

Quality Assurance Project Plan

Performance Test of Green Alternatives to Copper Antifouling Paints

By Mueed Jamal and Xianming Shi For the Hazardous Waste and Toxics Reduction Program Washington State Department of Ecology Olympia, Washington

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Contact Information

Washington State University

Xianming Shi Dept. of Civil and Environmental Engineering 410 E Dairy Road, Pullman, WA 99164-2910 Phone: 509-335-7088 Email: <u>xianming.shi@wsu.edu</u> Mueed Jamal Dept. of Civil and Environmental Engineering 410 E Dairy Road, Pullman, WA 99164-2910 Email: <u>mueed.jamal@wsu.edu</u>

Ecology's Hazardous Waste and Toxics Reduction Program

P.O. Box 47600 Olympia, WA 98504-7600 Phone: 360-407-6700 **Website:** <u>Washington State Department of Ecology</u>¹

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Table 1. Quality Assurance Project Plan approvers. Signatures and dates are not available on the Internet version.

Name	Title	Organization	Signature	Date
Xianming Shi	Author / Principal Investigator	Washington State University		
Mueed Jamal	Author / Project Lead	Washington State University		
Iris Deng	Client	Department of Ecology, Hazardous Waste and Toxics Reduction		
Nathan Lubliner	Client's Unit Supervisor	Department of Ecology, Hazardous Waste and Toxics Reduction		
Richelle Perez	Client's Section Manager	Department of Ecology, Hazardous Waste and Toxics Reduction		
Samuel Iwenofu	Program Quality Assurance Coordinator	Department of Ecology, Hazardous Waste and Toxics Reduction		

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2.0 Abstract

Copper oxide is commonly used in marine paints to reduce the growth of organisms like barnacles and algae on boat hulls. While copper-based antifouling paints are effective, they are toxic to salmon and other sensitive aquatic life. In addition to copper, other chemicals (biocides) that deter organic growth may damage the health of aquatic environments.

Washington State intends to phase out the use of copper-based antifouling paints on recreational vessels. To advance this work, and as directed by chapter 70A.445 RCW, Washington State Department of Ecology (Ecology) has begun conducting a review of information to search for safer, effective alternatives to copper-based antifouling paints.

This exploration has included reviewing information about antifouling paints and ingredients; exploring the feasibility of implementing best management practices and using non-biocidal antifouling alternatives; and evaluating any additional scientific or technical information and studies that are relevant to the review.

Over the past decade, the paint industry has developed new antifouling paint products, including non-copper alternatives, and marketed them as more environmentally-friendly. However, Ecology currently lacks performance data to evaluate these alternatives and determine whether they are safe and effective for use in Washington's waterways.

This performance test will build upon our review to date and help fill this data gap. We will compare the efficacy of copper-based, non-copper biocidal, and non-biocidal antifouling paints by testing up to 20 coating products in four sites in Puget Sound. The test will follow the Standard Test Method for Testing Antifouling Panels in Shallow Submergence, an American Society for Testing and Material method (ASTM, 2020).

We will monitor and evaluate the overall fouling condition monthly for a year in this field study. We will not evaluate efficacy of these paints based on a laboratory toxicity assessment; rather, we will evaluate efficacy based on the relative percentage of fouling coverage on the panels painted with individual paints in marine and lake waters. The test will provide data support to assess the feasibility of alternatives.

3.0 Background

3.1 Introduction and problem statement

This comparative study tests the efficacy of copper, non-copper, and biocidal-free antifouling paints in real waters around Puget Sound in Washington State. Researchers will test the same antifouling paint products at each test location.

Historical background

Copper was first widely used in the late eighteenth century to provide a solution to biofouling on Britain's navy. Before that, ancient Egyptians had used copper plates to avoid overgrowth of fouling organisms on their canoes (Strand & Solér, 2018). As the movement of ships in oceans increased over time, manufacturers developed more antifouling techniques. The first patent related to the use of copper, arsenic, and gunpowder in an antifouling technique was filed in 1654.

In the 1960s, biocides like tributyltin (TBT) and triphenyltin (TPhT), which belong to the group of organotin compounds (OTCs), began to replace copper (mainly Cu₂O) in antifouling paints. By the 1970s, most ships and boats around the world used TBT-based antifouling paint on their hulls. These OTCs were used in antifouling paints for over six decades. They were initially thought to be less toxic than copper and other heavy metals. Over time, however, researchers and legislative authorities began to recognize their toxicity. Around 2001, OTCs were banned from use as antifouling products in most parts of the world (Strand & Solér, 2018).

Today, despite the toxicological impacts of copper on marine life and humans, most antifouling paints still contain copper (Strand & Solér, 2018). The toxic effects of copper to aquatic life have been well documented. Strand & Solér (2018) found high mortality rates in snails and fishes exposed to copper from antifouling paints. Researchers also reported that dissolved copper at the level of 5-20 μ g/L is harmful to juvenile coho salmon and can reduce the olfactory response to smell by 82% (McIntyre et al., 2008, 2012).

When copper leaches from antifouling paints, it can contaminate waters and accumulate in sediments. Hull maintenance may add further copper contamination to the environment (Srinivasan & Swain, 2007). In boatyards, stormwater runoff from work areas and wastewater from pressure washing can contain large amounts of copper. The Boatyard General Permit restricts the amount of copper that can be discharged from boatyards by setting numeric discharge limits and by setting mandatory best management practices.

Figure 1 is a schematic illustration that shows how toxic biocides (including copper) used in antifouling paints contaminate water bodies. Boats are scraped and painted in the spring, then biocides leak into waterways during boating season. In the fall, boats are cleaned using high-pressure hosing. The contamination not only occurs in water, but also in unprotected soils around boatyards.



Figure 1. Toxic biocides leakage and accumulation in aquatic environment (Strand & Solér, 2018).

Scientific background

Copper is not lipophilic and only shows a slight tendency towards bioaccumulation, which explains why it has remained in antifouling paint formulations over the years (Almeida et al., 2007). However, continued use of antifouling paints with high copper content (40%-76% by weight) can introduce large amounts of copper into waters, thus posing a significant risk to aquatic species. Research indicates that antifouling paints add approximately 15 x 10⁶ kg/year of copper to seawater globally (Srinivasan & Swain, 2007).

In fish, both gills and guts can be sites of copper accumulation and toxicity (Bianchini et al., 2004). Free copper ion (unliganded or Cu²⁺) and the positively charged Cu(OH)⁺ are known toxic forms of copper, as they may pass through biological membranes (Brooks et al., 2007; Lee et al., 2010). Santos et al. also discussed that some aquatic organisms exhibited lower mortality when exposed to copper together with low NaCl concentrations, compared to copper alone (Santos et al., 2021). The study indicated that NaCl may protect organisms from copper toxicity due to the high availability of free ions and the competition at binding sites (biological target sites,

such as gills) in cell membranes between Na⁺ and Cu⁺ ions when the salinity levels are moderated (Santos et al., 2021).

In marine environment, copper can readily bind to sediments, leading to toxic impacts on several marine species, including the diversity of infaunal communities. For example, sediment spiked with 300 μ g/g Cu decreased the recolonization of polychaetas species (another type of biofouling) (Dafforn et al., 2011). Dafforn et al. also found that the increase of dissolved copper in marine water (at around 100 μ g/L Cu) reduces the growth of diatoms (a type of microfouling) by 50% (Dafforn et al., 2011).

Nevertheless, copper chemistry is complex, which makes it difficult to gauge its bioavailable fraction and effects on the environment. Models are available, such as the Biotic Ligand Model (BLM), that can help estimate the toxic amounts of bioavailable copper that may be harmful to the environment (Srinivasan & Swain, 2007). However, those studies and estimations are beyond the scope of this research work. As such, this study will not focus on the effects that dissolved copper and sediment-bound copper have on biofouling. Instead, researchers will use evidence from related literature to support this paint performance study, if needed.

Problem Statement

Washington State intends to phase out the use of copper-based antifouling paints and encourage the development of safer alternatives. However, we lack performance data around possible alternatives that are relevant to Washington's waters and fouling species.

In 2020, the Washington State Legislature amended the state's antifouling paints law (chapter 70A.445 RCW). As directed in the law, Ecology will conduct a review of:

- Information about antifouling paints and ingredients.
- Information on the feasibility of best management practices and nonbiocidal antifouling alternatives.
- Any additional scientific or technical information and studies that Ecology determines is relevant to that review.

Therefore, there is an immediate need to conduct field tests and gather data on the efficacy of antifouling paints. These field tests can help us determine whether there are feasible alternatives to toxic, copper-based paints.

3.2 Study area and surroundings

This study will take place at four test locations within Washington State, including three marine sites and one freshwater site. Below are descriptions of each test location:

1. Anacortes Ferry Terminal, Anacortes, Washington

Anacortes, a city in Skagit County, is located on Fidalgo Island in Washington State. It has average high and low summer temperatures of 70°F and 53°F, respectively. In winter, low temperatures average around 38°F. Average rainfall ranges from 0.8 inches to 6.7 inches, with most rain occurring in winter months. Anacortes does not receive much snow, with an average snowfall of 1.6 inches during winters.

The city's day length ranges between 8 hours and 16 hours. Longer days take place in the summer. Wind speed on average is normally below 7.0 mph on the windiest days. Water temperature, an important factor for this project, measures between 46° F and 56° F on average (Weather Spark, n.d., *Anacortes*).



Figure 2. Map and images of study area 1 – Anacortes, Washington (Google Maps, October 2022).

Topographically, Anacortes lies at an elevation range of 16 to 1500 feet, with an average of 65 feet above sea level. Geographical coordinates of Anacortes are 48.513 degrees latitude, - 122.613 degrees longitude. It is 49% surrounded by salt (ocean) waters. There are five weather stations near Anacortes (Weather Spark, n.d., *Anacortes*).

The tidal flux chart for this location indicates the highest tide height as 9.5 ft and the lowest as 3.5 ft, above and below the sea level respectively (Tide-Forecast.com, n.d.). The test site will maintain a minimum water level of 3 feet throughout the year.

Weather conditions and a number of small piers and docks make this location a strong and easily accessible test site that researchers can visit monthly. An exact location near Flounder

Bay Yacht Club on Fidalgo Island (Anacortes) has been confirmed after a site investigation and a pre-test rack installation.

2. Gig Harbor station, Gig Harbor, Washington

Gig Harbor Bay, located in the city of Gig Harbor, Washington, is another marine test location. The property that Washington State University (WSU) will use for testing (Figure 3) is owned by the Seattle Yacht Club.

On average, temperatures in Gig Harbor range from 78°F in summers to 57°F in winters. Average rainfall is between 0.8 inches in summer months to 7.8 inches during winters. The highest rainfall usually occurs in November, January, and February. Snowfall on average can be as high as 1.3 inches. Average wind speeds range between 3.1 and 5.0 mph and average water temperatures fall between 47°F and 57°F throughout the year. The geographical coordinates of Gig Harbor are 47.329 deg latitude, -122.580 deg longitude. Elevation averages 150 ft. above sea level within two miles of Gig Harbor (Weather Spark, n.d., *Gig Harbor*).

Tidal flux charts indicate that the lowest tide height is -3.5 ft. and the highest is 12.8 feet, below and above the sea level respectively (US Harbors, n.d., *Gig Harbor*). According to a representative at Gig Harbor, water level does not drop below 5 feet for the entire year at the pier chosen for installing racks.



Figure 3. Images and a map of study area 2 – Gig Harbor, Washington (Google Maps, January 2023).

As shown in Figure 3 (red circle in top left image), the Gig Harbor test location is surrounded by marine water and has a few piers that can be used as test sites.

3. Manchester Station, Port Orchard, Washington

The third test location is in Port Orchard, WA. Temperatures in Port Orchard average between 37° F and 69° F over the year. Port Orchard receives 1.6 inches to 2.9 inches of rainfall on average per year. Snowfall is almost negligible in this location. Water temperatures also remain comparatively higher, between 42° F to 62° F on average per year. Wind speeds on average remain between 9.7 and 13.7 mph year-round. The geographical coordinates of Port Orchard are 53.481 deg latitude, -2.237 deg longitude, and 164 ft elevation. There are four nearby weather stations.



Figure 4. Map and images of study area 3 – Port Orchard, Washington (Google Maps, October 2022). Photo credit: Dwayne Pappas, Aug. 2017 (bottom).

The tidal flux chart for this location indicates the lowest tide height reaches -4.0 feet and highest reaches 14 feet, below and above the sea level respectively (US Harbors, n.d., *Port Orchard*). However, the location indicated in Figure 4 (marked with a red line), as well as further away from shore, maintains a minimum water level of about 6 feet above sea level throughout the year. The site of submergence will have mild water movement with no strong tide currents throughout the year.

In Figure 4 above, the top left image shows the map of Port Orchard and the saltwater surrounding it. Researchers have confirmed a test site after a recent visit to the location for a trial rack installation.

4. Portage Bay, Seattle, Washington

The last location, Portage Bay in Seattle, is the only freshwater test area. It is surrounded by lake water. A testing site near Seattle Yacht Club, shown in the bottom image of Figure 5, has been finalized after a site investigation and a pre-test rack installation trial. The top left photo in figure 5 shows the area of Portage Bay (bounded in red dotted lines), which is easily-accessible by road from Seattle.



Figure 5. Map and images of study area 4 – Portage Bay, Seattle (Google Maps, October 2022).

The temperatures at Portage Bay range from 36°F to 76°F. According to the data collected from 1972 to 1998, in extreme cases, snowfall depth could be as high as 12 inches in winters at Portage Bay. Monthly averages for lowest and highest rainfall were 1.25 and 8.74 inches, respectively.

Portage Bay has an elevation of 16 to 90 feet above sea level and a latitude and longitude of 47.6478761° and -122.3142931°, respectively (Anyplace America, n.d.; Western Regional Climate Center, n.d.). According to the representative at Seattle Yacht Club, water level barely changes throughout the year at the testing site shown in Figure 5 (bottom image) and stays at a minimum of five feet high at all times. Water movement is almost negligible, except during festivals (such as a boat show that occurs in May), in which boat traffic increases.

Table 2 summarizes the study sites. The four test sites, including one freshwater site and three marine water sites, are geographically dispersed. We selected the test sites based on multiple criteria, where the test site:

- Allows researchers permission to access or right-of-entry.
- Is safe for researchers to access.
- Offers structures to host test panels for a year with low risks of loosing test setups.
- Is on public or private aquatic land with 0.3-3m water depth (with tidal areas, the site needs to have spots for 0.3-3m water depth for 90% of the time).
- Is a representative port area in Puget Sound that either has heavy boat traffic or serves as a long term boating moorage site.
- Has no ongoing construction or disturbing activities in the immediate vicinity.

Table 2. Test locations – water types, zip codes, and GPS.

Name	Туре	Location	Pier/Dock GPS
Manchester Station, Port	Saltwater	Port Orchard, WA	47.574038, -
Orchard, WA		98366	122.546467
Anacortes Ferry Terminal,	Saltwater	Anacortes, WA	48.491477, -
Anacortes, WA		98221	122.678800
Gig Harbor station, Gig Harbor,	Saltwater	Gig Harbor, WA	47.332959, -
WA		98405	122.577158
Portage Bay, Seattle, WA	Freshwater	Seattle, WA 98112	47.644555, - 122.308428

3.2.1 History of study areas

All of these locations were, and are currently, mostly used as yards and docks for boats, as can be seen in the previous images. Since the field test will be specific to each product, there are limited research publications focused on efficacy.

Hydraulic Project Approvals (HPAs) are required for hydraulic projects, which are construction or other work activities conducted in or near state waters that will "use, divert, obstruct, or change the natural flow or bed of any of the salt or fresh waters of the state" (chapter 77.55 RCW).

For testing in the above-mentioned locations, researchers submitted four HPA pre-applications to Washington Department of Fish and Wildlife (WDFW). The area biologist determined that Manchester Station at Port Orchard requires a standard HPA permit, while the other three test sites do not require permits. WDFW has approved a standard HPA permit for Manchester Station.

3.2.2 Summary of previous studies and existing data

Copper has been used as an antifouling agent for many years. In the past, it has been used as a sheathing on wood hulls, as a compound (with sulfide) in paints, as a metal, and as an alloy (Almeida et al., 2007). Copper-based antifouling paints were first identified as environmentally harmful in the twentieth century when they were replaced by OTCs. But after OTCs were also prohibited, copper-based antifouling paints were brought back to the market because copper was thought to be less harmful than organic tin (Gu et al., 2020; Strand & Solér, 2018).

Holm et al. (2008) tested BRA 640 (with copper as the biocide) antifouling paint and International Intersleek 425 (biocide free) fouling-release paint on PVC panels in four different locations. Researchers followed the ASTM standard test method (ASTM, 2020) to evaluate the efficacy of the paints. They found that the antifouling paint with copper as the biocide showed the least amount of fouling coverage (10% to 20%) on each panel in almost all of the locations. Moreover, the forms of fouling organisms were also different on fouling-release paint, antifouling copper-based paint, and anticorrosive control paint (Holm et al., 2008).

Two copper-based paints (A with 38.34% Cu, 6.23% Zn by mass and B with 42.75 % Cu, 4.25% Zn by mass) were tested alongside anticorrosion coatings to test the antifouling characteristics at Bali Bay in Indonesia. Both of the copper-based antifouling coatings provided better fouling resistance than the anticorrosion coatings. This study reported that copper as the biocide effectively reduces the growth of biofouling on steel in saltwater, whereas regular anticorrosion paints do not provide much resistance to fouling (Priyotomo et al., 2021).

A water-based, copper-free antifouling coating (containing metal-free organic biocide, ZnO and TiO₂) was used in another comparative study. This coating was compared to a polyurea coating (with no antibacterial component). The coated steel panels were immersed in saltwater at a Florida bridge site. The results indicated that the biocide-based copper-free antifouling paint showed the least signs of biofouling adhesion after 250 days of adhesion (Permeh, Lau, et al., 2019). Results from a similar study showed that steel panels with polyurea coating were no better than the uncoated steel panels in terms of resisting barnacles and growth of other fouling organism (Permeh et al., 2019). Moreover, the steel panels with antifouling coating were also in better condition, once cleaned after 250 days, compared to the uncoated ones and the ones coated with polyurea.

In another study, researchers found that copper release rates and fouling pressure increased with increased salinity. No significant difference in efficacy between the eight tested products was observed at the brackish and marine sites. Hence, the products with high release rates of copper were equally efficient as those with 4 - 6 times lower releases (Lagerström et al., 2020).

3.2.3 Parameters of interest and potential sources

In this project, antifouling paints may contain copper and/or zinc. Research conducted in the Baltic Sea region found that heavy metals like copper and zinc are toxic to several marine organisms (Strand & Solér, 2018).

Copper is toxic for marine life, including fishes and snails. Higher accumulation of copper may reduce the fertility rates in snails and increase their mortality rates. Higher levels of dissolved

zinc (Zn) may cause reduction in the growth rates of snails. Sea animals feeding on snails may therefore have higher levels of heavy metals. Copper, however, is considered more toxic than zinc because it can affect the organs of crustaceans and fish even at very low concentrations. Copper can also alter behavior (such as homing and mating search) in a large variety of marine organisms (Almeida et al., 2007; Strand & Solér, 2018).

The focus of this study will be to determine if a copper-free antifouling paint is effective enough to be considered as a replacement for copper-based biocidal antifouling paint.

3.2.4 Standards and regulatory criteria

There are several regulations and guidelines to follow when using paints.

- 1. This project will focus on the guidelines provided by ASTM standard method for testing antifouling paint (ASTM, 2020). We (the researchers) will keep to this industry standard for testing.
- 2. We will follow OSHA 1915.35 (OSHA, 2005) standard safety regulations for surface preparation and painting, and OSHA 1917.153 (OSHA, 2002) safety regulations for spray-painting operations. In general, researchers will use personal protective equipment (PPE) like coveralls, half-piece respirators with a minimum P95 filter cartridges, chemical-resistant gloves, and chemical-resistant goggles, in accordance with OSHA regulations.
- 3. In September 2018, the EPA released a Copper Compounds Interim Registration Review Decision. The EPA also adopted the copper leach rate limit set by the California Department of Pesticide Regulation (CDPR) in July 2018 (Burant et al., 2019). This Interim Decision required that paint manufacturers submit amended labels within 60 days, as well as submit additional leaching data to the EPA to register their products. The maximum allowable leach rate of 9.5 μ g/cm²/day is in effect and currently applies to most registered and new copper-based antifoulant products. It is possible that products registered prior to 2019 with higher leach rates are still available on the market. For this reason, product selection for this study will be limited to products that meet this leach rate cap.
- 4. We will follow OSHA standard safety regulations (OSHA, 2014) while sandblasting the steel panels.

4.0 Project Description

As discussed in Section 3.1, copper-based antifouling paints can be harmful to a wide range of aquatic species. Washington State would like to replace the copper-based antifouling paints that are dominant in the market with safer alternatives. This study will advance scientific understanding of the efficacy of copper-free antifouling paints.

As directed in chapter 70A.445 RCW, if Ecology determines that safer and effective alternatives to copper-based antifouling paints are feasible, reasonable, and readily available, then the copper ban will go into effect beginning January 1, 2026. The study outcomes will indicate

performance of copper and non-copper antifouling paints available in the market and provide data support to determine the feasibility of non-copper alternatives.

4.1 Project goals

The major goals for conducting this project, most of which are based on ASTM standard test method D3623 – 78a (ASTM, 2020), are provided as follows:

- Identify test locations in western Washington State and confirm up to four locations where painted steel panels can be submerged for 12 months.
- Obtain all antifouling paint products from the market with the assistance of Ecology representatives.
- Prepare the surface of the required number of steel panels before the application of antifouling paints.
- Apply control paints by carefully following ASTM testing standard (ASTM, 2020), supplemented with OEM's technical data sheets (TDS), and apply test paints by following the OEM's TDS to achieve the best performance.
- Transport all painted steel panels to desired locations and submerge the required number of panels into waters.
- Monitor the painted steel panels at all locations once a month (up to a year) for any kind of biofouling.

4.2 Project objectives

To complete this project, researchers will meet the following major objectives:

- 1. Purchase the necessary equipment and items required for this project. This includes, for example, the spraying setup (including an air compressor, pressure pot, etc.), testing meters (DO meter, water hardness testing kit, etc.), waterproof camera, etc.
- 2. Choose and finalize up to four test locations on the west side of Washington State.
- 3. With the assistance of Ecology representatives, obtain up to 20 antifouling paint products to test.
- 4. Collect the data from the performance testing of all 20 antifouling paint products.

4.3 Information needed and sources

We will collect required information from the literature, including published articles, reports, and books, to support this performance test. We will collect this new data by following the ASTM standard test method D3623 – 78a (ASTM, 2020). Environmental modeling will not be required for this project. However, if necessary, this project's data can be used to support future growth rate modelling.

4.4 Tasks required

To meet the four major objectives, researchers will complete several main tasks. For the **first** objective, the following main tasks will be completed:

- Gather information on application modes from OEM of paints (such as, International, Sea Hawk, Interlux, etc.). After confirming details, buy the right spraying setup.
- Confirm with WSU facilities which kind of air compressor should be installed to support paint spraying (specific requirements like CFM, 110 or 240 V, hosing sizes, etc.).
- If WSU does not offer proper spray-painting setup, look for a nearby outsource and discuss modes of paint application with them prior to purchasing any spray setups or equipment.
- Go through the safety regulations, waste and hazard management criteria, and purchase necessary items like, respirators, disposal pails, etc.

For the **second** objective, the following main tasks will be completed:

- With coordination of Ecology and the WSU research team, choose up to four locations in WA state based on the selection criteria defined in Section 3.2. The locations need to be relatively dispersed in four different directions around Puget Sound, WA.
- Conduct site investigations to verify accessibility and safety. Identify the exact access point to drop test panels at each location. The site investigation will also help researchers develop familiarity with possible challenges during testing. Take pictures of present conditions.
- Based on site investigations, design a rack that can carry the steel plates to submerge them underwater.

For the **third** objective, the following main tasks will be completed:

- Finalize up to 20 products (antifouling paints both copper and non-copper) after discussions through meetings between the principle investigator and an Ecology rep.
- While following the paint thickness and steel panel sizing requirements (ASTM, 2020), estimate how many gallons of paint will be required. The details of testing methods are discussed further in Section 9.2.
- Purchase up to 20 antifouling paint products. Use assistance from the Ecology representative, if needed.

For the **fourth** objective, the following main tasks will be completed:

• Make all necessary safety-related and technical purchases (for instance, ordering PPE to be used per OSHA and/or state protocols). Technical purchases include nylon rope, portable waterproof microscope with camera, a waterproof camera, paint thickness measuring gauge, etc.

- Locate a paint workspace that is currently in accordance with OSHA and/or following WA State safety protocols related to painting (for instance, a paint workshop installed with HEPA filters, proper paint waste disposal facility, etc). If WSU has no such paint workspace available, then set up a paint workshop or outsource the painting work. Researchers may have completed part of this task already while completing the first objective.
- Sandblast each steel panel in compliance with ASTM D3623 78a. Drill a hole in each steel panel before sandblasting them (ASTM, 2020).
- Paint each steel panel (estimate 9x9 sq. in) following the ASTM method (ASTM, 2020). Researchers might conduct a standard scratch test on a few additional painted panels to test the adhesion of applied products. Further details are provided in section 9.2.
- Transport the panels within two weeks of the topcoat (antifouling paint) application to the test locations.
- Submerge all the panels into the water for a year using a rack with dimensions indicated in the method (ASTM, 2020) and a highly-visible polypropylene rope. Researchers may take pictures of all panels before submerging panels into water.
- Monitor each panel individually each month, record the data, and report the biofouling (micro and/or macro) in compliance with the ASTM standard D3623 – 78a. Details of data recording are mentioned in Section 8.
- Continue such monitoring and recording results for at least one year. Researchers may also take photos upon monthly visits.
- The researchers will share quarterly email updates with Ecology. If needed, researchers will share preliminary data to support Ecology's draft determinations for the legislative report.
- Researchers will compile a summary report at the end of the project and submit it to the Ecology.

4.5 Systematic planning process

Not applicable to this study.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 3. The responsibilities of those who will be involved in the project.

Staff	Title	Responsibilities
Iris Deng HWTR Headquarter Office Department of Ecology Phone: 360-480-6555	Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Mueed Jamal Dept. of Civil & Environmental Eng. Washington State University, Pullman Phone: 425-499-8598	Research Associate	Writes the draft QAPP. Prepares the samples in the laboratory/painting facility and transports them to the sites. Oversees field sampling and transportation of samples back to the laboratory. Conducts QA review of data, analyzes and interprets data, and shares data online with Ecology on monthly basis. Writes the draft report and final report.
Xianming Shi Dept. of Civil & Environmental Eng. Washington State University, Pullman Phone: 425-499-8598	Principal Investigator	Oversees the entire project and provides troubleshooting and project management. Provides internal review of the QAPP and supervises the proper execution of the QAPP. Supervises the data QA, analysis and interpretation. Provides internal review of the draft report and final report.
Sydney Beaurivage Dept. of Civil & Environmental Eng. Washington State University, Pullman Phone: 319-325-5639	Field Assistant	Helps collect samples and records field information.
Samuel Iwenofu Department of Ecology 360-485-5487	Quality Assurance Coordinator	Conduct QA/QAPP review on behalf of the client and approve the final QAPP.
Nathan Lubliner HWTR Headquarter Office Department of Ecology 360-688-6703	Client's Unit Supervisor	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Richelle Perez HWTR Headquarter Office Department of Ecology 360-742-6794	Client's Section Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.

5.2 Special training and certifications

Dr. Xianming Shi has over a decade of experience in planning and conducting field trials and experiments. He is familiar with statistical approaches for managing complex and large data sets. He has a PhD in Chemistry and a M.S. in Industrial & Management Engineering and is a certified P.E. in Industrial Engineering.

Mr. Mueed Jamal, who will primarily be conducting field experiments and collecting data, has been working under Dr. Shi for two years. He has performed Field Operating Tests (FOTs) and has performed several laboratory-based experiments and tests while following standard operating procedures and ASTM standard methods. He has a background in metallurgy and materials science engineering that enables him to understand coatings and surface engineering.

5.3 Organization chart

Table 3 lists the key individuals and responsibilities.

5.4 Proposed project schedule

Tables 4 and 5 list key activities, due dates, and lead staff for this project.

Task	Due date	Lead staff
Field work	Jan. 2024	Mueed Jamal
Laboratory analyses	Jan. 2024	Mueed Jamal
Data validation	Feb. 2024	Xianming Shi

Table 4. Schedule for completing field and laboratory work.

Table 5. Schedule for the final report.

Task	Due date	Lead staff
Interim draft to supervisor	Dec. 2023	Mueed Jamal
Draft to client/ peer reviewer	Jan. 2024	Xianming Shi
Final draft to publications team	Feb. 2024	Iris Deng
Final report due on web	Apr. 2024	Iris Deng

5.5 Budget and funding

Ecology funded this study. Washington State University, Pullman (WSU) will carry out the actual implementation. The overall estimated project budget is summarized below in Table 6.

Funding for this study comes from the Washington State Hazardous Waste Assistance Account. Ecology and WSU have agreed upon project costs within their contracts. The total budget for the antifouling boat paint project is \$240,809. Of this total budget, \$192,327 is budgeted for direct costs, including \$80,400 for consumable supplies like test panels and paints. The budget for direct costs is detailed below:

- Salary and benefits for principle investigator: \$38,150
- Salary and benefits for research associate: \$41,493
- Salary and benefits for PhD student: \$10,776
- PhD student tuition: \$5,858
- Consumable supplies: \$80,400
- Travel (all travel based on current state per diem and privately-owned vehicle rates): \$15,650
- Total direct costs: \$192,327

The total budget, including both direct and indirect charges, is outlined in Table 6 below.

Table 6. Summary of budget

Budget Item	Amount
Total direct cost (including salary, benefits, PhD student tuition, consumable supplies, and travel)	\$192,327
Amount of direct costs subject to indirect charges (excludes PhD tuition)	\$186,469
Indirect Charges – F&A overhead 26%	\$48,482
Total project cost (sum of the total direct cost and indirect charges)	\$240,809

With Ecology's prior approval, and while staying within the total project cost, contractors may disperse budget amounts between items without amending the contract.

6.0 Quality Objectives

6.1 Data quality objectives

The main data quality objective (DQO)³ for this project is to collect the data for the efficiency of up to 20 antifouling paint products, after conducting experiments in marine and lake waters. Researchers will complete the analysis of these antifouling paint products by following the ASTM standard procedure (ASTM, 2020) to obtain a rating of fouling on painted steel test

³ DQO can also refer to **Decision** Quality Objectives. The need to identify Decision Quality Objectives during the planning phase of a project is less common. For projects that do lead to important decisions, DQOs are often expressed as tolerable limits on the probability or chance (risk) of the collected data leading to an erroneous decision. And for projects that intend to estimate present or future conditions, DQOs are often expressed in terms of acceptable uncertainty (e.g., width of an uncertainty band or interval) associated with a point estimate at a desired level of statistical confidence.

panels. Measurement quality objectives, as described below, will also be met once the standard procedure (ASTM D3623 – 78a) is followed.

6.2 Measurement quality objectives

MQOs for this project will also be based on the standard test method for testing antifouling panels in shallow submergence (ASTM, 2020). The major indicators for MQOs of this project are described in terms of precision, bias, sensitivity, representativeness, and completeness.

6.2.1 Targets for precision, bias, and sensitivity

MQOs for this project are summarized in Table 7, followed by descriptions

Parameter	Laboratory Duplicate (RPD)	Field Duplicate (RPD)	Matrix Spike Duplicate (RPD)	Lab Control Standard	Matrix Spike (Percent Recovery)	Lowest Value of Interest
Temperature	N/A	N/A	N/A	N/A	N/A	32°F
рН	N/A	N/A	N/A	N/A	N/A	8
Salinity	N/A	N/A	N/A	N/A	N/A	32 parts
Surface Roughness for Blasted Steel Panels	N/A	N/A	N/A	26 to 38 microns	N/A	26 microns
Film thickness for Primer Pretreatment	N/A	N/A	N/A	13 microns	N/A	N/A
Film thickness for primer coating	N/A	N/A	N/A	Varying based on products' TDS	N/A	Varying based on products' TDS
Film thickness for antifouling paint	N/A	N/A	N/A	Varying based on products' TDS	N/A	Varying based on products' TDS
Within laboratory SD	N/A	N/A	N/A	2.6	N/A	N/A

Table 7. Measurement quality objectives (for laboratory and on-site measurements).

6.2.1.1 Precision

Generally, researchers should judge precision based on the within-laboratory standard deviation (SD) and the between-laboratory SD. However, because only one research body is participating in this project, only the within-laboratory SD precision method will be followed.

On the basis of the within-laboratory SD, the criteria of "repeatability" will be used to judge the acceptability of results at the 95% confidence level (ASTM, 2020). Moreover, since this project

will test several antifouling paints against a standard test panel, the use of duplicates at the same location is not necessary. Rather, precision will be judged by rating fouling on four different but equal sections/areas within a test panel. The fouling rating of each area will be compared with the standard or control panel.

For each test location, researchers will prepare one standard panel and up to twenty test panels. On each test panel, there will be four equal areas as replicates. Altogether for one location, there will be 80 replicates representing the performance of 20 antifouling paint products.

Repeatability

Researchers will examine data if there is a difference of more than seven units between the results obtained from the mean of fouling ratings on each test panel. For instance, if the mean of fouling ratings obtained from the two equal areas (each 4.5" x 4.5") on the left side of a test panel is seven units higher than the mean obtained from the right side, researchers should repeat the test. In the method (ASTM, 2020), the precision criteria is slightly different, as only duplicates of standard test panels are compared. Here, we will be comparing the results obtained from different areas within the same test panels after determining the fouling rating as described in ASTM D3623 – 78a.

6.2.1.2 Bias

Bias is the difference between the sample mean and the true value. For this study, researchers will prepare one standard or control panel (for each location) by following the antifouling paint system mentioned in the method (ASTM, 2020). Fouling rating as the true value will, therefore, be obtained from the control panels and would usually be considered as 100. All 20 of the antifouling paint products will be tested by finding the bias of each using control panels.

6.2.1.3 Sensitivity

For this study, researchers will mostly collect data from the field. There will be very little or no laboratory work. In the field, standard and test panels should be submerged at a minimum depth of 1 foot (0.3m) in real waters (marine and lake). Moreover, if the panels are mounted side by side using a rack, the minimum distance between adjacent panels should be 1.5 mm. A minimum surface area (72 in²) of each test and standard panel should be exposed to fouling conditions for a minimum of 1 year. Paint films should be dried at a minimum temperature of 21°C. For most coats of each paint film, the minimum drying time should be 2 hours (ASTM, 2020).

Normalization

The rating system is based on the minimum test on one side area of 72 in². However, this project will study four equal test areas (20.25 in² each) within a single test panel. These four equal areas will be regarded as replicates. Therefore, percent ratings for a single test area (4.5" x 4.5") on each test panel shall be corrected using the normalization method described in the method.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

As discussed earlier, the standard testing method for testing antifouling panels in shallow submergence (ASTM D3623 – 78a) will be followed to prepare the standard (control) and test panels (ASTM, 2020). Standard (control) panels will then be used for comparison purposes and to determine the fouling rating on test panels. Researchers may use existing data from published articles to compare the results of this study with similar studies.

6.2.2.2 Representativeness

For this project, researchers will judge the performance of each antifouling paint by submerging the prepared standard and test steel panels into real waters. These waters include marine and lake waters. Real-life test locations may include boatyards, bays, or ferry slips. Since recreational boats may travel between marine and fresh lake water, researchers will test the selected antifouling paints in both environments.

The growth of fouling on test panels will be almost exactly the same as on boat hulks since the test panels will be placed in the same real-life conditions. Because the test will last for one calendar year, the test panels will be exposed to all seasons and weather conditions. The length of submergence time will be sufficient for fouling growth. The panels will stay submerged throughout the year except for a brief time once a month when researchers will inspect the fouling on painted panels. Flow conditions will be mild, as the test locations will be close to the shore or land areas, most likely against piers.

6.2.2.3 Completeness

The field work involved in this project requires that researchers travel to the test locations each month, pull the heavy, steel panels from the waters, and examine them for fouling. Examination includes taking pictures. Researchers may need a portable microscope to examine microfouling if any is present.

Usually in such scenarios, project completeness rates are higher than 90%, assuming there are no transportation issues and harsh ground conditions. Conditions like inclement weather, blocked roadways due to excessive snow, excessive turbulence in water by storms and/or boats and ferries, frozen lake waters, etc., could affect project completeness. Regardless of these reasons, researchers expect to complete 90% of the project within the time frame awarded.

6.3 Acceptance criteria for quality of existing data

Very limited data exist regarding the performance of antifouling paint. Researchers will only consider data from verifiable and cited sources. Acceptable existing data should meet these following requirements:

- 1) The data were produced based on the same ASTM method.
- 2) The data meet the measurement quality objectives defined in this QAPP.

3) The data were accompanied with a description of how the test was conducted, including test products and test location descriptions.

6.4 Model quality objectives

Not applicable to this study.

7.0 Study Design

7.1 Study boundaries

Researchers will perform this test on four test sites based on the selection criteria defined in Section 3.2. Biofouling is an issue particular to marine water, and antifouling paints are not generally needed for freshwater vessels. As such, the four test sites are selected to cover three marine water sites and one freshwater site where moored boats frequently travel to marine water. Please refer to Section 3.2 to view maps that show the possible study boundaries of each test location using red dotted lines. Section 3.2 also describes the topography for each study boundary. Ecology has confirmed the exact test location at each test site in Table 2.

This test will use up to 20 antifouling test products. The 20 products were identified through prior research, market surveys, boatyards outreach, and related regulations. Appendix A details the outreach and research used for product selection. Generally, these are popular and effective products recommended by boatyards and local retailers. The products contain up to 10 non-copper antifouling paints that represent different alternative ingredients, 6 typical copper antifouling paints, and 4 biocidal-free antifouling paints. The number of paints in non-copper and biocidal-free categories are mainly limited by the number of available products in the market. All the products claim to meet the copper leach rate requirements.

Products chosen for the study may be purchased online, through local sales representatives, or donated from manufacturers directly. The research team will make reasonable effort to purchase exact products as suggested in Appendix A. In the case that products are discontinued or unavailable, the research team may consult with Ecology to find substitute products with similar ingredients. If no substitutes are found, the proposed products will be excluded from the performance test.

7.2 Field data collection

At each site, three racks will be submerged to accommodate up to 20 test panels and one control panel. Researchers will plan travelling time so that test panels from different locations are installed and observed around the same dates. Two of the test racks will measure 1' x 4' (accommodating eight panels each) and the third rack will be 1' x 2.5' to accommodate five more panels. After submerging all of the panels in marine and lake waters, researchers will schedule monthly visits to collect data from all four locations. These visits will be divided into two visits to two test locations per day. A field assistant will accompany the project lead (Mueed Jamal) during the pre-testing visit and each monthly visit thereafter.

7.2.1 Sampling locations and frequency

The following locations will be used to submerge the test and standard panels for testing antifouling paint performance:

- 1. Anacortes (saltwater)
- 2. Gig Harbor (saltwater)
- 3. Port Orchard (saltwater)

4. Seattle (lake water)

We will examine the fouling on each submerged panel once a month, report the fouling, and take pictures of each panel as part of sampling (ASTM, 2020).

7.2.2 Field parameters and laboratory analytes to be measured

For this project, researchers will observe and record the amount and type of fouling present on each submerged panel. We will follow the rating system indicated in ASTM D3623 – 78a. Moreover, we will record the temperature, salinity (conductivity), and the pH of waters by following *Standard Operating Procedures for Measuring PH, Conductivity, and Temperature* (WA DOH, 2018) on each site before observing fouling. In addition, researchers may also record dissolved oxygen (DO) (ASTM, 2018) and water hardness.

7.3 Modeling and analysis design

Not applicable to this study.

7.3.1 Analytical framework

Not applicable to this study.

7.3.2 Model setup and data needs

Not applicable to this study.

7.4 Assumptions underlying design

Products used in this study reflect current available products from the market at the time of purchase. Manufacturing formulations and product registrations are subject to change in response to changes in the regulatory environment.

7.5 Possible challenges and contingencies

As discussed above, there may be interruptions due to inclement weather, unsuitable traveling conditions on the roads, etc. If any such contingency should occur, researchers will report as such in the final report.

It may also be challenging to pull steel panels out of the water without aids like hydraulic lifting. For this reason, no more than eight steel panels will be bolted to the polymer sheets (racks) for testing the performance of antifouling paint over the year.

Another contingency could be a change in design of the rack used for submerging the steel panels, according to the location or test site. The design of the testing rack for submerging panels in water may need to be changed depending on the form of piers at the test sites.

7.5.1 Logistical problems

The selected test locations do not have a very high tidal current. Still, there may be a risk of racks moving vertically underwater due to boat activities or storms. This movement could disturb the rack's position or depth, which should be between 0.3 m and 3 m during the testing

period. Therefore, researchers decided to use the maximum possible depth available, which is 3 m, whenever possible.

We may also add more weights to the sides of the rack (either on the ropes that are used to submerge it or on the rack itself) to keep it submerged within the standard depth range. Ideally, it would be best to keep the rack (and thereby all the panels bolted on it) submerged at a constant depth, but this may not be possible due to water turbulence caused by boat activities and/or any storms.

7.5.2 Practical constraints

Though researchers are prepared to find the most appropriate test locations, it is possible to have difficulties in finalizing a test site (e.g., pending property owner's approval, adequate open space without interference). If the researchers encounter challenges with any test site proposed in this QAPP, they may use an alternative site near the proposed location. It is also possible that unexpected conditions like water turbulence may cause test panels to collide with other structures, or lead to damages or loss of test panels. In these cases, the researchers will be prepared to investigate the test site thoroughly before test, try to reclaim the panels if possible, or try to restart the test if time allows.

As of now, researchers have found a few research examples and guidance to support this study. Researchers need to conduct a thorough literature review to gather useful information on existing data from similar studies.

There might be a need for a diver (or potentially a good swimmer) at the testing locations, in case a rack falls down in the water and needs to be reclaimed. To accommodate for this possibility, one of the testers should be able to swim and dive if needed.

Moreover, if it is not possible to drive to a test location due to inclement weather or poor road conditions, flying might be required. There is sufficient funding for this, and transportation should not be a problem.

ASTM standard test method D3623 – 78a proposes using a lead-based primer to prepare the standard (control) panels; however, several states across the country prohibit the use of lead-based paints and WSU does not have a facility to deal with lead-based paint. Additionally, both the lead-based primer and antifouling paint identified in this ASTM method have been discontinued.

Given these considerations, and after contacting ASTM directly, the WSU research team has picked a replacement antifouling paint system to use instead of the paint system recommended in the ASTM method. However, it's possible the replacement products (Seavoyage copper-free antifoulant and Seaguard 5000 HS primer) are not available as well. In this case, the research team will consult the qualified products list (QPL) that was referred by an ASTM member industrial leaders to find another suitable alternative.

Silica sand is not allowed for sandblasting purposes anymore due to health hazards. Therefore, researchers will use other suitable blasting media such as granite sand for blasting steel panels. However, the surface profile (Sa $2^{1/2}$) will be prepared according to the ASTM method (ASTM, 2020).

Additionally, the required spray setup for most of the test products chosen for this project is based on boat hulls. For these bigger jobs, manufacturers recommend airless sprayers with pressures up to 3000 psi or conventional spray guns with pressure pots. Since we have a small job (four small panels painted with one product), we will need to paint 1 quart of volume at most. Given this, we need to find a different setup for spraying the paints on both control and test panels. Researchers have contacted manufacturers directly to seek suggestions.

Limitations in receiving products through online purchases may occur due to unforeseen product unavailability and/or shipping delays after purchase. Some product purchases may need to be cancelled if the products are on back-order and not to be received within the proposed timeframe. Products may be reordered through a different online retailer or purchased at a retail store if this can be achieved within the purchase timeline mentioned in this QAPP.

7.5.3 Schedule limitations

Unexpected situations described in the practical constraints may require us to reanalyze a product. However, time constraints may limit this possibility. In this case, the results with be reviewed and accepted based on the data quality objectives as specified in this QAPP. From the time of submerging panels into water, it will take at least 14 months to complete the project. Delays in site investigation, rack design and modification or unexpected weather conditions may push back the proposed timeline. In this case, the researchers will update the timeline with Ecology promptly.

8.0 Field Procedures

8.1 Invasive species evaluation

Biofouling on boats can be a vector for the transfer of invasive aquatic species. However, in this study, all test panels will remain in the test locations. It is possible that invasive species or marine plants could be observed during monitoring. To avoid the spread of these species to other areas, we will implement procedures adapted from Ecology's Standard Operating Procedures to Minimize the Spread of Invasive Species (Parsons et al., 2021). Generally, researchers will wash and monitor the biofouling at the test location and will not anticipate transportation of invasive species.

8.2 Measurement and sampling procedures

Below is a brief procedure for measuring the fouling rate on steel panels submerged in water, based on ASTM standard test method D3623 – 78a:

- 1. Once the steel test panels are coated with the antifouling paints, they will be submerged into the marine and lake waters for one year. They will be visually examined for any form of fouling once per month.
- Each test panel will be divided (not physically, but in high quality photographs) into four equal areas (4.5" × 4.5"). Each of these areas will be rated for fouling according to ASTM D3623 – 78a.
- 3. Standard panels have the same dimensions with test panels. However, standard panels are evaluated based on the whole area $(9.0" \times 9.0")$, while test panels are evaluated on each quadruplet $(4.5" \times 4.5")$. The area differences will be considered in calculations based on the normalization guidelines specified in the method (ASTM, 2020).
- 4. Researchers will take pictures of all the test panels during each measurement, every month.
- 5. After a year of taking measurements each month and recording the fouling ratings, researchers will analyze the data by following ASTM D3623 78a.

Table 8. Reporting format for fouling on steel panels (ASTM, 2020).

Origin:
Series:
Basins:
Size:
Place of immersion:

Depth of immersion: Date immersed: Date Inspected: Inspected by:

Test Surface Number	Fouling on Surfaces*	Physical condition	% rating F.R.	% rating A.F.	% rating A.C.	% rating O.P.
	Barn:					
	Others:					
	Barn: E.B.:					
	Others:					
	Barn: E.B.:					
	Barn:					
	E.B.: Others:					
	Barn: E.B.: Others:					
	Barn: E.B.: Others:					
	Barn: E.B.: Others:					

* Fouling reported as found on the more heavily fouled surface. Solitary forms reported numerically; colonial forms by percent surface covered. Al: algae; Barn: barnacles; E.B.: encrusting bryozoans; Hyd: hydroids; Tun: tunicates; C.F.: completely fouled; CO: coelenterates; F.B.: filamentous bryozoans; Mol: molluscs; PC: polychaetes.

8.3 Containers, preservation methods, holding times

Table 9 presents the measurement parameters used to observe fouling on test and control panels, the panel material, the number of panels to be prepared, the approximate number of racks needed, the testing duration, and the number of paint products that will be tested.

Measurement parameter [*]	Matrix	Estimated number of panels [†]	Racks [‡]	Estimated number of products [§]	Submergence time
Fouling Resistance (F.R.)	Steel	21 (9"x9")	3	20	1 year
Antifouling Film (A.F.)	Steel	21 (9"x9")	3	20	1 year
Anticorrosive Film (A.C.)	Steel	21 (9"x9")	3	20	1 year
Overall Performance (O.P.)	Steel	21 (9"x9")	3	20	1 year

Table 9. Testing details and measurement parameters.

Notes:

* All four parameters will be measured for each test panel.

+ Number of panels are number of tested products plus one control paint. The number of tested products is subject to change due to availability and time constraints.

‡ Maximum of eight panels on each rack.

§ Researchers will test up to 20 products from the market. A standardized paint system is required for control panels, as per ASTM D3623 – 78a.

8.4 Equipment decontamination

When we submerge any equipment into waters to take DO, pH, or temperature readings, we will decontaminate the devices, probes, or meters according to Ecology's SOP EAP090 (Friese, 2020).

8.5 Sample ID

Researchers will give the test and standard panels individual identification numbers based on the antifouling paint system applied on each panel. Since there are multiple test locations and around 20 antifouling paint products, each panel's ID will indicate the paint formula, location code, and a code for each of the four areas on the panel. Different locations can have codes such as, A, B, C, D, etc. For instance, if a panel has been preserved with a paint system that has a formula of 121 and is submerged in location A, the panel ID will read "F121-A1", where 1 is indicating the area 1 out of 4 on each panel.

8.6 Chain of custody

This field test doesn't involve transportation of samples, or changes of possession. The test panels are not tracked with chain-of-custody forms during the field test, as they never leave the custody of WSU researchers. Instead, researchers will use laboratory logs in-house to record: (a) place of immersion; (b) depth of immersion; (c) date immersed; (d) date inspected; (e) inspected by, etc.

8.7 Field log requirements

Researchers will maintain field logs in a notebook while taking the measurements. Weather conditions may be wet or windy. We will prepare accordingly so we can still record in the field

log during these conditions. We will use permanent waterproof ink and waterproof notebooks. We will use a strikethrough to make any corrections. Later, we will transfer the logs to a laptop and then a desktop PC via USB. We will prepare the field logs according to ASTM D3623 – 78a (ASTM, 2020).

8.8 Other activities

These activities may include:

- Training for technical assistant for sandblasting and painting the panels.
- Commuting to the test locations using an official or rental vehicle and, if necessary, commuting by plane.
- Carefully disposing of the leftover and wasted paints. Disposal of any paint waste will follow the relevant U.S. EPA regulations (EPA, 2015). Researchers will also carefully follow guidelines mentioned on each military-grade paint product.
- Making necessary arrangements at the test sites to submerge the racks into the water. This may require site visit to test locations prior to the start of the research.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 10 presents lab procedures, including surface preparation, application of antifouling paints, types of material to be painted, number of panels, and other parameters of lab work.

Antifouling Paint	Sample Material	Samples Arrival Date	Expected Range of Results	Detection or Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
For all paint products	Low Carbon Steel (A569)	Sep 17, 2022	Sandblasted profile of Sa 2.5	Surface roughness of 1-1.5 mils before painting	Sandblasting steel to a profile of Sa 2.5	Sandblasting with garnet sand in accordance with ASTM D3623 – 78a, measuring surface roughness with standard gauge
For all paint products	Low Carbon Steel (A569)	Sep 17, 2022	Total of 263 µm thickness of the antifouling paint system	Total average thickness of paint films 260 ± 5 μm	Applying paint films in accordance with ASTM D3623 – 78a and TDS of selected products	Using paint spray booth (OSHA SOPs), measuring each and overall paint film/s thickness using standard gauge
For all paint products	Low Carbon Steel (A569)	Sep 17, 2022	Proper adhesion of paint after the final (top) coat	Adhesion strength (expected from 1.4 to 5.4 Mpa) or scratch resistance (from 1 to 8H)	Perform adhesion and scratch test on painted panels if possible	Use the standard testing methods for inspecting adhesion of paints

Tahle	10 Measurement	methods	(laboratory)	(ASTM	2020)
I UNIC		methods			2020).

Table	11. Measurement	methods	(field	testing)	(ASTM,	2020).
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Testing Parameter (for all paint products and test locations)	Sample Material	Panels Submerging Prospective Dates	Expected Range of Results	Detection or Reporting Limit	Sample Test Method	Analytical (Instrumental) Method
Temperature	Salt and lake waters	Nov 10, 2022 to Nov 20, 2022	34°F to 66°F	N/A	Handheld gun	Infrared
рН	Salt and lake waters	Nov 10, 2022 to Nov 20, 2022	6.5 to 8.5	N/A	Bucket collection of samples*	Portable pH meter
Salinity	Salt and lake waters	Nov 10, 2022 to Nov 20, 2022	32 to 37 ppt (for saltwater) 0.15 to 2 ppt (for lake water)	N/A	Bucket collection of samples*	Portable salinity or conductivity meter
Dissolved Oxygen (DO)	Salt and lake waters	Nov 10, 2022 to Nov 20, 2022	N/A	N/A	Bucket collection of samples*	Portable DO meter
Fouling resistance (F.R.)	Painted panels	Nov 10, 2022 to Nov 20, 2022	65 to 100	100 max. limit	ASTM D3623 – 78a	N/A
Antifouling Film (A.F.)	Painted panels	Nov 10, 2022 to Nov 20, 2022	70 to 100	100 max. limit	ASTM D3623 – 78a	N/A
Anticorrosive Film (A.C.)	Painted panels	Nov 10, 2022 to Nov 20, 2022	70 to 100	100 max. limit	ASTM D3623 – 78a	N/A
Overall performance (O.P.)	Painted panels	Nov 10, 2022 to Nov 20, 2022	70 to 100	100 max. limit	ASTM D3623 – 78a	N/A

* Researchers will collect salt and lake waters in a bucket and then measure their pH using a portable pH meter, salinity, hardness (total dissolved solids), and DO when the waters are beyond the reach of portable meters.

9.2 Sample preparation method(s)

In accordance with ASTM D3623 – 78a, researchers will prepare a surface sandblasted profile of Sa $2^{1/2}$ for each steel panel.

In accordance with ASTM D3623 – 78a, we will drill a small hole of 6 mm of diameter into each steel panel prior to the sandblasting. This will be used to hold each panel while painting.

For the measurement of surface roughness of 1 to 1.5 mils, we will use a standard and calibrated surface roughness gauge.

We will apply a standard antifouling coating system in accordance with ASTM D3623 – 78a. Paints that are prohibited (like lead-based primer) or that are not available on the market will be replaced after receiving suggestions from the ASTM technical manager and other researchers who have been involved in similar studies. The replacement paints will also meet military specifications.

We will apply three paint films and a total of seven coats to the prepared steel panels. The first paint film is a green pretreatment coating (one coat of 13 μ m thickness). The second film is the primer (four coats, each 37.5 μ m thick, and a total thickness of 150 μ m), and the third film is the antifouling paint as topcoat (two coats, each 50 μ m thick, and a total thickness of 100 μ m).

We will use up to 20 antifouling paints on the market as topcoats. Because some paints specified in the ASTM method are currently prohibited or unavailable, we will need to use a different paint system to prepare the test and standard (control) steel panels. Therefore, it could be useful to perform tests to inspect the bonding of the primers and topcoat individually. We will measure the adhesion strength and scratch resistance by performing standard adhesion (ASTM D4541 – 17) and standard scratch (ASTM D7027 – 20) tests. To perform these tests, we will either use an additional 20 panels, or panels that are already available, then re-sandblast and paint after obtaining test results.

Once we have prepared all panels (estimated 21 for each location), we will affix (bolt) them onto racks. We will need to use racks that can support the heavy steel panels (5 to 8, each 9" × 9" on each rack) and keep them submerged for a period of one year. These racks will most likely be made from polypropylene or a composite material large enough to accommodate at least 5 to 8 panels. The arrangement of panels (distance between them) on the racks will be in accordance with ASTM D3623 – 78a (ASTM, 2020).

After affixing all of the panels onto racks, we should transport them to test locations and submerge them within two weeks of the topcoat application. At least one marine water and one lake water site will be used.

The panels need to be submerged a minimum of 0.3 meter and maximum of 3 meters deep (ASTM, 2020). We may use the piers available on site to tie and secure the racks. We will use fouling-resistant nylon rope of adequate strength to lower and raise the racks.

We will note the fouling types and record the fouling rating. We will also take pictures of each panel.

After a year of examining the fouling on each submerged panel, we will compile and statistically evaluate the results.

9.3 Special method requirements

Not applicable to this study.

9.4 Laboratories accredited for methods

This study is a field test that doesn't involve laboratory instrumentation or chemical analysis. The preparation of the steel panels, including sandblasting and spray painting, will take place at Washington State University's Frank Innovation Zone. This is an institute with standard research facilities.

10.0 Quality Control Procedures

The Frank Innovation Zone (WSU) is equipped with a sandblasting shop and a painting booth. These workspaces provide standardized set-ups (for example, the paint booth is equipped with HEPA filters). The Frank Innovation Zone will upgrade as needed to meet the requirements for work specified in this study. For example, the painting booth lacks a 16 cfm air compressor required for handling the load of a pressure pot (50 to 60 psi). The installation is in progress now. Throughout the project, the PI will review interim reports and attend monthly meetings to discuss the progress of the project.

10.1 Table of field and laboratory quality control

Table 12 presents the number of control panels and replicate areas on test panels, as well as the standards required for this project.

Parameter	Field Blanks	Field Replicates	Laboratory Check Standards	Laboratory Method Blanks	Analytical Duplicates	Laboratory Matrix Spikes
Examination of fouling growth on location 1	One per location	4 equal areas on one steel panel. Total 20 panels per location.	ASTM D3623 – 78a, ASTM D2200	N/A	N/A	N/A
Examination of fouling growth on location 2	One per location	4 equal areas on one steel panel. Total 20 panels per location.	ASTM D3623 – 78a, ASTM D2200	N/A	N/A	N/A
Examination of fouling growth on location 3	One per location	4 equal areas on one steel panel. Total 20 panels per location.	ASTM D3623 – 78a, ASTM D2200	N/A	N/A	N/A
Examination of fouling growth on location 4	One per location	4 equal areas on one steel panel. Total 20 panels per location.	ASTM D3623 - 78a, ASTM D2200	N/A	N/A	N/A

10.2 Corrective action processes

For this project, researchers will follow a straightforward procedure from the standardized method (ASTM D3623 – 78a). It is unlikely that there will be any deviations or inconsistencies.

Still, in case of any data loss or inconsistencies in the methods or results, including any deviations from this QAPP, the following actions may be taken:

- Report to the PI exactly when and where the procedure was different from the one mentioned in the QAPP.
- Report the data loss in the final report. If a panel is lost in the water, we may not have sufficient time to re-start the study. Other than losing panels in the water or lacking measurements due to inclement weather or personal emergencies, there should be no other reason for data loss.
- Share discussions with Ecology's representative and principle investigator soon after the methodology changes from that indicated in the QAPP. This will keep everyone informed and ensure that everyone agrees with any new approach, if used.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

All electronic data, including documents, analytical output, statistical analysis, reports, etc. will be stored on project computers at WSU. The project team plans to share field results, images, and quarterly progress reports with Ecology through email.

Data entry errors will be detected by comparing laboratory notebook records and electronic data records. When the field test is completed, the project team will review and analyze the data for a final summary report.

11.2 Laboratory data package requirements

Researchers will provide a data package to Ecology, including all the results obtained from the year-long testing and a summary report. The data package will report the test results clearly and accurately. We will also prepare a short presentation of the results and useful findings. In addition to the title and abstract pages, the summary report may include the following information for interpretation and validation of data:

- I. Study background and project's narrative
- II. ASTM test method objectives
- III. Brief summary of test procedure
- IV. Detailed results and useful findings
- V. Discussion and conclusions
- VI. Future work

ASTM D3623 – 78a shows examples of a fouling census and bar graph to report the details of results collected over a period of one to two years. Based on those, researchers will compile similar data reporting, mostly using Microsoft Excel. Researchers will generate the behavior report of experimental surfaces using Figure 6 (ASTM, 2020).

11.3 Electronic transfer requirements

As mentioned above, researchers will enter data into Microsoft Excel and Word and record all monitoring events and extensive results from the year of testing electronically. Researchers will share electronic record with Ecology through email.

11.4 EIM/STORET data upload procedures

Not applicable to this study.

11.5 Model information management

Not applicable to this study.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

As of now, researchers have not planned any audits for this study, nor has Ecology required any. Regular quarterly email updates detailing the project's progress will serve as a mandatory check tool.

12.2 Responsible personnel

Ecology's QA Officer or designee will review the processes and results. The processes can include product acquisition, product documentation and data entry, test panel preparation, and adherence to this QAPP and related SOPs.

12.3 Frequency and distribution of reports

Per the requirements of this project, researchers will provide quarterly email updates to report the progress of this project throughout the year. Moreover, researchers will share the results of water salinity, pH, temperature measurements, and fouling ratings at different test locations in monthly quarterly updates via email.

12.4 Responsibility for reports

The following authors will participate in writing, editing, and organizing the final summary report:

- 1. Mueed Jamal (Research Associate, WSU)
- 2. Dr. Xianming Shi (Professor and Chair CEE WSU, WSU)
- 3. Dr. Iris Deng (Client and Contract Manager, Ecology)

13.0 Data Verification

Researchers from WSU will verify data for this project by comparing results with the MQOs defined earlier. Evaluation of project completion will be made once we have collected all the data at the end of the year-long field testing. All the mandatory requirements in the project's proposal will be checked and Ecology will receive a final confirmation of task completion. The project lead and PI will verify the data and its correctness against the defined procedures and contractual requirements at least twice.

13.1 Field data verification, requirements, and responsibilities

The project team from WSU will verify all the collected field data on a monthly basis. This data includes the efficacy of all the paints from all test locations in terms of fouling ratings. With complete dataset, the PI will also make sure the QAPP's MQOs are met.

13.2 Laboratory data verification

This is a field test. The processes completed at the lab will be sandblasting, profiling the panels (drilling holes, etc.), and spray painting the panels. These processes are not generating data from analysis. Additional scratch resistance and adhesion strength tests may be required. The project lead, and then the PI, will verify these lab tests and the work. Researchers will follow standard procedures and use standard measuring gauges for all the lab work completed at WSU Pullman.

13.3 Validation requirements, if necessary

Not applicable to this study.

13.4 Model quality assessment

Not applicable to this study.

Data Quality (Usability) Assessment 14.0

14.1 Process for determining project objectives were met

To evaluate whether the project outcomes have met the original objectives, the project lead will assess if the data were collected consistent with the study design (with no reason to question the study design assumptions), study methods, and study procedures described in the final approved QAPP. The PI will further evaluate the data and verify if all relevant MQOs are met.

14.2 Treatment of non-detects

This field study is based on biofouling monitoring through visual observation. The non-detects are based on analytical measurement, which is not applicable to this type of study.

14.3 Data analysis and presentation methods

Researchers will use statistics to analyze the monthly fouling performance data of the 20 selected antifouling paints at the four selected field locations. One statistical tool is correlation analysis, which aims to assess the correlation between the various factors of interest, such as the coating type, exposure conditions, and fouling behavior. Another statistical tool is principal component analysis (PCA), which is a common strategy to reduce the dimension of exploratory variables for making predictive models. The contribution of each principal component to the total variance and its correlation with original variables can be used as indicators for the variable selection.

Yet another statistical tool is ANOVA (Analysis of Variance), which aims to assess the differences between the means of two independent groups by differentiating the variability from random versus systematic factors. This helps researchers determine the effect of the fouling on the influential factors (coating type, exposure conditions, etc.) and identify the statistically significant factors and interactions. Finally, we will conduct a student's t-test to evaluate the level of significance between groups (for example, coating A vs. coating B, location 1 vs. location 2). If the data of interest does not follow a normal distribution, we will use an alternative to the student's t-test.

In addition, we will plot the monthly fouling data from coated samples at the four locations over time so we can illustrate temporal evolution. We will also use the time-series data of each coating group at a given location to develop quantitative models that predict the antifouling performance of the coating group in the subsequent months.

14.4 Sampling design evaluation

Researchers anticipate that the sampling design will provide sufficient statistical power to draw scientifically-sound conclusions. Multiple measurements on each coated sample and four different exposure locations provide the basis for statistical reliability of the field measurement data in terms of relative antifouling efficacy of the 20 antifouling paints of interest. Collecting data from four field locations near Puget Sound that represent diverse exposure scenarios (for

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example, fresh vs. marine water, different water temperatures) provides the statistical power to account for variability in fouling scenarios across the state of Washington.

14.5 Documentation of assessment

The data usability assessment will be documented in the final summary report. Researchers will provide an Excel file that incorporates all the results to facilitate proper assessment of the data.

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16.0 Appendices

Appendix A. Product selection for performance testing

Ecology's Hazardous Waste and Toxics Reduction Program (HWTR) provides this Appendix A to describe the product selection process. Test products for this performance testing are selected based on prior research, market surveys, community outreach, pesticides registration information, and recommendations from other state agencies. Two previous legislative reports identified DCOIT/Sea-Nine, Tralopyril/Econea, or zinc pyrithione as alternative ingredients that are available on the market. Ecology identified 133 biocidal antifouling paints in the Pesticide Information Center Online (PICOL) Database in August 2022. The majority of the antifouling paints available on the market are copper-based.

Active ingredients	Number of products
Cu -based (CUPROUS OXIDE,)	111
Tralopyril (Econea, 1H-PYRROLE-3-CARBONITRILE 4-BROMO-2-(4- CHLOROPHENYL)-5-TRIF	15
DCOIT (Sea-Nine 211, 4,5-DICHLORO-2-N-OCTYL-3-ISOTHIAZOLONE)	8
Cybutryne (Irgoral, CYCLOPROPYL-N-(1 1-DIMETHYLETHYL)-6- (METHYLTHIO)	13
Zinc pyrithione (Zinc Omadine, ZINC 2-PYRIDINETHIOL 1-OXIDE)	24

Table 13. Antifouling active ingredients and number of registered products in WA.

In September 2022, Ecology reached out to 24 boatyards and one paint retailer, asking for the popular and effective copper and non-copper paints sold and used in Washington. There are approximately 60 boatyards in Washington that are active with general boatyard permits. Based on previous community outreach, boatyards mainly purchase painting products from four major retailers: Fisheries Supply Co., West Marine Seattle, Land N' Sea Distributing, and Seattle Marine. Ecology sent this survey to one-third of the boatyards and one leading retailer. We received one reply from a paint retailer and nine responses from boatyards (40% response rate) via emails or phone calls. Some of the boatyards have multiple locations in Puget Sound areas.

Paint retailers sell bottom paint direct to boatyards, but rarely to consumers. One of the leading retailers shared sales information and revealed that the top nine products with the highest sales percentages all contain cuprous oxide or copper thiocyanate as active ingredients. Eight out of the nine boatyards that replied to our survey offer painting services and provided recommendations for one or more coating products. Six out of eight boatyards offer both copper and non-copper options. The other two boatyards are not offering non-copper paints because they don't find non-copper paints that work as effectively as copper paints, and they worry the customer will question their workmanship for non-copper paints.

In addition to Washington-based retailer and boatyards, we heard from American Coating's Association that Sherwin Williams would like to test their product named SeaVoyage Copper Free AF. We will consider this product in the final selection; however, this product seems to be unavailable through a preliminary online search.

Based on all the information collected, Ecology proposes to test a list of 20 products as follows. This list is subject to change, depending on availability and other unforeseen challenges in obtaining products.

Manufacture	Product Name	Ingredients
Pottit	Hydrocoat Eco. Copper Eree	6 00% Ecopes 4 80% Zinc
Fettit	Ablative Antifouling Paint	Pyrithione
Pettit	ECO HRT - Copper-Free	6% Econea; 4.8% Zinc
	Seasonal Antifouling Paint	Pyrithione
Interlux	Micron CF Copper-Free	3.90% Econea 4.12% Zinc
	Ablative Antifouling Paint	Pyrithione
Interlux	Pacifica Plus - Ablative	3.90% Econea 4.12% Zinc
	Seasonal Antifouling Paint	Pyrithione
Blue Water	Shelter Island Plus Copper	5.6% Econea, 4.0% Zinc
	Free Ablative	Pyrithione
Sherwin-Williams	Seavoyage Copper Free A/F	7.28% Econea; 6.38% Zinc
	Paint	Pyrithione
Seahawk	Smart Solution Ablative	2.90% Econea
	Antifouling Paint	
Seahawk	Mission Bay Copper-Free	3.80% Zinc Pyrithione
	Ablative Antifouling Paint	
EPAINT	EP-ZO Ablative Antifouling	4.80% Zinc Pyrithione
	Paint	
EPAINT	SN-1 Ablative Antifouling	2.91% DCOIT
	Paint	
EPAINT	EP-2000 Antifouling Paint	4.7% Zinc Pyrithione
International	Intersleek 1100 SR	non biocidal
Propspeed	Propspeed	non biocidal
International	Interspeed 640 Polish A/F	41.97% Cuprous Oxide
Seahawk	Cukote Ablative Antifouling	47.57% Cuprous Oxide
	Paint	
Seahawk	AF-33 Ablative Formula	33.60% Cuprous Oxide
	Antifouling Paint	
Seahawk	Sharkskin - Hard Modified	45.20% Cuprous Oxide
	Epoxy Antifouling Paint	
West Marine	PCA Gold Premium Ablative	47.50% Cuprous Oxide
	Antifouling Paint	
Interlux	Micron CSC - Ablative	37.20% Cuprous Oxide
	Antifouling Paint	
Interlux	Fiberglass Bottomkote NT -	25.00% Cuprous Oxide
	Ablative Antifouling Paint	

Table 14: A list of proposed products.

Appendix B. Glossaries, acronyms, and abbreviations

Glossary of general terms

Antifouling

A mechanism to prevent the growth and settlement of marine organisms.

Biofouling

Biofouling can generally be categorized as either microfouling (bacterial and diatomic biofilms) or macrofouling (macroalgae, barnacles, mussels, oysters, tubeworms, bryozoans).

Conductivity

A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen (DO)

A measure of the amount of oxygen dissolved in water.

рΗ

A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Salinity

Salinity is the dissolved salt content of a body of water

Acronyms and abbreviations

Table 15. Acronyms, abbreviations, and their meanings.

Term	Meaning
Alt.	Alternative
A.F.	Antifouling
BMP	Best management practice
CDPR	California Department of Pesticide Regulation
CEE	Civil and Environmental Engineering
DO	dissolved oxygen (see Glossary above)
DCOIT	4,5-dichloro-2-octyl-1,2-thiazol-3(2H)-one
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
FIZ	Frank Innovation Zone

Term	Meaning
i.e.	In other words
MQO	Measurement quality objective
OTCs	Organotin Compounds
PI	Principle investigator
PRF.	Performance
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SOP	Standard operating procedure
TBT	TriButyltin
TPht	TriPhenyltin
TriDurLE	Transportation Infrastructure Durability Longevity and
	Extension
WSU	Washington State University

Units of measurement

Table 16. Units of measure.

Unit	Meaning
°F	degrees Fahrenheit
Ft	feet
g	gram, a unit of mass
in	inch(es)
Kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mm	millimeter
mg	milligram
mL	milliliter
μm	micrometer or microns

Quality assurance glossary

Accreditation

A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)...that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy

The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (Jones, 1998).

Analyte

An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin, 2010).

Bias

The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Lombard and Kirchmer, 2004).

Blank

A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (Jones, 1998).

Calibration

The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Lombard and Kirchmer, 2004).

Check standard

A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Lombard and Kirchmer, 2004).

Comparability

The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 1997).

Completeness

The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

Continuing Calibration Verification Standard (CCV)

A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin, 2010).

Control chart

A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Lombard and Kirchmer, 2004).

Control limits

Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin, 2010).

Data integrity

A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin, 2010).

Data quality indicators (DQI)

Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA, 2006).

Data quality objectives (DQO)

Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA, 2006).

Data set

A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010).

Data validation

An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.
- Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

No qualifier – data are usable for intended purposes.

J (or a J variant) – data are estimated, may be usable, may be biased high or low.

REJ – data are rejected, cannot be used for intended purposes (Kammin, 2010; Lombard and Kirchmer, 2004).

Data verification

Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Lombard and Kirchmer, 2004).

Detection limit (limit of detection)

The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Lombard and Kirchmer, 2004).

Duplicate samples

Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 1997).

Field blank

A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Lombard and Kirchmer, 2004).

Initial Calibration Verification Standard (ICV)

A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin, 2010).

Laboratory Control Sample (LCS)

A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997).

Matrix spike

A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Lombard and Kirchmer, 2004).

Measurement Quality Objectives (MQOs)

Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA, 2006).

Measurement result

A value obtained by performing the procedure described in a method (Lombard and Kirchmer, 2004).

Method

A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (USEPA, 1997).

Method blank

A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Lombard and Kirchmer, 2004; Kammin, 2010).

Method Detection Limit (MDL)

This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, 1984).

Percent Relative Standard Deviation (%RSD)

A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

%RSD = (100 * s)/x

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

Parameter

A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin, 2010; Lombard and Kirchmer, 2004).

Population

The hypothetical set of all possible observations of the type being investigated (Lombard and Kirchmer, 2004).

Precision

The extent of random variability among replicate measurements of the same property; a data quality indicator (Jones, 1998).

Quality assurance (QA)

A set of activities designed to establish and document the reliability and usability of measurement data (Kammin, 2010).

Quality Assurance Project Plan (QAPP)

A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Lombard and Kirchmer, 2004).

Quality control (QC)

The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Lombard and Kirchmer, 2004).

Relative Percent Difference (RPD)

RPD is commonly used to evaluate precision. The following formula is used:

[Abs(a-b)/((a + b)/2)] * 100

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Lombard and Kirchmer, 2004).

Replicate samples

Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (Jones, 1998).

Representativeness

The degree to which a sample reflects the population from which it is taken; a data quality indicator (Jones, 1998).

Sample (field)

A portion of a population (environmental entity) that is measured and assumed to represent the entire population (Jones, 1998).

Sample (statistical)

A finite part or subset of a statistical population (USEPA, 1997).

Sensitivity

In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Lombard and Kirchmer, 2004).

Spiked blank

A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 1997).

Spiked sample

A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 1997).

Split sample

A discrete sample subdivided into portions, usually duplicates (Kammin, 2010).

Standard Operating Procedure (SOP)

A document that describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

Surrogate

For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin, 2010).

Systematic planning

A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA, 2006).

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