brushes or other washing systems to remove fouling organisms. This option also does not have the direct chemical effect on water quality and wildlife produced by toxic antifouling options.

Given the potential effects of sonic antifouling systems on marine mammals, Ecology cannot recommend them without further research.

Ecology is also unable to express an opinion about the safety of silicone-based and fluorinebased coatings without substantially more independent research about their persistence and environmental impacts. Based on the number of research articles on these and related substances, relevant research appears to be on-going.

Use of Leach Rates for Regulatory Purposes

SHB 2634 (2018) directed that Ecology's report, "may also include information about the advantages and disadvantages of using leaching rates as a regulatory standard. The department of ecology may include recommendations regarding the adoption of a leach rate standard but is not required to do so."

The main advantage to using leach rates as the basis for regulatory action is that it is the method most directly linked to environmental impacts. The effects of biocidal ingredients—both intentional and not—happen when the biocide leaches out of the paint and into the environment. Regulating paints based on how much biocide comes out into the water instead of how much was added during manufacturing makes for a closer alignment of regulation and environmental impact.

As noted above, USEPA is in the process of adopting a new leach rate standard for copper-based antifouling paints. Once that process is finished, paints that leach more than 9.5 μ g/cm²/day will not be allowed to be used on small recreational vessels. USEPA states, "Registrants with products above this leach rate standard will be required to either reformulate, voluntarily cancel [their FIFRA registration], or submit a label amendment to restrict the product's use from recreational boats under 65 feet in length."²³

There are two significant complexities to using leaching rates for regulatory purposes. First, leach rates are affected by a number of factors including salinity, acidity, temperature, and the presence of other substances. Second, leach rates also change, with higher leaching at the start and falling over time. A number of recent studies addressed these issues.⁶⁹ ⁷⁶

The ISO has developed a uniform standard for estimating the mean release rate of biocide from antifouling paints that accounts for these factors. ISO 10890:2010 generates estimates that "are suitable for use in general environmental risk assessments, and the application of appropriate correction factors will allow the most accurate and representative environmental risk assessment to be made in the relevant scenario and risk assessment case."^{*T*} The method works with all biocidal paints.

The MAMPEC model described above also takes these factors into account.

Ecology notes there are significant data gaps related to this issue. Ecology does not currently have information about the specific leach rates of existing paints currently sold in Washington State—how much copper and other biocides leach into the water and whether they contain other toxic chemicals that also leach out into the environment. Having this information would help better inform policy and regulatory decisions about these paints.

^{*T*} For more information, see <u>https://www.iso.org/standard/46281.html</u>.

Sources of Copper in Washington Marinas

During the 2018 legislative session, some stakeholders expressed concern that boatyards could be a significant source of copper entering marina waters. The 2018 legislation directed Ecology to examine additional information about sources of copper in Washington marinas:

(4) In developing the report and recommendations in subsection (1) of this section, the department of ecology is directed to consider any applicable data or other scientific information available about the sources of copper in Washington's marinas, including any available information related to upland sources of copper. This information may be included in the report, if appropriate.

Ecology reviewed one study that directly addressed this question: Ecology's "Copper, Zinc, and Lead Concentrations at Five Puget Sound Marinas" study released in 2018 found:

Dissolved [copper] concentrations in waters inside each of the five marinas studied are statistically higher than measurements taken outside each of the marinas. Suspended particulate matter and bottom sediments reliably showed higher [copper] concentrations inside the marinas compared to outside the marinas. Samples were not heavily influenced by stormwater inputs, and sampling consistently occurred during a neap tide, meaning that antifouling paints were likely the predominant source of [copper] inside the marinas. Antifouling paints are therefore the likely reason for significantly higher [copper] concentrations measured inside all five marinas over four separate sampling events.⁵⁸

It is important to note that of the five marinas examined in this study, only one had results (four out of 14 samples) exceeding the state water quality criteria for copper. $\frac{58}{58}$

Ecology was unable to locate any other studies that directly answered this question. To the contrary, the one study found, "The impacts of antifouling paint particles (APPs), which are generated during repair, cleaning, and painting procedures of vessel hulls…are still largely unknown."¹⁰⁸

USEPA's Interim Registration Review Decision on copper compounds, which includes copperbased antifouling paints, states:

In the Specific State Causes of Impairment database, there are currently 637 impaired waters in the U.S. due to copper... These include non-pesticidal sources of copper such as brake pads, municipal discharges/sewage, mining, industrial discharge and road construction, among others. While not all of these impairments are due to copper-based antifoulant paints, the source of impairment in a number of the waters, namely saltwater marinas, have been identified as copper-based antifoulant paints.²³

Although not as recent, a 2016 study of Swedish boatyards reported:

Statistical differences in soil concentration based on land use were consequently found: the areas used for boat storage and maintenance were significantly higher in [copper] and [zinc] than the areas used for car parking and transportation. The metal pollution in the boat storage areas is therefore shown to be directly linked to hull maintenance activities during which metal-containing antifouling paint particles are shed, end up on the ground, and consequently pollute the soil.⁷⁰

Although contamination of soil in boatyards is a concern, this study found the copper and zinc contamination inside the boatyard did not extend to adjoining parking areas. This might indicate that proper management of paint wastes at boatyards can prevent water contamination.

Without any other updated studies, Ecology also relied on older studies to address this issue. A 2004 study published in *Marine Pollution Bulletin* reports:

If managers wish to reduce dissolved copper emissions from hard vinyl or modified epoxy antifouling coatings on recreational vessels, it is most efficient to alter coating types rather than focus on hull cleaning BMPs. On a mass basis, 95% of the loading from recreational hull coatings occurs via passive leaching. Therefore, even if a BMP existed that reduced all of the dissolved copper emissions, the total cumulative reductions would amount to only 5%. Furthermore, most commercial hull cleaners attempt to clean coatings with minimal abrasiveness. They use these techniques to not only reduce copper emissions, but also to prolong the life of the coating. The use of BMPs may be more effective on softer coatings such as copper-based ablative paints.¹⁰³

While boatyards undoubtedly contribute some amount of copper to marina waters, Ecology was unable to find any studies that indicate this amount is significant when compared to contributions from passive leaching of copper from painted boats in the water.

Ecology's Recommendations

Based on the review summarized above, Ecology makes the following recommendations for possible future regulatory actions:

Regulation of biocidal antifouling paints

All recommendations regarding regulation of biocidal antifouling paints apply only to small recreational water vessels (those covered by the federal Clean Boating Act). Ecology does not make any recommendations for vessels that are subject to Coast Guard inspections and that are engaged in commercial use or carry paying passengers.

Recommendation 1: revise RCW 70.300.020 to delay current regulation of paint based on copper content

Except as noted below, the currently available science does not strongly support one regulatory approach over another. Therefore, Ecology recommends the Legislature delay the existing statutory restrictions based on copper content for a period of at least five years. This would allow for additional scientific research and review.

Recommendation 2: restrict the use of antifouling paints containing Cybutryne/Irgarol

Ecology recommends Washington State follow the lead of the IMO and prohibit the use of paints containing Cybutryne/Irgarol. While the IMO is in the process of adopting a worldwide ban, we note the mechanism for this prohibition is an international agreement. Ecology does not have the authority to enforce international agreements. Without a corresponding state law or regulation, Ecology would be unable to take enforcement against manufacturers or retailers selling paints containing Cybutryne/Irgarol.

Continued use of problematic chemicals despite international restrictions is not unprecedented. Ecology reviewed a 2019 study that indicates TBT is still being used as an antifouling ingredient and is detected in the environment, despite a 2008 IMO ban prohibiting its use.

Therefore, Ecology recommends Washington take steps to ensure Cybutryne/Irgarol paints are not sold in Washington for use on recreational water vessels, rather than simply relying on IMO action.^U

There are 16 antifouling paints containing Cybutryne/Irgarol currently registered in Washington State.

^U Ecology does not believe a ban on the use of TBT is needed due to its lack of general availability in the United States. However, a similar restriction on TBT would be consistent with the approach we recommend for Cybutryne/Irgarol.

Recommendation 3: give Ecology data collection authority

Ecology recommends any future legislation also include authority for Ecology to require paint manufacturers provide information to the department regarding ingredients, copper content, biocide leach rates, and other relevant data.

Currently, Ecology does not have the authority to require manufacturers of antifouling paints to disclose the ingredients in their products. Paint manufacturers are only required to disclose limited information, such as that found in a Safety Data Sheet or in registration documents with the Department of Agriculture or USEPA. In addition to the biocides (which are already disclosed), other paint ingredients such as phthalates, formaldehyde, and benzene would currently be disclosed only as "inactive ingredients," yet could still have negative effects on the environment.

Ecology believes it is necessary to obtain more information about antifouling paints, such as a full ingredient list, leach rate data, market share, and sales data. Without this type of information, Ecology will be unable to fill the current data gaps in evaluating the safety of antifouling paints. While obtaining this information from manufacturers will not fill all current data gaps, it will help Ecology answer some of the relevant questions. These answers will help support future regulatory or statutory changes and help inform the Legislature in their decision-making process.

This authority mirrors the authority already delegated to Ecology in Substitute Senate Bill 5135 (2018). The same protections for Confidential Business Information would presumably apply to data collected from antifouling paint manufacturers.

Recommendations for other biocides:

At this time, Ecology does not recommend taking any regulatory action on antifouling paints containing DCOIT/Sea-Nine, Tralopyril/Econea, or zinc pyrithione. Ecology recommends continued collection and monitoring of research on these biocides' possible environmental effects, especially Tralopyril/Econea's effects on mussels and other shellfish and zinc pyrithione's potential reproductive toxicity.

Additional considerations for regulatory actions

An additional important consideration for any potential regulatory action is to assess how biocide use might change as a result. More restrictive regulation of copper could result in paint manufacturers using more of other, more toxic biocides to meet market demands. This was an important finding of Ecology's 2017 report.

Given the work of the IMO on Cybutryne/Irgarol, as well as the new data on zinc pyrithione and expected future restrictions on its use in the EU, two of the four biocidal alternatives to copper could be removed from the market in the coming years. That would make copper one of three readily available biocides in paints (down from one of five). In that case, restrictions on copper would have an even bigger effect on the use of alternative biocides. This is why Ecology believes it is important to not ban copper-based paints at this time.
Other alternatives considered

In addition to the recommendation above to delay the effective date of the restrictions on copperbased paints, Ecology also considered the following options:

Alternative 1: Repeal—Revise RCW 70.300.020 to allow for future copper paint restrictions to be made in rule

Current law would ban the sale and application of antifouling paints containing more than 0.5 percent copper beginning January 1, 2021. Instead of delaying this effective date, the Legislature could consider repealing the content-based statutory restriction and directing Ecology to adopt any needed restrictions on antifouling paints through rulemaking under the authority established under SSB 5135 (2018).

Ecology did not adopt this as a primary recommendation because we are currently developing the review and rulemaking process to implement SSB 5135. We believe it is prudent to fully develop that process and complete one full rulemaking cycle instead of trying to add a second round of review and rulemaking, focused on antifouling paints, which would run simultaneously with the initial SSB 5135 review.

Alternative 2: Replace—Revise RCW 70.300.020 to adopt a leach rate restriction on copper-based paints and conduct a pilot study

Setting a copper leach rate standard that limits the amount of copper reaching marine waters could accomplish the same goals as the original ban while offering greater simplicity and consumer choice to the boating community and the maritime industry. The Legislature could consider replacing the existing statutory restrictions based on copper content with restrictions based instead on a copper leach rate. The Legislature could also direct Ecology to conduct a study of environmental conditions both before and after the leach rate takes effect, potentially providing information to help evaluate whether adopting a leach rate standard for antifouling paints makes a difference in environmental copper levels.

Ecology did not adopt this as a primary recommendation for two reasons. First, since USEPA is in the process of adopting the 9.5 μ g/cm²/day leach rate standard, it seemed duplicative to adopt the same standard at the state level without some other reason to do so. Second, Ecology believes conducting a study with a sufficiently large scope, while informative, would have a significant fiscal impact.

Alternative 3: Do nothing

If no legislation is passed, the existing statutory ban on the sale and use of copper-based antifouling paints will take effect January 1, 2021. Ecology does not recommend this alternative, as it could lead to increased use of antifouling paints with potentially more significant and detrimental environmental effects.

Additional comments

Invasive species

When discussing the need for a wide variety of antifouling options, some stakeholders have expressed concern about invasive species. This point is well taken. Transport of invasive species is more likely to occur in larger commercial vessels (including large recreational vessels that are outside the scope of the underlying legislation) that travel long distances between countries and continents. Smaller vessels can still spread invasive species around an area once they have been introduced, including transporting species from a coastline to inland waters.¹¹⁷

However, this concern does not warrant a change to any of Ecology's recommendations. Implementation of our recommendations will not eliminate biocidal antifouling options and there are no indications that any of the recommendations would lead to an increased threat from invasive species.

Conclusion

There is a significant amount of research being conducted worldwide on issues related to fouling. This research continues to reveal new information about antifouling substances and how they work in the environment. Taken as a whole, this research to date has shown that copper and other antifouling substances have complex interactions with each other and the environment. These interactions are not easy to predict and may have serious consequences on environmental health. Significant data gaps still exist, especially relating to the various chemicals found in antifouling paints, how those chemicals enter the environment, and their effects once in the environment.

Ecology continues to be concerned about the potential environmental effects of biocidal antifouling paints on non-target species. The concerns expressed in our 2017 report are still relevant. Based on the scientific information available to date, Ecology continues to be concerned that in some circumstances, alternatives to copper-based antifouling paints may be more harmful to the environment than the copper paints they replace.

This concern is especially applicable to Cybutryne/Irgarol. Ecology recommends restricting the use of this antifouling ingredient on recreational vessels in Washington State.

Regarding possible restrictions on copper-based paints, Ecology continues to believe that a content-based ban is not appropriate at this time. Ecology recommends that the Legislature delay the ban for an extended period and give Ecology the authority to require information from paint manufacturers regarding chemicals, leach rates, and other relevant data about their products. These actions will allow more scientific information to be developed to help fill existing data gaps before the Legislature makes a final determination on whether to allow, prohibit, or restrict the use of copper-based paints on Washington recreational vessels.

Appendices

Appendix A. Available Antifouling Paints

The following are the antifouling paints currently registered for sale in Washington State. In addition to the paint name, the current EPA Registration number and active ingredients are also provided.

The three paints highlighted in green are the non-copper paints identified in the Washington State Antifouling Boat Paint Alternatives Assessment with an overall recommendation of "likely to meet expectations."

Paints noted as "Appears to meet $<9.5 \ \mu g/cm^2/day$ Leach Rate" are those listed on the California Department of Pesticide Regulation's approved antifouling paints containing copper as of July 30, 2019:

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Antifouling Seaforce 100 AV - Various Colors	2568-102	31.94% Cuprous Oxide	
Antifouling Seaforce 200 AV - Various Colors	2568-93	44.59% Cuprous Oxide	Yes for Black, Blue, Dark Red
Antifouling Seaforce 300 AV - Various Colors	2568-99	39.59% Cuprous Oxide 2.19% DCOIT	
Aquagard Alumi-Koat Off White	9339-31- 70383	3.71% Copper Thiocyanate 0.80% Irgarol	
Aquagard Waterbase A-F Paints Alumi-Koat - White	9339-22- 70383	3.88% Cuprous Oxide	
Aquagard Waterbase Antifouling Paints Bottom Boat	9339-19- 70383	26.37% Cuprous Oxide	Yes
Armor Antifoulant Paint	9339-33- 70383	5.60% Econea 4.10% Zinc Pyrithione	Yes
C-Flex 1-2-3 AF - Various Colors	48302-7-8186	49.00% Cuprous Oxide	
CMP Sea Grandprix 220 HS - Light Brown S	48302-15	23.75% Cupric Oxide	
CMP Sea Grandprix 660 HS - Light Brown S	48302-14	19.00% Cupric Oxide 1.50% DCOIT	
Copper Pro SCX	74681-4	67.00% Cuprous Oxide 1.96% Irgarol	
Copper Shield	74681-2	45.00% Cuprous Oxide	
E Paint Sn-1 w/Sea-Nine 211	64684-5	2.91% DCOIT	Yes
E Paint Zo-Antifouling Paint	64684-4	4.80% Zinc Pyrithione	Yes
Ep2000 - A/F Paint/Boat Bottoms w/Zinc Omadine	ns 64684-6 4.70% Zinc Pyrithione		Yes

Table 4 Antifouling paints currently available in Washington State

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Flexdel Bottom Gard Anti-Fouling Paint-Black	9339-20- 70383	24.70% Cuprous Oxide	
Flexgard X Copper Paint	9339-20	24.70% Cuprous Oxide	
Flexgard XI Waterbase Preservative Copper Paint	9339-19	26.37% Cuprous Oxide	
Hempaguard X7 89900 Part A - Various Colors	10250-57	8.47% Copper Pyrithione	
Hempels A/F Globic 81920 - Black Blue Brown Red	10250-56	36.10% Cuprous Oxide 1.86% DCOIT	Yes
Hempels A/F Globic 81950 - Blk Blu Brn Red	10250-55	37.00% Cuprous Oxide 1.86% DCOIT	Yes
Hempels Antifoul Olympic Hi - Red Lt. Red Blk Brgt Blue	10250-54	48.79% Cuprous Oxide	Yes
Interlux A/F Pacifica Plus - Various Colors	2693-220	3.90% Econea 4.12% Zinc Pyrithione	Yes
Interlux A/F Trilux 33 Paint/Outdrives Outboards & Props	2693-226	6.54% Copper Thiocyanate 1.33% Zinc Pyrithione	Yes
Interlux Act - Various Colors	2693-142	41.97% Cuprous Oxide	
Interlux Act w/Slime Fighter - Various Colors	2693-227	29.73% Cuprous Oxide 0.98% Irgarol	Yes
Interlux Aqua-One - Various Colors	2693-193	28.45% Cuprous Oxide	
Interlux Bottomkote Pro - Various Colors	23566-6	25.00% Cuprous Oxide	
Interlux Fiberglass Bottomkote Aqua - Various Colors	2693-172	46.45% Cuprous Oxide	
Interlux Fiberglass Bottomkote NT - Various Colors	2693-228	25.00% Cuprous Oxide	Yes
Interlux Fiberglass Bottomkote Y999 Bronze	2693-179	28.32% DCOIT	Yes
Interlux Micron 66 - Various Colors	2693-187	40.41% Cuprous Oxide 3.80% Zinc Pyrithione	Yes
Interlux Micron 99 Biolux SPC - Various Colors	2693-232	43.51% Cuprous Oxide 4.56% Copper Pyrithione	
Interlux Micron CF - Various Colors	2693-230	3.90% Econea 4.12% Zinc Pyrithione	Yes
Interlux Micron CSC - Various Colors	2693-132	37.20% Cuprous Oxide	Yes
Interlux Micron Extra VOC - Various Colors	2693-190	38.62% Cuprous Oxide 2.00% Irgarol	Yes
Interlux Micron Optima/Base Part A - Various Colors	2693-193	28.45% Cuprous Oxide	Yes
Interlux Micron WA - Various Colors	2693-175	48.80% Cuprous Oxide	

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Interlux Ultra - Various Colors (- 192)	2693-192	66.65% Cuprous Oxide 1.59% Irgarol	
Interlux Ultra - Various Colors (- 212)	2693-212	55.00% Cuprous Oxide 0.98% Irgarol	Yes
Interlux Ultra-Kote - Various Colors	2693-119	57.00% Cuprous Oxide	
Interlux VC 17M Extra/Part A - Various Colors	2693-197	20.35% Copper, as Elemental	
Interlux VC 17M Extra - Red/Part A Base - Tank Mix w/2693-195	2693-198	20.35% Copper, as Elemental	
Interlux VC 17m - V105U Original V106U Blue	45168-5	2.38% Irgarol	Yes
Interlux VC 17M - V107U Red	45168-6	2.38% Irgarol	Yes
Intersmooth 460 A/F -Various Colors	2693-187	40.41% Cuprous Oxide 3.80% Zinc Pyrithione	Yes for Black, Blue, Dark Brown, Dark Red
Interspeed 340 NA Polishing A/F - BQA357 Red	2693-180	38.63% Cuprous Oxide 3.00% DCOIT	
Interspeed 5640 - Various Colors	2693-220	3.90% Econea 4.12% Zinc Pyrithione	Yes
Interspeed 6200NA A/F - Red Black	2693-176	21.31% Cuprous Oxide	Yes
Interspeed 640 Polish A/F - Various Colors	2693-142	41.97% Cuprous Oxide	Yes for Red, Blue, Black, Green, Ocean Gray
Interspeed 6400NA Controlled Depletion Polymer A/F - Red Black	2693-132	37.20% Cuprous Oxide	Yes
Juggernaut Copper Ablative Bottom Paint/Blue	74681-32- 89049	35.00% Cuprous Oxide	
Marlin Antifouling Velox Plus - Various Colors	86015-1	13.30% Zinc Pyrithione	
Micron CSC 5586 Dark Blue	2693-132	37.20% Cuprous Oxide	
Micron CSC HS - Various Colors	2693-225	33.40% Cuprous Oxide	Yes
Micron Extra - Various Colors	2693-190	38.62% Cuprous Oxide 2.00% Irgarol	Yes
Nautical Proguard Ablative - Various Colors	2693-142	41.97% Cuprous Oxide	Yes
Nautical Super Proguard - Various Colors	23566-20	55.00% Cuprous Oxide	
Pettit A/F Paint/Inflatable Boats - 1841 Black	60061-135	25.25% Cuprous Oxide	Yes
Pettit Black Widow Ultra-Slick Racing A/F Finish	60061-116	6 25.00% Copper Thiocyanate Y 2.50% Zinc Pyrithione Y	

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Pettit Horizons Ablative A/F Bottom Paint - Various Colors	60061-14	40.50% Cuprous Oxide	
Pettit Hydrocoat Ablative A/F Paint - Various Colors	60061-87	40.34% Cuprous Oxide	Yes
Pettit Hydrocoat Eco Copper-Free Multi-Season Ablative - Various Colors	60061-137	6.00% Econea 4.80% Zinc Pyrithione	Yes
Pettit Hydrocoat SR Dual Biocide Ablative A/F Paint - Various Colors	60061-141	40.00% Cuprous Oxide 2.00% Irgarol	Yes
Pettit Hydrocoat SR Dual-Biocide Ablative A/F	60061-136	25.25% Cuprous Oxide 2.00% Irgarol	
Pettit Marine Paint A/F 1933 Copper Bronze	60061-86	33.26% Cuprous Oxide	
Pettit M-P Copper-Guard A/F - Various Colors	60061-86	33.26% Cuprous Oxide	
Pettit M-P Prof Coat Trinidad 75 A/F - Various Colors	60061-49	65.00% Cuprous Oxide	
Pettit M-P Prof Coatings Trinidad 75 A/F - Various Colors	60061-66	55.60% Cuprous Oxide	
Pettit M-P Sea Mate Tri-Polymer A/F Bottom Paint—1825BLK 1625RED 1225BLU	60061-31	24.50% Cuprous Oxide	
Pettit M-P Unepoxy Plus A/F Bottom Paint - Various Colors	60061-63	45.70% Cuprous Oxide	
Pettit Neptune 5 Hard Hybrid Ablative A/F Paint - Various Colors	60061-142	25.25% Cuprous Oxide	Yes
Pettit Prof Coatings Trinidad 75 A/F - Various Colors	60061-57	60.90% Cuprous Oxide	
Pettit Trinidad Pro A/F Paint - Various Colors	60061-94	60.00% Cuprous Oxide 2.00% Irgarol	Yes
Pettit Trinidad SR A/F Bottom Paint - Various Colors	60061-94	60.00% Cuprous Oxide 2.00% Irgarol	Yes
Pettit Ultima Ablative A/F Paint - Various Colors	60061-71	37.50% Cuprous Oxide	
Pettit Ultima Eco Ablative A/F Paint - Various Colors	60061-134	6.00% Econea 4.80% Zinc Pyrithione	Yes
Pettit Ultima SR 40 A/F - Various Colors	60061-101	47.50% Cuprous Oxide	Yes
Pettit Ultima SR 60 - Various Colors	60061-94	60.00% Cuprous Oxide 2.00% Irgarol	
Pettit Ultima SR 60 A/F - Various Colors	60061-49	65.00% Cuprous Oxide	
Pettit Ultima SSA A/F Paint - Various Colors	60061-71	37.50% Cuprous Oxide	

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Pettit Unepoxy Standard Hard A/F Paint - Various Colors	60061-86	33.26% Cuprous Oxide	
Pettit Vivid A/F Paint - Various Colors	60061-116	25.00% Copper Thiocyanate 2.50% Zinc Pyrithione	
PPG Amercoat 214 Marine A/F Paint - Black	7313-18	47.99% Cupric Oxide	
PPG Amercoat ABC 3 Marine A/F Paint - Type 223 Black	7313-18	47.99% Cupric Oxide	Yes
PPG Amercoat ABC 3 Marine A/F Paint - Various Colors	7313-18	47.99% Cupric Oxide	Yes
PPG Amercoat ABC 4 Marine A/F Paint - Various Colors	7313-12	29.20% Cuprous Oxide	Yes
PPG Amercoat Amercoat 214 Marine A/F Paint - Various Colors	7313-13	38.46% Cupric Oxide	Yes
Pro-Line Vinyl Copper Antifouling 1088C Paint - Black	577-551	55.70% Cuprous Oxide	Yes
Pro-Line Vinyl Copper Antifouling 1088C Paint - Various Colors	577-550	66.90% Cuprous Oxide	
Regatta Baltoplate Racing Finish - Various Colors	2693-148	41.15% Cuprous Oxide	
Rust-Oleum Marine Coatings Boat Bottom Antifouling Paint/Various Colors	60061-63- 69587	45.70% Cuprous Oxide	Yes
Sea Hawk Biocop Extreme (Various Colors)	44891-20	31.08% Cuprous Oxide 6.17% Econea	
Sea Hawk Biocop TF	44891-15	38.06% Cuprous Oxide 4.14% Zinc Pyrithione	Yes
Sea Hawk Islands 44TF (Various Colors)	44891-20	31.08% Cuprous Oxide 6.17% Econea	
Sea Hawk Mission Bay	44891-16	3.80% Zinc Pyrithione	Yes
Sea Hawk Mission Bay CSF	44891-17	4.02% Zinc Pyrithione	Yes
Sea Hawk Prem Quality Cukote Biocide Plus Slime Resistant A/F Coating	44891-14	47.57% Cuprous Oxide 2.00% Irgarol	
Sea Hawk Single Season Protection Talon Paint	44891-12	33.60% Cuprous Oxide	Yes
Sea Hawk Yacht Finishes AF 33 A/F Paint	44891-12	33.60% Cuprous Oxide	Yes
Sea Hawk Yacht Finishes Cukote A/F Coating - Black	44891-7	47.57% Cuprous Oxide	Yes
Sea Hawk Yacht Finishes Eco Kote Copper-Free	44891-17	4.02% Zinc Pyrithione	Yes
Sea Hawk Yacht Finishes Monterey Water Borne A/F Coating	44891-9	54.67% Cuprous Oxide	Yes

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Sea Hawk Yacht Finishes Sharkskin A/F Paint	44891-11	45.20% Cuprous Oxide	Yes
Sea Hawk Yacht Finishes Smart Solution	44891-19	2.90% Econea	Yes
Sea Hawk Yacht Finishes Tropikote A/F Bottom Paint	44891-10	75.80% Cuprous Oxide	Yes
Seaguard Ablative A/F Coating/Blk Blu Red L. Red	10250-54-577	48.79% Cuprous Oxide	
Seaguard Copper Bottom A/F Paint No. 45 Blk/Blu/Red	577-569	44.70% Cuprous Oxide	
Seaquantum Ultra SP - Various Colors	2568-103	48.20% Cuprous Oxide 2.23% Copper Pyrithione	Yes
Seavoyage 100 Anti-Fouling Paint - Var Colors	577-572	21.05% Cuprous Oxide 4.12% Copper Pyrithione	
Seavoyage Copper Free A/F Paint - Red & Black	577-570	7.28% Econea 6.38% Zinc Pyrithione	Yes
Sigma Ecofleet 238 Marine A/F Paint - Blue	7313-12	29.20% Cuprous Oxide	Yes
Sigma Ecofleet 238 Marine A/F Paint - Various Colors	7313-12	29.20% Cuprous Oxide	Yes
Sigma Ecofleet 530 - Various Colors	7313-24	39.00% Cuprous Oxide 2.40% DCOIT	Yes
Sigma Nexeon 610 - Various Colors	7313-26	5.23% DCOIT 5.42% Econea	Yes
Spartan Multi-Season Ablative Bottom Paint/Black	74681-2- 89049	45.00% Cuprous Oxide	
Tefcite	89101-1	56.50% Cuprous Oxide 0.02% Silver 0.05% Zinc, Elemental	Yes
Trilux 33 - Various Colors	2693-203	16.95% Copper Thiocyanate 3.39% Zinc Pyrithione	
Ultra Gard	9339-34- 70383	37.50% Cuprous Oxide	
VC - Offshore Teflon AF - Various Colors	2693-148	41.15% Cuprous Oxide	
West Marine Bottomshield A/F Paint Easy Appl Tech	60061-135	25.25% Cuprous Oxide	Yes
West Marine CPP Ablative A/F Paint - Various Colors	60061-132	23.70% Cuprous Oxide	Yes
West Marine PCA Gold! Ablative A/F Paint - Various Colors	60061-101	47.50% Cuprous Oxide	Yes
Woolsey Ablative Plus A/F Paint - Various Colors	60061-132	23.70% Cuprous Oxide	
Woolsey Defense A/F Finish - Various Colors	60061-129	28.86% Cuprous Oxide	
Woolsey Defense HC A/F Finish - Various Colors	60061-58	52.60% Cuprous Oxide	

Paint Name	EPA Registration Number	Active Ingredients	Appears to meet <9.5µg/cm²/day Leach Rate
Woolsey Yacht Shield Ablative A/F Bottom Paint - Various Colors	60061-43	35.00% Cuprous Oxide	
Woolsey Yacht Shield H20 Ablative A/F Bottom Paint - Various Colors	60061-135	25.25% Cuprous Oxide	
Woolsey Yacht Shield SF Ablative A/F Bottom Paint - Various Colors	60061-117	47.50% Cuprous Oxide	Yes
Woolsey Yacht Shield SF Ablative A/F - Various Colors	60061-101	40.00% Cuprous Oxide 2.00% Irgarol	Yes

Appendix B. Risk assessments, scientific studies, and other relevant analyses consulted and reviewed in developing this Report to the Legislature

Ecology staff consulted and reviewed the following peer-reviewed studies, assessments, technical documents, and other reports and information in developing this report and its recommendations. Each citation below is noted whether it is:

- Externally peer reviewed (conducted by persons who are external to and independent of the author or author's institution, but who may have been suggested by the author).
- Independently peer reviewed (conducted by one or more independent third parties selected by the journal editors).
- Internally peer reviewed (conducted by staff internal to the author's institution).
- Subject to open review (a documented open public review process that is not limited to invited organizations or individuals).
- Legal and policy document (such as statutes, administrative rules, and court decisions).
- Data from primary research, monitoring activities, or other sources that has not been published or subjected to peer review.
- Records of the best professional judgment of Ecology employees or other individuals.
- Other sources of information that do not fit into one of the categories identified above, including those where peer review is not applicable.

Chemical risk assessments consulted

- European Chemicals Agency. Evaluation of Active Substance Assessment Report: 4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT), Product-Type 21 (Antifouling products). March 2014. <u>https://echa.europa.eu/documents/10162/d9e8d38f-d5b3-c469-4419-f2a687832c07</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- 2. European Chemicals Agency. Evaluation of Active Substance Assessment Report: Copper Flakes (Coated with Aliphatic Acid), Product-Type 21. January 2016. https://echa.europa.eu/documents/10162/2e655db6-b1c6-6c09-4fbd-c926b6cca54f, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- 3. European Chemicals Agency. Evaluation of Active Substances Assessment Report Public Version: Copper Pyrithione, Product Type 21. May 2015. <u>http://dissemination.echa.europa.eu/Biocides/ActiveSubstances/1275-21/1275-21_Assessment_Report.pdf</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)

- European Chemicals Agency. Evaluation of Active Substances Assessment Report: Cybutryne, Product Type PT21 (Antifouling). May 2014. <u>https://echa.europa.eu/documents/10162/aebe6f3b-0992-cd67-3588-13311e8c12ff</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- 5. European Chemicals Agency. Evaluation of Active Substance Assessment Report: Dicopper Oxide, Product-Type 21. January 2016. <u>http://dissemination.echa.europa.eu/Biocides/ActiveSubstances/1289-21/1289-21_Assessment_Report.pdf</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- 6. European Chemicals Agency. Evaluation of Active Substances Assessment Report: Medetomidine, Product-Type 21 (Antifouling Products). February 2015. <u>http://dissemination.echa.europa.eu/Biocides/ActiveSubstances/1327-21/1327-21_Assessment_Report.pdf</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- European Chemicals Agency. Evaluation of Active Substances Assessment Report: Tolylfluanid, Product-Type 21 (Antifouling Products). June 2014. <u>https://echa.europa.eu/documents/10162/6dc15617-6986-8a61-3a9a-ef782a0d66f1</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- European Chemicals Agency. Evaluation of Active Substances Assessment Report: Tralopyril, Product-Type 21 (Antifouling Products). April 14, 2014. <u>http://dissemination.echa.europa.eu/Biocides/ActiveSubstances/1403-21/1403-21_Assessment_Report.pdf</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- 9. European Chemicals Agency. Evaluation of Active Substances Assessment Report: Tralopyril, Product-Type 21 (Antifouling Products). January 2019. <u>https://echa.europa.eu/documents/10162/edf62568-dafb-73a2-51b7-b3118505dab3</u>, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- European Chemicals Agency. Evaluation of Active Substances Assessment Report: Zineb, Product-Type 21(Anti-Fouling Products). December 2013. <u>https://circabc.europa.eu/sd/a/0c0693e1-f677-484d-b6ce-ed5d85d2d0c9/Zineb%20(assessment%20report%20as%20finalised%20on%2013.12.13).</u> pdf, retrieved July 9, 2019. (All EU Member States "technical experts" peer review.)
- 11. European Chemicals Agency, Biocidal Products Committee. Opinion on the Application for Approval of the Active Substance: Copper Flakes (Coated with Aliphatic Acid), Product Type: 21. December 8, 2015, ECHA/BPC/080/2015. <u>https://echa.europa.eu/documents/10162/92507327-1852-a002-e98b-7f95f60e02b6</u>, retrieved July 9, 2019. (Legal and policy document.)

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- European Chemicals Agency, Biocidal Products Committee. Opinion on the Application for Approval of the Active Substance: Cybutryne, Product Type: 21. June 17, 2015, ECHA/PC/065/2015. <u>https://echa.europa.eu/documents/10162/912c9ab0-a3d7-88e0-ed90-50061c850784</u>, retrieved July 9, 2019. (Legal and policy document.)
- European Chemicals Agency, Biocidal Products Committee. Opinion on the Application for Approval of the Active Substance: Dichlofluanid, Product Type: 21. October 11, 2016, ECHA/BPC/120/2016. <u>https://echa.europa.eu/documents/10162/3b2ea206-8dc2-</u> c47a-4f4b-4dfbba57aa23, retrieved July 9, 2019. (Legal and policy document.)
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- European Chemicals Agency, Committee for Risk Assessment (RAC). Opinion Proposing Harmonised Classification and Labelling at EU Level of Pyrithione Zinc. September 14, 2018. <u>https://echa.europa.eu/documents/10162/6405ddd0-2429-9e13-31bd-4e0752fe7430</u>, retrieved July 9, 2019. (Subject to open review by "Concerned parties and Member State Competent Authorities.")
- 20. European Commission on the Environment. Selection of Chemical Substances to be Screened in the Context of the Impact Assessment on Criteria to Identify Endocrine Disruptors. January 13, 2016. <u>https://ec.europa.eu/health/sites/health/files/endocrine_disruptors/docs/impactassessment_chemicalsubstancesselection_en.pdf</u>, retrieved July 22, 2019. (Legal and policy document.)

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Appendix C. MAMPEC modeling technical memo



July 18, 2019

TO:	Brian Penttila and Kimberly Goetz, Clients, HWTR Program Kara Steward, Lead Client Unit Supervisor, HWTR Program Ken Zarker, Lead Client Section Manager, HWTR Program
THROUGH:	Jim Medlen, Unit Supervisor, Environmental Assessment Program Jessica Archer, Section Manager, Environmental Assessment Program
FROM:	Dave Serdar, Environmental Assessment Program
CC:	Annette Hoffmann Melissa Peterson
SUBJECT:	Technical Memo: Calculation of Acceptable Leaching Rates for Vessel Antifoulants

Summary

Vessel hull leaching rates for the antifouling biocides copper, cybutryne (Irgarol), DCOIT (Seanine), zinc pyrithione, and tralopyril (Econea) were evaluated for five Washington marinas using the Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC). The model was used to back-calculate the maximum allowable leaching rates (MALRs) that would result in concentrations at the chronic marine water quality criterion for copper and the predicted no effect concentrations (PNECs) for the other biocides. Post-model adjustments were applied to each of the MALRs to account for five possible hull-cleaning scenarios that could increase biocide loading.

The five marinas selected for modeling have recently measured data on metals concentrations in water and other parameters used in the model calculations (Hobbs et al. 2018). Four of the five marinas evaluated are in enclosed or semi-enclosed settings with low tidal flushing. Tidal flushing is a dominant driving force for biocide removal in the MAMPEC model. As a result, these low-flush marinas represent worst-case or near worst-case scenarios for biocide concentrations among Puget Sound marinas.

The mean and median copper MALRs are $6.3-15.4 \,\mu g/cm^2/d$ and $6.5-15.8 \,\mu g/cm^2/d$, respectively, for the low-flush marinas. The ranges in concentrations reflect the different inwater hull cleaning scenarios. The single open harbor marina evaluated had a much higher threshold for copper leaching (up to $100 \,\mu g/cm^2/d$) due to its high flushing rate.

Non-copper biocides are toxic at lower concentrations than those for copper. Therefore, modeled MALRs for non-copper biocides are lower than those for copper—more than two orders of magnitude lower in some cases. Like copper, these biocides have much lower MALRs in enclosed marinas compared to the open harbor marina.

Background

Vessel antifouling paints (AFPs) are used to deter marine organisms, such as barnacles, oysters, mussels, shipworms, or algae, from attaching to the submerged portion of boat hulls. These paints are available in a variety of forms (e.g., hard, ablative, self-polishing) and are typically formulated with biocides intended to leach from the paint in order to prevent fouling. Copper-based chemicals are the most common biocide currently used in AFPs, although other biocidal ingredients are approved for use in Washington waters.

Leaching of biocides from AFPs can adversely affect water quality and marine life, particularly in marinas where high boat densities and poor flushing can lead to elevated biocide concentrations in water and sediments. Copper has been measured at levels above background concentrations and aquatic life criteria in a number of saltwater marinas in Washington (Johnson 2007; Hobbs et al. 2018). Elevated copper in marina environments is not limited to Washington; numerous studies have shown copper enrichment in marinas in California, the East Coast, Europe, and New Zealand (Srinivasan & Swain 2007; Singhasemanon et al. 2009; NZEPA 2012; Daehne et al. 2017).

The largest copper loads in marinas are generally due to passive leaching of copper from vessels with copper-containing AFPs. In-water cleaning of vessel bottoms can result in high episodic releases of copper and can increase the rates of passive leaching through surface refreshment of the AFP hull coatings (Schiff et al. 2004; Earley et al. 2014). Upland activities, such as vessel maintenance in boatyards, may also account for some of the copper delivered to the marina aquatic environment. However, these sources are likely to be a relatively small portion of the overall copper load to marinas (CRWQCB 2005) and are regulated in Washington under the NPDES permit process.

In recognition of the potential adverse effects of copper released from AFPs, the Washington State Legislature passed Substitute Senate Bill (SSB) 5436 in 2011, banning the sale of recreational vessels with copper AFPs beginning January 1, 2018. SSB 5436 also banned the sale and use of AFPs containing more than 0.5% copper effective January 1, 2020. The bill required Ecology to survey the types of AFPs sold in Washington, including those with biocides other than copper, and assess their potential to harm marine life.

In its report to the Legislature, Ecology identified 30 non-copper biocidal AFP products currently registered for use in Washington (Penttila 2017). Included among these registered products are four biocides that can be used in place of or as boosters to copper: zinc pyrithione, tralopyril (trade name Econea), cybutryne (trade name Irgarol 1051), and DCOIT ("Seanine"; trade name SEA-NINE 211N). The assessment also showed that some of the non-copper biocides may pose a significant risk to marine life and water quality, especially in and around recreational boat marinas. Ecology concluded that the AFPs containing non-copper biocides are potentially as harmful, or more harmful, than AFPs containing copper. Sampling data obtained from marinas in Washington suggest that zinc concentrations are generally not present at levels that would adversely affect aquatic life (Hobbs et al. 2018), and the other biocidal chemicals have rarely, if ever, been analyzed in Washington waters.

The Legislature responded to this information by passing Substitute House Bill (SHB) 2634, which delayed the copper AFP bans until January 2021. SHB 2634 directs Ecology to further assess and report on the environmental impacts from AFP uses in Washington waters. The bill

also directs Ecology to conduct modeling and other analyses as needed to "inform regulatory standards for antifouling paints and coatings and their ingredients, such as a leaching standard." Leaching standards for copper in AFPs have been established in California and in Europe, but SHB 2634 directs Ecology to conduct Washington-specific studies, including Washington-specific leaching evaluations. The bill broadens the need to understand whether the loadings of any approved biocide, including non-copper biocides, are a cause for concern.

This technical memorandum provides results of a modeling study conducted by Ecology to estimate acceptable leach rates for copper and other biocides from recreational vessels in Washington. Results of this modeling yield the maximum allowable leaching rates (MALRs) for copper and other AFP biocides that would be protective of aquatic life.

Methods

OVERVIEW OF METHODS

MALRs for copper and other biocides were calculated using the Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC, version 3.1.0.5). MAMPEC is specifically designed to predict environmental concentrations of chemicals leached from AFPs in typical marine environments, such as marinas.

The basic design of MAMPEC allows the user to input environmental characteristics of a marina (e.g., physical dimensions, water characteristics), physicochemical properties of a biocide (e.g., solubility, degradation rates), and emissions of the biocide (e.g., application rates, leaching rates) to predict biocide concentrations in marina waters. With other parameters held constant, the user can vary biocide leaching rates until a target concentration, such as a water quality criterion, is reached. This back-calculation approach was used for the present effort and has been used by California Department of Pesticide Regulation (CDPR) to calculate MALRs for copper (Zhang & Singhasemanon 2014) and in guidance proposed by the Environmental Protection Agency (USEPA 2017). Additional details of the MAMPEC model are described in Appendix A.

MAMPEC was used to evaluate leaching rates at five Puget Sound area marinas for copper, Irgarol, Seanine, zinc pyrithione, and Econea. Leaching rates determined from MAMPEC calculations were then adjusted for five possible cleaning scenarios. The following sections describe the methods and data in more detail.

DATA

To calculate Washington-specific MALRs using the MAMPEC model, water and sediment characteristics were obtained from a recent survey of five Puget Sound area marinas conducted by Ecology during 2016 and 2017 (Hobbs et al. 2018; Table 1). These data were selected for the following reasons:

- The data set includes a number of water quality characteristic which are specific to the marinas.
- The data are recent, having been collected in the past two years.
- The data are of high quality. Both laboratory-generated data and *in situ* monitoring, using a Hydrolab multi-probe, met the measurement quality objectives as outlined in the Quality Assurance Project Plan (Hobbs and McCall 2016).

- Background copper concentrations are available.
- Copper concentrations inside the marinas are available, which can be compared with model results.
- Three of the marinas are highly enclosed, with relatively small rates of flushing and thereby representing worst-case or near worst-case scenarios.
- Some of the most important model parameters are difficult and time-consuming to estimate (e.g., vessel wetted surface areas). Limiting these to five marinas is a reasonable undertaking given budget and time constraints.
- Nearly all of the vessels in the marinas are pleasure craft <65 feet length overall, which are the type and length of the vessels addressed in the legislation.
- The marinas are of substantial size, with approximately 300 to 750 moorage slips and occupancy rates averaging >80%.

		No. of	Date	Associated	Environmental
Marina	Location	Moorage Slips	Established	Boatyard?	Setting
Swantown	Olympia	~ 650	1983	Yes	Semi-enclosed
City of Des					
Moines	Des Moines	~ 750	1970	Yes	Enclosed
John Wayne	Sequim	~ 300	1985	No	Enclosed
Skyline	Anacortes	~ 400	1960s	Yes	Enclosed
Friday Harbor	San Juan Island	~ 500	1970s	No	Open harbor

Table 1. Summary of marinas used for modeling.

A map and photos of the modeled marinas are shown in Appendix B.

Additional sources of water column data (e.g., chlorophyll) were obtained from the Puget Sound Ecosystem Monitoring Program (PSEMP). PSEMP data are considered reliable and are generated by a monitoring program guided by a detailed Quality Assurance Monitoring Plan (Bos et al. 2015).

Data on marina dimensions and physical characteristic of the marina environment (e.g., wind speeds), were obtained from satellite imagery (Google Maps), NOAA, values recommended by MAMPEC authors, or best professional judgement. With the exception of tralopyril, MAMPEC includes default values for biocide data. Tralopyril data were obtained through literature searches. All of the data used for model input and their sources are in Appendix C.

Wetted surface areas (WSAs) of vessel hulls, a key parameter to estimate biocide emissions, was obtained using several methods. First, the boat population for each marina was estimated from information provided by each marina's harbormaster. This included the numbers and sizes of slips, the proportion of sail and power boats, and the seasonal occupancy rates. For Skyline marina, this information was unavailable because the harbor is a conglomeration of small marinas managed by different entities. A survey of boats using Google Maps was therefore used to estimate vessel types, numbers, and sizes at Skyline.

Once the vessel population was estimated at each marina, formulas predicting WSAs based on boat length (length overall, LOA) were applied. For sailboats, the formula (Equation 1) was developed using known LOAs and WSAs from 30 sailboats, each available from a builder of traditional and contemporary sailboats (Dudley Dix, <u>https://www.dixdesign.com/designs.htm</u>)

and from Offshore Racing Congress certificates (ORC, <u>https://www.orc.org/</u>). Only monohull sailboats 25 to 65 feet were considered. Sailboat data obtained from ORC certificates were only considered if the model was also listed as an active Northwest Pacific Handicap Racing Fleet member (PHRF, <u>https://phrf-nw.org</u>) to ensure they resembled the make-up of local boats.

(Eq. 1) *WSA = 0.2117·(LOA)² + 0.2831·(LOA)* Where:

LOA = length overall

For powerboats, WSAs were estimated using a modification of the Holltrop-Mennen equation as recommended by Bakker & van Vlaardingen (2017). This formula (Equation 2) uses a number of hull coefficients to estimate WSAs from the hull form, and includes terms for estimating WSAs for the skeg and rudder. Recommended default values are provided by Bakker & van Vlaardingen (2017).

(Eq. 2)

$$WSA = L \cdot (B + 2 \cdot T) \cdot \sqrt{C_M} \cdot \left(0.453 + 0.4425 \cdot C_B - 0.2862 \cdot C_M - 0.003467 \cdot \frac{B}{T} + 0.3696 \cdot C_W \right) + 1.12 \cdot (C_M \cdot T \cdot B_{WL})$$

Where:

$$\begin{split} L &= L_{WL} = length \ at \ waterline\left(\frac{LOA}{1.12}\right) \\ B &= B_{WL} = beam \ at \ waterline\left(\frac{L_{WL}}{0.8827 \cdot \ln(L_{WL}) + 0.7941}\right) \\ T &= Draft\left(\frac{B_{WL}}{4.0}\right) \\ C_M &= midship \ area \ coefficient \ of \ the \ underwater \ hull \ (0.71) \\ C_B &= block \ coefficient \ of \ the \ underwater \ hull \ on \ the \ basis \ of \ length \ on \ the \ waterline \ (0.45) \\ C_W &= water \ plane \ area \ coefficient \ based \ on \ length \ on \ the \ waterline \ (0.80) \end{split}$$

While other WSA formulas are available, the formulas presented here appear to be well-suited to the purposes of this modeling exercise. Sailboat WSAs were evaluated using other formulas, but Equation 1 was found to consistently have the best fit with known WSAs ($R^2 = 0.90$). A lack of available powerboat WSAs precludes evaluating the ability of Equation 2 to accurately predict WSAs. However, a thorough analysis of numerous formulas by Bakker & van Vlaardingen (2017) concludes that Equation 2 consistently offers the best results over a range of hull forms.

GENERAL ASSUMPTIONS

Some important model inputs use assumptions and best professional judgement, due to a lack of information on actual values. Application factors (AFs) are used to describe the rates of application (i.e., percentage of boats using a particular biocide) as a term to calculate the overall emissions from leaching. For copper, the AF input has a directly proportional effect on predicted environmental concentrations (PECs) (e.g., doubling the AF results in double the PEC) if all of the copper stems from passive leaching. In lieu of known AFs, the AF was fixed at 100% for copper and 20% for the other biocides. This is the approach used by California Department of Pesticide Regulation (CDPR) for copper and by New Zealand Environmental Protection Authority (NZEPA) for copper and other compounds. Consistent with CDPR and NZEPA, all

leaching was assumed to be emitted from vessels at berth.

ASSUMPTIONS FOR BOATYARD INPUTS

For marinas with associated boatyards, biocide emissions due to onshore repair and maintenance activities can also be estimated using MAMPEC. This requires a number of additional input parameters, including the number of boats undergoing maintenance, fraction of paint removed by pressure-washing and by abrasion, and the concentration of active ingredient in the paint being removed. Few, if any, of these details are available for local marinas, and therefore recommended default values designed for MAMPEC were used. These default values can be found in the harmonized scenario recommended for all OECD (Organization for Economic Cooperation and Development) countries (van de Plassche & van der Aa 2004).

Active ingredient concentrations were based on AFPs registered in Washington and listed in the Washington State University's Pesticide Information Center Online database (<u>http://cru66.cahe.wsu.edu/labels/Labels.php</u>). The arithmetic mean of active ingredient concentrations were calculated for each biocide. Product technical or safety data sheets were used to obtain product densities in order to convert active ingredient concentrations from percent (by weight) to grams per liter (g/L). For copper, the active ingredient was converted to a metallic copper equivalent. The following active ingredient concentrations were used for the boatyard component of the model:

- copper 800 g/L
- Irgarol 37 g/L
- Seanine 43 g/L
- zinc pyrithione 76 g/L
- Econea 79 g/L

Since the fraction of fugitive paint materials released to surface water is required for model input, 1% was used based on best professional judgement. Model runs using a more conservative estimate of 10% were also included. These fugitive emissions are generated by sanding and pressure-washing existing paint; they are not due to overspray during new paint application.

TARGET WATER CONCENTRATIONS

Table 2 shows the target biocide water concentrations used to back-calculate maximum allowable leaching rates (MALRs). For copper, the most appropriate target concentration is the Washington State marine chronic aquatic life criterion (3.1 μ g/L dissolved copper). This was also the target used by CDPR to establish MALRs in California (Zhang & Singhasemanon 2014).

Target concentrations for Irgarol, Seanine, and Econea were developed in European Union (EU) regulation and reported as predicted no effect concentrations (PNECs) for marine waters. Aside from Econea, these PNECs were also used by NZEPA (2012) for their AFP risk assessment. The zinc pyrithione target is the PNEC reported by NZEPA (2012). The USEPA has not developed applicable criteria or threshold concentrations for these biocides.

MAMPEC predicts maximum, 95th percentile, mean, median, and minimum biocide concentrations in water. Predicted mean concentrations were used to back-calculate MALRS. Mean values were selected because all target concentrations are based on chronic toxicity endpoints, and therefore mean rather than maximum localized exposures were deemed more appropriate.

	Target Water	
Biocide	Concentration (µg/L)	Source
Copper	3.1 (dissolved)	Marine AWQC (Chapter 173-201A WAC)
Cybutryne (Irgarol)	0.0058 (total)	PNEC; EU (2011), NZEPA (2012)
DCOIT (Seanine)	0.0068 (total)	PNEC; EU (2014a), NZEPA (2012)
Zinc pyrithione	0.046 (total)	PNEC, NZEPA (2012)
Tralopyril (Econea)	0.0017 (total)	PNEC, EU (2014b)

Table 2. Target marine water biocide concentrations used to back-calculate maximum allowable leaching rates (MALRs).

AWQC = Ambient Water Quality Criterion

PNEC = Predicted No Effect Concentration

ADJUSTMENTS FOR IN-WATER HULL CLEANING

Studies have shown that underwater hull cleaning increases copper release from AFPs both during and after cleaning (Schiff et al. 2004; Earley et al. 2014). MAMPEC is designed to estimate biocide concentrations due to passive leaching from AFPs but does not have the capability to calculate additional releases due to underwater hull cleaning. To account for additional copper releases as a result of cleaning, MALRs calculated by MAMPEC are multiplied by the cleaning adjustment factors shown in Table 3.

Copper releases from underwater hull cleaning are largely dependent on the rate of cleaning and methods used. More frequent cleaning releases more copper from both hard and ablative paints, and aggressive cleaning (e.g., using an abrasive 3M[™] scouring pad) releases more copper than cleaning using a Best Management Practice (BMP), such as soft-pile carpet (Earley et al. 2014).

CDPR derived the cleaning adjustment factors in Table 3 from the data reported by Earley et al. (2014) and applied them to their MALRs for copper (Zhang & Singhasemanon 2014). The result was that for each marina scenario, five possible MALRs are calculated; no cleaning, frequent cleaning using a BMP, frequent cleaning without BMP, less frequent cleaning using a BMP, and less frequent cleaning without BMP.

This cleaning adjustment approach assumes that all vessels in a marina are cleaned at the frequency and methods described by Zhang & Singhasemanon (2014). Although releases due to cleaning were originally measured only for copper, these adjustment factors were applied to other biocides in the present analysis.
Table 3. Adjustment factors applied to MALRs to account for in-water hull cleaning method and frequency.

	No cleaning	BMP – every 3 weeks in summer (JJA), every 4 weeks remainder of year	No BMP – every 3 weeks in summer (JJA), every 4 weeks remainder of year	BMP – monthly	No BMP – monthly
Adjustment factor	1	0.57	0.41	0.71	0.45

BMP = Best Management Practice: scrubbing using soft-pile carpet

No BMP = Without Best Management Practice: scrubbing using abrasive 3M[™] scouring pad JJA = June, July, August

MODEL SENSITIVITY TESTING

MAMPEC does not include a module to assess sensitivity to varying parameter inputs. Therefore, in order to assess sensitivity, a simplified iterative process of manual inputs was used to gauge model response to parameter variations.

Two marinas, Des Moines and Friday Harbor, were used for sensitivity testing. Des Moines was selected because its design best represents a closed marina layout used by MAMPEC. Friday Harbor was selected because it is the only marina modeled using an open harbor layout.

Three biocides were used for sensitivity testing: copper, zinc pyrithione, and Econea. These chemicals were tested because they have very different physicochemical properties and might be expected to respond differently to parameter changes.

Sensitivity tests were conducted by entering all applicable parameters in the MAMPEC "environment" module at values one-half and double ($\times 0.5$ and $\times 2$) the values used to calculate MALRs. The predicted water concentration resulting from each entry was then compared to the target concentration for each biocide. Applications factors and leaching rates were also tested using the same procedure. Results of the model response to these tests are shown in Appendix D.

Results

CALCULATION OF MALRS WITHOUT BOATYARD INPUTS

Tables 4 through 8 show MALRs calculated for the biocides modeled using MAMPEC. Biocide emissions are from passive leaching and the cleaning scenarios described previously. Figure 1 shows relative MALR patterns among the five marinas.

For the five marinas evaluated, MALRs for copper range from $6.5 - 100 \,\mu\text{g/cm}^2/\text{d}$, assuming no in-water cleaning, and $2.6 - 71 \,\mu\text{g/cm}^2/\text{d}$ with adjustments applied for cleaning (Table 4). MAMPEC predicts that leaching rates at Friday Harbor could be much higher than other marinas before the marine water quality criterion is reached, likely due to the model setting (open harbor) used at this location. The other more confined marinas were modeled using a marina setting which predicts much lower rates of flushing and therefore less assimilative capacity for copper. Des Moines marina is predicted to reach the marine water quality criterion at the lowest leaching rates among the five marinas, likely a reflection of the high vessel density at this marina.

Marina	No cleaning	More frequent cleaning using BMP	More frequent cleaning, NO BMP	Less frequent cleaning using BMP	Less frequent cleaning, NO BMP
Swantown	23.4	13.3	9.59	16.6	10.5
Des Moines	6.47	3.69	2.65	4.59	2.91
John Wayne	15.1	8.58	6.17	10.7	6.77
Skyline	16.6	9.48	6.82	11.8	7.48
Friday Harbor	100.3	57.2	41.1	71.2	45.1
Mean =	32.4	18.5	13.3	23.0	14.6
Median =	16.6	9.48	6.82	11.8	7.48

Table 4. MALRs (μ g/cm²/d) predicted by MAMPEC to result in the target water concentration for copper, with adjustments for in-water hull cleaning scenarios.

MALRs for Irgarol range from $0.058 - 0.86 \,\mu\text{g/cm}^2/\text{d}$, assuming no in-water cleaning, and $0.024 - 0.61 \,\mu\text{g/cm}^2/\text{d}$ with adjustments applied for cleaning (Table 5). Patterns for Irgarol MALRs among the five marinas are similar to those for copper, with Friday Harbor predicted to have a much higher leaching rate before the PNEC is reached.

Table 5. MALRs ($\mu g/cm^2/d$) predicted by MAMPEC to result in the target water concentration for Irgarol, with adjustments for in-water hull cleaning scenarios.

Marina	No cleaning	More frequent cleaning using BMP	More frequent cleaning, NO BMP	Less frequent cleaning using BMP	Less frequent cleaning, NO BMP
Swantown	0.162	0.092	0.066	0.115	0.073
Des Moines	0.058	0.033	0.024	0.041	0.026
John Wayne	0.078	0.044	0.032	0.055	0.035
Skyline	0.111	0.063	0.046	0.079	0.050
Friday Harbor	0.862	0.491	0.353	0.612	0.388
Mean =	0.254	0.145	0.104	0.180	0.114
Median =	0.111	0.063	0.046	0.079	0.050

MALRs for Seanine range from $0.96 - 2.6 \,\mu\text{g/cm}^2/\text{d}$, assuming no in-water cleaning, and $0.39 - 1.9 \,\mu\text{g/cm}^2/\text{d}$ with adjustments applied for cleaning (Table 6). MALRs among the five marinas were much closer than the spread patterns observed for copper and Irgarol. Friday Harbor has the highest MALR, but only slightly higher than Skyline, and less than three times the lowest MALR (Des Moines).

Marina	No cleaning	More frequent cleaning using BMP	More frequent cleaning, NO BMP	Less frequent cleaning using BMP	Less frequent cleaning, NO BMP
Swantown	1.74	0.99	0.71	1.24	0.78
Des Moines	0.96	0.55	0.39	0.68	0.43
John Wayne	1.00	0.57	0.41	0.71	0.45
Skyline	2.29	1.31	0.94	1.63	1.03
Friday Harbor	2.63	1.50	1.08	1.87	1.18
Mean =	1.72	0.98	0.71	1.22	0.78
Median =	1.74	0.99	0.71	1.24	0.78

Table 6. MALRs (μ g/cm²/d) predicted by MAMPEC to result in the target water concentration for Seanine, with adjustments for in-water hull cleaning scenarios.

MALRs for zinc pyrithione range from $1.2 - 8.1 \,\mu g/cm^2/d$, assuming no in-water cleaning, and $0.48 - 5.7 \,\mu g/cm^2/d$ with adjustments applied for cleaning (Table 7). Patterns for zinc pyrithione MALRs among the five marinas are intermediate between those for copper and Seanine, with the highest MALR (Friday Harbor) seven times higher than the lowest (Des Moines).

Table 7. MALRs (μ g/cm²/d) predicted by MAMPEC to result in the target water concentration for zinc pyrithione, with adjustments for in-water hull cleaning scenarios.

Marina	No cleaning	More frequent cleaning using BMP	More frequent cleaning, NO BMP	Less frequent cleaning using BMP	Less frequent cleaning, NO BMP
Swantown	2.52	1.44	1.03	1.79	1.13
Des Moines	1.18	0.67	0.48	0.84	0.53
John Wayne	1.39	0.79	0.57	0.99	0.63
Skyline	2.74	1.56	1.12	1.95	1.23
Friday Harbor	8.08	4.61	3.31	5.74	3.64
Mean =	3.18	1.81	1.30	2.26	1.43
Median =	2.52	1.44	1.03	1.79	1.13

MALRs for Econea range from $0.09 - 0.38 \ \mu g/cm^2/d$, assuming no in-water cleaning, and $0.037 - 0.27 \ \mu g/cm^2/d$ with adjustments applied for cleaning (Table 8). Patterns for Econea MALRs among the five marinas are intermediate between those for Seanine and zinc pyrithione, with the highest MALR (Friday Harbor) four times higher than the lowest (Des Moines).

Marina	No cleaning	More frequent cleaning using BMP	More frequent cleaning, NO BMP	Less frequent cleaning using BMP	Less frequent cleaning, NO BMP
Swantown	0.174	0.099	0.071	0.124	0.078
Des Moines	0.090	0.051	0.037	0.064	0.041
John Wayne	0.100	0.057	0.041	0.071	0.045
Skyline	0.218	0.124	0.089	0.155	0.098
Friday Harbor	0.385	0.219	0.158	0.273	0.173
Mean =	0.193	0.110	0.079	0.137	0.087
Median =	0.174	0.099	0.071	0.124	0.078

Table 8. MALRs (μ g/cm²/d) predicted by MAMPEC to result in the target water concentration for Econea, with adjustments for in-water hull cleaning scenarios.



Figure 1. MALRs for each biocide relative to the median MALR among marinas. The median is indicated by a value of 1.0. Missing values for Skyline (copper and Irgarol) and Swantown (Seanine, zinc pyrithione, and Econea) indicate those marinas have the median MALR for the respective biocide.

CALCULATION OF MALRS WITH BOATYARD INPUTS

Three marinas with associated boatyards – Swantown, Des Moines, and Skyline – were analyzed for potential biocide emissions due to boatyard activities. John Wayne and Friday Harbor marinas do not have associated boatyards.

Estimates of boatyard-related biocide emissions were calculated by MAMPEC using values recommended by van de Plassche & van der Aa (2004), based on surveys of boatyard activities in Europe. All boatyard emission were assumed to stem from paint removal activities. No effort has been made to gauge how these input values compare with actual boatyard activities for the marinas modeled for this report. Because this is a preliminary examination of the potential effects from boatyards, estimates were made for the "no cleaning" scenario only.

Results show that for copper, Seanine, and zinc pyrithion, the boatyard emissions contribute only small amounts to overall loads, and therefore have little effect on MALRs (Table 9). For these biocides, the boatyard contributions are small even when 10% of the fugitive material generated during paint removal is delivered to marina waters.

For Irgarol and Econea, boatyard discharges might represent a substantial load relative to the assimilative capacity of the marina. As a result, there is less "room" for loading from passive hull leaching, resulting in lower MALRs. This effect is especially pronounced at Des Moines marina, which has about one-half the volume of either Swantown or Skyline, and therefore a much lower assimilative capacity for biocide inputs.

Table 9. Effects of boatyard inputs on MALRs (μ g/cm²/d) for all biocides. Scenarios include no boatyard inputs (0%) and boatyard fractions to surface waters of 1% and 10%. All scenarios assume no in-water cleaning of vessel hulls.

	Fraction to				Zinc	
Marina	surface water	Copper	Irgarol	Seanine	pyrithione	Econea
Swantown	0%	23.4	0.162	1.74	2.52	0.174
"	1%	23.3	0.160	1.73	2.52	0.170
"	10%	23.3	0.144	1.72	2.49	0.139
Des Moines	0%	6.47	0.058	0.96	1.18	0.090
"	1%	6.45	0.056	0.96	1.17	0.086
"	10%	6.37	0.037	0.94	1.14	0.052
Skyline	0%	16.6	0.111	2.29	2.74	0.218
"	1%	16.6	0.108	2.29	2.73	0.214
u	10%	16.5	0.087	2.27	2.69	0.175

MODEL SENSITIVITY

Table 10 shows parameters that result in changes >10% to predicted biocide concentrations for at least one marina/biocide when their values are decreased by 50% or increased by 100%. Results of this simplified analysis indicate that biocide concentrations predicted for the open harbor layout (Friday Harbor) are generally more sensitive than those from the marina layout (Des Moines). Not surprisingly, the greatest response results from changes to application factors and leaching rates. The responses to these inputs are directly proportional for zinc pyrithione and Econea, but less so for copper due to the influence of background copper concentrations.

Aside from suspended particulate matter (SPM) concentrations and temperature, water characteristics play a comparatively small role in driving predicted biocide concentrations. MAMPEC fate and flux analysis shows that, next to hydrodynamic exchange (flushing), sedimentation is the major process removing copper from marina water, whereas degradation drives zinc pyrithione and Econea removal.

Of note is the effect that flow velocity has on predicted biocide concentrations in the open harbor scenario. A flow velocity of 0.01 m/s was used to calculate MALRs based on a simple estimate, because no data could be found on current velocities in Friday Harbor.

		Des Moines Marina						Friday Harbor Marina					
	Cop	oper	Zinc py	Zinc pyrithione		Econea		Copper		Zinc pyrithione		Econea	
Parameter	×0.5	×2	×0.5	×2	×0.5	×2	×0.5	×2	×0.5	×2	×0.5	×2	
Flow velocity	1.0%	-1.3%	0.7%	-0.9%	0.0%	-0.6%	82.6%	-44.8%	66.7%	-44.6%	42.4%	-37.6%	
Waterbody width beyond marina or harbor	*	0.3%	*	0.0%	*	0.0%	-10.0%	-7.7%	-10.7%	-8.5%	-10.0%	-8.2%	
Marina depth	3.5%	-1.9%	48.3%	-38.3%	70.6%	-43.9%	87.7%	-45.8%	99.8%	-50.0%	100.6%	-49.9%	
Marina mouth width	7.1%	-13.9%	3.0%	-7.2%	1.2%	-4.1%	na	na	na	na	na	na	
Average wind speed	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.3%	-10.6%	2.2%	-10.9%	2.4%	-9.4%	
Suspended particulate matter concentration	9.4%	-14.5%	0.0%	0.0%	0.0%	0.0%	7.7%	-12.9%	0.0%	0.0%	0.0%	0.0%	
Temperature	0.0%	0.0%	2.4%	-7.8%	10.0%	-24.7%	0.0%	0.0%	0.4%	-1.5%	3.5%	-8.8%	
Dissolved copper, background	-5.8%	11.6%	na	na	na	na	-3.2%	6.5%	na	na	na	na	
Application factor (%)+	-44.2%	**	-50.0%	100.0%	-50.1%	99.4%	-46.8%	**	-50.0%	99.8%	-49.9%	100.6%	
Leaching rate (µg/cm²/d)‡	-44.2%	88.7%	-50.0%	100.0%	-50.1%	99.4%	-46.8%	93.5%	-50.0%	99.8%	-49.9%	100.6%	

Table 10. Parameters that result in changes >10% to predicted biocide concentrations for at least one marina/biocide when these parameters are changed by -50% (×0.5) or +100% (×2).

Light shading = change of 1% – 10%

Medium shading = change of >10% - 50%

Dark shading = change of >50%

* Original value is the minimum recommended by MAMPEC

⁺ Original application factors are 100% for copper and 20% for other biocides

****** Original value is the maximum possible (100%)

+ Original leaching rate at Des Moines = 6.47 for copper, 1.175 for zinc pyrithione, 0.090 for Econea; Original leaching rate at Friday Harbor = 100.3 for copper, 8.08 for zinc pyrithione, 0.385 for Econea

na = not applicable

Discussion

MALRs derived from modeling poorly flushed enclosed marinas are likely to be lower than those from open marinas, and would therefore be more protective of aquatic life if they are applied broadly. Of the five marinas modeled using MAMPEC, three are highly enclosed marinas and one is semi-enclosed. These marinas represent worst-case or near worst-case scenarios in terms of flushing and, hence, copper enrichment due to leaching from vessel hulls. Indeed, Hobbs et al. (2018) showed high copper concentrations in these marinas compared to an open-harbor marina.

MALR results from the four enclosed or semi-enclosed marinas are fairly similar – within a factor of 3.5 – suggesting that the results provide a reasonable range of estimates for worst-case or near worst-case scenarios. For these marinas, the range of copper MALRs falls within the range of MALRs reported by California Department of Pesticide Regulation (CDPR) for each of the matching in-water cleaning scenarios (Zhang & Singhasemanon 2014). For instance, in the "no cleaning" scenario, the results from this study are $6.5 - 23 \,\mu g/cm^2/d$, compared to $1.1 - 25 \,\mu g/cm^2/d$ reported by CDPR. However, median values reported by CDPR were lower than in this study (8 versus $16 \,\mu g/cm^2/d$). Lower values for MALRs might be expected for the California marinas due to lower tidal ranges (less flushing) and higher background copper compared with Puget Sound marinas. Other differences might also drive MALRs, and while a detailed comparison with California marinas is beyond the scope of the present analysis, this limited comparison indicates that results are in the same range.

MALRs for copper and other biocides at Friday Harbor are clear outliers among the five marinas due to the environmental setting for this particular marina. This marina sits at the mouth of a small embayment, itself within a bay. If fits into neither MAMPEC's marina setting nor open harbor setting, although the latter is a more appropriate choice for modeling. It has a much higher flushing capacity than other marinas, and is much deeper as well. The MAMPEC open harbor setting makes it very sensitive to the user input value for flow velocity, and as mentioned in the Methods section, the value used was based on best professional judgement.

Even considering these uncertainties, the MALR results for Friday Harbor seem reasonable when compared to the other marinas. Hobbs et al. (2018) reported average dissolved copper concentrations three to ten times lower in Friday Harbor Marina compared to the other four marinas. In addition, MAMPEC predicts that copper concentrations outside Friday Harbor marina would decrease less gradually than the steep decrease in copper concentrations predicted for waters outside other marinas. These predicted patterns are similar to those found by Hobbs et al. (2018) for inner versus outer copper concentrations.

Copper MALRs among the enclosed or semi-enclosed marinas are much closer to each other than Friday Harbor. For these marinas, the relative pattern for MALRs might be expected to demonstrate the inverse of measured dissolved copper concentrations (i.e., a higher MALR would be expected at a marina with a lower dissolved copper level, and vice versa). However, these relationships are not always consistent. For instance, Skyline and Swantown have the highest measured dissolved copper concentrations but also comparatively high MALRs.

Underwater hull surface (i.e., wetted surface areas, or WSA) densities of each marina partially explain some of the copper concentrations predicted by MAMPEC. Table 11 shows qualitative

comparisons of MALRs, measured copper concentrations, and WSA densities among the enclosed and semi-enclosed marinas. The underwater hull surface densities (expressed as WSA divided by marina surface area or volume) are much lower for Skyline and Swantown, resulting in lower predicted copper concentrations and higher MALRs.

While this observation might be useful for explaining predicted values, it still fails to explain inconsistencies with measured copper concentrations. For Skyline, the discrepancy may be due to this marina's complex shape. MAMPEC may overpredict the hydrodynamic exchange at Skyline because it does not account for the presence of its numerous embayments and overall unusual geometry. This might account for the relatively high MALR for Skyline even though measured copper concentrations are high.

A large uncertainty in the model parameterization is the input values for copper biocide application factors, assumed to be 100% for all marinas. Application factors are nearly directly proportional to MAMPEC output for copper concentrations in water. Given the paucity of information on actual biocide usage rates, there is no way to gauge the validity of this input value.

Table 11. Patterns of MALRs, measured copper concentrations, and wetted surface area (WSA) densities among the enclosed and semi-enclosed marinas.

Variable	Qualitative Comparison
Copper MALRs	Swantown > Skyline ≈ John Wayne >> Des Moines
Measured dissolved copper concentrations	Skyline >> Swantown > Des Moines > John Wayne
WSA density (WSA/marina surface area)	Des Moines > John Wayne >> Skyline ≈ Swantown
WSA density (WSA/marina volume)	Des Moines ≈ John Wayne >> Swantown > Skyline

BOATYARD INPUTS

Based on the modeling results, boatyards are unlikely to account for substantial copper loads to marinas compared to loads from passive leaching. The assumptions used for the boatyard module in MAMPEC are fairly conservative (active ingredient levels of 800 g/L metallic copper; up to 10% discharged to the marina during paint removal), yet they still represent <2% of the total load. However, investigating actual copper loads from boatyards was beyond the scope of this exercise.

For Irgarol and Econea, boatyard discharges are potentially more important given the model assumptions. MAMPEC predicts that, at a boatyard fraction of 10% emitted to marinas, MALRs would need to be reduced by up to 40% in order to assimilate the additional biocide load. This is due to the large composition of these biocides in paints (i.e., active ingredient) relative to the target concentrations (Table 2). For instance, paint was assumed to contain 79 g/L of Econea, which has a target concentration of 0.0017 μ g/L, resulting in an active ingredient to target ratio of about 50 billion. By comparison, copper has an active ingredient to target ratio of about 300 million. Since MAMPEC assumes that biocide discharges from boatyards are independent of leaching rates (they have a direct effect on water concentration), boatyard discharges have more influence when active ingredient to target concentrations are greater.

Conclusions and Recommendations

Vessel hull leaching rates for the antifouling biocides copper, cybutryne (Irgarol), DCOIT (Seanine), zinc pyrithione, and tralopyril (Econea) were evaluated for five Washington marinas using the Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC) model. The marine water quality criterion for copper and the predicted no effect concentrations (PNECs) for the other biocides were used as target concentrations to back-calculate matching leaching rates. These leaching rates are the highest allowable (i.e., maximum allowable leaching rates [MALRs]) that would be protective of aquatic life.

For the four enclosed and semi-enclosed marinas evaluated using MAMPEC, the mean and median copper MALRs were found to be $6.3 - 15.4 \,\mu g/cm^2/d$ and $6.5 - 15.8 \,\mu g/cm^2/d$, respectively. These marinas are likely to be representative of worst-case or near worst-case scenarios in terms of flushing and, hence, copper enrichment due to leaching from vessel hulls. The range in concentrations represents adjustments due to in-water hull cleaning, which previous studies have found to enhance copper loading by as much as 60%.

An open harbor type marina was also evaluated for leaching of copper and found to have a much higher threshold for copper leaching (up to 100 μ g/cm²/d) due to its high flushing rate. The relative MALRs between enclosed and open marinas are consistent with relative copper concentrations measured in the same marinas during a recent survey.

Non-copper biocides are toxic at concentrations lower than copper. Therefore, modeled MALRs are lower than for copper — more than two orders of magnitude lower in some cases. Like copper, these biocides have much lower MALRs in enclosed marinas compared to the open harbor marina. However, one noticeable difference is that boatyard inputs, based on modeled values, may play a substantial role in Irgarol and Econea concentrations in marina waters.

Overall, it appears that the MALRs reported here are suitable for evaluating paint products based on their reported leaching rates. MALRs provided in this analysis are based on recent highquality data from worst-case or near worst-case scenarios in terms of flushing, which is the main driving force for removing copper from marina waters according to the MAMPEC model. Among the four enclosed and semi-enclosed marinas, modeled MALR results are relatively close, suggesting that they are good representations of this type of environment. If a goal of future modeling efforts is to provide representative MALRs for all marinas, then additional open harbor marinas (and perhaps other marina settings) should be sampled and evaluated with MAMPEC.

Boatyard inputs should also be evaluated further, because it is possible that inputs from boatyards could be substantial for some biocides. However, Washington-specific boatyard data were unavailable for use as model inputs, and values recommended for OECD countries were used instead. Boatyards are permitted in Washington under the National Pollutant Discharge Elimination System (NPDES) and those permits are managed by Ecology. A first-tier investigation to obtain information from the boatyards and possibly to collect environmental samples could be readily executed. This could provide improved data for input, or insights about whether current model inputs are suitable for local situations.

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Appendices

APPENDIX A. THE MAMPEC MODEL

The following is adapted from the MAMPEC 3.1 Technical Documentation (van Hattum et al. 2016):

Introduction

MAMPEC is a steady-state 2D integrated hydrodynamic and chemical fate model, originally developed for the exposure assessment of antifouling substances (van Hattum et al. 2002, 2006).

The model predicts concentrations of antifoulants in generalized "typical" marine environments (open sea, shipping lane, estuary, commercial harbor, yachting marina, open harbor). The user can specify emission factors (e.g., leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound-related properties and processes (e.g., dissociation constant [Kd], octanol-water partition coefficient [Kow], organic carbon partition coefficient [Koc], volatilization, speciation, hydrolysis, photolysis, biodegradation), and properties and hydrodynamics related to the specific environment (e.g., currents, tides, salinity, dissolved organic carbon, suspended matter load, port dimensions).

MAMPEC includes options for advanced photolysis modeling, incorporation of wind-driven hydrodynamic exchange, and other nontidal exchange processes important for areas without tidal action or inland freshwater environments. Included are also service-life emission and other scenarios developed by an OECD-EU working group (van der Plassche & van der Aa 2004) and adopted by the European Union as the standard environmental emission scenarios to be used for evaluation of the biocides under the Biocidal Products Directive (BPD, Directive 98/8/EC) and the more recent Biocidal Product Regulation (BPR, Regulation (EU) 528/2012).

The model has been validated for a number of compounds and is today recognized by regulatory authorities in the European Union, United States, Japan, and other OECD countries. The documentation of formulations and backgrounds in MAMPEC has been described in different reports issued with new updates (e.g., van Hattum et al. 1999, 2002, 2006; Baart et al. 2003; Boon et al. 2008) and with additional explanations in release notes or documents prepared for the technical meetings of competent European authorities for the Biocidal Products Directive.

Structure of the Model

The basic structure of the MAMPEC model consists of a central user interface (UI), from which data are entered to or retrieved from a database, submodels are run, and calculation results are presented. The UI guides the user via different panels, menus, and screens, and helps to provide the required input settings for 1) environments, 2) compound properties, and 3) emission scenarios. The user-supplied information and the results of the calculations are stored in a database, which is shielded from the user.

Interaction with the database is through the UI in order to maintain integrity of the database. From the UI various hydrodynamic and chemical fate modules are called upon for the calculations of water quality and hydraulic exchange and transport processes (DELWAQ and SILTHAR programmed in FORTRAN). The calculations are executed on a user-defined grid basis. The UI results and export screens allows the user to compose the input for MAMPEC and to run its computational part, or view, print, or file results from previous runs, and to export and import scenario and compound settings. Each combination of environment, compound, and emission scenario is assigned automatically a unique identifying label, in order to keep track of the different runs of the model. Basic sets of (read-only) default settings for prototype environments and default emission scenarios are provided for reasons of standardization and can be used for comparisons between different compounds.

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APPENDIX B. MAP AND PHOTOS OF THE FIVE MARINAS USED IN THE MAMPEC MODEL

Figure B-1. Locations of the five marinas used in the MAMPEC model (adapted from Hobbs et al. 2018).



Figure B-2. Photos of the five marinas used in the MAMPEC model.

References for Appendix B

Hobbs, W., M. McCall, and J. Lanksbury. 2018. Copper, Zinc, and Lead Concentrations at Five Puget Sound Marinas. Publication No. 18-03-001. Environmental Assessment Program, Washington State Department of Ecology, Olympia. <u>https://fortress.wa.gov/ecy/publications/SummaryPages/1803001.html</u>. APPENDIX C. INPUT DATA USED FOR MAMPEC

Table C-1. Environmental data	input for MAMPEC. See Table (C-1 Supplement for data sources.

Hydrodynamics and Transport Modeling (Environmental Data) Input	Swantown	data source	Des Moines	data source	John Wayne	data source	Skyline	data source	Friday Harbor	data source
Environment Type (harbor type)	Marina	-	Marina	-	Marina	-	Marina	-	Open Harbor	_
Tidal period (hour)	12.41	а	12.41	а	12.41	а	12.41	а	12.41	а
Tide amplitude (difference, m)	3.194	b	2.456	с	1.629	d	1.408	e	1.469	f
Max. density difference tide (kg/m ³)	0.6	g	0.1	g	0.1	g	0.2	g	0.05	g
Non tidal daily water level change (m)	0	h	0	h	0	h	0	h	0	h
Flow velocity (F, m/s)	0.1	h	0.1	h	0.1	h	0.1	h	0.01	h
Coast length on each side of marina or harbor (x1, m)	809	i	908	j	543	j	836	j	348	i
Marina or harbor length (x2, m)	809	k	605	k	362	k	557	k	348	k
Marina or harbor width (y1, m)	315	k	196	k	175	k	344	k	280	k
Waterbody width beyond marina or harbor	150	Ι.	106		175		244		560	
(yz, m)	158		190	m	2.1	m	344	m	560	n
Marina depth (m)	3.2	U k	5.5	U k	5.1	0	4.9	p a	9.1	-
Average wind speed (m/s)	70	r	50	ĸ	50	к +	27	Ч	5	V
Eraction of time wind perpendicular	4	r	4	S	4	ι +	4	u	0.25	v
	0.02	h	0.02	s h	0.02	L 14/	0.0001	u h	0.35	v h
Max density difference flush (ka/m^3)	17	av	21	av	24	av	23	av	0	h
Height of submorged dam (m)	17	g,^	0	g,^	0	g,^	0	g,^	0	
Width of submerged dam (m)	70	v v	50	k	50	v v	27	0	na	-
Depth below mean sea level in harbor entrance (m)	3.2	0	3.5	0	3.1	0	4.9	р	na	_
Exchange area harbor mouth below mean sea level (m ²)	224	У	175	у	155	у	132.3	y.	na	-
Latitude (dec. deg., northern hemisphere)	47.05544	z	47.39964	z	48.0628	z	48.49235	z	48.53837	z
Cloud coverage (class 0-10)	7	аа	7	ab	7	ас	7	ас	7	ас
Suspended particulate matter conc. (mg/L)	5.28	ad	4	ad	12.15	ad	4.7	ad	4.53	ad
Particulate organic carbon conc. (mg/L)	0.26	ae	0.14	ae	0.58	ae	0.14	ae	0.10	ae
Dissolved organic carbon conc. (mg/L)	1.47	ad	1.1	ad	2.91	ad	1	ad	0.78	ad
Chlorophyll (µg/L)	12.7	af	6.77	af	9.72	af	2.68	af	2.34	af
Salinity (psu)	22.91	ad	26.78	ad	31.86	ad	30.35	ad	31.16	ad
Temperature (°C)	11.23	ad	11.32	ad	10.55	ad	10.28	ad	9.21	ad
рН	7.3	ad	7.5	ad	7.7	ad	7.6	ad	7.3	ad
Depth mixed sediment layer (m)	0.1	ag	0.1	ag	0.1	ag	0.1	ag	0.1	ag
Sediment density (kg/m ³)	304	ad	907	ad	730	ad	441	ad	703	ad
Degradation rate for organic carbon in sediment (1/day)	0	ah	0	ah	0	ah	0	ah	0	ah
Net sedimentation velocity (m/day)	9.07	ae	1.64	ae	3.95	ae	6.41	ae	11.97	ae
Fraction organic carbon in sediment	0.037	ai	0.008	ai	0.013	ai	0.021	ai	0.017	ai
Total copper, background (μg/L)	0.8	aj	0.48	aj	0.24	aj	0.33	aj	0.27	aj
Dissolved copper, background (µg/L)	0.55	ad	0.38	ad	0.21	ad	0.24	ad	0.22	ad
Initial sediment copper (µg/g, dw)	93.3	ad	33.4	ad	58.3	ad	66.5	ad	22.3	ad

Table C-1 Supplement: Data sources for Table C-1.

Code	Source
а	NOAA. https://oceanservice.noaa.gov/education/kits/tides/tides05_lunarday.html
b	NOAA. <u>https://tidesandcurrents.noaa.gov/datums.html?units=1&epoch=0&id=9446969&name=OLYMPIA%2C+BUD+INLET%2C+PUGET+SOUND&state=WA</u> . Olympia.
с	NOAA. <u>https://tidesandcurrents.noaa.gov/datums.html?units=1&epoch=0&id=9446484&name=Tacoma&state=WA</u> . Tacoma.
d	NOAA. https://tidesandcurrents.noaa.gov/datums.html?units=1&epoch=0&id=9444900&name=Port+Townsend&state=WA. Port Townsend.
e	NOAA. <u>https://tidesandcurrents.noaa.gov/datums.html?units=1&epoch=0&id=9448614&name=BOWMAN+BAY%2C+FIDALGO+ISLAND&state=WA</u> . Bowman Bay, Fidalgo Island.
f	NOAA. <u>https://tidesandcurrents.noaa.gov/datums.html?units=1&epoch=0&id=9449880&name=Friday+Harbor&state=WA</u> . Friday Harbor.
g	Derived from data reported by Hobbs et al. (2018) and isohaline curves by water density and temperature. Max. density difference tide based on mean annual inner and outer salinities.
h	Best professional judgement
i	Estimated as equal to marina or harbor length
j	Estimated as 150% of the marina or harbor length
k	Google Maps, accessed 8/24/18
I	Estimated as one-half the marina or harbor width
m	Estimated as equal to marina or harbor width
n	Estimated as twice the marina or harbor width
0	Based on navigation logs during Hobbs et al. (2018) sampling. Depths confirmed by Harbormaster.
р	Based on navigation logs during Hobbs et al. (2018) sampling.
q	Google Maps, accessed 8/24/18. Marina opening width is based on low tide. At high tide, the opening width is estimated to be 54 m.
r	Estimated from Olympia Airport wind rose
S	Estimated from Seattle Tacoma International Airport wind rose
t	Estimated from Port Angeles International Airport wind rose
u	Estimated from Burlington Skagit Airport wind rose
v	Estimated from Friday Harbor Airport wind rose
w	Based on area of parking lots that drain to marina basin per Ron Amundson (Harbormaster) and data from Western Regional Climate Center (<u>https://wrcc.dri.edu/cgi-bin/cliMAIN.pl?wa7544</u>)
х	Assumes a density of 1000 kg/m ³ for stormwater
У	Marina mouth width × marina depth
z	Hobbs et al. (2018). Data were verified using Google Maps (8/24/18).
аа	OWSC. http://www.climate.washington.edu/cloudcover/. Office of the Washington State Climatologist. Olympia Airport 1973-2000.
ab	OWSC. http://www.climate.washington.edu/cloudcover/. Office of the Washington State Climatologist. SeaTac Airport 1973-2000.
ас	OWSC. http://www.climate.washington.edu/cloudcover/. Office of the Washington State Climatologist. Whidbey Island NAS 1971-2000.
ad	Hobbs et al. (2018). Annual mean values.
ae	Derived from data reported by Hobbs et al. (2018).
af	Ecology Marine Waters group. Data provided by Skip Albertson (11/20/18).
ag	MAMPEC default value for low sedimentation environments
ah	MAMPEC User's Manual. Recommend default value for first-tier assessments.
ai	Value reported by Hobbs et al. (2018). MAMPEC uses a calculated value that may differ from the reported value.
aj	Annual mean values reported by Hobbs et al. (2018). MAMPEC calculates total copper value when dissolved copper is input, which may differ from the reported value.
na	not applicable

Chemical (Biocide) Data Input	Copper	data source	Irgarol	data source	Seanine	data source	Zinc Pyrithione	data source	Econea	data source
Compound description	Copper (example)	_	Irgarol (example)	_	Seanine (example)	-	Zinc Omadine (example)	_	Econea	-
Compound name	Copper	-	Irgarol	-	Seanine	-	Zinc- pyrithione	-	Tralopyril	-
Molecular mass (g/mol)	63.5	а	253.37	а	282	а	317.7	а	349.54	b
Saturated vapor pressure at 20°C (Pa)	0.0E+00	а	8.8E-05	а	4.5E-06	а	1.0E-06	а	1.90E-08	с
Solubility at 20C (g/m³)	0.001	а	7	а	4.7	а	6.3	а	1.60E-01	с
CAS number	_	-	_	-	_	_	_	-	122454- 29-9	b
EINECS number	-	-	-	-	-	-	-	-	-	-
Reference	-	-	-	-	-	-	-	-	-	-
Dissociation constant (Kd, m ³ /kg)	30	а	na	-	na	-	na	-	na	_
Hydrol./other abiotic rate const. (diss. water, 20°C, 1/day)	na	-	0.00E+00	а	5.00E-02	а	3.82E-02	а	1.11E+00	d
Hydrol./other abiotic half-life (diss. water, 20°C, day)	na	-	Infinity	а	1.39E+01	а	1.81E+01	а	6.25E-01	с
Hydrol./other abiotic rate const. (sediment, 20°C, 1/day)	na	-	0.00E+00	а	0.00E+00	а	8.13E+00	а	1.11E+00	d
Hydrol./other abiotic half-life (sediment, 20°C, day)	na	-	Infinity	а	Infinity	а	8.53E-02	а	6.25E-01	с
Photolysis rate constant (diss. water, 20°C, 1/day)	na	-	0.00E+00	а	0.00E+00	а	9.20E-01	а	1.87E+00	d
Photolysis half-life (diss. water, 20°C, day)	na	-	Infinity	а	Infinity	а	7.53E-01	а	3.70E-01	е
Photolysis rate constant (sediment, 20°C, 1/day)	na	-	0.00E+00	а	0.00E+00	а	0.00E+00	а	1.87E+00	d
Photolysis half-life (sediment, 20°C, day)	na	-	Infinity	а	Infinity	а	Infinity	а	3.70E-01	е
Biodegradation, aer. and anaer. rate const. (diss. water, 20°C, 1/day)	na	-	2.80E-02	а	1.65E+01	а	1.76E-01	а	7.79E-01	d
Biodegradation, aer. and anaer. half-life (diss. water, 20°C, day)	na	-	2.48E+01	а	4.20E-02	а	3.94E+00	а	8.90E-01	е
Biodegradation, aer. and anaer. rate const. (sediment, 20°C, 1/day)	na	-	2.80E-02	а	1.65E+01	а	6.30E-01	а	7.79E-01	d
Biodegradation, aer. and anaer. half-life (sediment, 20°C, day)	na	-	2.48E+01	а	4.20E-02	а	1.10E+00	а	8.90E-01	е
Octanol-water partition coefficient (Kow, 10 log Kow)	na	-	2.80E+00	а	2.85E+00	а	9.00E-01	а	4.66E+00	b
Organic carbon partition coefficient (Koc, 10 log Koc)	na	-	3.10E+00	а	4.19E+00	а	4.00E+00	а	3.32E+00	e
Henry's Constant at 20°C (Pa m³/mol)	na	-	3.19E-03	а	5.00E-09	а	5.00E-05	а	5.68E-04	b
Melting temp. (°C)	na	-	130	а	41	а	260	а	253.4	с
Acid dissociation constant (pKa)	na	-	5.16	а	14	а	0	а	7.08	с

Table C-2. Chemical data input for MAMPEC. See Table C-2 Supplement for data sources.

Table C-2 Supplement: Data sources for Table C-2.

Code	Source
а	MAMPEC default value
b	EPA. https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID6041503#properties
с	Kempen (2011)
d	Calculated by MAMPEC
е	EU Regulation No. 528/2012 (EU 2014)
na	not applicable

Table C-3 Emissions	data input for MAMPEC	See Table C-3 Sunn	lement for data sources
Table C-5. Ellissions (Jala IIIpul IOI IVIAIVIPEC	. See Table C-S Supp	iement for uata sources.

		a source	Des	a source	lohn	a source		a source	Friday	a source
Emissions Data Input	Swantown	dat	Moines	dat	Wayne	dat	Skyline	dat	Harbor	dat
Service Life Emissions									L	
Length class (m)	varies	a,b	varies	a,c	varies	a,d	varies	a,e	varies	a,f
Surface (wetted) area (m ²)	17973	a,b	15905	a,c	7133	a,d	13732	a,e	12296	a,f
No. ships at berth (per day)	597	b	656	с	264	d	478	e	395	f
No. ships moving (per day)	0	g,h	0	g,h	0	g,h	0	g,h	0	g,h
Application factor (%)	100/20	I,h,j	100/20	I,h,j	100/20	l,h,j	100/20	I,h,j	100/20	I,h,j
Leaching rate at berth (μ g/cm ² /day)	varies	k	varies	k	varies	k	varies	k	varies	k
Leaching rate while moving (µg/cm ² /day)	0	g,h	0	g,h	0	g,h	0	g,h	0	g,h
Non-Service Life Emissions –						0.	•	0.		
Maintenance & Repair										
Painting period (professional, day)	183	1	183	Ι	na	-	183	I	na	-
Painting period (nonprofessional, day)	91	I	91	I	na	-	91	I	na	-
No. days to paint one boat	1	1	1	Ι	na	-	1	I	na	-
Painting frequency per year (professional)	0	1	0	Ι	na	-	0	I	na	-
Painting frequency per year (nonprofessional)	0	1	0	Ι	na	-	0	I	na	-
No. boats treated per period (professional)	50	Ι	50	-	na	-	50	Ι	na	-
No. boats treated per period (nonprofessional)	5	1	5	Ι	na	-	5	Ι	na	-
Conc. active ingredient in paint (professional, g/L)	varies	m	varies	m	na	-	varies	m	na	-
Conc. active ingredient in paint (nonprofessional, g/L)	varies	m	varies	m	na	Ι	varies	m	na	-
Amount of paint applied per boat (professional, L)	4.5	I	4.5	Ι	na	-	4.5	I	na	-
Amount of paint applied per boat						_				_
(nonprofessional, L)	2.5		2.5		na		2.5		na	
Fraction to surface water (professional)	0	I	0	I	na	-	0	I	na	-
Fraction to surface water (nonprofessional)	0		0		na	-	0		na	-
Non-Service Life Emissions – Removal										
Removal period (professional, day)	183	I	183	I	na	-	183	I	na	-
Removal period (nonprofessional, day)	91	I	91	I	na	-	91	I	na	-
No. days to remove paint from one boat	1	I	1	I	na	-	1	I	na	-
No. boats treated per period (professional)	50	1	50	Ι	na	-	50	I	na	-
No. boats treated per period (nonprofessional)	350	I	350	Ι	na	-	350	I	na	-
Fraction paint removed by high pressure wash						_				_
(professional)	0.2	Ι	0.2	Ι	na		0.2	Ι	na	
Fraction paint removed by high pressure wash						_				_
(nonprofessional)	0.2		0.2		na		0.2		na	
Fraction paint removed by abrasion (protessional)	0.1		0.1		na	_	0.1		na	
Fraction paint removed by abrasion (nonprofessional)	0.1	1	0.1		na	_	0.1	1	na	_
Conc. active ingredient in paint (professional, g/L)	Varies	m	varies	m	na	_	varies	m	na	_
Eraction active ingredient in paint (nonprofessional, g/L)	varies	m	varies	m	na	_	varies	m	na	
removed by high pressure wash (professional)	0.05	1	0.05	1	na	-	0.05	1	na	-
Fraction active ingredient remain. in exhausted paint				-						
removed by high pressure wash (nonprofessional)	0.05	1	0.05	Т	na	-	0.05	1	na	-
Fraction active ingredient remain. in exhausted paint						1				_
removed by abrasion (professional)	0.3	I	0.3	1	na		0.3		na	
Fraction active ingredient remain. in exhausted paint	0.2		0.2		-	-	0.2		-	-
Amount of point applied per best (applied per best (0.3		0.3		na		0.3		na	\vdash
Amount of paint applied per boat (protessional)	4.5		4.5		ria	<u> </u>	4.5		na	<u> </u>
Eraction to curface water (professional)	2.5	~	2.5	~	na		2.5	~	na	<u> </u>
Fraction to surface water (professional)	0.1	<u></u> б	0.1	<u>б</u> а	na	_	0.1	<u>б</u> л	na	<u> </u>
	0.1	Б	0.1	Б	ild	ı –	0.1	б	i i d	1 -

Code	Source
а	Length classes and related wetted surface area calculations are available upon request
b	Bruce Marshall, Swantown Marina Harbormaster, verbal and written communication 12/13/18
с	Scott Wilkins, Acting City of Des Moines Marina Harbormaster, written communication 12/13/18
d	Ron Amundson, John Wayne Marina Harbormaster, written communication 11/27/18
е	Estimated using Google Maps, accessed 12/21/18
f	Tami Hayes, Friday Harbor Marina Harbormaster, written communication 11/28/18
g	Best professional judgement
h	Consistent with NZEPA
i	100% for copper, 20% for other biocides
j	Consistent with CDPR for copper
k	Range-finding to meet target water concentrations
I	Values recommended by van der Plassche & van der Aa (2004)
m	Copper – 800 g/L (metallic equiv.), Irgarol – 37 g/L, Seanine – 43 g/L, zinc pyrithione – 76 g/L, Econea – 79 g/L
na	not applicable

Table C-3 Supplement: Data sources for Table C-3.

References for Appendix C

- Kempen, T. 2011. Efficacy, chemistry and environmental fate of tralopyril, a non-metal antifouling agent. European Coatings Conference "Marine Coatings III," Berlin, 28 February 2011.
- EU [European Union]. 2014. Regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products. Evaluation of active substances. Assessment Report, Tralopyril, Product-type 21 (Antifouling Products). 14 April 2014.
- Hobbs, W., and M. McCall. 2016. Quality Assurance Project Plan: Copper, Zinc, and Lead in Five Marinas within Puget Sound. Publication No. 16-03-120. Washington State Department of Ecology, Olympia. <u>https://fortress.wa.gov/ecy/publications/SummaryPages/1603120.html</u>.
- van de Plassche, E., and E. van der Aa. 2004. Harmonisation of Environmental Emission Scenarios: An Emission Scenario Document for Antifouling Products in OECD countries (ESD PT21). Royal Haskoning, Nijmegen, the Netherlands. Available from http://ihcp.jrc.ec.europa.eu/ and MAMPEC support site. <u>https://echa.europa.eu/documents/10162/16908203/pt21_antifouling_products_en.pdf/54_a7f413-dca9-4382-b974-1eed342315f5</u>.

APPENDIX D. SENSITIVITY TESTS FOR MAMPEC

Environmental Inputs – Des Moines I	Marina	Сорр	ver	Zinc Py	rithione	Ecor	Econea	
Parameter	Original Value	x 0.5	x 2	x 0.5	x 2	x 0.5	x 2	
Max. density difference tide (kg/m ³)	0.1	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Flow velocity (F, m/s)	0.1	1.0%	-1.3%	0.7%	-0.9%	0.0%	-0.6%	
Coast length on each side of marina or harbor (x1, m)	908	0.0%	*	0.0%	*	0.0%	*	
Waterbody width beyond marina or harbor (y2, m)	196	+	0.3%	+	0.0%	+	0.0%	
Marina depth (m)	3.5	3.5%	-1.9%	48.3%	-38.3%	70.6%	-43.9%	
Marina mouth width (x3, m)	50	7.1%	-13.9%	3.0%	-7.2%	1.2%	-4.1%	
Average wind speed (m/s)	4	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Fraction of time wind perpendicular	0.02	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Flush (m ³ /s)	0.01	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Max. density difference flush (kg/m ³)	21	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Width of submerged dam (m)	50	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Depth below mean sea level in harbor entrance (m)	3.5	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Cloud coverage (class 0–10)	7**	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Suspended particulate matter conc. (mg/L)	4	9.4%	-14.5%	0.0%	0.0%	0.0%	0.0%	
Particulate organic carbon conc. (mg/L)	0.14	0.0%	0.0%	0.2%	-0.4%	0.0%	0.0%	
Dissolved organic carbon conc. (mg/L)	1.1	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Chlorophyll (µg/L)	6.77	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Salinity (psu)	26.78	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Temperature (°C)	11.32	0.0%	0.0%	2.4%	-7.8%	10.0%	-24.7%	
pH	7.5	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Depth mixed sediment layer (m)	0.1	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Sediment density (kg/m ³)	907	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Net sedimentation velocity (m/day)	1.64	3.9%	-6.8%	0.0%	0.0%	0.0%	0.0%	
Dissolved copper, background (µg/L)	0.38	-5.8%	11.6%	na	na	na	na	
Initial sediment copper (μg/g, dw)	33.4	0.0%	0.0%	na	na	na	na	
Emissions – Des Moines Marina								
Application factor (%)	100/20‡	-44.2%	§	-50.0%	100.0%	-50.1%	99.4%	
Leaching rate (µg/cm²/day)	Varies [#]	-44.2%	88.7%	-50.0%	100.0%	-50.1%	99.4%	
Indicates change of 10/ 100/								

Table D-1. Changes to target water concentrations predicted by MAMPEC in a marina scenario using decreased (×0.5) or increased (×2) parameter inputs.

Indicates change of 1% – 10%

Indicates change of 10% – 50%

Indicates change of >50%

* Original value at maximum recommended by MAMPEC

⁺ Original value at minimum recommended by MAMPEC

** Maximum cloud coverage category is 10

‡ Original application factor 100% for copper, 20% for other compounds

§ Original value is maximum possible (100%)

Leaching rate = 6.47 for copper, 1.175 for zinc pyrithione, 0.090 for Econea

na = not applicable

Environmental Inputs – Friday Harbor M		1	Copper			Zinc Pyr	ithione	Econea		
Parameter	Original Value		x0.5	x2		x0.5	x2	x0.5	x2	
Max. density difference tide (kg/m ³)	0.05		na	na		na	na	na	na	
Flow velocity (F, m/s)	0.01		82.6%	-44.8%		66.7%	-44.6%	42.4%	-37.6%	
Coast length on each side of marina or harbor (x1, m)	348		-2.3%	*		-2.2%	*	-0.6%	*	
Waterbody width beyond marina or harbor (γ 2, m)	560		-10.0%	-7.7%		-10.7%	-8.5%	-10.0%	-8.2%	
Marina depth (m)	9.1		87.7%	-45.8%		99.8%	-50.0%	100.6%	-49.9%	
Marina mouth width (x3, m)	na		na	na		na	na	na	na	
Average wind speed (m/s)	5		2.3%	-10.6%		2.2%	-10.9%	2.4%	-9.4%	
Fraction of time wind perpendicular	0.35		1.9%	-3.2%		1.7%	-3.3%	1.8%	-2.4%	
Flush (m³/s)	0		na	na		na	na	na	na	
Max. density difference flush (kg/m ³)	0		na	na		na	na	na	na	
Width of submerged dam (m)	na		na	na		na	na	na	na	
Depth below mean sea level in harbor entrance (m)	9.1		na	na		na	na	na	na	
Cloud coverage (class 0-10)	7†		0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	
Suspended particulate matter conc. (mg/L)	4.53		7.7%	-12.9%		0.0%	0.0%	0.0%	0.0%	
Particulate organic carbon conc. (mg/L)	0.10		0.0%	0.0%		0.0%	-0.2%	0.0%	0.0%	
Dissolved organic carbon conc. (mg/L)	0.78		0.0%	0.0%		-0.2%	0.0%	0.0%	0.0%	
Chlorophyll (µg/l)	2.34		0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	
Salinity (psu)	31.16		0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	
Temperature (°C)	9.21		0.0%	0.0%		0.4%	-1.5%	3.5%	-8.8%	
рН	7.3		0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	
Depth mixed sediment layer (m)	0.1		0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	
Sediment density (kg/m ³)	703		0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	
Net sedimentation velocity (m/day)	11.97		1.6%	-3.2%		0.0%	-0.2%	0.0%	0.0%	
Dissolved copper, background (µg/L)	0.22		-3.2%	6.5%		na	na	na	na	
Initial sediment copper (µg/g, dw)	22.3		0.0%	0.0%		na	na	na	na	
Emissions - Friday Harbor Marina										
Application factor (%)	100/20‡		-46.8%	**		-50.0%	99.8%	-49.9%	100.6%	
Leaching rate (µg/cm²/d)	Varies [#]		-46.8%	93.5%		-50.0%	99.8%	-49.9%	100.6%	

Table D-2. Chang	es to target water co	oncentrations predicted	by MAMPEC in an open	harbor scenario
using decreased (×0.5) or increased (×2) parameter inputs.		

Indicates change of 1% – 10%

Indicates change of 10% – 50%

Indicates change of >50%

* Original value at maximum recommended by MAMPEC

+ Maximum cloud coverage category is 10

‡ Original application factor 100% for copper, 20% for other compounds

** Original value is maximum possible (100%)

Leaching rate = 100.3 for copper, 8.08 for zinc pyrithione, 0.385 for Econea na=not applicable