DEPARTMENT OF ECOLOGY
State of Washington

Report to the Legislature on Non-copper Antifouling Paints for Recreational Vessels in Washington

December 2017
Publication 17-04-039

Publication and Contact Information

This report is available on the Department of Ecology website at
https://fortress.wa.gov/ecy/publications/SummaryPages/1704039.html

For more information contact:

Publications Coordinator
Hazardous Waste & Toxics Reduction Program
P.O. Box 47600
Olympia, WA 98504-7600

E-mail: hwtrpubs@ecy.wa.gov
Phone: 360-407-6700

Washington State Department of Ecology - www.ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Accommodation Requests:

To request ADA accommodation including materials in a format for the visually impaired, call Ecology at 360-407-6700 or visit https://ecology.wa.gov/accessibility. People with impaired hearing may call Washington Relay Service at 711. People with speech disability may call TTY at 877-833-6341.

Report to the Legislature on Non-copper Antifouling Paints for Recreational Vessels in Washington

by
Brian Penttila

Hazardous Waste and Toxics Reduction Program
Washington State Department of Ecology
Olympia, Washington

This page intentionally left blank.

Table of Contents

List of Tables

List of Figures

Executive Summary

Antifouling paints help prevent the growth and attachment of marine plants and organisms on boats moored in water. In recent decades, the active ingredient in most of these paints has been copper. These paints continually release copper, which can build up in and near marina waters and harm marine animals and plants. Copper is the basis for a number of antifouling biocide additives, but there are several other biocides available in Washington. All of these biocides destroy or inhibit the growth or activity of some marine organisms.

Copper Boat Paint Ban Scheduled for 2020

In 2011, the Washington State Legislature passed the Recreational Water Vessels – Antifouling Paints Law, Revised Code of Washington (RCW) Chapter 70.300, to phase out the use of copper-based antifouling paints on recreational boats.

In the first phase, effective January 1, 2018:

- New recreational boats may not be sold with copper-based antifouling paints.

The second phase, effective January 1, 2020:

- Bans the sale of antifouling paints for recreational boats if they contain more than 0.5 percent copper.

Banning copper in antifouling paints eliminates one source of boatyard stormwater contamination.

The law directed the Department of Ecology to survey the types of antifouling paints sold in Washington, study how antifouling paints affect marine life, and report our findings to the Legislature by December 31, 2017. This report fulfills that directive.

Potential Hazards of Non-copper and Non-Biocidal Antifouling Paints

We identified 30 non-copper biocidal antifouling paints registered for use in Washington. These paints include six types, each containing either one non-copper biocide or a combination of two non-copper biocides.

Studies in other countries show that several of the biocides may pose a significant risk to marine life and water quality, especially in and around recreational boat marinas. Much of the adverse data on these alternative biocides are based on modeling results that do not exactly match the conditions found in Washington waters.

Several non-biocidal paints are also available. Because they do not include a biocide, they are widely believed to be safer for the marine environment, but there are potential hazards to using these paints. There has not been much study of their impact on marine life. Additional aquatic toxicity testing is needed to determine if the non-biocidal antifouling paints might have harmful effects on marine life.

Ecology Proposes Delaying Copper Boat Paint Ban

Our review of recent studies and available science on non-copper antifouling boat paints raises significant concerns that, in trying to move away from a known toxic chemical, we are pushing the boating industry toward regrettable substitutes that could worsen environmental degradation in state marinas. We recommend delaying the copper boat paint ban, giving us time to study the relative impacts of copper versus non-copper biocides, using models based on Puget Sound marina designs and water quality conditions.

Introducing a leach rate limit could reduce the amount of copper pollution from antifouling paints. The state of California recently applied such a limit on paints used on recreational vessels. The U.S. Environmental Protection Agency has also proposed a similar approach.

Any approach that restricts copper must also consider restricting non-copper biocides, which may pose their own risks.

If the ban on copper antifouling paint proceeds as directed under current law, we conclude that additional monitoring and testing will be needed to investigate the impacts of non-copper biocides. Based on the findings of further research, regulatory or legislative action may be needed to address any emerging concerns.

Background

Review of Chapter 70.300 RCW

Antifouling paints help prevent the growth of marine plants on boats moored in the water. They also limit the attachment and growth of marine animals such as barnacles. The most commonly used antifouling paints contain large quantities of copper-based biocides. Leaching from painted boat hulls is a major source of copper both in water and in sediment near marinas and boatyards (Schiff et al., 2004). The effects of copper extend into the nearby marine environment, where they can harm aquatic plants, animals, and fish.

In 2011, the Washington State Legislature passed the Recreational Water Vessels – Antifouling Paints Law, Revised Code of Washington (RCW) Chapter 70.300 to address the impacts from using copper-based antifouling paints on recreational water vessels.

Chapter 70.300 RCW has two main provisions:

- After January 1, 2018, new recreational water vessels with antifouling paint containing copper may not be sold in the state.
- Beginning January 1, 2020, all antifouling paints containing more than 0.5 percent copper will be prohibited from being sold or applied to recreational water vessels.

A recreational water vessel is defined as a vessel that is less than 65 feet in length, and used primarily for pleasure, or leased, rented, or chartered to a person for pleasure. Commercial vessels are not affected by the law.

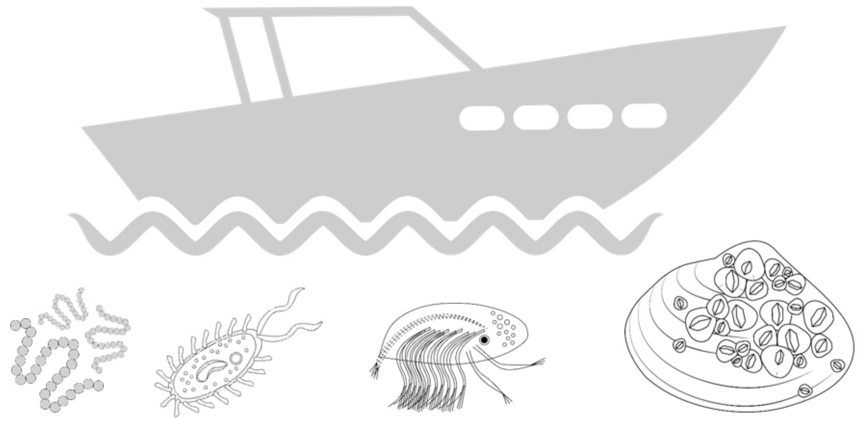
RCW 70.300.050(2)(a) requires that Ecology "…determine the types of antifouling paints that are available in this state. The department shall also study how antifouling paints affect marine organisms and water quality. The department shall report its findings to the legislature … by December 31, 2017."

Antifouling Boat Paints

Why are antifouling paints needed?

Any structure immersed in water will immediately attract marine organisms looking for a stable place to live and feed. This colonization starts with the smallest life forms, like bacteria or algae. These microorganisms produce a slimy, living film (Figure 1). Over time, larger species such as mollusks, tube worms, and barnacles attach and grow. This living layer that coats underwater structures is called *marine fouling* and affects not only fixed structures such as seawalls and pilings, but also ships and boats of all kinds (Johnson & Gonzalez, 2004).

Marine fouling increases the roughness of boat hulls. This can then increase the drag, causing increased fuel consumption for power boats, and reduced maximum speed or maneuverability of sailboats. Over time, fouling organisms can damage the hull coating or the underlying hull. In fresh water, fouling is mostly an esthetic concern and antifouling paints are generally not needed.



Seconds	Hours	Days	Weeks
Biomolecules	Bacteria	Larvae	Invertebrates

Figure 1. It takes just a few minutes for the smallest marine organisms to attach to a surface in the sea. Within a few weeks, larger organisms such as mollusks have begun to attach.

How do antifouling paints work?

There are two classes of antifouling paints: biocidal and non-biocidal.

Biocidal paints

Biocidal paints continuously release a toxic substance into the water near the boat hull surface. This toxic boundary layer discourages the approach and attachment of fouling organisms. Biocidal paints do not completely eliminate fouling, but they can reduce how fast it builds up over time.

There are many types of fouling organisms, and no single biocide works well on all of them. For example, copper works on most problem organisms, but does not work well against many aquatic plants. Use of a second *booster biocide* can increase overall effectiveness, allowing reductions in the main biocide, and reduce overall cost (Ranke & Jastorff, 2000).

Non-biocidal paints

These are a bit more complicated. There are two main types of non-biocidal antifouling paints:

- **Soft non-biocidal**: Paints that create a slippery surface designed to make it hard for marine life to stick. The underlying coating may also be flexible, which causes organisms to peel off when the boat is in motion. Self-cleaning is a valued attribute of non-biocidal paints, but it doesn’t eliminate all fouling (Bressy & Lejars, 2014).
- **Hard non-biocidal**: Paints designed to endure frequent, aggressive cleaning (Madsen et al., 2000). These are often epoxies and may contain ceramic or glass for toughness.

Why are copper-based antifouling paints a problem?

Copper, in the form of cuprous oxide, is the most widely used antifouling biocide for recreational boats. Copper-based paints typically contain about 40 percent cuprous oxide, but the content can be as high as 76 percent in Washington State.[1] Painted boat hulls continuously release copper into marina waters. When large numbers of boats are berthed together, the copper level in the local water rises. Studies have attributed over 90 percent of this copper to leaching from copper-based paints (California RWQCB, 2005; Schiff et al., 2004).

Impacts of copper on water quality

To protect aquatic life, the state established maximum levels (concentrations) for certain pollutants for both short-term (acute) and long-term (chronic) periods in Washington's surface waters. These water quality standards were established in Chapter 173-201A Washington Administrative Code (WAC).

For dissolved copper in marine waters, the state's maximum allowable levels are:

- Acute limit: 4.8 micrograms per liter
- Chronic limit: 3.1 micrograms per liter

These concentration limits are generally known as water quality criteria.

Effects of copper toxicity on the marine environment and aquatic life

Copper is most toxic to the early life stages of mussels, oysters, and sea urchins. It can build up (bioaccumulate) in algae, plankton, and crustaceans (Ranke & Jastorff, 2000; Thomas & Brooks, 2010). Copper in the water column can attach to particle matter and settle into sediment, where bottom-feeding organisms can absorb or ingest it. These same organisms, through their normal movement and activity, resuspend sediment copper, causing recurring exposure to marine plants and animals (Fetters et al., 2016; Roberts, 2012). When copper binds to sediment or water particles, it can be inactivated, but the nature of this effect in seawater is a topic of ongoing research beyond the scope of this report.

Copper does not bioaccumulate in fish, as they are able to regulate the level of copper in their systems. However, it can affect the sense of smell (olfaction) in juvenile salmon returning to freshwater spawning streams, which can affect their ability to avoid predators.

Salmon somehow detect and avoid water with levels as low as 17 micrograms per liter of copper, but the overall impact of this on salmon fitness or survival is not known (Sommers et al., 2016). The levels at which these effects have been observed are far above copper levels measured in Puget Sound recreational marina waters (Washington State Department of Ecology, 2017).

In salt water, other dissolved substances can help protect against this effect on olfaction up to at least 50 micrograms per liter of dissolved copper (Baldwin, 2015). Further details on the effects of copper are available in recent reviews and pesticide registration summaries (Arai et al., 2009; Dafforn et al., 2011).

Water quality at marinas

Marinas are more likely to exceed copper water quality criteria if they have:

---

[1] There are 123 antifouling paints containing some form of copper registered for use in Washington State. The paint survey results beginning on page seven (Non-copper Paints Available in Washington State) identify the five types of copper-based biocides.

1. High boat occupancy, and
2. Restricted water flows.

Breakwaters, used to provide protection from wakes and wind-driven waves, can reduce the normal tide-driven flow of marina waters. A marina with a single entrance won't flow as well as a marina with multiple entrances (Washington State Department of Ecology, 2007).

Achieving copper limits at marinas

As shown in Figure 2, preliminary results from a study underway at Ecology shows copper levels in water across multiple marinas in the Puget Sound were significantly higher inside marinas compared to outside (Washington State Department of Ecology, 2017).

In addition, copper levels were significantly higher in more protected marinas when Ecology sampled suspended sediment, sediments deposited on the bottom of marinas, and algae growing in these marinas.

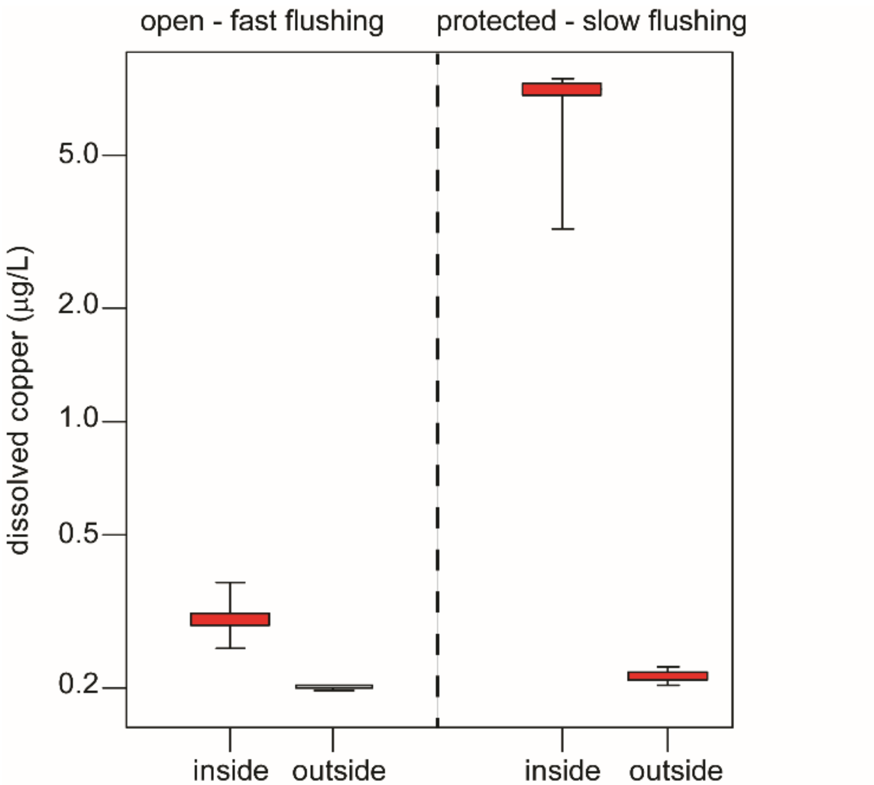


Figure 2. Dissolved copper in water during September 2016. Left panel is an open, fast flushing marina; the right panel is a protected, slow flushing marina. Results are the averages and ranges of copper from multiple samples inside and outside the marinas.

Copper levels in marina waters will vary with the season as boating activity varies (see Figure 3). Generally, waters near marinas are the most biologically active in the spring and summer, which is when boating activity is the highest. Regardless of the time of year, copper levels are consistently greater inside a marina compared to outside the marina.

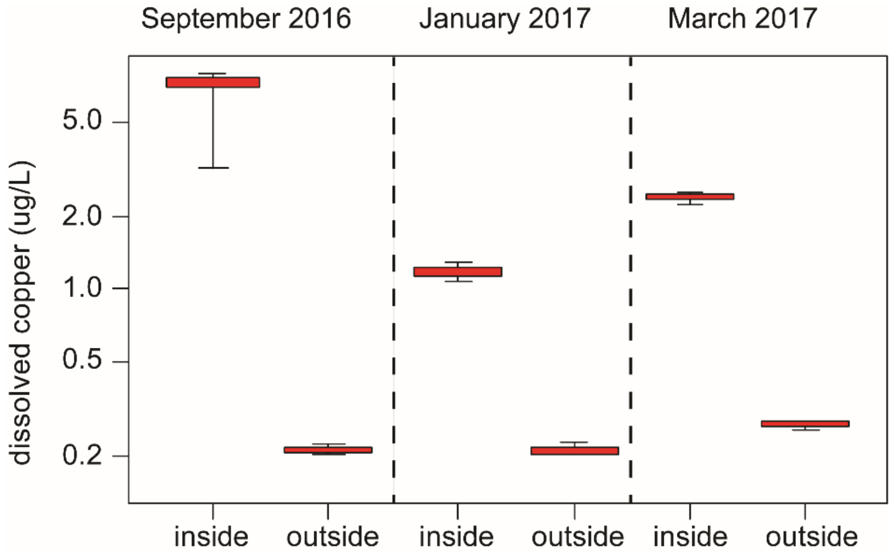


Figure 3. Copper levels in marinas vary throughout the year. This data, from one protected marina, shows higher levels during times of greater boating activity. Levels inside the marina are consistently higher than outside.

Other events that drive copper levels up:

- Accidental releases
- Runoff from pressure-washing boats
- Illegal in-water cleaning
- Paint particles that collect in sediment

Runoff from pressure-washing boats, which can be high in copper, should be properly treated and disposed. Paint particles that collect in sediment are an ongoing source of copper (Earley et al., 2014; Turner et al., 2009).

Non-copper Paints Available in Washington State

Biocidal paints

How was the survey of paints done?

Biocidal paints must be registered with the U.S. Environmental Protection Agency (USEPA) and the Washington State Department of Agriculture (WSDA). WSDA staff review labels and documents from manufacturers for compliance with state law. Selected data are stored in the Pesticide Information Center Online (PICOL) Database (Washington State University, 2017).

We identified 153 biocidal antifouling paints in the PICOL database. Both manufacturer and "store brand" labels may be used for the same paints, so the true number of products is likely fewer. To retrieve the full list of products and their associated biocide concentrations from the PICOL database, see the Appendix for instructions.

There are 11 biocides registered for use in antifouling paints in Washington State (Table 1), including several copper-based biocides. Out of the 153 paints in the PICOL database, 123 products contained one or more copper-based biocides. About 90 paints were based on copper alone, mostly in the form of cuprous oxide. Silver and zinc occurred in only one product in combination with cuprous oxide. Since silver and zinc are not approved for use in biocidal antifouling paints in New Zealand or the European Union, there were no comparable data available for these biocides for this review. They are not considered further.

None of these copper-containing paints meet the 0.5 percent copper maximum limit described in RCW 70.300.020. Therefore, they would all be subject to the law's 2020 ban on use and sale.

Table 1. Biocides registered for use in antifouling paints in Washington State.

Pestidice Active Ingredient[2]	PC Code[3]	Target Organisms[4]
Copper (flakes or powder)	22501	Broad effect, some algae resistant
Copper pyrithione (Copper Omadine)[5]	88001	Algae, marine plants
Copper thiocyanate	25602	Broad effect, some algae resistant
Cupric Oxide, Copper(II) Oxide	42401	Broad effect, some algae resistant
Cuprous Oxide, Copper(I) Oxide	25601	Broad effect, some algae resistant
Tralopyril (Econea)	119093	Molluscs
Cybutryne (Irgarol 1051)	128996	Algae, marine plants
DCOIT (Sea-Nine 211)	128101	Broad effect
Silver	72501	Slime (microorganisms)
Zinc	129015	Algae, marine plants
Zinc pyrithione (Zinc Omadine)	88002	Algae, marine plants

What non-copper biocidal antifouling paints are available?

There are 30 non-copper biocidal paints registered for use in Washington State (Table 2). These included six different types of products. Four types contain only one biocide, but two types contain a combination of two biocides. Most of the paints contained Zinc Pyrithione alone or in combination with Tralopyril.

Table 1 briefly lists the organisms controlled by the individual biocides. The mechanism, or way it controls organisms, is different for each biocide (European Chemicals Agency, 2017a):

- **Copper-based biocides**: Copper ions release into the surrounding water. These ions slow organisms from settling on the hull surface. Copper ions interfere with some enzyme and protein functions in living systems
- **Tralopyril (Econea)**: Disrupts energy systems at the cellular level.
- **Cybutryne (Irgarol)**: Interferes with photosynthesis in algae and plants. This leads to decreased nutrient production and inhibits growth.
- **DCOIT**: Reacts with proteins and inhibits processes that organisms use to attach to surfaces.
- **Silver**: Interacts with and deactivates certain enzymes. It is particularly effective against bacteria.
- **Zinc pyrithione**: Zinc is released from zinc pyrithione in water and interferes with some enzyme functions. It is thought to disrupt the membranes of cells, which makes it an effective algaecide and fungicide.

---

[2] Common names appear in parentheses. The Appendix identifies the database name for each biocide.
[3] USEPA assigns a PC Code (pesticide chemical code) for each unique pesticide or pesticide combination.
[4] Based on European Union biocide approval documents (European Chemicals Agency, 2017b).
[5] Restricted to boats larger than 25 meters (81 feet).

Table 2. Types of non-copper biocidal paint products registered in Washington State. A count of the registered products appears in the first column. The percentage of active ingredient varies among the products in each group.

Number of Registered Paint Products	Biocidal Active Ingredient(s) in the Paint
4	Cybutryne (Irgarol 1051)
12	Zinc Pyrithione and Tralopyril (Econea)
10	Zinc Pyrithione
1	Tralopyril (Econea)
2	DCOIT (Sea-Nine 211)
1	DCOIT (Sea-Nine 211) and Tralopyril (Econea)

Impacts of biocidal paints on water quality and marine organisms

For biocidal paints, we assume that the active ingredients will be the primary source of any environmental impact during use. This report does not evaluate individual paints, but potential concerns can be inferred from the biocide type and concentration.

The ideal biocide has:

- A short lifetime in the environment (low persistence).
- Low potential to build-up in the food chain (low bioaccumulation).
- Low toxicity to non-target species, *i.e.*, nonfouling plants, oysters, and fish.

Antifouling paints contain a variety of chemicals with different purposes. Components such as solvents and polymers are not expected to impact marine life during boat use because they evaporate and disappear, or they are converted to plastic-like coating materials that are too large to enter living cells.

Biocides prevent fouling because of their toxicity, but we want that toxicity to diminish over time and distance away from the boat hull.

Persistence

Once released to seawater, biocides begin to break down by various mechanisms. These include:

- **Photolysis**: Breakdown by ultraviolet light from the sun.
- **Hydrolysis**: Breakdown by chemical reactions in water.
- **Biodegradation**: Breakdown by microbes or other life that consume and transform the biocide.

These mechanisms often operate in parallel, but there is usually a dominant mechanism.

Pesticide registration requires data on how quickly biocide chemicals break down, usually reported as a half-life value. Half-life is the amount of time it takes to remove one-half of the original amount of biocide in the water. A short half-life means that the biocide will break down quickly. Washington State's PBT Rule, Chapter 173-333 WAC states that a chemical is persistent if its half-life in water is greater than or equal to 60 days.

Marine life can also be harmed by the by-products of biocide breakdown, called degradates. Degradates may be more toxic, more bioaccumulative, and more persistent than the parent biocide.

Bioaccumulation

Fatty tissues attract many organic chemicals. Marine plants and animals can absorb organic biocides from eating contaminated food and from the water they live in. These organic biocides are then stored in body fat or lipids. When chemicals are absorbed from water it is called bioconcentration. A buildup of stored chemicals over time from either ingestion or absorption is called bioaccumulation.

Chemical levels can increase as you go up the food chain, from plants to insects to fish, and this can lead to increasingly harmful effects. Metals do not bioaccumulate in the same way as organic chemicals, but they do build up in some marine life.

Bioaccumulation is usually assessed using a bioaccumulation factor (BAF) or bioconcentration factor (BCF). Washington State's PBT Rule, Chapter 173-333 WAC, states that a chemical has high potential to bioaccumulate if the BAF or BCF is greater than 1,000. We use this standard to classify the bioaccumulation potential of biocides.

Toxicity

While a biocide might be used to target certain organisms, such as marine plants, most of them are also toxic to other types of marine life. Toxicity to some common species is discussed below.

Regulators usually combine data for many species, and for different life stages (e.g., juvenile vs. adult), to determine acceptable water and sediment concentrations. These water quality and sediment criteria are used for regulatory purposes in Washington State. The non-copper biocides addressed in this report do not have established water quality criteria since they are not yet common in the marketplace.

Marina Risk Assessments

To protect boats, marinas provide a small, sheltered area with docks. Water does not flow as freely in and out of a marina as it does in other areas of Puget Sound, so biocides can build up in marina waters. To understand biocide impacts, we need to know the levels of the biocide in marina waters. Regulators use models to predict these levels.

A computer-based marina model is used to calculate a predicted environmental concentration (PEC). This is the average level a biocide is expected to build up over time in marina waters. Marina antifouling models consider characteristics of the paint, the size and occupancy of the marina, and the local water conditions. Paint variables include the concentration of biocide and the biocide release (leach) rate. A "typical" marina has a fixed physical size, number of boats, and the boats have a predetermined painted area. Water temperature, tide levels, and other factors are also included (Van De Plassche & Van Der Aa, 2004).

First, a "safe" concentration, called the predicted no-effect concentration (PNEC) is established for each biocide. This is similar to a water quality criterion, but is usually determined by toxicity to the most sensitive species in the marine environment. Calculations for the PNEC also include adjustment factors that address the quality of the data set. PNECs are designed to be conservative.

If the model results show the predicted concentration is above the “safe” concentration, harmful effects on aquatic life in the marina are expected. If high biocide concentrations reach waters outside the marina, the concern is more serious. While models aren’t perfect, research has shown that the predictions are reasonable and should provide fair comparisons among different biocides (Gadd & Cameron, 2012).

Results for Non-copper Biocidal Paints

PBT Properties

Persistence

WSDA pesticide registrations identify four non-copper biocides:

- DCOIT (Sea-Nine 211)
- Cybutryne (Irgarol 1051)
- Tralopyril (Econea)
- Zinc Pyrithione

To assess persistence, we reviewed data from European Union biocide evaluations to identify the most likely (dominant) breakdown mechanism (European Chemicals Agency, 2017a). The half-life[6] for the dominant breakdown mechanism is reported in Table 3. Any information provided on biocide breakdown products is noted in the “Degradates” column.

Table 3. Approximate half-life for each biocide in seawater. A shorter half-life means faster breakdown in water.

Biocide	Half-Life (days)	Dominant Breakdown Mechanism	Degradates
Cybutryne (Irgarol)	Infinite	Biological breakdown	Likely to be persistent and toxic
DCOIT (Sea-Nine)	<1	Biological breakdown	Not persistent; less toxic
Tralopyril (Econea)	<1	Photolysis/Hydrolysis	Possibly persistent; less toxic
Zinc Pyrithione[7]	<3-4	Photolysis/ Biological breakdown	Zinc is persistent and toxic, but pyrithione degradates are not.

Cybutryne is expected to persist in seawater for a very long time. While the half-life is listed as “infinite,” this is due to the difficulty measuring breakdown when the half-life extends into hundreds of days. Breakdown products are also expected to be long-lived and toxic. DCOIT and Tralopyril break down relatively quickly and there are no indications that their degradates are long-lived or very toxic.

Zinc pyrithione is an organic metal compound. Zinc can separate from the pyrithione portion in water. Pyrithione rapidly degrades by exposure to sunlight, in as quickly as a few hours, but this effect decreases with depth and depends on the overall water quality. In the absence of light, biological breakdown is more important and pyrithione degrades within a few days.

---

[6] In some cases, we used data from die-away studies, where biocide is added to seawater and the loss measured over time. This die-away time is roughly equivalent to a half-life, but reflects all of the mechanisms of breakdown operating in parallel.

[7] The half-life for zinc pyrithione is based on the pyrithione data contained in the EU assessment of Copper Pyrithione. Zinc and other elements like copper do not degrade and are persistent.

Zinc, like copper, is a metal and doesn't break down. Over time, metals from biocides and other sources accumulate, adversely affect sediment quality, and harm marine life. This is also a concern for persistent biocides like cybutryne.

Bioaccumulation Potential

As noted above, bioaccumulation potential is based on BAF or BCF factors reported in EU biocide assessments (European Chemicals Agency, 2017a). Following Washington State PBT criteria, BAF or BCF values above 1,000 were identified as "High" in Table 4. Results were otherwise shown as "Low." A "–" indicates that no data was available.

Table 4. Bioaccumulation potential for biocides in marine organisms. Data was not available for all cases.

Biocide	Potential to Bioaccumulate (for select members of each aquatic life group)		
	Plants	Invertebrates	Fish
Cybutryne (Irgarol)	High	Low	Low
DCOIT (Sea-Nine)	–	–	Low
Tralopyril (Econea)	–	–	Low
Zinc Pyrithione[8]	–	pyrithione - Low	pyrithione - Low

DCOIT and tralopyril break down rapidly in seawater, so while there is limited data on bioaccumulation, they are not expected to build up in marine plants or animals. Pyrithione shows very low values for bioaccumulation in oysters and fish.

Zinc bioaccumulates in some marine organisms, but the results for bioaccumulation are highly variable by species (Cardwell et al., 2013). Zinc is an essential mineral, so most organisms need zinc to survive and have developed special ways to move it in and out of tissues to prevent harmful accumulation.

Toxicity

Biocides are toxic to many species, even non-fouling organisms like the Eastern oyster (Table 5). Products often contain multiple biocides so that one biocide's strengths complement another biocide's weaknesses. However, "biocide boosters" like cybutryne or zinc pyrithione, designed to target plants, also affect marine animals.

Table 5. Data on toxicity of each biocide on marine species (USEPA, 2017).

Lower values indicate higher toxicity. All figures are parts per billion (ppb).[9]

Organism[10] \ Biocide	DCOIT (Sea-Nine)	Cybutryne (Irgarol)	Tralopyril (Econea)	Zinc Pyrithione
Marine plant, EC50	18	0.452	2.7	0.65
Marine shrimp lifecycle, LOEC	1.224	260	0.51	4.2
Marine shrimp, LC50	4.7	400	0.98	4.7
Eastern oyster, EC50	9.4	3200	0.64	22

[8] The half-life for zinc pyrithione is based on the pyrithione structure data in the EU assessment of copper pyrithione. Zinc and copper are persistent and do not degrade.

[9] LC50 (lethal concentration) refers to concentrations that are lethal for 50 percent of organisms. EC50 (effective concentration) refers to non-lethal effects that occur in 50 percent of organisms. The LOEC (lowest observed effect concentration) is based on non-lethal adverse effects, such as reproduction (in this case for shrimp).

[10] The marine plant is a diatom: *Skeletonema costatum*; the marine shrimp is *Americamysis bahia*; the oyster is *Crassostrea virginica*.

The predicted no-effect concentration, used in the marina risk assessments below, considers a wider range of toxicity data for each biocide. This toxicity evaluation together with exposure determines the impact of antifouling paint use on the marine environment.

Marina Modeling Results for Non-copper Biocidal Paints

Estimates for biocide concentration in marina waters are based on well-established marina models. Results reported here are based on publications from two regulatory authorities:

- New Zealand Environmental Protection Agency's re-evaluation of antifouling biocides from 2012 (New Zealand EPA, 2012).
- European Union (EU) Biocidal Products Commission evaluations from 2012-2016 (European Chemicals Agency, 2017a).

Each set of assessments provides estimates for different "scenarios," involving selected marina designs and boat types with calculations for each biocide.

Table 6 shows results from the New Zealand assessment. The scenario considers average marina concentrations calculated for an average recreational marina. The biocide leach rate is set to an average of measured values (or estimated when measurements are not available). Note that each biocide is evaluated independently, so the values shown in the table assume that only one biocide is used at a time in the marina.

Different use assumptions are applied for copper than for the other biocides. The copper line item assumes that 100 percent of boats in the model marina use antifouling paint and that no other biocides are used. For the other biocide line items, it is assumed that only 20 percent of boats use a single biocidal paint and that no other biocides are used. This simulates a low-level use of the alternatives as the market transitions to non-copper biocidal paints. In a real marina, the overall risk would need to consider the simultaneous use of multiple biocides, but this is beyond the capability of the current modeling tools.

Marina concentrations are shown in the "Estimated Level" column of Table 6. The "Safe Level" is estimated from toxicity data (the predicted no-effect concentration discussed earlier), not from model calculations. The quotient of these two values gives a measure of risk:

$$Risk = \ Estimated\ Level/Safe\ Level$$

A "Risk" value greater than 1.0 indicates potential concern. Risk values less than 1.0 indicates that the estimated concentrations are likely to be safe. Risk values (or quotients) are shown in Table 6 and plotted in Figure 4.

Table 6. Recreational marina modeling results from the New Zealand assessment. Estimated Level and Safe Level are concentrations in units of micrograms per liter. A risk greater than 1 receives a "No" in the "Safe?" column. These calculations assume that only one biocide is used at a time in the model marina.

Biocide[11]	Estimated Level	Safe Level	Risk	Safe?	Source
DCOIT	0.0263	0.0068	3.87	No	New Zealand
Cybutryne/Irgarol	0.0915	0.0058	15.8	No	New Zealand
Zinc Pyrithione	0.0761	0.046	1.65	No	New Zealand
Copper	1.73	2.6	0.66	Yes	New Zealand

[11] The New Zealand assessment identifies cybutryne as Irgarol, and DCOIT as Sea-Nine.

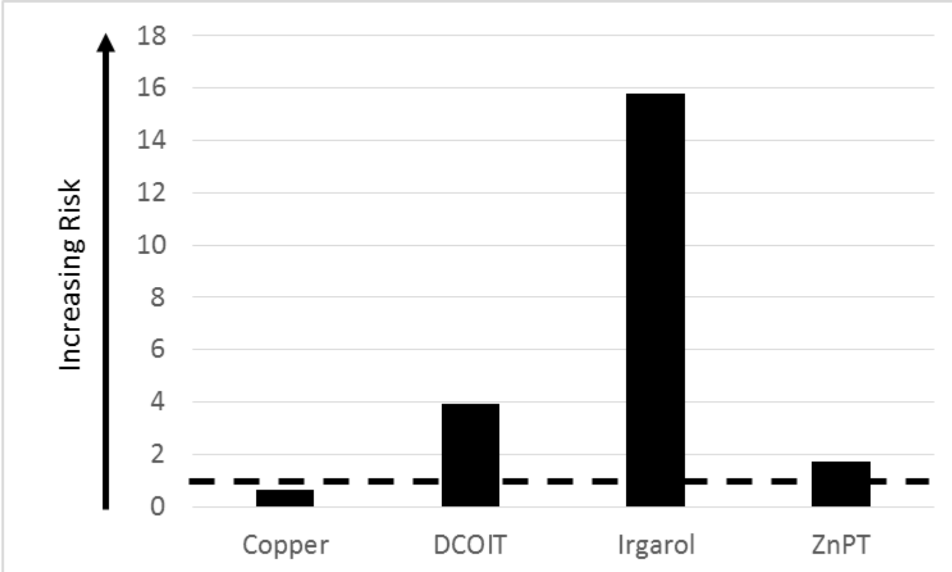


Figure 4. Estimates of risk for the New Zealand average marina scenario.

The dashed line in Figure 4 indicates a "safe" level of risk. DCOIT and Irgarol far exceed safe levels in these calculations.

EU biocide approvals are based on risk calculations similar to the marina modeling results described above. Approval requires additional data and studies, including sediment impacts (which are not reviewed here) (European Chemicals Agency, 2017b). Three of the four non-copper biocides registered in Washington State cannot be used on recreational boats in the EU:

- **Cybutryne (Irgarol):** Denied registration for any antifouling use as the evaluation process determined its use posed "unacceptable risks to marine waters and sediment organisms..."
- **Tralopyril and DCOIT**: Evaluated as safe for use on boats in shipping lanes and outside commercial harbors (areas with high dilution), but risks were identified for waters inside commercial and smaller vessel harbors. Tralopyril and DCOIT are not approved for use on boats less than 81 feet long. In other words, no use would be allowed on the recreational vessels addressed in Chapter 70.300 RCW, which defines recreational vessels as vessels less than 65 feet in length.

The risk attributed to the use of cuprous oxide-based paints were considered acceptable in the average saltwater recreational marina model calculations.

The United States Environmental Protection Agency is developing similar modeling assessments, but recreational marina results have not been finalized in time for this report. The New Zealand and EU data suggest that there may be good reason to take a closer look at the potential hazards of the non-copper biocides in Washington State waters.

Non-biocidal paints

There is no requirement to register non-biocidal antifouling paints since they contain no toxic active ingredients. As part of a larger study, Northwest Green Chemistry identified five non-biocidal alternatives to copper-based antifouling paints, shown in Table 7 (Northwest Green

Chemistry, 2017).[12] While this list is not exhaustive, it provides representative examples of the types of non-biocidal approaches that are available on the market.

Table 7. Non-biocidal alternatives to copper-based antifouling paints in the NGC study.

Product	Type	Comment
Aurora VS721	Polymer/wax	Not a hull paint; applied like a car wax or polish.
Coval Marine & Hull	Ceramic-epoxy	Requires professional application
CeRam-Kote 54 SST	Ceramic-epoxy	
Oceanmax Propspeed	Silicone	For metal running gear
ePaint EP21	Photoactive	UV sensitized zinc oxide

The Aurora product is a wax-like surface treatment rather than an alternative paint. Oceanmax Propspeed is designed for use on metallic running gear (e.g., propellers). Of the remaining three products, only ePaint EP21 was available in online stores for marine paints.[13] This ePaint product uses a modified form of zinc oxide (ZnO) treated with a special UV sensitizer (Ciriminna et al., 2015). The treated ZnO generates hydrogen peroxide in the presence of sunlight to help prevent fouling. Though the effect is chemical in nature, the treated ZnO is not registered as a pesticide.[14]

Several studies over the past decade or so have evaluated other non-biocidal paints for their antifouling performance (Johnson & Gonzalez, 2004; San Diego Unified Port District, 2011). Some products mentioned in previous studies appear to be surface treatments rather than true bottom paints, such as urethane, polyurethane, and wax/polymer treatments, and are excluded from this report. Based on information found through web searches, many of the products in these earlier studies do not appear to be commercially available at this time.

Recent articles on developments in non-biocidal antifouling paints also identify 20 or more non-biocidal products, though nearly all of these target the commercial vessel market (Ciriminna et al., 2015; Lejars et al., 2012). Those products whose websites address the recreational boat market include Interlux Intersleek Pro (fluoropolymer-based) and Seacoat SEA-SPEED (a polysiloxane fluoro-polymer technology). These paints may only be available to marine service businesses.

Impacts of non-biocidal paints on water quality and marine organisms

Impacts of biocidal paints were derived from studies of the biocide active ingredients. In most cases, these biocides have been studied for decades. Pesticide registrations require at least a minimum set of toxicity and other environmental test data, however, non-biocidal paints are not required to register and there has been little study of their marine impacts.

Some non-biocidal "foul-release" coatings are based on silicone or fluorine compounds that create a very slippery surface (Bressy & Lejars, 2014). In some cases, the paints contain oils that are continually released to the environment and may settle to the sediment. Since they are not soluble in water and last a long time in the environment, oils could accumulate and smother the sediment or otherwise impact its permeability (Lejars et al., 2012; Nendza, 2007).

---

[12] Northwest Green Chemistry (NGC) evaluated alternatives to copper-based antifouling paints under contract to Ecology. The NGC study considered hazards of the paint chemicals, antifouling performance, exposure during application, cost, and availability. The final report from NGC was completed September 30, 2017.

[13] Websites searched: West Marine, Jamestown Distributors, Yachtpaint.com, SMSDistributors.com, and Fisheries Supply.

[14] Many antifouling paints also include zinc oxide (ZnO). ZnO is most often used as a paint pigment, ultraviolet light (UV) protectant, or to control the rate of paint dissolution. ZnO is not regulated as a biocide.

Coating polymers may use toxic and persistent tin-based catalysts or other harmful processing additives. These may remain in the finished product at low levels and impact the marine environment. Recent reports suggest that foul-release coating formulations now use safer, non-toxic catalysts (Bressy & Lejars, 2014).

Bioassays are tests that can identify toxicity from antifouling paints on organisms. In these tests, residual chemicals from dried paint are extracted by soaking samples in water. Marine animals or plants are then exposed to the paint extract to look for toxicity or growth effects. At least three studies have found toxicity to marine organisms from non-biocidal paints using these techniques (Karlsson et al., 2006; Madsen et al., 2000; Watermann et al. 2005). Further testing of non-biocidal paints may be important if changes in regulations drive their large-scale adoption in Washington State.

Conclusion

Thirty non-copper biocidal antifouling paint products are registered for use in Washington State. Current data are not sufficient to show that these non-copper paints are less harmful to marine environments than paints that contain copper. In some cases, these non-copper paints contain biocides that may pose a significant risk to water quality and marine life. A small number of non-biocidal antifouling paints are also available. While these paints are widely believed to be safer than biocidal paints, there is little data to show how these paints affect aquatic life or water quality.

The EPA is considering leach rate regulations for copper in antifouling paints. This action will result in an overall copper reduction, but may increase the use of non-copper biocides that are considered worse for the environment. Studies on the impacts of these biocides are needed to help Ecology understand whether current or future paint product formulations pose an unacceptable risk to Washington State waters.

Recommendations

Legislative and Budget Requests

- **Investigate and model biocide risk based on Washington State data**. High quality scientific models are available that can quantify the risk of biocides in marina environments. Ecology recommends using these models with data for Washington State water conditions and marina characteristics to validate whether the high risk estimated in other countries is relevant to marinas here. This work will extend the antifouling paint alternatives assessment completed by Northwest Green Chemistry to incorporate exposure considerations and will address toxicity to a wider-range of marine species. These models can also be used to address biocide sediment impacts and freshwater marina considerations.
- **Incorporate findings from recent antifouling paint assessments**. Northwest Green Chemistry, a nonprofit organization, worked with Ecology, industry, and other organizations to conduct research and publish an alternatives assessment of copper-based antifouling paints. Ecology should integrate the results of their biocide exposure analysis with the completed antifouling paint alternatives assessment.
- **Evaluate efforts by EPA and other states to adopt leach rate limits**. In order to mitigate the effects of copper, the state of California has recently implemented a leach rate limit for copper-based antifouling paints used on recreational vessels. Interim reports from the registration review of copper at EPA suggest that similar leach rate limits may be proposed

nationally for saltwater recreational antifouling applications. Ecology should evaluate these regulatory actions for applicability in Washington State.

- **Report to the Legislature on leach rate findings.** Ecology should use the assessment to make recommendations on whether risk mitigation measures, such as leach-rate limits, may be required for biocidal paints.

Actions for Ongoing Program Work

- **Collect additional scientific data and information about biocides**. Biocide assessments conducted by governments in other countries suggest that the use of paints with certain non-copper biocides may have an adverse effect on water quality and marine life in the Puget Sound. Ecology recommends working with the EPA, other regulatory authorities, paint manufacturers, and other interested parties to collect scientific data and information on the use and safety of these biocides.
- **Collaborate with the private sector to promote safer alternatives and best practices.** The Clean Boating Foundation's Clean Boatyard Program works to disseminate best management practices for boatyards to reduce the impact of toxic substances on nearby waters (Clean Boating Foundation, 2017). Ecology recommends promoting this program through website links, internal promotion to boatyard permit inspectors, and support to Public Participation Grant awardees currently promoting source control and reduction strategies. Ecology also recommends sharing current and future findings on the safest available antifouling paint alternatives. We do not anticipate this would require new financial resources.
- **Promote the use of alternatives assessments**. Ecology recommends continuing to promote and share the Northwest Green Chemistry report with a broad range of stakeholders through website links and references to the report when speaking about antifouling paints. Ecology will also continue to monitor developments in new paint technologies and non-paint alternative technologies such as boat washing stations. Efforts in this area can help avoid the use of regrettable substitutes and, where possible, identify non-chemical solutions to our environmental challenges. We do not anticipate the need for additional financial resources for this recommendation.

Possible Future Actions

- **Investigate the possibility of a public-private collaboration to assess the performance of antifouling paints**. NGC assessments of the performance of antifouling paints rely on limited data, mostly from warm-water locations. Ecology recommends exploring the possibility of a public-private collaboration to conduct performance field tests of antifouling paints in Washington waters to assess whether performance data from other jurisdictions is relevant to Washington waters and fouling species. As performance testing can be very expensive, a collaboration might involve funding provided by the private sector with Ecology performing the day-to-day work to conduct the testing. An arrangement like this could provide Ecology with additional data about the use of antifouling paints in Washington waters, and could assist industry in evaluating and improving product performance by using Ecology's environmental expertise.

References

Arai, T., Harino, H., Ohji, M., & Langston, W. J. (2009). Ecotoxicology of Antifouling Biocides. Tokyo; New York: Springer. https://doi.org/10.1007/978-4-431-85709-9

Baldwin, D. (2015). Effect of Salinity on the Olfactory Toxicity of Dissolved Copper in Juvenile Salmon. Retrieved from http://www.sfei.org/sites/default/files/biblio_files/754 Baldwin Cu Olfactory Toxicity.pdf

Bressy, C., & Lejars, M. (2014). Marine Fouling: An Overview. Journal of Ocean Technology, 9(4), 19–28. Retrieved from https://www.researchgate.net/profile/Marlene_Lejars/publication/271179593_Marine_Fouling_An_Overview/links/54bf69850cf28ce68e6b4e8d/Marine-Fouling-An-Overview.pdf

California Regional Water Quality Control Board San Diego Region. (2005). Total Maximum Daily Load for Dissolved Copper in Shelter Island Yacht Basin, San Diego Bay Basin Plan Amendment and Technical Report. Retrieved from http://www.waterboards.ca.gov/sandiego/water_issues/programs/watershed/docs/swu/shelter_island/techrpt020905.pdf

Cardwell, R. D., DeForest, D. K., Brix, K. V., & Adams, W. J. (2013). Do Cd, Cu, Ni, Pb, and Zn Biomagnify in Aquatic Ecosystems? In Reviews of Environmental Contamination and Toxicology, vol. 226 (pp. 101–122). Springer, New York, NY. https://doi.org/10.1007/978-1-4614-6898-1_4

Ciriminna, R., Bright, F. V., & Pagliaro, M. (2015). Ecofriendly Antifouling Marine Coatings. ACS Sustainable Chemistry & Engineering, 3(4), 559–565. https://doi.org/10.1021/sc500845n

Clean Boating Foundation. (2017). Clean Boatyard Program. Retrieved August 14, 2017, from http://www.cleanboatingfoundation.org/clean-boatyard-program

Dafforn, K. A., Lewis, J. A., & Johnston, E. L. (2011). Antifouling strategies: History and regulation, ecological impacts and mitigation. Marine Pollution Bulletin, 62(3), 453–465. https://doi.org/10.1016/j.marpolbul.2011.01.012

Earley, P. J., Swope, B. L., Barbeau, K., Bundy, R., McDonald, J. A., & Rivera-Duarte, I. (2014). Life cycle contributions of copper from vessel painting and maintenance activities. Biofouling, 30(1), 51–68. https://doi.org/10.1080/08927014.2013.841891

European Chemicals Agency. (2017a). Biocidal Active Substance Assessment Reports - ECHA. Retrieved August 6, 2017, from https://echa.europa.eu/information-on-chemicals/biocidal-active-substances

European Chemicals Agency. (2017b). Biocidal Products Committee opinions on active substance approval - ECHA. Retrieved August 13, 2017, from https://echa.europa.eu/regulations/biocidal-products-regulation/approval-of-active-substances/bpc-opinions-on-active-substance-approval

Fetters, K. J., Costello, D. M., Hammerschmidt, C. R., & Burton, G. A. (2016). Toxicological effects of short-term resuspension of metal-contaminated freshwater and marine sediments. Environmental Toxicology and Chemistry, 35(3), 676–686. https://doi.org/10.1002/etc.3225

Gadd, J., & Cameron, M. (2012). Antifouling biocides in marinas: Measurement of copper concentrations and comparison to model predictions for eight Auckland sites. Auckland. Retrieved from http://www.aucklandcouncil.govt.nz/SiteCollectionDocuments/aboutcouncil/planspoliciespublications/technicalpublications/TR2012033Antifoulingbiocidesinmarinas.pdf

Johnson, L. T., & Gonzalez, J. A. (2004). Staying Afloat with Nontoxic Antifouling Strategies for Boats. Retrieved from https://caseagrant.ucsd.edu/sites/default/files/Seagrant_Nontoxic_AntifoulingII.pdf

Karlsson, J., Breitholtz, M., & Eklund, B. (2006). A practical ranking system to compare toxicity of anti-fouling paints. Marine Pollution Bulletin, 52(12), 1661–1667. https://doi.org/10.1016/j.marpolbul.2006.06.007

Lejars, M., Margaillan, A., & Bressy, C. (2012, August 8). Fouling release coatings: A nontoxic alternative to biocidal antifouling coatings. Chemical Reviews. https://doi.org/10.1021/cr200350v

Madsen, T., Samsøe-Petersen, L., Gustavson, K., & Rasmussen, D. (2000). Ecotoxicological Assessment of Antifouling Biocides and Nonbiocidal Antifouling Paints.

Nendza, M. (2007). Hazard assessment of silicone oils (polydimethylsiloxanes, PDMS) used in antifouling-/foul-release-products in the marine environment. Marine Pollution Bulletin, 54(8), 1190–1196. https://doi.org/10.1016/j.marpolbul.2007.04.009

New Zealand EPA. (2012). Antifouling paints reassessment. Retrieved from http://epa.govt.nz/Publications/Antifouling paints reassessment Preliminary Risk Assessment.pdf

Northwest Green Chemistry. (2017). Fourth Stakeholders Call: WA State Antifouling Boat Paint AA — Northwest Green Chemistry. Retrieved August 14, 2017, from https://www.northwestgreenchemistry.org/event/fourth-stakeholders-call-wa-state-antifouling-boat-paint-aa

Ranke, J., & Jastorff, B. (2000). Multidimensional risk analysis of antifouling biocides. Environmental Science and Pollution Research, 7(2), 105–114. https://doi.org/10.1065/espr199910.003

Roberts, D. A. (2012). Causes and ecological effects of resuspended contaminated sediments (RCS) in marine environments. Environment International, 40, 230–243. https://doi.org/10.1016/j.envint.2011.11.013

San Diego Unified Port District. (2011). Safer Alternatives to Copper Antifouling Paints for Marine Vessels. San Diego. Retrieved from http://www.boatus.com/gov/pdf/EPA-CopperPaint.pdf

Schiff, K., Diehl, D., & Valkirs, A. (2004). Copper emissions from antifouling paint on recreational vessels. Marine Pollution Bulletin, 48(3–4), 371–377. https://doi.org/10.1016/j.marpolbul.2003.08.016

Sommers, F., Mudrock, E., Labenia, J., & Baldwin, D. (2016). Effects of salinity on olfactory toxicity and behavioral responses of juvenile salmonids from copper. Aquatic Toxicology (Amsterdam, Netherlands), 175, 260–8. https://doi.org/10.1016/j.aquatox.2016.04.001

Thomas, K. V., & Brooks, S. (2010). The environmental fate and effects of antifouling paint biocides. Biofouling, 26(1), 73–88. https://doi.org/10.1080/08927010903216564

Turner, A., Pollock, H., & Brown, M. T. (2009). Accumulation of Cu and Zn from antifouling paint particles by the marine macroalga, Ulva lactuca. Environmental Pollution, 157(8–9), 2314–2319. https://doi.org/10.1016/j.envpol.2009.03.026

USEPA. (2017). OPP Pesticide Ecotoxicity Database. Retrieved August 14, 2017, from http://www.ipmcenters.org/Ecotox/DataAccess.cfm

Van De Plassche, E., & Van Der Aa, E. (2004). Harmonisation of Environmental Emission Scenarios: An Emission Scenario Document for Antifouling Products in OECD countries (ESD PT21). Royal Haskoning, Nijmegen. Retrieved from https://echa.europa.eu/documents/10162/16908203/pt21_antifouling_products_en.pdf/54a7f413-dca9-4382-b974-1eed342315f5

Washington State Department of Ecology. (2007). Dissolved Copper Concentrations in Two Puget Sound Marinas. Retrieved from https://fortress.wa.gov/ecy/publications/documents/0703037.pdf

Washington State Department of Ecology. (2017). Copper, Zinc, and Lead in Five Marinas within Puget Sound, report in preparation.
Washington State Legislature. (n.d.). Chapter 173-333 WAC: Persistent Bioaccumulative Toxins. Retrieved July 9, 2017, from http://apps.leg.wa.gov/WAC/default.aspx?cite=173-333
Washington State University. (2017). Pesticide Information Center Online (PICOL). Retrieved August 14, 2017, from http://cru66.cahe.wsu.edu/LabelTolerance.html
Watermann, B., Daehne, B., Sievers, S., Dannenberg, R., Overbeke, J., Klijnstra, J., & Heemken, O. (2005, 9). Bioassays and selected chemical analysis of biocide-free antifouling coatings. Chemosphere, 60(11), 1530-1541.

Appendix A

Marine antifouling paints are registered pesticides in Washington State. Records of these registrations are included in an online database, the Pesticide Information Center Online (PICOL), maintained by Washington State University (WSU, 2017). Queries to this database can identify paints currently registered in Washington State using the PICOL Simple Search link: http://cru66.cahe.wsu.edu/labels/Labels.php.

From the Simple Search page:

1. Set the "Item to search on" field to "Crop."
2. Select "Boat" in the "Common Name" field.
3. Click "Submit Query" and the search returns a count of "matching labels."
4. Refine the query, or view directly using the "Format Labels" button.
5. Option buttons on the next screen control the type of label information displayed in the final results.

Each individual label record includes a hyperlink to an image of the product label at EPA.

Results for "Boat" as "Crop" will also return pesticides used for common insect pests. The "PICOL Database Name" column of Table A1 provides chemical names for the non-copper antifouling biocides found in the PICOL database.

Table A-1. Identifying information for non-copper biocides in antifouling paints.

Name	Common Name	CAS Number	PC Code	PICOL Database Name[15]
Tralopyril	Econea	122454-29-9	119093	1H-PYRROLE-3-CARBONITRILE 4-BROMO-2-(4-CHLOROPHENYL)-5-(TRIF
DCOIT	Sea-Nine 211	64359-81-5	128101	4 5-DICHLORO-2-N-OCTYL-3-ISOTHIAZOLONE
Cybutryne	Irgarol 1051	28159-98-0	128996	CYCLOPROPYL-N-(1 1-DIMETHYLETHYL)-6-(METHYLTHIO)-
Zinc pyrithione	Zinc Omadine	13463-41-7	88002	ZINC 2-PYRIDINETHIOL 1-OXIDE

[15] Note that these chemical names are incomplete. For full names, search the CAS number at any number of chemical data portals online, such as ChemSpider.com, or the NIST Chemistry WebBook: http://webbook.nist.gov/chemistry/.