PNNL-30285

Pacific Northwest
NATIONAL LABORATORY

Naval Information Warfare Center
PACIFIC

ENVVEST Ambient Monitoring Program

In-Progress Summary 2009–2019

September 2020

JE Strivens
N Hayman
M Colvin
G Rosen
J Frew
T Richardson

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

ENVVEST Ambient Monitoring Program

In-Progress Summary 2009–2019

JE Strivens [a*]
N Hayman [b]
M Colvin [b]
G Rosen [b]
J Frew [b]
T Richardson [c]

September 2020

[*] To whom correspondence may be addressed (Jonathan.Strivens@pnnl.gov)
[b] Naval Information Warfare Center Pacific, San Diego, CA[1]
[c] Puget Sound Naval Shipyard and Intermediate Maintenance Facility, Bremerton, WA

Prepared for
The Puget Sound Naval Shipyard & Intermediate Maintenance Facility
Project ENVVEST

Suggested citation:
Strivens, J.E., Hayman, N., Colvin, M., Rosen, G., Frew. J., Richardson. T. 2020. ENVVEST Ambient Monitoring Program: *In-Progress Summary 2009–2019*. PNNL-30285, prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Pacific Northwest National Laboratory
Sequim, Washington 98363

[1] This document's content represents work performed under Space and Naval Warfare Systems Center Pacific (SSC Pacific). SSC Pacific formally changed its name to Naval Information Warfare Center Pacific (NIWC Pacific) in February 2019.

Foreword

The ENVVEST Project is designed to develop and demonstrate strategies for protecting and improving the health of aquatic ecosystems in partnership with the U.S. EPA and the Washington State Department of Ecology. The primary objectives of the ENVVEST Project serve to establishing environmentally protective levels for chemicals-of-concern and incorporate them into decision making processes. The objectives are achieved through the use of sound ecological science and risk-based management. The ENVVEST Ambient Monitoring Program (stewarded by long-standing technical stakeholders, MSL and NIWC) is a singular component of the Project and should be considered holistically within ENVVEST's large scale environmental monitoring efforts.

This report is a periodic update and supersedes:

Strivens, J.E., Johnston R.K., Schlafer N., and Brandenberger J.M. 2018. *ENVVEST Ambient Monitoring Program: In-Progress Summary 2009–2017*. PNNL-28116, prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Primary updates in this summary consist of:

(1) The addition of chemistry from five AMB Events (AMB25–AMB29) conducted from 2018–2019,
(2) Incorporation of long-term whole effluent toxicity and receiving water toxicological evaluations,
(3) A review of the Sinclair/Dyes Inlet's water-effects-ratio toward protective effluent thresholds, and
(4) Demonstration of DGT-labile marine Toxics Substances Criteria and fractionation in setting NPDES effluent limits that are protective toward surface waters and the mass balance of the inlets.

The current report provides a basis for determining the need for improvements, a means of assessing of the effectiveness of corrective actions and informs on adaptive management actions needed to improve environmental quality and to protect aquatic resources of the Sinclair and Dyes inlets.

Recent companion reports (i.e., those that report status and trends most current toward confluence-approach decision making) include:

1. Brandenberger J.M., Metallo D., Rupert B., Johnston R., Gebhart C., and J.E. Strivens. 2018. *Non-Dry Dock Stormwater Monitoring Report for Puget Sound Naval Shipyard, Bremerton, Washington 2010-2013*. PNNL-27900, prepared for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

2. Johnston R., Brandenberger J., Guerrero J., Rosen G., and Colvin M. 2019. *Sediment Quality Verification Study and Baseline for Process Improvement at the Puget Sound Naval Shipyard and Intermediate Maintenance Facility, Bremerton, Washington*. PNNL-29156, prepared for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

3. Strivens, J.E. and Johnston R. 2019. *ENVVEST Mussel Watch Program In-Progress Summary 2010–2018*. PNNL-29110, prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Executive Summary

This report summarizes the in-progress findings (2009–2019) of effluent and surface water chemistry and toxicological evaluations within the Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF, part of Naval Base Kitsap-Bremerton [NBK]) and surrounding marine waters (Sinclair and Dyes Inlets), collected under Project ENVironmental inVESTment's (ENVVEST) Ambient Monitoring Program (AMB). Project ENVVEST was initiated as a cooperative effort among the PSNS&IMF, regulatory agencies, and local stakeholders to protect beneficial uses of Sinclair and Dyes Inlets. The overall goal of the Ambient Monitoring Program, under Project ENVVEST, is monitoring and tracking environmental water quality to support characterization of the status and trends of ecological resources, assess the effectiveness of cleanup and pollution control measures, and determine whether discharges from all sources are protective of beneficial uses, including those related to aquatic life and human health, in the receiving waters of the Inlets—all in the context of U.S. Environmental Protection Agency (EPA) National Pollution Discharge and Elimination System (NPDES) regulations, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) cleanup requirements, and EPA aquatic life criteria. This report is provided by the Pacific Northwest National Laboratory's (PNNL) Marine Sciences Laboratory (MSL) and the Naval Information Warfare Center (NIWC) Pacific's Bioassay Laboratory. MSL and NIWC have been instrumental in designing the field sampling programs for biota, sediments, freshwaters, and marine waters for Project ENVVEST. Additionally, MSL provides chemical analyses of metals and organics at the required low levels of detection to meet Project goals and under NELAC accreditation through NJDEP (laboratory Certification ID. No. WA004) and by reciprocity the State of Washington's Department of Ecology (Ecology) (Laboratory ID. No. F560). NIWC Pacific provides evaluations of whole effluent toxicity (WET) tests and is a certified laboratory under the State of California Department of Health Services Environmental Laboratory Accreditation Program (ELAP), Certification ID. No. 2601, and Ecology's accreditation program, Laboratory ID. No. F893.

The succinct ENVVEST Ambient Monitoring Program objectives include:

- Extending the baseline for assessing continuous process improvement of the PSNS&IMF operations and other sources of contamination into Sinclair and Dyes Inlets;
- Providing data for validation and verification of mixing zone models (ambient data are needed to inform the development of discharge limits, verify and validate discharge models, and assess total loading of all contaminants into the two Inlets);
- Obtaining data and information about the toxicity of effluents and receiving waters for NPDES permitting for the PSNS&IMF (specific toxicity tests of effluents and ambient waters are needed to inform the permit process); and
- Developing procedures needed to meet ambient monitoring requirements for water, sediment, and biota in support of adaptive management actions.

Investigative Activities

2009–present

Under the Ambient Monitoring Program, the PSNS&IMF, MSL and NIWC initiated marine water sampling in August 2009 and proceeding collections have captured wet and dry periods (i.e., summer/fall [dry] and winter/spring [wet]) for a total of 29 campaigns over 10-years. Monitored stations, to date, have been grouped into five main zones based on proximity to industrial activities: 1) end-of-pipe NPDES-regulated

PSNS&IMF outfalls; 2) nearshore along the industrialized waterfront of the PSNS&IMF and within 30 m of a monitored outfall; 3) along the floating security barrier of the PSNS&IMF; 4) nearshore in Sinclair Inlet along the Bremerton and Port Orchard waterfront, the mouth of the Port Washington Narrows, and reference locations in Dyes Inlet, Port Orchard Passage, and Rich Passage; and 5) central marine waters in Sinclair and Dyes Inlets and the passages to central Puget Sound. The 29 sampling campaigns conducted are identified as AMB01 through AMB29.

Sampling has consisted of composite or grab samples for permit-specific trace metals (Hg, Cu, Pb, and Zn), ancillary parameters (total suspended solids, total organic carbon, dissolved organic carbon, salinity, ammonia as nitrogen, nitrate + nitrite as nitrogen, total Kjeldahl nitrogen, total phosphorous, and oil/grease) and supporting metals (Al, Ag, As, Cd, Cr, and Ni). It should be noted that at the time of this report, NPDES permit guidance is only in effect for Cu; other metals classified as permit-specific in this report are those included in historic and/or current NPDES draft permits. This report summarizes data for these permit-specific metals as both spatial and temporal trends to highlight areas of concern and to inform on long-term improvements to the waterbody.

The Ambient Monitoring Program has also consistently performed acute and chronic endpoint toxicological evaluations on a subset of stations within Sinclair Inlet and whole effluent testing on PSNS industrial discharges. This approach allows for detection of ecological impacts that can occur from constituents not targeted for chemical quantification, both illicit (e.g. contaminated wastewater discharges) and natural (e.g., harmful algal bloom toxins), and is critical for comprehensive long-term protection strategies. These evaluations include: 1) acute 96-h mysid (*Americamysis bahia*) survival, 2) chronic 48-h bivalve (*Mytilus galloprovincialis*) embryo-larval development, 3) chronic 96-h echinoderm (*Strongylocentrotus purpuratus*) embryo-larval development, 4) QwikLite (*Pyrocystic lunula*) 24-h bioluminescence, and 5) giant kelp (*Macrocystis pyrifera*) 48-h germination and growth. Test method and species selection was based on those outlined in the draft working NPDES permit for PSNS (2008a) and/or deemed as appropriate surrogates for such tests. Test method selection also considered sensitivity to likely contaminants of concern including Cu and Zn, with embryo-larval development tests with sea urchins and mussels being particularly sensitive and relevant to the geographical area.

2016–present

Toward fulfilling a cornerstone objective of Project ENVVEST, the novel, scientifically progressive, and cost-effective approach of water quality assessment by passive sampling has been instituted with an initial focus on Cu bioavailability in surface waters. The specific approach relies on diffusive gradients in thin-films (DGT), which are capable of measuring 30+ metals (including Cd, Cu, Ni, Pb, and Zn) and a variety of organic contaminants-of-concern in a time-averaged manner and can then be expressed as ambient concentrations through understanding of Fick's First Law of Diffusion. To date, ENVVEST has successfully developed toxicological endpoints for Cu when monitoring the operationally defined "labile" fraction, which is integrated by DGT through a mechanism that reflects in situ ligand competition. This threshold allows for assessment of surface water health within the PSNS&IMF and at Kitsap Basin reference sites stewarded by ENVVEST stakeholders (e.g., the Port of Silverdale, Port of Illahee, and WA State Ferry Maintenance Terminal). Beginning in March of 2016, in partnership with the Navy's Environmental Sustainability Development to Integration Program (Project #523), DGT passive samplers were co-deployed during eight Ambient Monitoring Program events. The dataset that has been established allows for labile fraction-based loading to become a fundamental component of multiple-line-of-evidence approaches and can be readily adopted for use by Naval Installations, and others, following legal adoption by ENVVEST partners (Strivens et al. 2020a).

Findings

The following primary conclusions can be drawn, pertaining to PSNS&IMF, from this in-progress summary:

Mercury

In relation to Toxics Substances Criteria, the marine chronic value for Hg has been exceeded at PSNS Nearshore Station PS03 twice in the last decade (AMB01 [08/31/2009] and AMB17 [04/07/2015]). PS03 has been the subject of multiple investigations (e.g., Brandenberger et al. 2018; Conn et al. 2018) and is thought to be impacted by intrusion and leaching of legacy contaminated soil. All other stations within the study area met protection thresholds for surface waters and there has been no significant difference between the long-term monitoring results for PSNS&IMF Barrier and the nearshore or marine stations of the Inlets; indicating that elevations within PSNS are not, on average, significantly transported within the surface layer from the barrier downstream. The PSNS&IMF's nearshore mean total Hg levels fell within the expected ranges for Puget Sound waters; however, dissolved levels were, on average, four times greater in the PSNS Nearshore impact zone and two times greater in the Sinclair and Dyes Inlet's surface waters in comparison to the broader Puget Sound. These results are in agreement with the finding of Johnston et al. (2019) and Strivens and Johnston (2019) and are majorly influenced by legacy deposition currently being addressed under CERCLA. Long-term water concentrations display stable trends of both total and dissolved Hg, and the PSNS&IMF drydock outfalls are not significantly contributing to immediate surface water conditions.

Copper

Predominately, surface water data show few exceedances of default Toxic Substances Criteria for Cu over the last decade. Importantly, ENVVEST water-effect ratio (WER) efforts for the Sinclair/Dyes Inlet show that grab samples do not indicate the occurrence of any acute effects (Rosen et al. 2009), earlier concerns about olfactory response to salmon have been alleviated based on studies focused on relevant life stage and water chemistry in the region (Sommers et al. 2016; Rosen et al. 2009), and 4-years of labile Cu data have also demonstrate protection of the environment. Long-term, dissolved Cu concentrations of surface waters within the PSNS&IMF are trending downward, with the exception of direct receiving zones for OF018 and OF019. The datasets, herein, suggest that reasonable potential (before consideration of mixing) exists to exceed both default and biological response modulated Toxics Substances Criteria at these two locations. Toward derivation of a conservatively protective NPDES benchmark for loading from drydock outfalls it is demonstrated and recommended that the agreement between WER and DGT-labile Cu derived water quality-based effluent limits should be acknowledged as the genesis for their use. Following adoption of this practice, incorporation of CH3D dilution ratios and bioavailability criterion should be used to adjust the waste load allocation within the confines of a protective mass balance loading scenario.

Lead

All sites with the ENVVEST study area have remained an order of magnitude below the Toxic Substances Criteria over the last 10-years. There has been no significant difference between the PSNS Barrier and the Sinclair/Dyes Nearshore impact zones. In comparison to five other Puget Sound shipyard areas, mean dissolved Pb in inner shipyards was 0.0653 µg L^{-1} (Hobbs et al. 2018) and PSNS averages 0.0231 µg L^{-1}; additionally, Puget Sound marine areas have been shown to average 0.0819 µg L^{-1} and Sinclair/Dyes Marine averages 0.0173 µg L^{-1}. No NPDES limits are currently in place for this analyte and reasonable potential assessment indicates that previous draft water quality-based effluent limits are not essential.

Zinc

The ENVVEST dataset shows a statistically significant difference across surface water impact zone delineations and the average dissolved Zn over time. Gradients digress from the PSNS Nearshore (5.19 µg L^{-1}) to the PSNS Barrier (3.09 µg L^{-1}) to the Sinclair/Dyes Nearshore (1.89 µg L^{-1}) and then to the Sinclair/Dyes Marine (1.19 µg L^{-1}) impact zone. Elevated Stations within the PSNS display the same trend as Cu, and are those nearest to drydock effluent points, but no data have exceeded the marine chronic criterion of 81.0 µg L^{-1} over the span of the Ambient Monitoring Program and the effectual NPDES limit has never been breached. However, the variability in OF018 total Zn (average 36.8 ± 14.4 µg L^{-1}) and OF019 total Zn (average 22.0 ± 15.2 µg L^{-1}), over the last decade, drive reasonable potential for concern toward Toxic Substances Criteria encroachment. As is recommended for Cu, CH3D dilution factors should be applied to drydock effluent statistics for Zn, to adjust the draft waste load allocations, followed by consideration of transport and fate (i.e., for both mass balance and focusing).

Purple Sea Urchin Embryo-Larval Development

For the sea urchin embryo-larval development test, with percent normal larval development as the endpoint, significant toxicity (>25% toxic effect) has been observed infrequently at OF019 early in the monitoring period and more recently at OF018. A total of 27, 26, 28, and 4 samples have been tested for OF018, OF019, OF021, and OF096, respectively. Following EPA (1995) procedures (significant adverse effect compared to the control), 33.3%, 15.4%, 0%, and 50.0% of tested samples have been toxic for OF018, OF019, OF021, and OF096, respectively. Although there was no clear statistically significant relationship between observed toxicity and dissolved Cu or Zn concentrations, because sea urchins are relatively sensitive to both copper and zinc, a simplistic toxic unit (TU) analysis was conducted herein. Summing of copper and zinc TUs suggested that these constituents may explain at least some of the toxicity, with the highest TUs occurring as OF018>OF019>OF021>OF096, comparable to the order for dissolved Cu and Zn concentrations. Verification of the cause of toxicity would require other testing strategies such as toxicity identification evaluations (TIEs). Further, the use of the TU approach here is somewhat limited due to the fact that water chemistry characteristics, such as dissolved organic carbon, that have resulted in models to estimate potential reduction of the bioavailability of Cu are not well developed for Zn. In samples from the receiving environment, toxicity was rarely observed, except in the presence of planktonic red tide organisms (e.g. *Gymnodinium sp., Psuedo-nitzschia sp.*) at densities reported to cause toxicity to co-occurring species, presumably associated with saxitoxin (*Gymnodinium*) or domoic acid (*Pseudo-nitzschia*) production in the toxicity test vessels. Such events occurred in summer months (typically August-September) and were present most commonly in the middle of Sinclair Inlet, but also were found at high densities at PSNS Nearshore sites periodically. Incidence of sea urchin (and the other test species evaluated in this program) toxicity was almost exclusively limited to the documentation of elevated concentrations red tide organisms following microscopic identification and determination of densities for comparison to thresholds reported in the literature.

Mediterranean Mussel Embryo-Larval Development and Survival

For the mussel embryo-larval development test, two endpoints are reported: percent normal-alive and percent normal development. Significant toxicity (>25% toxic effect) has been observed infrequently at OF019 and OF021 earlier in the monitoring period and more recently at OF018. A total of 15, 16, 17, and 2 samples have been tested for OF018, OF019, OF021, and OF096, respectively. Following EPA (1995) procedures (significant adverse effect compared to the control), 20.0%, 6.3%, 11.7% and 0% tested samples have been toxic for OF018, OF019, OF021, and OF096, respectively. There are instances where toxicity was observed in the sea urchin test, but not in the mussel. Most reports show that mussel embryos are less sensitive to zinc than purple sea urchins, which may explain the reduced instance of adverse effects with

mussel embryos. Similar to the other tests, toxicity observed in near-shore surface samples was attributed to the presence of harmful algal species (red tide events).

Dinoflagellate Bioluminescence

The bioluminescent test using the dinoflagellate was conducted 22, 21, 22 and 4 times for outfall samples OF018, OF019, OF021 and OF096, respectively. Significant reductions in bioluminescence, when compared to controls, were observed intermittently for all the outfall samples. 22.7%, 9.5%, 4.5% and 50% tested samples have been toxic for OF018, OF019, OF021, and OF096, respectively. It should be noted that this test tended to be more variable than the other standard methods employed in this monitoring program, and it maybe be appropriate to put less weight on this test with respect to decision making. As with the other test methods, several instances of reduced bioluminescence were observed in the near-shore surface samples but are not related to outfall discharges and likely a result of red tide occurrences.

Giant Kelp Germination and Growth

Two endpoints are reported for the giant kelp bioassay: spore germination and spore growth. Toxicity testing using this species was conducted for ambient monitoring events AMB01 through AMB10. OF018, OF019 and OF021 were tested a total of 10, 8 and 10 times, respectively. While the test for significant toxicity (TST) statistical analysis was not conducted on samples during these events, the significant toxicity threshold of 25% was used for comparative purposes. The percent difference from controls never exceeded 25% for the samples from the outfalls. Following EPA (1995) procedures (significant adverse effect compared to the control), OF018 exhibited toxicity during a single event (AMB06) for the growth endpoint, out of the 10 events conducted. Samples from OF019 and OF021 never exhibited toxicity using the EPA (1995) method. A single near-shore surface water sample showed toxicity for the growth endpoint during AMB01, and consistent with the other species evaluated, toxicity was likely due to the red tide event observed. This test was ultimately eliminated from the monitoring program after AMB10, in 2012, due to redundancy with the bioluminescence test, which fills the gap for an algal species.

Mysid Shrimp Survival

The mysid survival tests demonstrated no significant toxicity (>20% mortality) in any of the outfall samples over the 10-year period. Assuming Cu and Zn are the primary contaminants of concern in the outfalls, this result is not surprising considering relatively low sensitivity in comparison with the embryo-development test methods, with LC50s higher by an order of magnitude. This said, the mysid shrimp is widely employed in NPDES permits for Navy discharges (e.g. the metro Naval bases in San Diego) due to its overall sensitivity to effluents and general lack of false positives. Periodically, toxicity was observed in some ambient samples, but these were attributed to toxic red tide events occurring during collection events. A total of 27, 27, 28, and 4 samples have been tested for OF018, OF019, OF021, and OF096, respectively, and none were determined to be toxic following EPA (2002) procedures (significant adverse effect compared to the control).

Summary Recommendations

The Ambient Monitoring Program interlaces with the ENVVEST Sediment Quality, Mussel Watch, Non-Dry-Dock Stormwater, Mass Balance, and CH3D Modelling Programs. The datasets described herein provide baselines for assessing continuous process improvement of the PSNS&IMF operations and other sources of contamination entering Sinclair and Dyes Inlets. The Ambient Monitoring Program is critical for stewarding this waterbody and can be continually used to this end, with each event in turn demonstrating

protection of beneficial uses to all stakeholders. Currently, copper is denominated the primary analyte-of-concern within the AMB datasets and will be the focus of impending stormwater characterizations – toward an updated perspective of total loading reflective of AKART completion.

In recognition that recent NPDES regulations have been developed with generic reference values, toward the reduction of potential for toxicologically significant micronutrient-level exceedances of trace metals in Shipyards (e.g., EPA 2008a; Ecology 2016, 2019) and strong statistical differences between PSNS&IMF Nearshore and Barrier grab samples, continuous monitoring efforts should promote this location for maintaining the ENVVEST ambition to demonstrate novel approaches toward environmental protection that can sequentially benefit the local waterbody and also be adopted by others on a larger scale. Continued development of labile fraction criteria has considerable potential to benefit coastal communities, at large, where current operationally defined dissolved fraction reference values potentially under- or overestimate toxicological impacts – leading to either ecological damage or non-essential remediation costs. Draft guidelines on their use, herein, are not regulations and do not impose any new requirement. Rather, these biologically relevant assessment thresholds are presented to initiate public involvement and intergovernmental coordination toward adopting novel, and superior, approaches to ecological risk assessment.

For NPDES permit renewal, the site-specific Cu translators and resulting water quality-based effluent limits discussed in Section 5.2.2 should be given primary consideration. These results provide direct assessment of OF018 and OF019 drydock effluents and can, in combination with CH3D, the results of Brandenberger et al. (2018), and relevant indicators of habitat protection (e.g., Johnston et al. 2019; Strivens and Johnston 2019), be adapted to conservatively regulate drydock and stormwater outfalls for protection of surface waters.

For all end users of this report, it is imperative to recognize that the ENVVEST Project should be considered holistically, as it was designed to provide multiple-line-of-evidence approaches for risk assessors, regulators, compliance managers, and stakeholders toward attainment and preservation of beneficial uses of the Sinclair and Dyes Inlets waterbody. For further understanding of the ENVVEST strategy, the *Puget Sound Naval Shipyard Project ENVVEST Technical Work Master Plan*, which was written by the Project ENVVEST Technical Steering Committee, is available from the PSNS Public Affairs Office (POC: pao@psns.navy.mil).

Abbreviations and Acronyms

AKART	All Known, Available, and Reasonable Methods of Treatment
AMB	AMBient monitoring
AML	average monthly limit
AN	ammonia as nitrogen
ANOVA	analysis of variance
AVS-SEM	acid-volatile sulfide-simultaneously extracted metals
BMP	best management practice
CASS	coastal Atlantic seawater standard
CBR	critical body residue
C_{DGT}	concentration in µg L^{-1}, as measured by DGT
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CETIS	Comprehensive Environmental Toxicity Information System
CFR	Code of Federal Regulations
CMC	criterion maximum concentration
CRM	certified reference material
CVAF	cold vapor atomic fluorescence
CWA	Clean Water Act
DD	dry dock
DGT	diffusive gradients in thin-films
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	U.S. Department of Defense
DOE	Washington Department of Ecology
DWE	dry weather event
DWSE	dry weather storm event
EC50	Median Effective Concentration
ELAP	Environmental Laboratory Accreditation Program
ENVVEST	ENVironmental inVESTment
EPA	Environmental Protection Agency
F_D	fractional difference
FFCA	Federal Facility Compliance Agreement
FIAS	flow-injection atomic spectroscopy
HEM	hexane extractable material
HGAA	hydride generation atomic absorption
HSD	honest significant difference
HTCO	high temperature catalytic oxidation

IC	inorganic carbon
ICP-MS	inductively coupled plasma mass spectrometry
KPUD	Kitsap Public Utility District
LC50	Median Lethal Concentration
LCS	laboratory control sample
MB	method or procedural blank
MDL	maximum daily limit or method detection limit
MLLW	mean lower low water
MS	matrix spike or mass spectrometry
MSD	matrix spike duplicate or minimum significant difference
MSL	Marine Sciences Laboratory (PNNL)
NBK	Naval Base Kitsap
NIWC	Naval Information Warfare Center
NNN	nitrate + nitrite as nitrogen
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollution Discharge Elimination System
NPOC	non-purgeable organic carbons
OC	organic carbon
OF	outfall
PNNL	Pacific Northwest National Laboratory
POC	point of contact
Ppt	parts-per-thousand
PSNS	Puget Sound Naval Shipyard
PSNS&IMF	Puget Sound Naval Shipyard & Intermediate Maintenance Facility
PSU	practical salinity unit
QAPP	quality assurance project plan
QC	quality control
RPD	relative percent difference
SOP	standard operating procedure
SRM	standard reference material
TIE	toxicity identification evaluation
TKN	total Kjeldahl nitrogen
TOB	test of bioequivalence
TOC	total organic carbon
TP	total phosphorous
TRM	total recoverable metals
TSS	total suspended solids
TST	test for significant toxicity

WER	water effect ratio
WET	whole effluent toxicity
WQBEL	water quality-based effluent limit
WWBF	wet weather base flow
WWSE	wet weather storm event

Contents

Figures

Tables

1.0 Introduction

The Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF), a tenant command operating within Naval Base Kitsap (NBK) and also referred to as the "Bremerton Naval Complex" (BNC) in U.S. Environmental Protection Agency (EPA) Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) documents, is located on Sinclair Inlet in Bremerton, Washington, and is referred to, herein, as "PSNS" for brevity and continuity with previous Ambient Monitoring reports. PSNS is the largest industrial facility on Sinclair Inlet and has been in operation since 1896; it functions primarily to repair, refuel, and decommission naval ships. Critically, the PSNS' Drydock No. 6 is the largest drydock on the U.S. west coast and the only drydock that can service aircraft carriers. In stewarding this DoD capability, the PSNS has committed to a culture of continuous process improvement for all aspects of operations, including preventing releases of hazardous materials and waste in marine discharges. Toward maintaining those values, and in response to 1998 303(d) survey findings (i.e., listings As, Cd, Cu, Pb, Hg, Ag, Zn, and PCBs), in 2000 under the EPA Project XL (eXcellence in Leadership) Program (which offered "federal facilities the opportunity to propose novel and cost-effective ways of protecting the environment"), the Project ENVVEST (ENVironmental inVESTment) Final Project Agreement was signed as a cooperative program among PSNS, the EPA, the Washington State Department of Ecology (Ecology), and local stakeholders to leverage and extend efforts to help improve environmental quality and assist in meeting water quality goals for Sinclair and Dyes Inlets and their surrounding watersheds (EPA 2000; PSNS, EPA and Ecology 2000).

Sinclair and Dyes Inlets in Puget Sound receive pollution from a variety of Naval and non-Naval sources including PSNS operations, marina and vessel traffic, storm event runoff, discharges from municipal wastewater treatment plants, industrial outfalls, and surface streams, as well as legacy sources such as contaminated sediments that are being addressed by CERCLA cleanup and restoration activities (e.g., URS 2008; Paulson and Keys 2009; Paulson et al. 2010; US Navy 2012a, 2017). Toward addressing such a complex and diverse series of input streams, Project XL Program projects are tailored to demonstrate in situ results of innovative environmental compliance strategies and develop line-of-evidence approaches to guide EPA evaluations of protection efforts and inform on the need to replace or modify regulatory benchmarks and policy-setting approaches. ENVVEST is specifically aimed toward advancing the science behind current National Pollutant Discharge Elimination System (NPDES) default guidance: the current report fulfills the foundational ENVVEST objectives of assessing ecosystem health by determining the relative contributions and effects of prioritized industrial and stormwater discharge sources, supporting modeling of contaminant loading into the Inlets and development of mixing zone isopleths (Johnston and Wang 2004; Katz et al. 2004, Johnston et al. 2009b; Wang et al. 2011), demonstrating protection of beneficial uses required under the Clean Water Act (Johnston et al. 2009, 2018a) and the XL Program objective of demonstrating alternative tools for the NPDES Program. In addition, multiple assessment endpoints and ecological responses relevant to NPDES objectives have been tracked by the ENVVEST Project through a number of long-term programs (e.g. stormwater [Brandenberger et al. 2018], marine receiving waters [Strivens et al. 2018a], sessile biota [Strivens and Johnston 2019d,e], and silt/sediments [Johnston et al. 2019]). The current report should be considered within the entirety of the aforementioned components.

Due to expansive contaminant source control measures conducted in the Inlets following the ENVVEST agreement (e.g., new pollution prevention measures, hazardous waste minimization, combined sewer overflow reduction, sediment cleanup, dredging, and sediment capping activities [all of which are comprehensively documented in Johnston et al. 2019]), current PSNS NPDES guidance has not been updated under the ENVVEST Agreement. In this interim period, discharges from the PSNS are being regulated by the EPA under the Clean Water Act NPDES Industrial Permit No. WA-000206-2, issued April 1, 1994 and administratively extended since 1999. This permit covers all PSNS operations and authorizes

the discharge of dry dock drainage, non-contact cooling water, treated steam plant wastewater, stormwater runoff, demineralized water, steam condensate, saltwater from the supply system, and potable water from the facility. Toward updating the permit, in May 2008 the EPA issued a Working Draft NPDES Permit (EPA 2008a), for the PSNS' consideration, with draft loading thresholds for As, Hg, Cu, Pb, and Zn, and in which comprehensive knowledge of sediment quality in NPDES receiving zones was the primary concern and is actively being addressed through targeted ENVVEST sediment collection efforts (e.g., Brandenberger et al. 2011, Johnston et al. 2019, Strivens et al. 2020b). The limits drafted in 2008 reflected updated 303(d) listings for the Inlets, informed by the ENVVEST efforts and reported by Kohn et al. (2004, 2006, 2008), and reasonable potential assessments. The driver for sediment characterization was the potential need for mixing-zone inclusion in NPDES updates (Podger 2009) and to facilitate NPDES mixing-zone best management practices (BMP), on March 23, 2013, PSNS and EPA entered into a Federal Facilities Compliance Agreement (FFCA, EPA Docket No. CWA-10-2013-0045) to complete Military Construction projects to upgrade the dry dock process water control system, increase the capacity of oily waste treatment systems, and make other improvements to BMPs to meet All Known, Available, and Reasonable Methods of Treatment (AKART) for preventing, controlling, or abating the pollutants discharged from the Shipyard (Jabloner et al. 2009, US Navy 2012b).

Prior to initiating AKART efforts, ENVVEST drafted contaminant mass balances for Cu, Pb, Zn, and Hg in the Inlets (Crecelius et al. 2003, Brandenberger et al. 2008) and calculated water-effect-ratios (WER) for Cu (Rosen et al. 2009), which is a primary concern due to hull leaching of Naval antifoulant paint formulations – and becomes the focal point of the current report. The most recent mass balance indicated that Naval operations accounted for roughly 55% of Cu and Zn introduced to the Inlets surface waters, while Pb and Hg inputs were dominated by extraneous factors (e.g., atmospheric deposition and/or precipitation). Despite ongoing national defense efforts, baseline WER and mass balance results indicated that Cu contributions to the Inlets were both buffered by the prevailing organic carbon levels and already declining (i.e., a steady decrease in central deposition began as early as 1950). These results indicate that, while improvements to BMPs were essential, environmental awareness prior to Project ENVVEST had begun to alleviate pressures on the ecosystem.

During the second half of the FFCA agreement period (from 2016–2019), ENVVEST made additional efforts toward quantifying and confirming Cu bioavailability in receiving waters by establishing the criterion maximum concentration (CMC) for novel time-integrative passive samplers (Strivens et al. 2019c, 2020a). The long-term ENVVEST ambient water (grab sampling [36 continuous stations from 2009–2019] and passive sampling [nine continuous stations from 2016–2019]) datasets in the current report provide defensible data and guidance for management of facility upgrades, track progress of novel remediation and prevention efforts, and demonstrate alternative tools for the NPDES Program.

Provided, herein, is an in-progress summary of the Ambient Monitoring Program data collected under the *Sampling and Analysis Plan for Ambient Monitoring and Toxicity Testing for Sinclair and Dyes Inlets, Puget Sound, Washington* (referred to, herein, as the Quality Assurance Project Plan [QAPP]) (Johnston et al. 2009, updated 2018a). The QAPP for ambient monitoring was developed to assess toxicological response at major effluent sources and the receiving and central waters of Sinclair and Dyes Inlets. This document serves to update Strivens et al. (2018a) by addition of five grab-sampling events, inclusion of corresponding toxicological test results, and confirmation of Cu bioavailability in receiving zone surface waters. The results and summary are focused on the water quality measurements for NPDES trace metals of concern (Hg, Cu, Pb, and Zn) in the context of Marine Aquatic Life Criteria and Human Health Criteria for Consumption of Organisms. Ancillary parameters (total suspended solids [TSS], total organic carbon [TOC], dissolved organic carbon [DOC], salinity, ammonia as nitrogen [AN], nitrate + nitrite as nitrogen [NNN], total Kjeldahl nitrogen [TKN], total phosphorous [TP], and oil/grease [HEM]) and supporting metals (Al, Ag, As, Cd, Cr, and Ni) are summarized in the appendices. Furthermore, to assist in focused

investigations and integration of Program datasets, all data grab sampling has been provided to the PSNS in EIM format (POC: pao@psns.navy.mil).

2.0 Objectives

The ENVVEST Ambient Monitoring Program objectives are as follows:

1. Extend the baseline for assessing continuous process improvement of the PSNS operations and other sources of contamination into Sinclair and Dyes Inlets.

2. Provide data for validation of proposed mixing zones and model verification; ambient data are needed to inform the development of discharge limits, verify and validate discharge models, and assess total loading of all contaminants into the Inlets.

3. Obtain data and information about the toxicity of effluents and receiving waters for NPDES permit requirements for the PSNS. Specific toxicity tests of effluents and ambient waters are needed to inform the permit process.

4. Develop the procedures needed to meet ambient monitoring requirements for water, sediment, and biota in support of adaptive management actions.

The data obtained from this sampling effort are used to assess the impact of all sources of pollution on environmental quality of the two inlets, support further development of the integrated watershed and receiving water models developed for the Sinclair and Dyes Inlet watershed (Wang et al. 2005; Skahill and LaHatte 2006, 2007; Johnston et al. 2009b; Wang et al. 2011), and provide the basis for calculating total maximum daily loads for key environmental contaminants within the watershed (e.g., Brandenberger et al. 2008; Lawrence et al. 2012). A key aspect of this work is to quantify trace metal concentrations in saltwater at levels well below marine water quality standards. Data from the network of ambient monitoring stations are evaluated to assess the impact of contaminants discharged into Sinclair and Dyes Inlets, characterize the status and trend of ecological resources, and determine whether discharges from all sources are protective of beneficial uses including aquatic life. The data also provide a basis for determining the need for improvement, assessing the effectiveness of corrective actions, and informing adaptive management actions needed to improve environmental quality and protect aquatic resources.

3.0 Sampling Design

This section addresses the technical approaches taken, defines stations at which samples were collected, and summarizes quality objectives for all AMB efforts from 2009-2019. All aspects of the ENVVEST Ambient Monitoring program adhere to the QAPP (Johnston et al. 2010 [initial]; 2018 [current update]) and are periodically reviewed by MSL and NIWC scientists for reconciliation with dynamic regulatory and scientific conclusions.

3.1 Technical Approach

Marine water sampling was initiated by Project ENVVEST in August 2009, and proceeding grab and drydock composite collections have captured wet and dry periods (i.e., summer/fall [dry] and winter/spring [wet]) (Noble et al. 2013) for a total of 29 campaigns over 10 years (Figure 1). When ENVVEST was instituted, the wet season was operationally defined as the months of November through April, and dry season as May through October. In the interim, Ecology has shifted their seasonal definitions (e.g., Ecology 2016); however, for continuity of the Project, season ranges have not been shifted in the current report. ENVVEST AMB stations are grouped into five classifications based on local activities: 1) NPDES-regulated PSNS outfalls; 2) nearshore along the industrialized waterfront of PSNS and within 30 m of a monitored outfall; 3) along the floating security barrier of PSNS; 4) nearshore in Sinclair Inlet along the Bremerton and Port Orchard waterfront, the mouth of the Port Washington Narrows, and reference locations in Dyes Inlet, Port Orchard Passage, and Rich Passage; and 5) central marine waters in Sinclair and Dyes Inlets and the passages to central Puget Sound (Table 1). This design allows for spatial analysis moving away from the shorelines to determine the dilution gradient within the water body, as well as temporal analysis (which captures BMP effectiveness and allows for early indication of new source inputs).

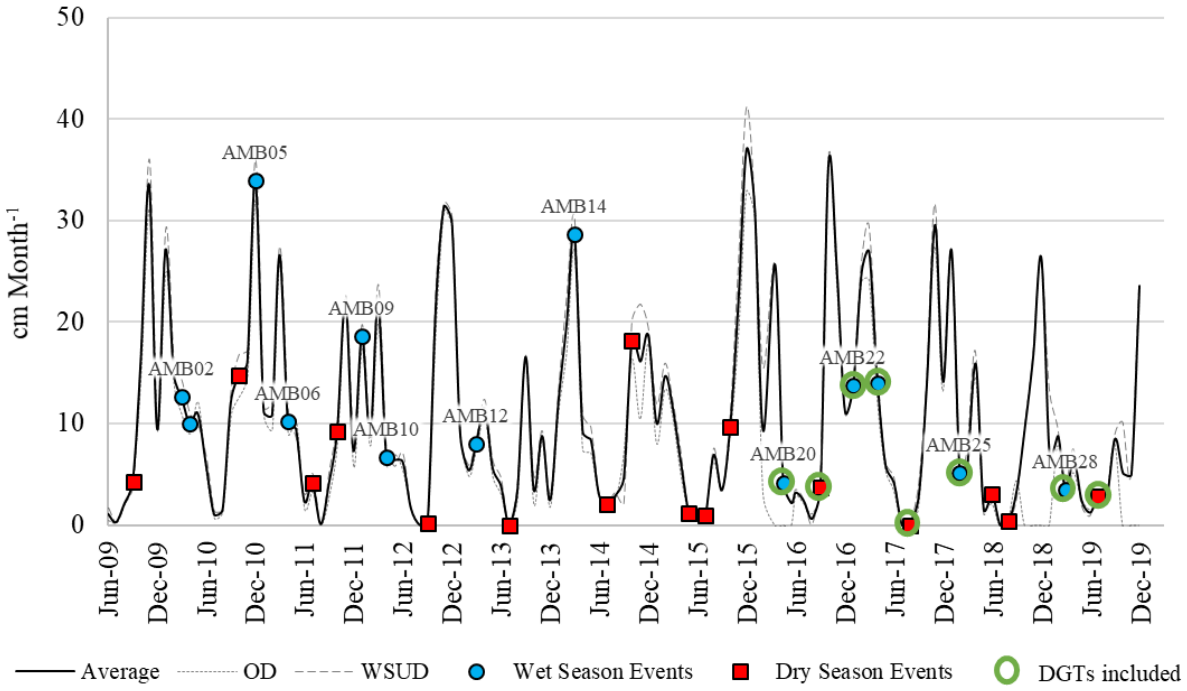

Figure 1. Monthly rainfall at the PSNS, with AMB sampling events overlaid. The average rainfall is calculated from Kitsap Public Utility District stations Olympus Drive (OD) and West Sound Utility District (WSUD); these tipping buckets are located 4 miles north and south of the PSNS, respectively.

Concurrent with grab sampling windows for AMBs 20–25, 28, and 29 (Figure 1), in situ time-averaged labile concentrations of Cd, Cu, Ni, Pb, and Zn were monitored at select nearshore stations within PSNS and reference stations at the Ports of Silverdale (adjacent to urban/commercial land use) and Illahee (adjacent to rural/residential land use), and a dock in Eagle Harbor (adjacent the WA State Ferry Maintenance Facility) (Table 1) using diffusive gradients in thin-films (DGT). DGT is a technique by which the operationally defined labile fraction of select metals are captured over toxicologically relevant windows. While Marine Aquatic Life Criteria are based on an operationally defined dissolved fraction (which excludes substantially less toxic particulates, respective to the total fraction [e.g. Cu-clay, Cu-organic matter, Cu-silicates, Cu-Me-oxides, Cu-Alga, etc.]), the concentration measured by DGT (C_{DGT}) excludes measurement of Cu in the form of Cu-DOM, with the exception of some weakly bound ions, resulting in an approximation of free ion, Cu-carbonates, Cu-hydroxides, and labile Cu-DOM over a selected exposure period, thereby providing a better indication of bioavailability over calculations that use the dissolved fraction from grab sampling (e.g. biotic ligand models). Use of DGT to monitor Cu against a CMC was pioneered by Project ENVVEST (Strivens et al. 2019) and can effectively reflect ligand competition in situ without the need to assess dissolved organic carbon (DOC) quality (Strivens et al. 2020). Furthermore, the time-scale sensitivity of this approach was also reported by ENVVEST (Strivens et al. 2018b, 2019b) for Cd, Cu, Ni, Pb, and Zn – using PSNS sites to demonstrate sensitivity at ambient concentrations and temperatures relevant to that installation's waters. Additionally, novel modifications have been explored by ENVVEST for quantification of organic contaminants by this method (Kuo et al. 2019). Outside of Project ENVVEST, researchers are working toward integrating DGT into the European EQS (e.g., Belzunce-Segarra et al. 2019) and deployment methodologies have been explored by the EPA (Burgess et al. 2017). The current report focuses on the use of this technique to (1) validate previous Cu WER calculations for the Inlets, (2) demonstrate ecosystem health on time scales more relevant to chronic

Sampling Design

exposure, and (3) capture both short-term fluxes and temporal baselines of bioavailability in NPDES receiving zone surface waters.

Table 1. Marine water monitoring stations listed by zone designations 2–5.

Station ID	Zone	Latitude	Longitude	Land-Use Runoff Regime	Jurisdiction
PS01 [a]	2	47.55401	-122.65725	Urban/ Industrial Nearshore	NBK-BREM
PS02	2	47.55456	-122.65452	Urban/ Industrial Nearshore	NBK-BREM
PS03 [ab]	2	47.55592	-122.65182	Urban/ Industrial Nearshore	NBK-BREM
PS04 [b]	2	47.55458	-122.64752	Urban/ Industrial Nearshore	NBK-BREM
PS05	2	47.55606	-122.64491	Urban/ Industrial Nearshore	PSNS&IMF
PS06 [ab]	2	47.55310	-122.64225	Urban/ Industrial Nearshore	PSNS&IMF
PS07	2	47.55598	-122.64134	Urban/ Industrial Nearshore	PSNS&IMF
PS08 [ab]	2	47.55784	-122.63880	Urban/ Industrial Nearshore	PSNS&IMF
PS09 [ab]	2	47.55996	-122.63626	Urban/ Industrial Nearshore	PSNS&IMF
PS10	2	47.56046	-122.63322	Urban/ Industrial Nearshore	PSNS&IMF
PS10.1 [b]	2	47.56123	-122.63132	Urban/ Industrial Nearshore	PSNS&IMF
PS11 [b]	2	47.56048	-122.62986	Urban/ Industrial Nearshore	PSNS&IMF
PS12	2	47.56052	-122.62836	Urban/ Industrial Nearshore	NBK-BREM
PS13	3	47.55199	-122.65407	Urban/ Industrial Marine/Nearshore	PSNS&IMF
PS14	3	47.55241	-122.64371	Urban/ Industrial Marine/Nearshore	PSNS&IMF
PS15 [a]	3	47.55562	-122.63658	Urban/| Industrial Marine/Nearshore	PSNS&IMF
PS16 [b]	3	47.55872	-122.62844	Urban/ Industrial Marine/Nearshore	PSNS&IMF
ANCOVE [c]	4	47.57929	-122.64624	Urban/ High Residential Nearshore	City of Bremerton
BJEST [a]	4	47.54360	-122.62754	Urban/ High Residential Estuarine	City of Port Orchard
CLMBAY	4	47.57133	-122.54950	Rural/Industrial Estuarine	EPA/DOE/NOAA/Navy
DY07 [c]	4	47.58081	-122.66123	Urban/ High Residential Nearshore	City of Bremerton/ Kitsap County

Sampling Design

Station ID	Zone	Latitude	Longitude	Land-Use Runoff Regime	Jurisdiction
DYOTS [b]	4	47.64193	-122.69395	Urban/ Commercial Nearshore	Port of Silverdale/ Kitsap County
HRPT [c]	4	47.56555	-122.61383	Urban/ High Residential Nearshore	City of Bremerton
POPIPD [b c]	4	47.61295	-122.59480	Rural/ Residential Nearshore	Port of Illahee
ILSP [c]	4	47.60046	-122.59414	Rural/ Forested Nearshore	WA State Parks
PWNLP [c]	4	47.58426	-122.64405	Urban/ Commercial Nearshore	City of Bremerton
SN03	4	47.54658	-122.67124	Urban/ Commercial Nearshore	City of Bremerton/ Kitsap County
SN05	4	47.53143	-122.68687	Urban/ Commercial Nearshore	City of Bremerton
SN08	4	47.54008	-122.66242	Rural/ Forested Nearshore	City of Port Orchard
SN10	4	47.54095	-122.64264	Urban/ Commercial Nearshore	City of Port Orchard
SN11	4	47.54338	-122.63549	Urban/ Commercial Nearshore	Port of Bremerton
WP	4	47.58397	-122.57182	Rural/ Residential Nearshore	Sinclair Inlet
M1	5	47.63276	-122.58203	Marine	Port Orchard Passage
M2	5	47.57424	-122.53654	Marine	Rich Passage
M3.1 [a]	5	47.55978	-122.61121	Marine	Sinclair Inlet
M3.3	5	47.54958	-122.64303	Marine	Sinclair Inlet
M4 [a]	5	47.54487	-122.66686	Marine	Sinclair Inlet
M5	5	47.61044	-122.66637	Marine	Rocky Point
M6	5	47.59767	-122.68472	Marine	Ostrich Bay
M7	5	47.62447	-122.69194	Marine	Dyes Inlet
M8	5	47.57256	-122.67512	Marine	Oyster Bay
EAGLE b	N/A	47.62105	-122.51780	Urban/ Industrial Nearshore	WA State

[a] Stations selected for bioassay (in addition to OFs)
[b] Stations selected for passive sampling focus
[c] Stations removed from statistical assessment due to aperiodic inclusion in AMB events

3.2 Sampling Station Maps

Sinclair and Dyes Inlets are located along the west side of central Puget Sound, and include the cities of Bremerton, Silverdale, and Port Orchard, along their shorelines. These Inlets are connected by the Port Washington Narrows and joined to the main basin by Port Orchard and Rich Passages. The watershed drains 252.3 km^2 (Figure 2), of which 80% is routed through streams, and 20% drains directly into marine waters (May and Culinan 2005). Major streams draining to Sinclair Inlet include Blackjack and Gorst Creeks. The maximum depth of both inlets is ~42 m. ENVVEST hydrodynamic modeling studies have concluded that there is significant exchange of water and transport of sediment between Sinclair and Dyes Inlets (Wang and Richter 1999); therefore, the two inlets are treated as a single water body with respect to TMDLs. Station maps in Sections 3.2.1 and 3.2.2 depict primary stations that have been included for the duration of Project ENVVEST AMB monitoring.

Primary stations of interest toward NPDES renewal encompass those in the PSNS Nearshore zone. Sampling location selection has been thoroughly detailed in previous reports (e.g., Brandenberger et al. 2018; Johnston et al. 2019; Strivens and Johnston 2019d) and incorporates receiving zones for both the industrial outfalls reported, herein, and the stormwater outfalls of concern discussed in Brandenberger et al. (2018). To summarize the upstream contributions to these stations:

PS01—is (1) the receiving zone for the Bremerton Callow Avenue (B-ST28) stormwater outfall and NPDES stormwater outfalls-of-concern 022 and 089 (primary upstream work activities: parking/steam plant/truck traffic), (2) located in the inactive fleet mooring section, and (3) an area with low flushing.

PS02— is (1) the receiving zone for NPDES stormwater outfall-of-concern 015, (2) located in the inactive fleet mooring section, and (3) an area with low flushing.

PS03—is (1) the receiving zone for NPDES stormwater outfalls-of-concern 013, 014 and 040 (primary upstream work activities: municipal/commercial/residential services), (2) located near active ships moored at Pier D, and (3) an area with low flushing.

PS04—is (1) the receiving zone for NPDES stormwater outfalls not considered to be of concern in the 23/156 discharges focused on under the ENVVEST Project, (2) a tug-boat operations area, and (3) located near active ships moored at pier C.

PS05—is (1) the receiving zone for NPDES stormwater outfall-of-concern 012 (primary upstream work activities: vehicle and equipment movement and parking, material storage, air comp. facility, mixed waste storage facility and general warehousing), (2) a tug-boat operations area, (3) located near active ships moored at Pier B, and (4) an area with low flushing.

PS06—is the receiving zone for NPDES industrial discharge 019 (DD6 operations).

PS07—is (1) the receiving zone for NPDES stormwater outfall-of-concern 010 (primary upstream work activities: non-aircraft carrier support services) and (2) located near an active barge moored at Pier 9.

PS08—is (1) the receiving zone for NPDES stormwater outfall-of-concern 030 (primary upstream work activities: vessel, equipment and materials recycling), (2) an area-of-concern for shoreline stabilization, (3) at the mouth of DD5, (4) located near inactive ships at mooring A, and (5) an area with low flushing.

PS09—is (1) the receiving zone for NPDES industrial discharge 018 (DD1-5 operations) and stormwater outfalls-of-concern 008 and 052 (primary upstream work activities: vessel maintenance), (2) located at the mouth of DD4, (3) located near active ships moored at Pier 3, and (4) an area with low flushing.

PS10—is (1) the receiving zone for NPDES industrial outfall 096 and stormwater outfall-of-concern 028, (2) at the mouth of DD2, and (3) located near active ships moored at Pier 4.

PS10.1—is (1) the receiving zone for NPDES stormwater outfalls-of-concern 006 and 025 (primary upstream work activities: materials storage [outdoors], various shops and training center, water front support activities, dry-dock support activities, crane, vehicle and equipment traffic, laydown and staging areas), (2) located at the mouth of DD1, and (3) located near active ships moored at Pier 5.

PS11—is (1) the receiving zone for NPDES stormwater outfall-of-concern 003 (primary upstream work activities: material storage, pipe/boiler/forge/nuclear repair shops, Chem Lab, DD3 cutting facility), (2) located at the mouth of DD3, and (3) located near inactive ships and barges moored at Pier 6.

PS12—is the receiving zone for City of Bremerton Storm Drains B-ST29 and B-ST14 and NPDES stormwater outfall-of-concern 095 (primary upstream work activities: materials storage [outdoor]).

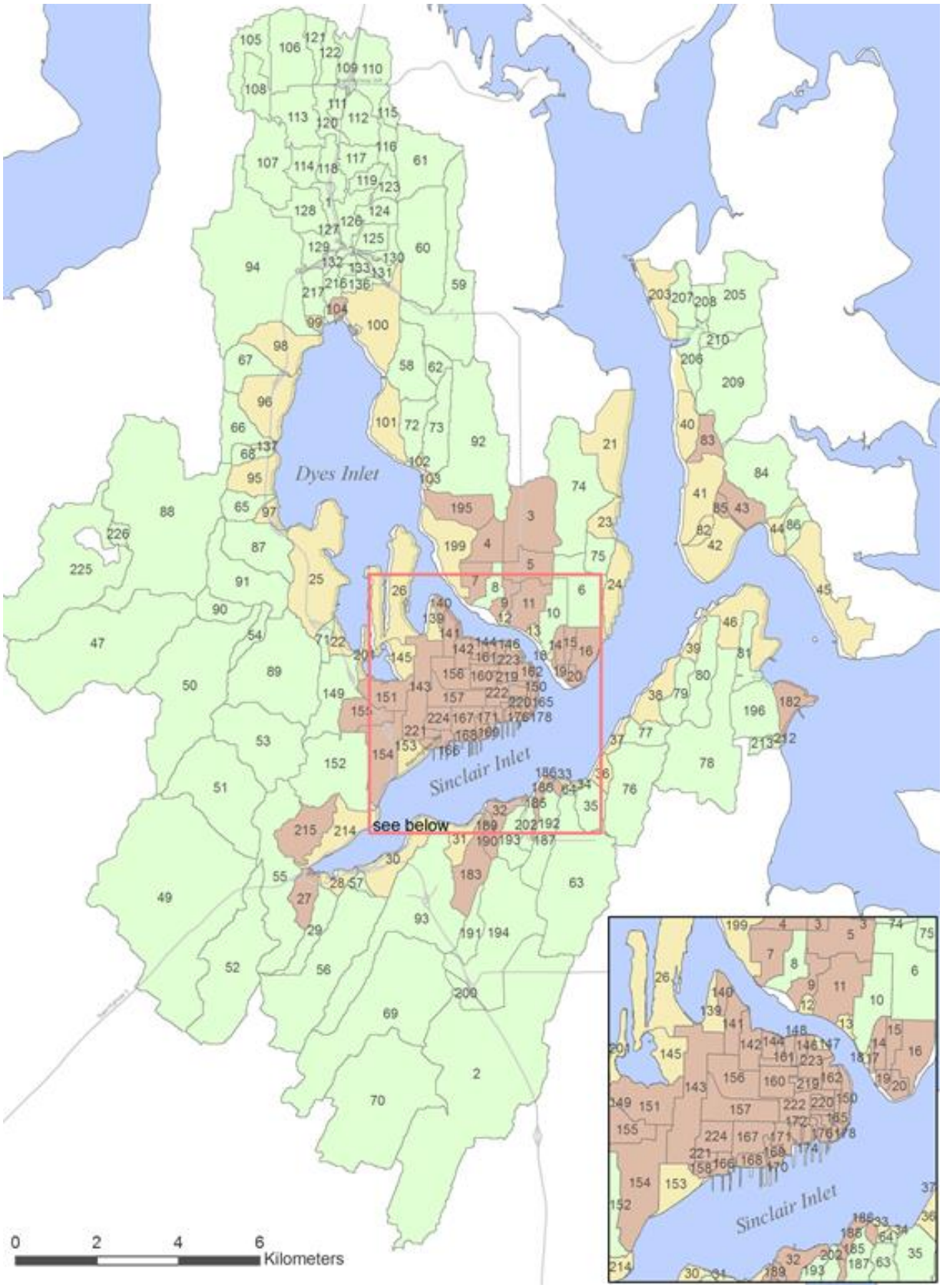

Figure 2. Sinclair-Dyes Inlet sub-watershed delineations with a 30 percent blowout of Bremerton.

Sampling Design

3.2.1 PSNS Outfalls

The four major industrial outfalls (OFs; OF018, OF019, OF021, and OF096 [Figure 3]) at PSNS are included in the seasonal AMB sampling plan and lead pump-well lines are screened weekly by the PSNS onsite laboratory. OF018 is partitioned into OF018A and OF018B, both of which discharge the effluents collected from PSNS Dry Docks (DDs) 01 through 05 (total area drained is 57,292 m^2); this is a redundant system (one outfall is operational at a time). The character of the discharge does not change with alternation of the pump-wells; therefore, the data refer to OF018 for either discharge location. Both outfalls discharge just west of DD04 at PSNS Nearshore sampling station PS09. Discharges cycle ~1-h on:3-h off and are triggered by the well level. At the discharge points, OF018A discharges below mean lower low water (MLLW) at a height of 5.79 m above the bottom, while OF018B discharges above MLLW at 6.52 m. OF096, located east of Pier 5, is also used for direct discharge from DDs 01–05, and empties at PSNS Nearshore sampling station PS10.1 (this site is incorporated in Section 5.2 plots of OF018 and in respective WQBEL calculations, as the drainage source is identical). OF019 discharges water from DD06 at the end of Pier 9 (the total area drained is 19,263 m^2); the PSNS Nearshore sampling station ID is PS06. The pump cycles ~7.5 min on:50 min off (but increase to 11 min on: 15 min off when a carrier is in DD) and discharges below MLLW at a height of 7.28 m above the bottom. Water from these DD OFs is composed of hydrostatic relief water (seepage from groundwater and inlet water), vessel cooling water, water from industrial operations, and stormwater during rainy conditions (upgrades to these systems have resulted in water from industrial operations and stormwater being largely redirected to the City of Bremerton's waste water treatment plant).

OF021 previously discharged treated demineralization water from a steam plant at PSNS, north of Mooring E. The treated water was discharged through a 0.1 m pipe with a 12.1 m long diffuser starting 279.8 m from the shore at a depth of 10.67 m (at PSNS Barrier station PS13). PSNS AKART actions shifted from demineralization to reverse-osmosis in 2011 and have redirected boiler blowdown to the sanitary sewer.

Figure 3. PSNS outfall, pump-well, and dry-dock locations. (Google [n.d.]. [Google Maps Puget Sound]. Retrieved November 1, 2017, from https://google/maps.)

3.2.2 Ambient Waters

As shown in Figure 4, nearshore stations within PSNS (those located within 30 m of a monitored outfall) include identifiers PS01–PS12 (west to east). Moving outward from the waterfront are four stations located near the PSNS security barrier (PS13–PS16). Nearshore sampling stations within Sinclair Inlet, outside of the PSNS security barrier, are identified as SN##; Blackjack Estuary (station ID: BJEST) and Waterman Point (WP). Other stations included as non-PSNS nearshore (Category 4) include nearshore areas of adjoining passages (Port Orchard and Rich Passages) and Dyes Inlet (Table 1). To complete the gradient, stations centrally located in the Inlets and passages are sampled and are identified as M#.

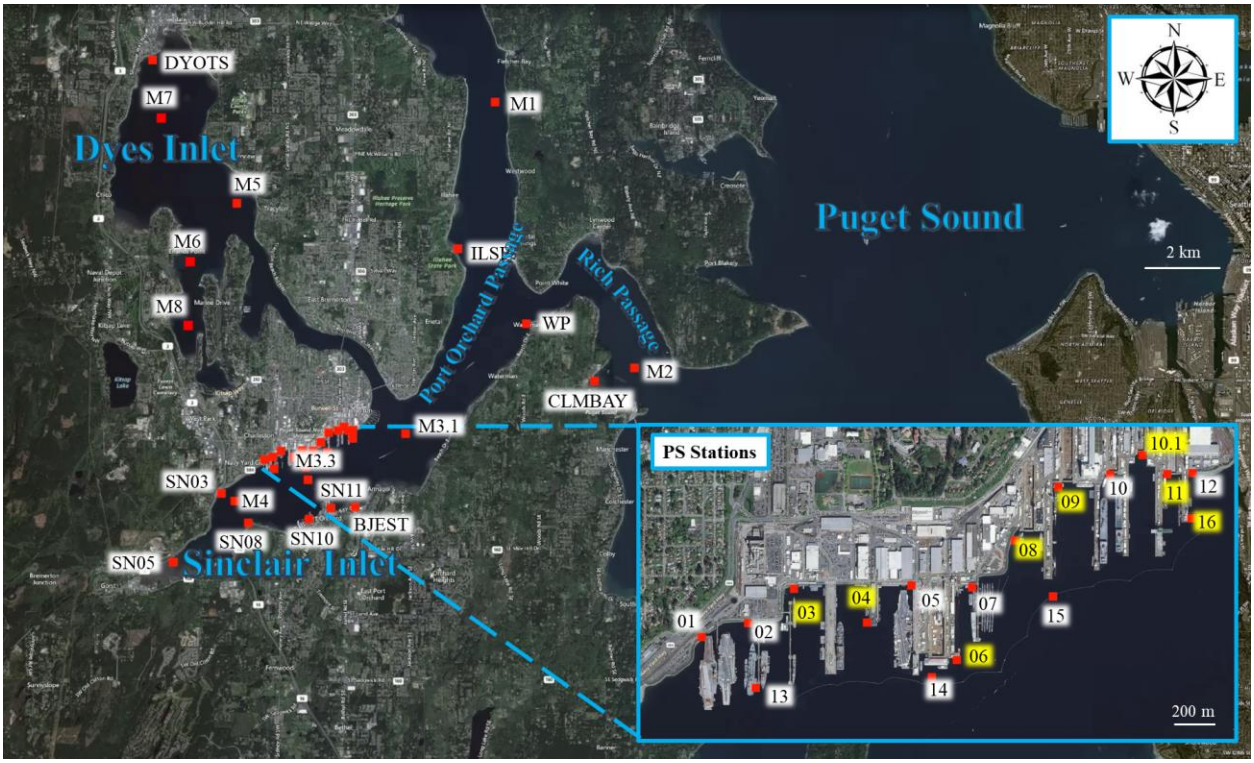

Figure 4. Marine grab sampling stations included in the spatial summary analysis. Highlighted PS stations indicate inclusion in the 2016-2019 passive sampling effort. (Google [n.d.]. [Google Maps Puget Sound]. Retrieved November 1, 2017, from https://google/maps.)

3.3 Quality Objectives and Criteria for Measurement Data

3.3.1 Regulatory

The current PSNS NPDES permit was issued in September 1986, then reissued in April 1994 (#WA-003716-8 or WA00206-2), and covers drydock discharges, steam-plant discharges, and stormwater from non-drydock areas. This 1994 permit[1] is the current authoritative stormwater discharge guidance for the PSNS, and limits Cu (at all DD outfalls) and Zn (at OF021) effluents to daily maximums of 33 µg L^{-1} and 1,000 µg L^{-1}, respectively; future limits covering Hg, Cu, Pb, and Zn are being drafted through ENVVEST stakeholder discussions (EPA 2008a,b). Under the current permit, Zn monitoring ceased prior to ENVVEST

[1] Current (1994) NPDES permit for the Shipyard:
https://www.epa.gov/npdes-permits/npdes-permit-puget-sound-naval-shipyard-wastewater-treatment-plant-washington

monitoring based on process modifications. The Cu limit, which was intended to maintain receiving water concentrations below the marine chronic toxic substance criteria defined in Table 2 (which also provides human health criteria for seafood consumption), is still used as the default benchmark for weekly screening.

Table 2. Toxics Substances Criteria[(a)]

	Aquatic Life Criteria – Marine Waters (µg L^{-1})		Human Health Criteria for Consumption of Organisms[(b,c)]
Metal	**Acute[(b)]**	**Chronic**	
Hg	1.8	0.025[(d)]	0.15
Cu	4.8	3.1[(b)]	1300
Pb	210	8.1[(b)]	[(e)]
Zn	90.0	81.0[(b)]	2900
Cd	42.0	9.3[(b)]	[(e)]
Cr (VI)	1100	50.0[(b)]	[(e)]
Ni	74.0	8.2[(b)]	190

(a) Summary reprint of data from WAC 173-201A-240 and 40 CFR 131.36.
(b) The ambient criteria in the table are for the dissolved fraction.
(c) The human health criteria in the table were calculated using a fish consumption rate of 175 g/day.
(d) These criteria are based on the total recoverable fraction of the metal.
(e) EPA is not promulgating human health criteria for this contaminant. However, permit authorities should address this contaminant in NPDES permit actions using the State's existing narrative criteria for toxics.

Toward reissuance of the NPDES permit for PSNS, EPA (2008b) initially proposed to calculate updated maximum daily (MDL) and average monthly (AML) waste-load allocations for As, Cu, Pb, Zn, and Hg from Marine Aquatic Life Criteria, as opposed to a technological feasibility derived limit – using guidance from EPA's *Technical Support Document for Water Quality-Based Toxics Control* (1991). The current long-term datasets show that Cu and Zn are of moderate concern in PSNS industrial effluents and a thorough discussion of the path forward is given within Section 5.0 and documented in Appendix C; there is a lack of reasonable potential for exceedances of As, Pb, or Hg. Toward that end, the current report allows for site-specific total → dissolved, or in the case of Cu total → labile (by WER and/or C_{DGT}), translators to be applied (following EPA 1996c guidance). In addition, AKART may be used to supersede a WQBEL approach for select discharge sources and ENVVEST has recently summarized many of its multiple-line-of-evidence approaches, which were developed to model distribution and measure environmental endpoints within Kitsap Basin impact zones in order to overcome water quality-based effluent limit uncertainties imposed by the magnitude of outfalls at this installation, toward mixing zone inclusion and development of TMDL criteria for the Inlets (i.e., sediment and water column biological effects studies [Johnston et al. 2019; Strivens and Johnston 2019]). The results shall be weighted into the update of effluent limit derivation during Project ENVVEST stakeholder discussion (as established in PSNS, EPA and Ecology 2000).

3.3.2 Analytical

The following sections summarize the field quality control, laboratory quality control, and the overall usability of the data. Measurement quality objectives for the analyses conducted for this study are expressed in terms of accuracy, precision, and sensitivity goals. Accuracy and precision are monitored through the analysis of quality control samples (Appendix A, Table A.1) and are parameterized in Appendix A, Table A.2. Measurement quality criteria. Analytical parameters, holding times, and detection limits are provided in event Quality Control Narratives (Appendix E), which contains complete campaign reports as provided

to PSNS by PNNL's MSL; holding times are defined in Table A.3. The datasets were found to have acceptable measures of each of these variables.

Accuracy is defined as the degree of agreement between an observed value and an accepted reference value. Accuracy is achieved through the use of laboratory control samples (LCS), matrix spikes (MS), matrix spike duplicates (MSD), and standard reference materials (SRM). The trace metals LCSs and MSs/MSDs results are summarized in Appendix B; recovery of OC, TSS, and nutrient reference material are also summarized in Appendix B. The recovery of contaminants of concern, Hg, Cu, Pb, and Zn in SRMs are provided below to demonstrate the overall high quality of the data set. Figure 5 shows the results for National Institute of Standards and Technology SRM 1641 Mercury in Water, and Figure 6, Figure 7, and Figure 8 illustrate the results from the seawater reference material CASS (coastal Atlantic seawater standard).[1] Ancillary metal SRM recoveries are depicted in Appendix B (Figure B.1, Figure B.2, and Figure B.3).

Figures 6, 7, and 8 also illustrate a move to an online-preconcentration method for trace metals during AMB20, which minimized sample preparation and eliminated correction errors when accounting for trace impurities. The reproducibility of the online-preconcentration method described by Strivens et al. (2019a), coupled with low blanks and detection limits, demonstrated an effective move to an automated procedure using ethylenediaminetriacetic and iminodiacetate acid chelation exchange resin and multi-analyte determination via ICP-MS for total and dissolved Ni, Cu, Zn, Cd, and Pb in marine water samples.

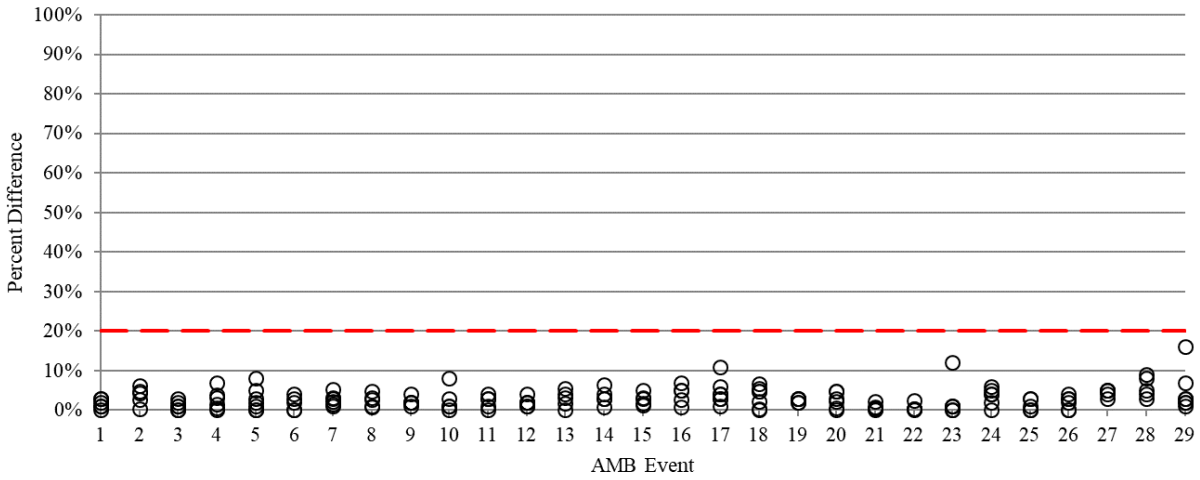

Figure 5. Analytical recovery of National Institute of Standards and Technology SRM 1641 for AMB events 1–29 Hg. Limits are defined by the ENVVEST QAPP as ± 20% recovery from the certified value.

[1] CASS was obtained from the National Research Council of Canada (NRC, Ottawa, ON) and is intended for use during the analysis of nearshore seawater for trace metals; salinity 33.5PSU. This water was collected from Halifax Harbour; at a depth of 12 m. ENVVEST samples had a salinity range of 8.2-31.8 PSU.

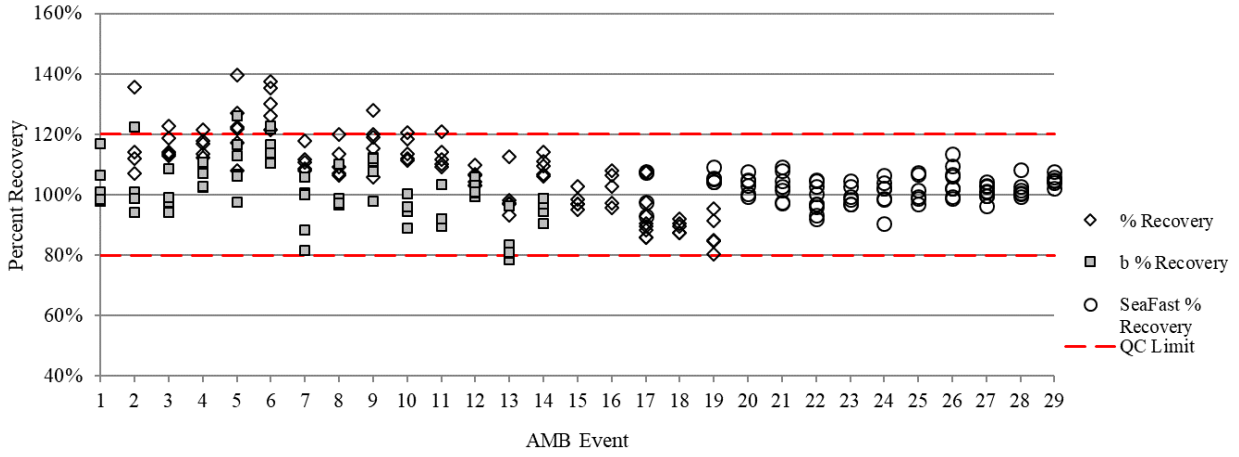

Figure 6. Analytical recovery of CRM CASS for AMB events 1–29 Cu. Events 1–14 were analyzed after Fe-Pd preconcentration, and blank corrected post-analysis; events 15–19 were analyzed after Fe-Pd preconcentration, and blank corrected via inclusion of reagents in the calibration curve; events 20–29 were analyzed via online preconcentration and did not require blank correction. QC limits are defined by the ENVVEST QAPP and may be greater or smaller than the certified ranges.

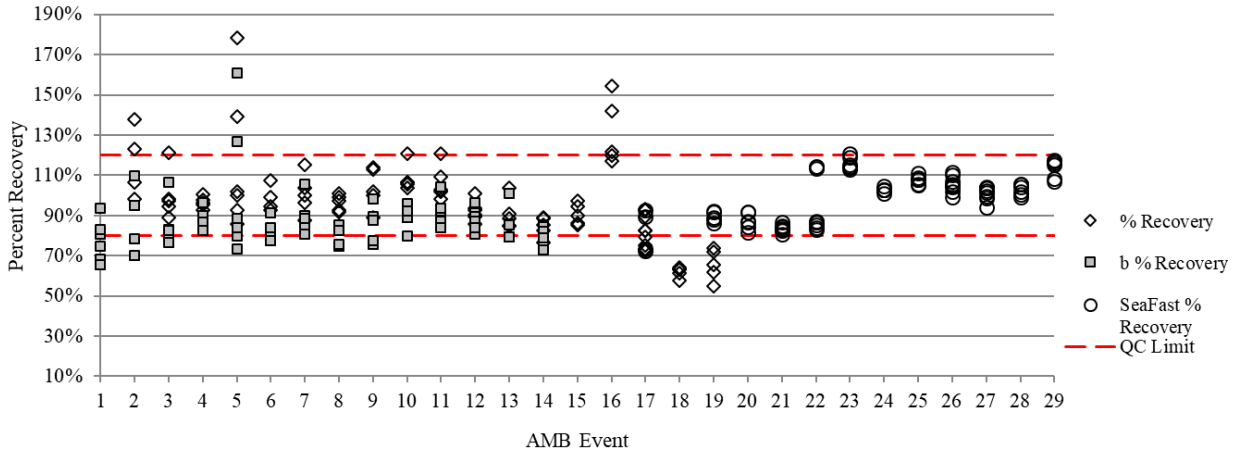

Figure 7. Analytical recovery of CRM CASS for AMB events 1–29 Pb. Events 1–14 were analyzed after Fe-Pd preconcentration, and blank corrected post-analysis; events 15–19 were analyzed after Fe-Pd preconcentration, and blank corrected via inclusion of reagents in the calibration curve; events 20–29 were analyzed via online preconcentration and did not require blank correction. QC limits are defined by the ENVVEST QAPP and may be greater or smaller than the certified ranges.

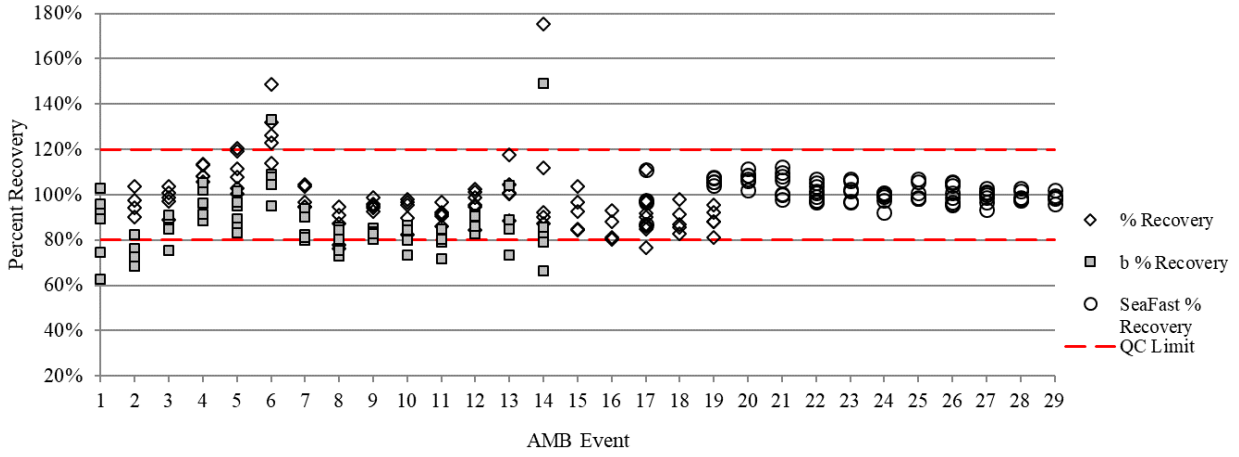

Figure 8. Analytical recovery of CRM CASS for AMB events 1–29 Zn. Events 1–14 were analyzed after Fe-Pd preconcentration, and blank corrected post-analysis; events 15–19 were analyzed after Fe-Pd preconcentration, and blank corrected via inclusion of reagents in the calibration curve; events 20–29 were analyzed via online preconcentration and did not require blank correction. QC limits are defined by the ENVVEST QAPP and may be greater or smaller than the certified ranges.

Precision is defined as the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is achieved through both field and laboratory replication to assess the field variability as well as the laboratory method precision (see Appendix B). The mean relative percent differences (RPD) for laboratory replication met the criteria given in the QAPP (Table A.2).

Sensitivity is the capability of a test method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. Sensitivity is addressed primarily through the selection of appropriate analytical methods, equipment, and instrumentation. The methods selected for the Sinclair and Dyes Inlet study were chosen to provide the sensitivity required for the end use of the data (Johnston et al 2009a; 2018). This is a quantitative assessment and is monitored through the instrument calibrations and calibration verification samples and the analysis of procedural blanks with every analytical batch (Appendix E).

Method detection limits (MDL) for trace metals are determined annually according to 40 CFR Part 136 Appendix B for each method of interest by instrument, matrix, and compound of interest. Laboratory MDLs for seawater are reported from Annually Verified Seawater MDL Studies as determined by seven replicates of CASS, Sequim Bay Seawater, or spiked SeaBlank. The freshwater MDLs are reported from the Annually Verified Freshwater MDL Study determined using seven replicates of deionized water prepared using total recoverable metals (TRM) protocol. Reporting limits are determined as 3.18 times the laboratory achieved MDL. Campaign-specific MDLs are listed on each data report in Appendix E.

Data in Appendix E are evaluated and flagged with qualifiers as follows:

Table 3. Analytical Data Qualifiers

Flag	Definition
--	Not analyzed
&	Accuracy result outside QC criterion of ≤20% PD
*	Precision result outside QC criterion of <30%
B	Analyte detected in the method blank > RL and sample concentration < 10 times detected blank value
b	Data are blank corrected using the batch specific procedural blank
J	Analyte detected above the MDL, but less than the RL
N	Spiked sample recovery outside QC criterion of 70-130%
NA	Not applicable/available
NC	Not Certified
NS	Sample not spiked for this analyte
U	Analyte not detected at or above the MDL, MDL reported
c#	Exceeds data quality objective but meets one of the following contingency criterion:
	1 SRM certified <10x MDL or
	2 Insufficient spiking level relative to native sample concentrations
	3 Sample concentration <10x MDL

3.3.3 Toxicological

The quality assurance/quality control (QA/QC) requirements based on EPA guidelines for aquatic bioassays, specifically whole effluent toxicity (WET) testing as intended for compliance for NPDES permits are of utmost importance for this project. In brief, the QA/QC requirements ensure that the laboratory provides high-quality data and is in compliance with standard operating procedures (SOPs) for sampling handling, equipment calibration and proper use, record keeping, and data handling.

Reference toxicant tests were performed concurrently for each monitoring event, and for each species evaluated, as quality control measures to assess the health of the organisms and technical performance of the methods. Ideally, results fall within two standard deviations of the laboratory's' historical performance (i.e. control charts) for the specific toxicant and species combination, however, this is not a test acceptability criterion. Test acceptability criteria are method dependent and are provided in section 4.3.3**.**

4.0 Methods

4.1 Grab and Composite Sample Collection Methods

A detailed description of the sampling methods is provided in the QAPP (Johnston et al. 2009a, 2018). Briefly, sampling followed ultra-clean collection procedures recommended for trace metals at EPA water quality criteria levels in EPA Method 1669 (EPA 1996a). Sampling bottles were double bagged in a Class 100 clean room and shipped to the PSNS. All sample bottles were handled using clean gloved hands following the "dirty hands/clean hands" technique (EPA 1996a). Surface grab (~1 m depth) samples were collected directly into sample bottles by hand from a small boat using a pre-cleaned polyvinyl chloride sampling pole. Industrial effluent composite samples were originally collected using Sigma® automated samplers. After AMB18, a Teledyne-Isco® 6700 series sampler with a custom back-pressure modulation chamber assembled by Cardno TEC (Charlottesville, Virginia) (Figure B.4) was installed in OF019, and after AMB22 OF018A&B were equipped with in-line piston style Sentry ISOLOK SAB Automatic Fixed Volume Samplers.

The auto-samplers were programmed to collect water when discharge pumps were activated, such that a 10 L composite sample was collected over 24 hours into glass barrels. The composite effluent water was then subsampled for chemical analysis. Auto-samplers in pump-wells were subject to some collection variation (i.e., when an auto-sampler failed to collect a composite, grab sampling was implemented for a single pump-down phase or a combination of grab samples was collected over multiple pump-downs).

Samples were held at < 6 °C during transit to MSL and were delivered immediately after collection by MSL staff. Sample custody records associated with the physical possession and/or storage history of each individual sample are documented in accordance with MSL-A-001 *Sample Login Procedures* and MSL-A-002 *Sample Chain-of-Custody* (Battelle 2016b, 2013) and are available upon request.

4.2 Passive Sampler Deployment Methods

DGT deployments followed the methodology discussed in Strivens et al. (2020). Briefly, a subset of 9 continuously monitored stations was selected (additional exploratory stations appear in the data reports [Appendix E.2] for select events), which were nearshore and nonstochastic, positioned within the PSNS effluent receiving zones and corresponding to surface grab sampling locations. As this was not a previously standardized approach, various deployment durations were used — however, the approaches settled on for the primary analyte (labile Cu) were to either (1) to use consecutive 3-day deployments for the desired monitoring window, which reflects the midpoint between bivalve (*Mytilus*) and sea urchin (*Strongylocentrotus*) embryo-larval bioassay protocol durations, or (2) to use imbricated 3-day deployments when input fluxes were of interest (e.g., Strivens et al. 2018b). In addition to deployments reflective of highly sensitive biological development stage durations, coinciding longer-term deployments were always included to validate baselines. The longer term (~7 and 14-day) deployments are used in the current report to summarize labile Pb; this is due to the time-integrated nature of the device, where an inverse relationship exists between C_{DGT} background levels and deployment times (i.e., PSNS Nearshore waters were not loaded with Pb to quantifiable levels over short-deployments, however, the deployments can be shortened dramatically in situations where this metal is at a level of toxicological concern). For all events where passive samplers were utilized, deployments began and ended ~ 1-week pre- and post-grab sampling.

The standard depth of deployment was 1 m, to reflect grab sampling efforts. For select events (AMB28 and 29) profiles of bioavailable Cd, Cu, Ni, Pb and Zn were captured to determine if classical distributions were interrupted by the varying fresh- and saltwater inputs, upwelling, run-off, impediments to natural circulation, in-water work, and algal blooms that contribute to uncertainty of transport-and-fate due to altered metal and ligand inputs, as well as changes to temperature, pH, salinity, and dissolved oxygen.

Protection of samplers from large debris was achieved by placement inside polypropylene cages (2.0-cm mesh) and temperature was recorded every 5-min by co-deployed HOBO™ loggers. At collection, the DGT membrane filters were rinsed with a stream of deionized water. Reflective of grab sampling efforts, when not in the water DGTs were transported in individual clean room certified zip pouches and double bagged, and all deployment/retrieval steps used clean gloved hands following the "dirty hands/clean hands" technique. Samples were held at < 6 °C during transit to MSL and were delivered immediately after collection by MSL staff. Sample custody records associated with the physical possession and/or storage history of each individual sample are documented in accordance with MSL-A-001 (Battelle 2016b, 2013) and all records are maintained in accordance with SOP MSL-D-003 *Archiving Documented Information* and MSL-D-004 *Data Reporting/Reduction and Information Backup/Archiving* for 10 years (Battelle 2020a,b), with the MSL Project Manager serving as the Administrative Custodian.

4.3 Analytical Methods

4.3.1 Trace Metals

Trace metals analysis was performed in state-of-the-art class-100 clean-air laboratory facilities, which MSL has designated for preparation, handling, and analysis of environmental samples for ultra-trace level determinations of metals and metalloids.

4.3.1.1 Grab and Composite Sampler

Immediately upon receipt, in the laboratory, each trace metals sample was shaken vigorously and approximately 500 mL was filtered through a pre-cleaned 0.45 µm polyvinylidene fluoride filter membrane inside a Class-100 clean bench. The dissolved and total fractions were then acidified to a pH of < 2.0 using Optima™ grade nitric acid (Fisher, Pittsburgh, PA, USA).

For events AMB01–AMB24, samples were analyzed for total and dissolved Hg using Cold Vapor Atomic Fluorescence (CVAF) in accordance with Battelle Standard Operating Procedure (SOP) MSL-I-013, *Total Mercury in Aqueous Samples by CVAF* (Battelle 2011). Post-AMB24 the process was automated and Battelle SOP MSL-I-042 (Battelle 2020c), *Automated Analysis of Total Mercury by Cold Vapor Atomic Fluorescence (CVAF)* replaced MSL-I-013. Both methods follow EPA Method 1631 and have equivalent sensitivity.

Freshwater samples, identified as < 5% seawater, were prepared for metals analysis (other than Hg) following the preparation method for TRM described in EPA Method 1640 (EPA 1997).

Prior to analyses of marine water metals—Ag, Al, As, Cd, Cu, Ni, Pb, and Zn—samples were either preconcentrated in accordance with Battelle SOP MSL-I-025, *Methods of Sample Preconcentration: Iron and Palladium/APDC Coprecipitation and Borohydride Reductive Precipitation for Trace Metals Analysis in Water* (AMB01–AMB19) (Battelle 2003), or using an online preconcentration via the seaFast™ chelation column method for Cd, Cu, Ni, Pb, and Zn (AMB20-29) (Strivens et al. 2019a). After AMB19,

marine samples were analyzed for Al using ICP-MS direct injection at 15x dilution; as was the case with Cr for all events.

Preconcentrated and diluted marine samples were analyzed by ICP-MS in accordance with Battelle SOP MSL-I-022, *Determination of Elements in Aqueous and Digestate Samples by ICP/MS* (Battelle 2016a); the base methods for this procedure are EPA Method 1638 and EPA Method 1640 (EPA 1996b; 1997). Samples were analyzed for As by flow-injection atomic spectroscopy (FIAS) in accordance with Battelle SOP MSL-I-030, *Determination of Metals in Aqueous and Digestate Samples by Hydride Generation Atomic Absorption (HGAA) with Flow Injection (FIAS)* (Battelle 2009); the base method for this procedure is EPA Method 270.3 (EPA 1986).

4.3.1.2 Passive Samplers

Upon receipt at MSL, the Chelex binding phase was immediately removed from the DGT units in a class 100 clean bench using Teflon forceps, placed into an acid cleaned micro-centrifuge tube, and stored at 4±2˚C until elution in 1 mL 15.8 mol Optima™ grade nitric acid (within 14-days). During the course of this Project EPA made the recommendation that elutions be performed in 1 M HNO_3 (Burgess et al. 2017), however, after adjusting elution coefficients this modification has no meaningful effect to the end result, thus for continuity the methodology change was not implemented by ENVVEST.

DGT were analyzed for five metals (Cd, Cu, Ni, Pb, and Zn) in accordance with SOP MSL-I-022 (Battelle 2016a). The DGT data were reported in units of µg L^{-1} C_{DGT}, the conversion of which is based on Fick's First Law (Zhang and Davison 1995). After laboratory verifications, elution factors were adopted from Garmo et al (2003) and temperature dependent diffusion coefficients from a table provided by the sole commercial manufacturer (DGT Research Ltd, Skelmorlie, Quernmore, Lancaster, UK [later published in Davison 2016]). To blank correct C_{DGT}s, the average values in µg of analytes on 8 blank Chelex resins were subtracted from the mass of metals accumulated on each field sampler.

4.3.2 Ancillary Parameters

The TSS concentrations were determined by gravimetric analysis in accordance with Battelle SOP MSL-I-041 *Total Suspended Solids Measures* (Battelle 2012); the base method for this procedure is SM2540D (Eaton et al. 2005). A method modification was made beginning with AMB12: the use of polycarbonate filters replaced glass fiber filters to reduce the error of weighing very small amounts of particles on a much higher mass filter.

The salinity was measured using a YSI-30 S-C-T probe. Salinity is reported in ppt (parts per thousand) calculated from the instrument's conductivity and temperature values using algorithms found in Standard Methods for the Examination of Water and Wastewater.

For AMB01–AMB09, OC samples were analyzed by Persulfate-Ultraviolet or Heated-Persulfate Oxidation SM5310 C, by ALS Environmental, Kelso, WA (APHA 1998). Beginning with AMB10, TOC and DOC samples were analyzed using a High Temperature Catalytic Oxidation (HTCO) method, in accordance with Battelle MSL-W-011 *Determination of Total and Dissolved Organic Carbon in Seawater by high Temperature Catalytic Oxidation* (Battelle 2014). The instrument is specially equipped with a high-salt sample combustion tube kit and halogen scrubber for seawater analysis. Briefly, seawater samples are acidified to pH <2 by concentrated hydrochloric acid (trace metal grade, Fisher Chemical) prior to analysis, then sparged for 2 minutes to remove inorganic carbon (IC). The non-purgeable organic carbons (NPOCs) in samples are then converted to CO_2 by HTCO with a platinum catalyst. A nondispersive infrared detector then is used to detect the converted CO_2 for quantification of NPOC.

Analyses of AN, NNN, TKN, TP, and HEM were also conducted by ALS Environmental or GEL Laboratories, following EPA Methods 350.1, 353.2, 351.4, 365.3, (or 365.4), and 1664 (O'Dell 1993; 1993b; Schlueter 1977; EPA 1978, 1983, 1999), respectively.

4.3.3 Toxicological Evaluations

Toxicity testing was conducted in accordance with standard methods (ASTM 2004, EPA 1995, EPA 2002) at the NIWC Pacific Bioassay Laboratory. The laboratory is certified under the State of California Department of Health Services, Environmental Laboratory Accreditation Program (ELAP), Certificate No. 2601 and State of Washington Department of Ecology, Laboratory ID. No. F893.

Chronic toxicity tests on effluent and ambient water samples from PSNS&IMF were performed using purple sea urchin (*Strongylocentrotus purpuratus*) and Mediterranean mussel (*Mytilus galloprovincialis*) embryos. Acute tests were conducted using mysid shrimp (*Americamysis bahia*) and bioluminescent dinoflagellate (*Pyrocystis lunula*) using a QwikLite® 200 Toxicity Test System. The giant kelp spore (*Macrocystis pyrifera*) germination and growth test was performed on samples collected from September 2009 through March 2012 (AMB01 through AMB10). Giant kelp tests were performed at the Nautilus Environmental, LLC Bioassay Laboratory (ELAP Certificate No. 1802).

Samples were either shipped or hand couriered overnight to the NIWC laboratory in San Diego, CA. Upon receipt of the samples at the laboratory, water quality parameters of the samples were measured prior to toxicity testing and included pH, dissolved oxygen (DO), salinity and temperature. For toxicity exposures using the purple sea urchin, mussel and the dinoflagellate, samples with salinities < 34 ppt were adjusted with the addition of hypersaline brine to increase salinities to 34 ppt. For mysid shrimp toxicity exposures, salinities < 30 ppt were adjusted with the addition of Bioassay Grade Crystal Sea Marine Mix®.

For the purple sea urchin, mussel, dinoflagellate and kelp spore toxicity exposures, effluent samples were tested in a 0.5 dilution series (i.e. 6.25, 12.5, 25, 50% and the highest possible concentrations – due to the addition of hypersaline brine to increase salinity) and ambient samples were tested at the highest possible concentration only. For the mysid shrimp exposures, effluent and ambient samples were typically tested at the 100% concentration only.

Statistical analyses were conducted using Comprehensive Environmental Toxicity Information System (CETIS) Software. First, samples underwent a comparison analysis against the appropriate control to determine if a significant difference was present (EPA 1995) where data type determined analysis was performed (i.e. Dunnet Multiple Comparison Test, Two-Sample T-Test, Steel Many-One Rank Sum Test; parametric or non-parametric, depending on data). When a dilution series on a given sample was conducted, a point estimate analysis was conducted to determine EC_{50}/LC_{50} values (Linear Regression, Trimmed Spearman-Karber, or Linear Interpolation).

Starting in June 2015 (AMB18), for the tests with the purple sea urchin, Mediterranean mussel and mysid shrimp, a Test for Significant Toxicity (TST) analysis was conducted on the highest concentration tested for each sample and the appropriate control (EPA 2010). TST analyses tests examine whether the results of a given sample relative to its respective brine control differs by an *a priori* prescribed amount rather than whether they are the same, as in traditional hypothesis testing. For the purple sea urchin test, the mussel, the giant kelp and the mysid shrimp, the *a priori* critical percent difference is set at 25, 25, 25 and 20%, respectively. No TST method exists for the dinoflagellate bioluminescence bioassay.

Summaries of test conditions and test acceptability criteria are provided in Appendix A: Tables A.4 – A.8.

4.4 Presentation of Data Trends

Spatial and temporal graphical representation of seawater data use the following log transformations for resolution of both data gradients and respective regulatory limits: (1) Hg and Pb are expressed as bases of 10 (with the exception of C_{DGT} Pb), (2) Cu data is given in base 2; and (3) Zn is expressed as base 5 (with the exception of C_{DGT} Zn). Effluent records, with the exception of Cu are plotted using base 10.

To provide the overall descriptive statistics for this interim report, the spatial data were reviewed and the following were removed from the data set for statistical analyses: 1) sites omitted from more than four events (see Table B.7); 2) all samples labeled as duplicates or deep stations because the analysis was for surface water trends; and 3) multiple samples taken during the same AMB event and sampling location that were averaged as one sample (e.g., B, C, or D samples). The overall range of spatial data are displayed in box and whiskers plots where lower and upper hinges correspond to the first and third quartiles. Whiskers extend from the upper and lower hinges to the largest value no farther than 1.5x the inner quartile range. Data plotted beyond the whiskers are considered to be outliers. Temporal data are displayed as mean values and maxima of the total set and for concordance between plots the datasets trimmed for spatial statistics were used for temporal assessment (Strivens et al. [2018] included non-routine reference stations in the temporal trends).

5.0 Results

Surface water results are subdivided into spatial (Section 5.1.1) and temporal (Section 5.1.2) analyses and outfall results are given in Section 5.2. A summary of station-specific data is provided in Appendix B, Table B.7 (including reference stations eliminated from statistical analysis, which may be of interest in targeted investigations).

Arsenic results are not presented in detail in the current report and have not been monitored by surface water grab sampling or drydock compositing since 2012. Data collected from 2009-2012 provided that As levels from these locations were an order of magnitude below the 21 µg L^{-1} chronic threshold suggested in WAC 173-201A-240; likewise, stormwater monitoring did not indicate a significant loading concern (Brandenberger et al. 2018). Arsenic analysis remains in the ENVVEST Mussel Watch suite of metals to verify that no upward trajectories appear in long-term status and trends; PAH and PCB levels are also tracked through Mussel Watch to inform on trends of 303(d) contaminants-of-concerns (Strivens and Johnston 2019).

For Hg (Sections 5.1.1.1, 5.1.2.1, and 5.2.1), neither receiving waters nor industrial effluent trends have significantly shifted trajectory over the 2-year window from AMB25–29 (Strivens et al. 2018a). Notations of outliers and exceedances of the chronic endpoint at PS03 paraphrase the previous discussion and drydock effluents remain a non-concern against a WQBEL assessment. Likewise, Pb ambient spatial, ambient temporal, and effluent trends (Sections 5.1.1.3, 5.1.2.1, and 5.2.3) do not justify remedial action. Reasonable potential evaluations are included in Appendix C. For Hg and Pb, sediment evaluations in PSNS have demonstrated reasonable protection toward benthos in the form of toxicological evaluations and AVS-SEM ratios (which by default is also true for Ag, Cd, Cu, Ni, and Zn). Impacts to passing species may be considered from sessile tissues reported in Strivens and Johnston (2019) and are chronic in stormwater station specific localities (Brandenberger et al. 2018).

Zn data presented in Sections 5.1.1.4, 5.1.2.1, and 5.2.4 demonstrate environmental protection under Project ENVVEST and that average ambient dissolved levels have remained stable over time. However, even with the exclusion of known mechanically induced outliers, there is reasonable potential to continue targeted monitoring of Zn at OF018 and to set a threshold for protection of aquatic life.

A comprehensive discussion of WQBELs is focused on Cu and is divided among Sections 5.1.1.2, 5.1.2.1, and 5.2.2. While spatial trends highlight minor concern near drydock outfalls, and temporal trends show an improving baseline within the PSNS, drydock effluents indicate an initial concern that must be understood through the context of significant bioavailability factors (e.g., EPA 2016) which should then be applied to mixing zone adjusted WQBELs to achieve protective waste load allocations while also preserving uses beneficial to national defense. This should not be construed as a request to lower the water quality standards under the WAC. Rather it is a correction to the default parameter that has been recognized and acknowledged through the EPA's recent drafting of biotic ligand model-based criteria.

5.1 Surface Water

Nearshore stations within PSNS, identified as PS01–PS12 are plotted from west to east, as are PSNS Barrier stations PS13–PS16 and nearshore stations within Sinclair Inlet. Dyes Inlet nearshore stations are given west to east, and adjoining passage nearshore stations are plotted south to north. To complete the gradient, stations centrally located in the Inlets and passages are plotted in an "inner-to outer" fashion in relation to the PSNS (i.e., Sinclair, Dyes, passages). The sub-sectioning overlay in Figure 9 further delineates impact zones 4 and 5 (Sinclair/Dyes Nearshore and Sinclair/Dyes Marine, respectively) for visualization assistance.

5.1.1 Spatial Comparison

Spatial data set impact zones' variance of metals, regulated under WAC 173-201A-240, were compared using one-way analysis of variance (ANOVA) followed by post hoc Tukey when applicable. Statistical significance is indicated as yes or no in tables accompanying each spatial narrative; no meaning $p > 0.05$.

5.1.1.1 Mercury

The trends in Figure 9 and Figure 10 show Hg variation between the PSNS industrial areas and the receiving waters. For Hg_{diss}, there are statistically significant differences among impact zones [$F_{(3,953)} = 9.2$, $p = <0.00001$]. There is, however, no significant difference between the PSNS Barrier (average = 0.314 ± 0.112 ng L^{-1}) and the nearshore/marine stations of the Inlets (averages = 0.345 ± 0.225 ng L^{-1} and 0.310 ± 0.201 ng L^{-1}, respectively) (Table 4); meaning greater levels within PSNS (average = 0.704 ± 1.70 ng L^{-1}) are not, on average, significantly transported, in the surface layer, from the barrier downstream. Station PS03, the elevated point within the PSNS, is affected by tidal and rainwater flushing through Hg containing backfill (making ambient conditions highly variable over time) and is the subject of ongoing focused investigations (Brandenberger et al. 2018; Conn et al. 2018).

For Hg_{tot}, there are statistically significant differences within the sum of impact zones, where $\alpha = 0.05$, [$F_{(3,952)} = 14.7$, $p = <0.00001$]. The significance mirrors the dissolved fraction when comparing PSNS Nearshore to Sinclair/Dyes Nearshore stations, with averages of 1.60 ± 2.65 and 0.985 ± 0.807 ng L^{-1}, respectively, but again when comparing the Sinclair/Dyes Nearshore to Sinclair/Dyes marine stations (average = 0.744 ± 0.451 ng L^{-1}) there is a lack of significant gradient. Non-PSNS point sources (e.g., Sinclair Inlet nearshore Stations SN03–SN05, which are impacted by the Bremerton Wastewater Treatment Plant's West Outfall) are evident within the sampling area. In relation to Toxics Substances Criteria, the marine chronic value was exceeded only at PS03 (AMB01 [08/31/2009] and AMB17 [04/07/2015]). The impact zones' mean Hg levels fall within the expected ranges for Puget Sound waters with respect to total levels; however, dissolved levels are, on average, four times greater in the PSNS Nearshore impact zone and two times greater in the remaining zones in comparison to the Puget Sound review by Sedar (2009). Reflective of elevated surface water Hg concentrations at PS03, ENVVEST Mussel Watch data indicate that in situ photochemical reduction of $Hg(II)_{aq}$ has caused intermittent exceedances of scope-for-growth endpoints (Strivens and Johnston 2019).

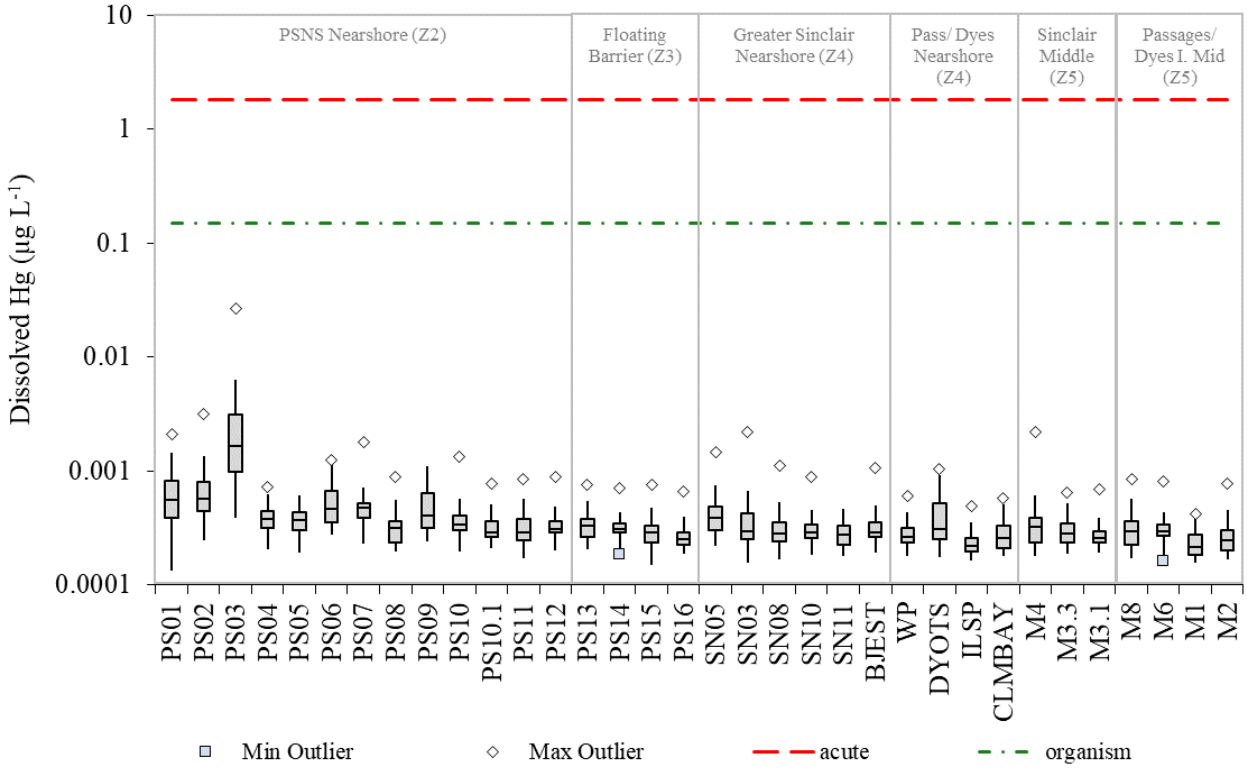

Figure 9. Hg_{diss} as the average of 29 sampling events over 10 years moving (left-to-right) from high to low impact zones of Sinclair and Dyes Inlets. Regulatory limits are those described in WAC 173-201A-240 and 40 CFR 131.36 and provided in Table 2 of the current report.

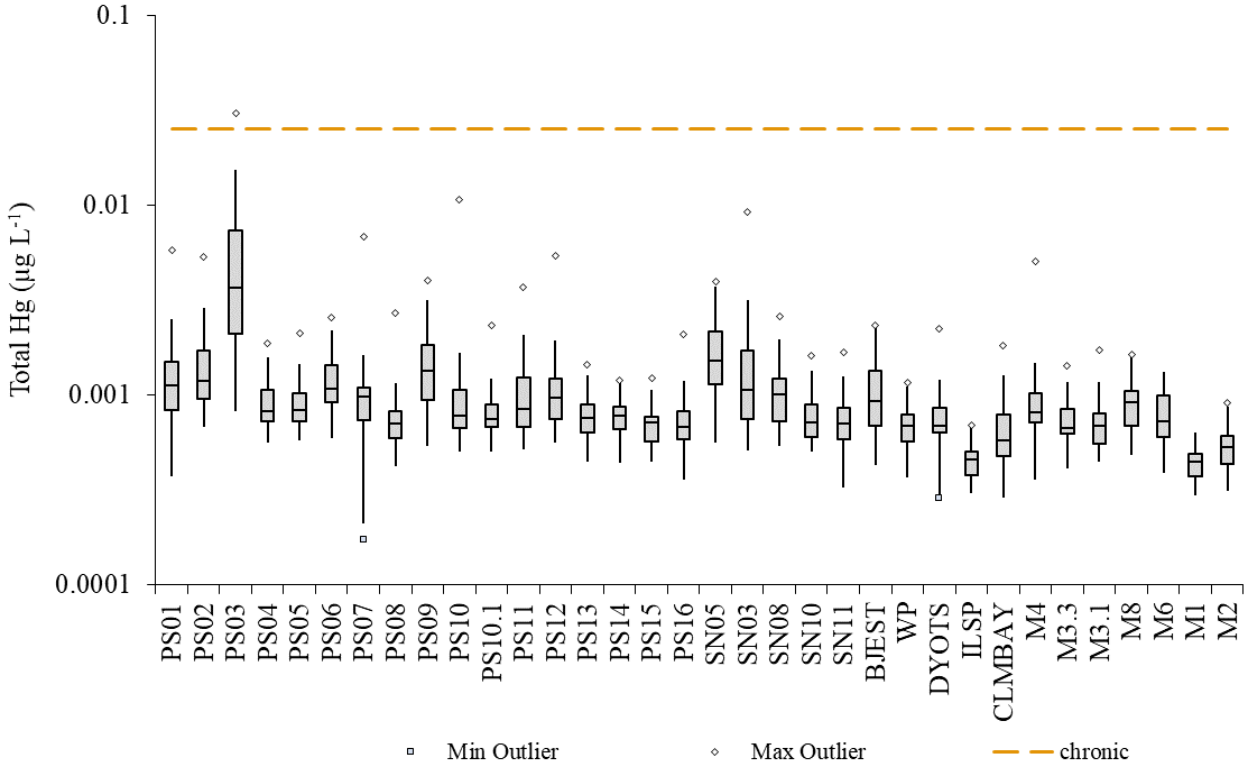

Figure 10. Hg_{tot} as the average of 29 sampling events over 10 years moving from the high to low impact zones of Sinclair and Dyes Inlets. Regulatory limits are those described in WAC 173-201A-240 and 40 CFR 131.36 and provided in Table 2 of the current report.

Table 4. Tukey analysis of the differences between impact zones for Hg_{diss}.

Contrast	Difference (µg L^{-1})	Lower bound (95%)	Upper Bound (95%)	Significant ($\alpha = 0.05$)
PSNS Nearshore vs Sinclair/Dyes Marine	0.000394	0.000148	0.000639	Yes
PSNS Nearshore vs PSNS Barrier	0.000390	9.35E-05	0.000686	Yes
PSNS Nearshore vs Sinclair/Dyes Nearshore	0.000359	0.000139	0.000579	Yes
Sinclair/Dyes Nearshore vs Sinclair/Dyes Marine	3.49E-05	-0.000225	0.000295	No
Sinclair/Dyes Nearshore vs PSNS Barrier	3.10E-05	-0.000277	0.000339	No
PSNS Barrier vs Sinclair/Dyes Marine	3.88E-06	-0.000323	0.000331	No

Table 5. Tukey analysis of the differences between impact zones for Hg_{tot}.

Contrast	Difference (µg L^{-1})	Lower bound (95%)	Upper Bound (95%)	Significant ($\alpha = 0.05$)
PSNS Nearshore vs Sinclair/Dyes Marine	0.000857	0.000462	0.001251	Yes
PSNS Nearshore vs PSNS Barrier	0.000845	0.000369	0.001320	Yes
PSNS Nearshore vs Sinclair/Dyes Nearshore	0.000616	0.000262	0.000970	Yes
Sinclair/Dyes Nearshore vs Sinclair/Dyes Marine	0.000241	-0.000178	0.000659	No
Sinclair/Dyes Nearshore vs PSNS Barrier	0.000229	-0.000267	0.000724	No
PSNS Barrier vs Sinclair/Dyes Marine	1.18E-05	-0.000514	0.000537	No

5.1.1.2 Copper

The trend in Figure 11 shows Cu_{diss} variation between the PSNS industrial areas and the proximate waters. For Cu_{diss}, there are statistically significant differences determined as a one-way ANOVA among impact zones [$F_{(3,953)}$ = 270, p = <0.00001]. Post hoc comparisons using a Tukey test indicated that the mean differences were significant for all impact zone comparisons (Table 6). Elevated stations within the PSNS are the direct receiving zones of DD discharges, but are also affected by collocated stormwater outfalls and rare overflow events (e.g., in 2018 PSNS disclosed the discovery of a 2-year grey water leak estimated to have contributed 1.7 ML to the PS08 receiving zone and earlier that year a 0.3 ML spill occurred into the PS03 area due to sewage intrusion into a stormwater system). Elevated areas outside of the PSNS (SN10 and SN11) are collected from the Port Orchard Sinclair Marina within the City of Port Orchard and the Port Orchard Marina foot-ferry terminal within the Port of Bremerton, respectively. In general, the data show few exceedances of the default Toxic Substances Criteria (i.e., PS07–09); these exceedances occurred during AMB04 (09/08/2010), AMB05 (11/18/2010), AMB09 (12/06/2011), AMB12 (02/12/2013), AMB13 (06/08/2013), and AMB27 (08/22/18). Importantly, ENVVEST Cu Water Effect Ratio (WER) efforts for the Sinclair/Dyes Inlet show that grab samples do not indicate the occurrence of acute effects during these events (EPA 1994, Rosen et al. 2009). In comparison to five other Puget Sound shipyard areas (Friday Harbor, Skyline, John Wayne, Des Moines, and Swantown Marinas), as reported in Hobbs et al. (2018), mean inner shipyard Cu_{diss} concentrations were 1.57 µg L^{-1} and PSNS averages 1.46 µg L^{-1}; additionally, Puget Sound marine averages were 0.323 µg L^{-1} and Sinclair/Dyes Marine is 0.536 µg L^{-1}.

Biennial samplings of whole *Mytilus* tissue at PS06, 08, and 09 have historically shown exceedances of Cu critical body residue (CBR) benchmarks, but not after 2014 (Strivens and Johnston 2019); the early CBR exceedances were linked to in-water construction and have not recurred post-construction. Mussel tissue analysis from March 2020 collections will be available in late 2020 for further confirmation of biota health.

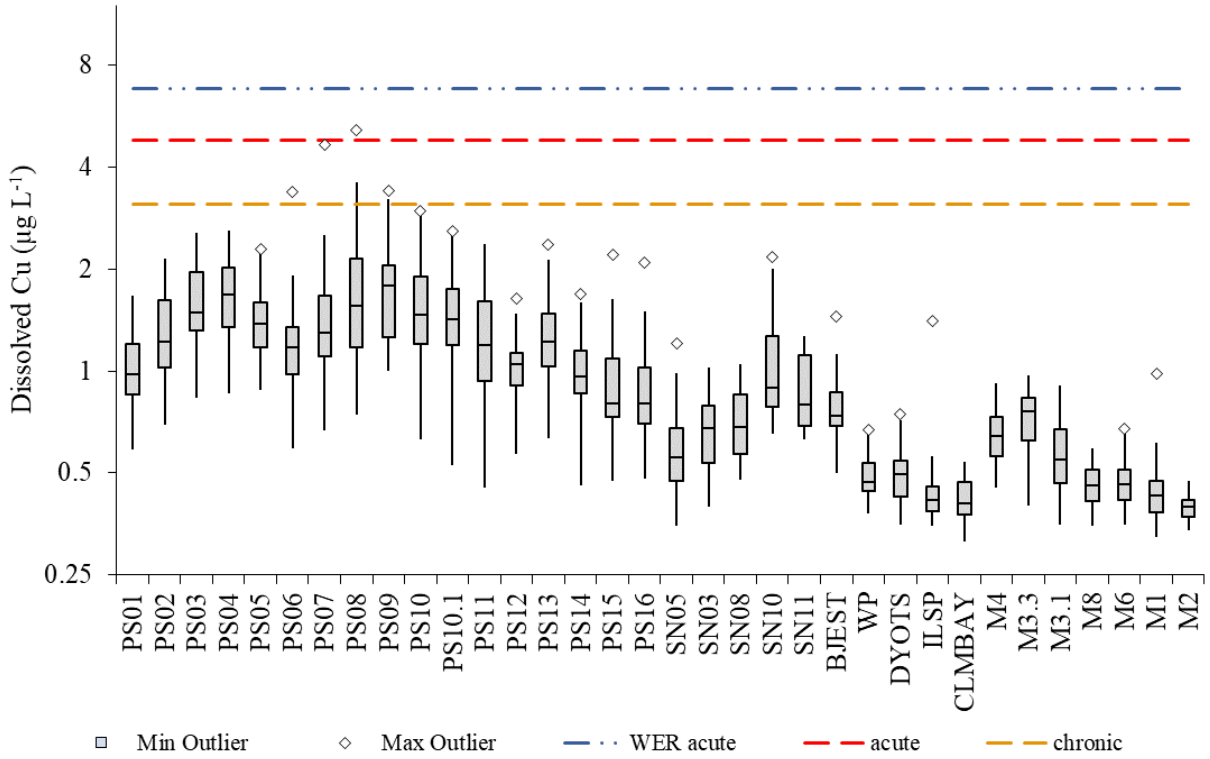

Figure 11. Cu_{diss} as the average of 29 sampling events over 10 years moving from the high to low impact zones of Sinclair and Dyes Inlets. Regulatory limits are those describe in WAC 173-201A-240 and 40 CFR 131.36 and provided in Table 2 of the current report; human health criteria for consumption of organisms is three orders of magnitude greater than the data range. The WER adjusted acute criterion is also depicted.

Table 6. Tukey analysis of the differences between impact zones for Cu_{diss}.

Contrast	Difference (µg L^{-1})	Lower bound (95%)	Upper Bound (95%)	Significant ($\alpha = 0.05$)
PSNS Nearshore vs Sinclair/Dyes Marine	0.925	0.826	1.024	Yes
PSNS Nearshore vs Sinclair/Dyes Nearshore	0.805	0.716	0.893	Yes
PSNS Barrier vs Sinclair/Dyes Marine	0.491	0.359	0.623	Yes
PSNS Nearshore vs PSNS Barrier	0.434	0.314	0.553	Yes
PSNS Barrier vs Sinclair/Dyes Nearshore	0.371	0.247	0.495	Yes
Sinclair/Dyes Nearshore vs Sinclair/Dyes Marine	0.120	0.015	0.225	Yes

Toward demonstration of novel NPDES tools and validation of the Cu WER study, ENVVEST C_{DGT} results (Strivens et al. 2019, 2020) have been incorporated into compliance assessments. The long-term health of the Sinclair Inlet study area, shown in Figure 12, demonstrates successful adoption of the DGT technique into a regulatory compliance program. Inclusion of reference points, reflective of differing land use adjacent to the receiving waters (i.e., industrial vs commercial or rural), provides a qualitative comparison. The Ports of Silverdale and Illahee demonstrate a labile baseline for non-industrial use waters, while Eagle Harbor was not significantly different from Sinclair Inlet by Tukey ($p = 0.05$). Although clear baseline shifts are evident, the data indicate that successful protection of beneficial uses is occurring with respect to the proposed CMC calculation.

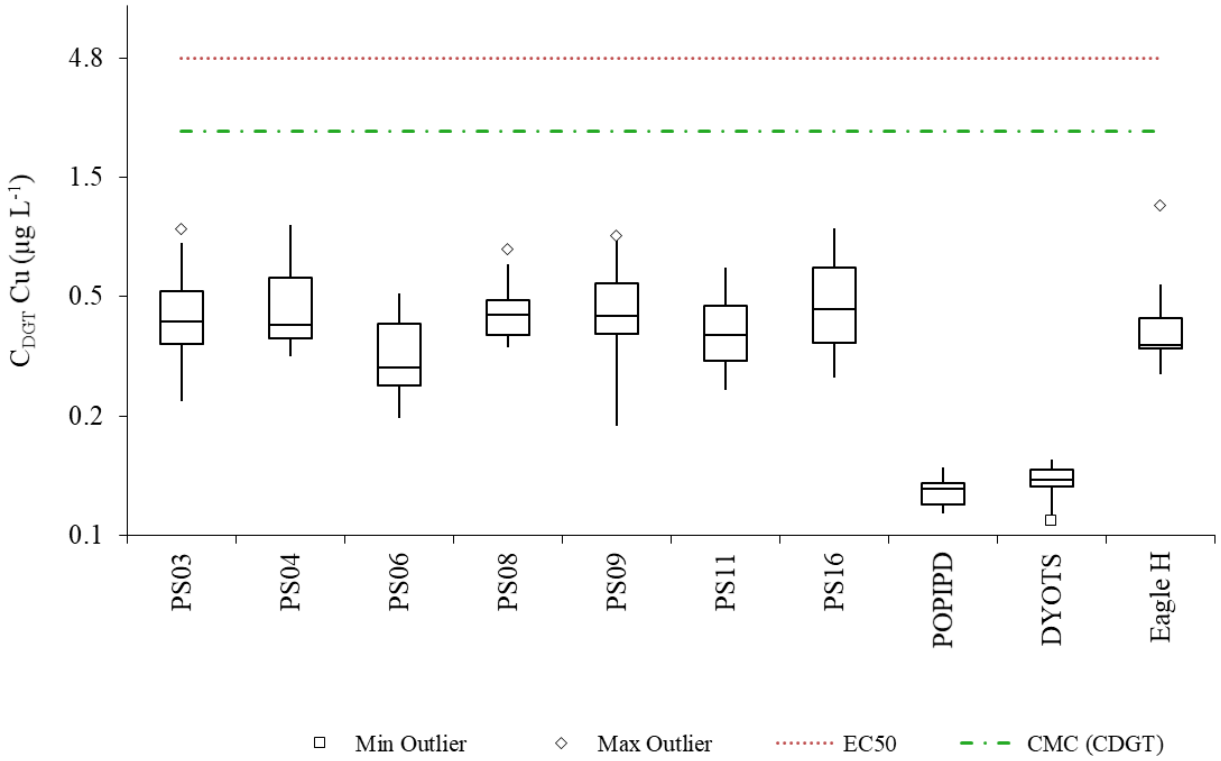

Figure 12. Long-term health of PSNS Nearshore and reference stations within the Kitsap Basin, with respect to labile Cu. The compiled data consist of 3-d DGT deployments (PSNS stations; *n* = 28/station) and 14-d deployments (reference locations; *n* = 5–7/station) between December 2016 and July 2019. (Reprinted from Strivens et al. 2020, with the addition of Eagle Harbor)

Calculated C_{DGT} precision at the ambient levels within PSNS (and over the respective temperature dependent diffusion range) can be summarized through average RPDs of duplicate samplers that have been included in campaigns in PSNS waters, where 1-day averages were 15 ± 17% (*n* = 10), 3-days 11 ± 19% (*n* = 31), 7-days 8 ± 7% (*n* = 11), and 14-days 7 ± 7% (*n* = 14); meaning sampling requirements for ambient waters can conveniently be scaled to represent a 24-h composite if deemed pragmatic. Additionally, Dunn et al. (2007) has demonstrated the precision of marine field deployments over 6-h periods; however, as is inherently true of all sampling methods, the significance of tidal flushing becomes extreme when averaging periods are shortened and transient time to steady state will be limiting due to organic complexes in seawaters. Brief discussion of deployment duration is pretext to highlighting some disagreement in scientific consensus, where the current opinion in draft Aquatic Life Criterion (e.g., EPA 2016) is that the standard 24-h averaging period be shifted to 1-h (to account primarily for ammonia toxicity); however, that notion is not relevant to C_{DGT} Cu and recent work establishes that pulsed trace metal inputs can be tolerated when offset over biologically relevant windows (e.g., Angel et al. 2015).

In addition to a monitoring strategy reflective of grab sampling protocol, select AMB events have included labile assessments of vertical profile distributions to (1) determine if classical distribution was occurring in the dynamic sampling environments and (2) resolve the representativeness of the standard sampling protocol. Figure 13 shows a subset of those efforts and highlights the difference in lability that is experienced when moving from the thin near-surface layer to the standard use of “upper 1 m” grab sampling. Labile concentrations at all stations, as is observed by the PS06, PS08, and PS09 summary, were uninfluenced by impediments to natural distribution. Inclusion of this approach at all PSNS sites during March and August of 2019 showed that only PS03 was ever of-concern with regard to Cu lability

in the upper 2 cm (i.e., levels slightly above the threshold determined by Strivens et al. [2020] were observed [exceedances of ~ 20% for two consecutive 3-day averaging period] however, water quality at the 1 m mark was ~ 34% of the C_{DGT} CMC). This type of analysis demonstrates the utility of DGT and provides better understating of the total ecosystem.

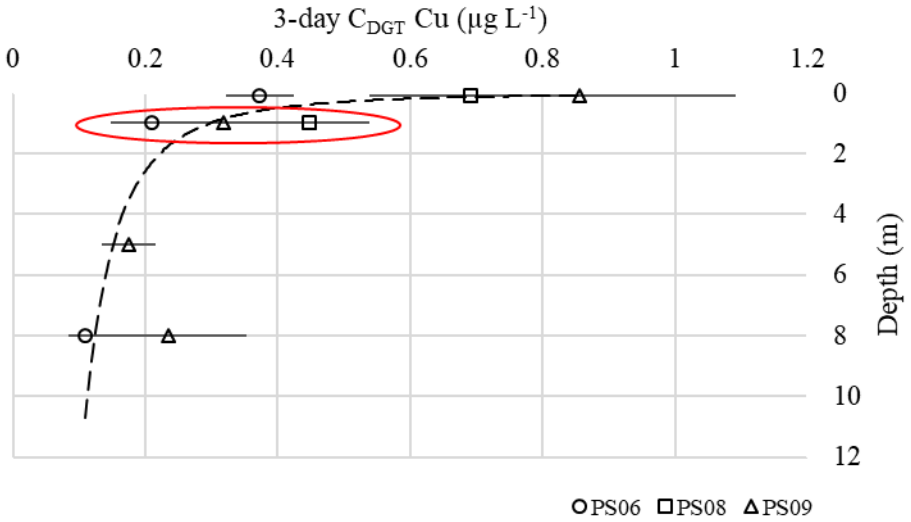

Figure 13. C_{DGT} Cu profiles captured at PS06, PS08, and PS09 during AMB28 as four 3-day deployments per site over 12 days.

5.1.1.3 Lead

The trend in Figure 14 shows Pb_{diss} variation between the PSNS industrial areas and the adjoining waters. For Pb_{diss}, there are statistically significant differences among impact zones within the waterbody [$F_{(3,952)}$ = 14.4, p = <0.00001], but samples have shown all areas to be an order of magnitude below the Toxic Substances Criteria. There is no significant difference between the PSNS Barrier and the Sinclair/Dyes Nearshore impact zones (Table 7). In comparison to five other Puget Sound shipyard areas, mean Pb_{diss} in other inner shipyards was 0.0653 µg L^{-1} (Hobbs et al. 2018) and PSNS is 0.0231 µg L^{-1} (n = 373); Puget Sound marine averages were 0.0819 µg L^{-1} and Sinclair/Dyes Marine is 0.0173 ± 0.0140 µg L^{-1} (n = 192). The long-term lability of Pb, as measured by DGT, is provided in Figure 15 for data posterity toward interpretation in a toxicological effects context – the PSNS data are plotted as 7-day averages due to the number of low-lability induced non-detects over 3-day deployments. These trends support negation of Pb effluent limits for industrial- and storm- waters at this facility.

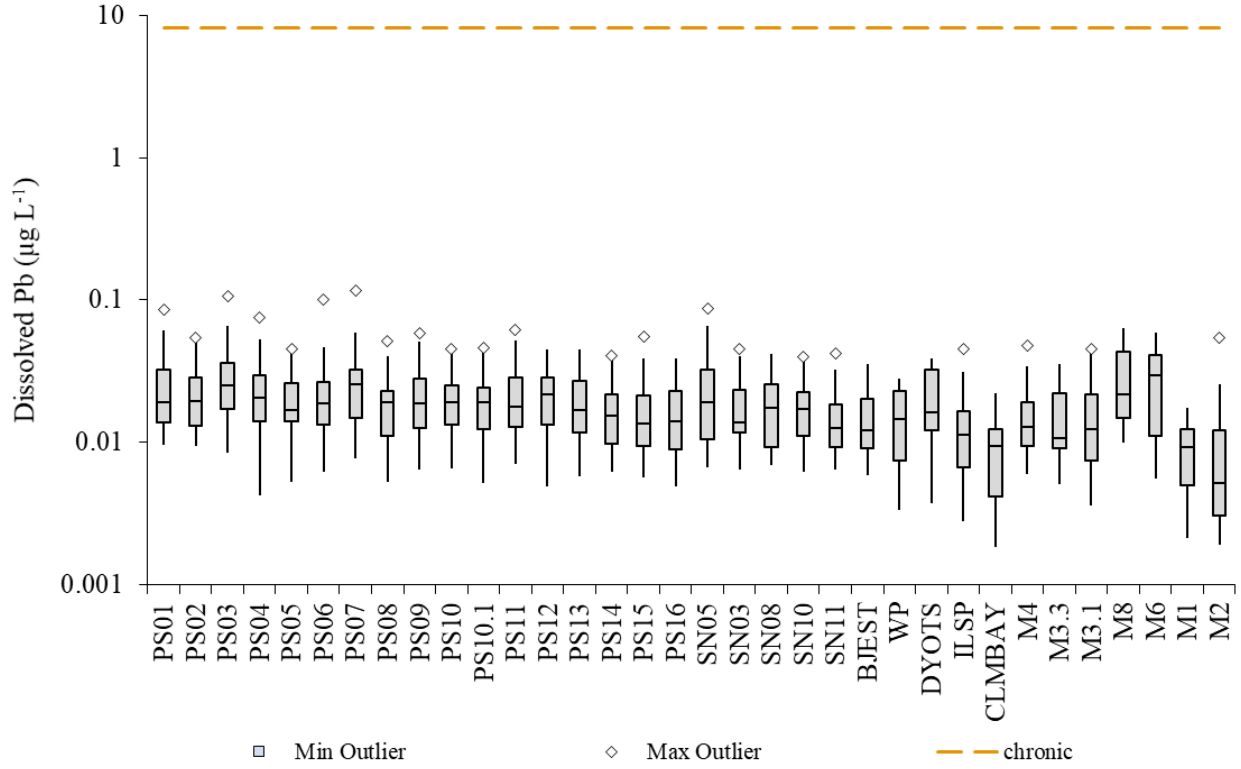

Figure 14. Pb_{diss} as the average of 29 sampling events over 10 years moving from the high to low impact zones of Sinclair and Dyes Inlets. Health limits are those describe in WAC 173-201A-240 and 40 CFR 131.36 and provided in Table 2 of the current report; the acute threshold (210 µg L^{-1}) exceeds the given scale by an order of magnitude.

Table 7. Tukey analysis of the differences between impact zones for Pb_{diss}.

Contrast	Difference (µg L^{-1})	Lower bound (95%)	Upper Bound (95%)	Significant ($\alpha = 0.05$)
PSNS Nearshore vs Sinclair/Dyes Nearshore	0.00601	0.00327	0.00875	Yes
PSNS Nearshore vs Sinclair/Dyes Marine	0.00576	0.00270	0.00882	Yes
PSNS Nearshore vs PSNS Barrier	0.00562	0.00194	0.00931	Yes
PSNS Barrier vs Sinclair/Dyes Marine	0.00013	-0.00394	0.00421	No
Sinclair/Dyes Nearshore vs Sinclair/Dyes Marine	-0.00025	-0.00349	0.00299	No
Sinclair/Dyes Nearshore vs PSNS Barrier	-0.00038	-0.00422	0.00346	No

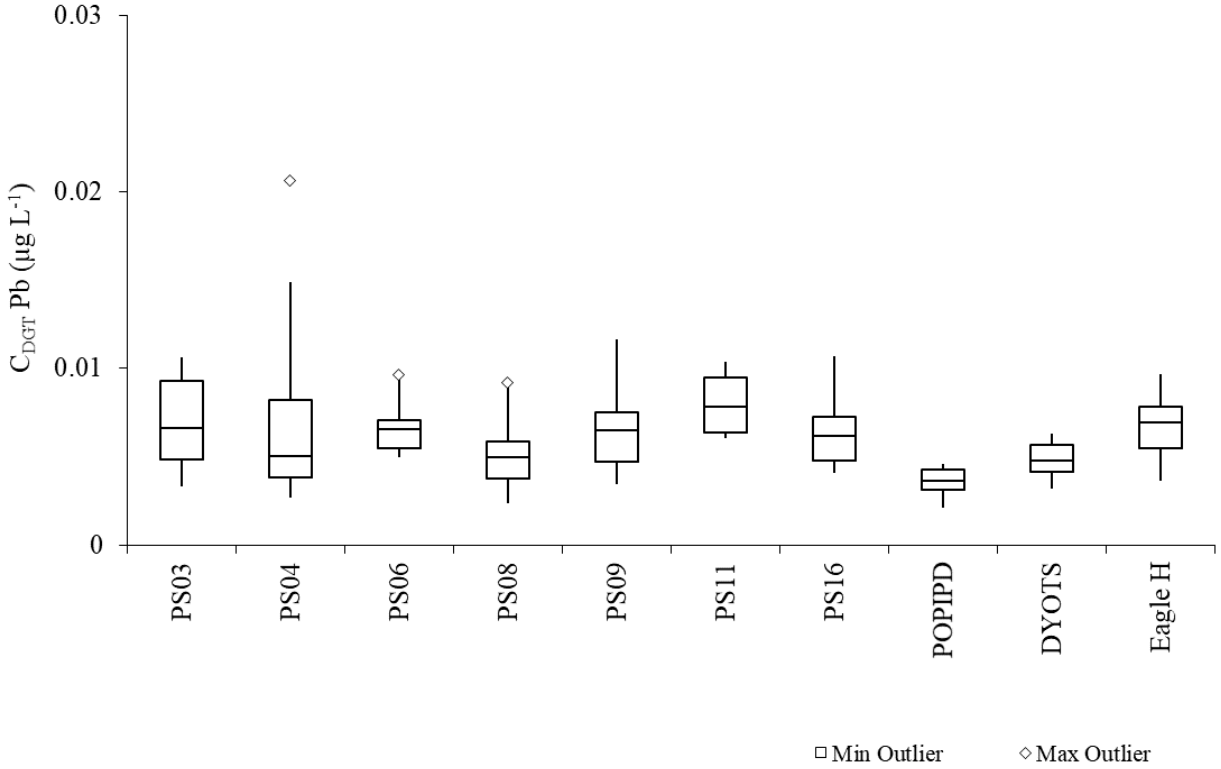

Figure 15. Long-term lability of Pb in the PSNS Nearshore and reference stations within the Kitsap Basin. The compiled data consist of 7-d DGT deployments (PSNS stations; *n* = 12/station) and 14-d deployments (reference locations; *n* = 5–8/station) between December 2016 and July 2019.

5.1.1.4 Zinc

The trend in Figure 16 shows Zn_{diss} variation between the PSNS industrial areas and the receiving impact zones. There is a statistically significant difference among the four zones [$F_{(3,952)} = 123$, $p = <0.00001$]; and the averages display a gradient from PSNS Nearshore (5.19 ± 3.30 µg L^{-1}) to the PSNS Barrier (3.09 ± 2.21 µg L^{-1}) to the Sinclair/Dyes Nearshore (1.89 ± 2.87 µg L^{-1}) and the Sinclair/Dyes Marine (1.19 ± 0.891 µg L^{-1}); post hoc Tukey analysis shows the variation between Sinclair/Dyes Nearshore and Sinclair/Dyes Marine is the least significant (Table 8). Elevated Stations within the PSNS display the same trend as Cu, and are those nearest to DD effluent points; those outside of the PSNS, SN10 and SN11, are again collected from the Port Orchard Sinclair Marina within the City of Port Orchard and the Port Orchard Marina foot-ferry terminal within the Port of Bremerton, respectively – and likely result from shedding of antifoulant paints. No data exceed the marine chronic criterion of 81.0 µg L^{-1}. In comparison to five other Puget Sound shipyard areas, mean inner shipyards were 3.91 µg L^{-1} versus PSNS at 5.19 µg L^{-1}; additionally, Puget Sound marine areas averaged 0.812 µg L^{-1} versus the Sinclair/Dyes Marine zone at 1.19 µg L^{-1} (Hobbs et al. 2018). Of additional significance, the levels of total Zn within the PSNS Nearshore have been demonstrated to have minimal scope-for-growth effects on filter feeders (Strivens and Johnston 2019).

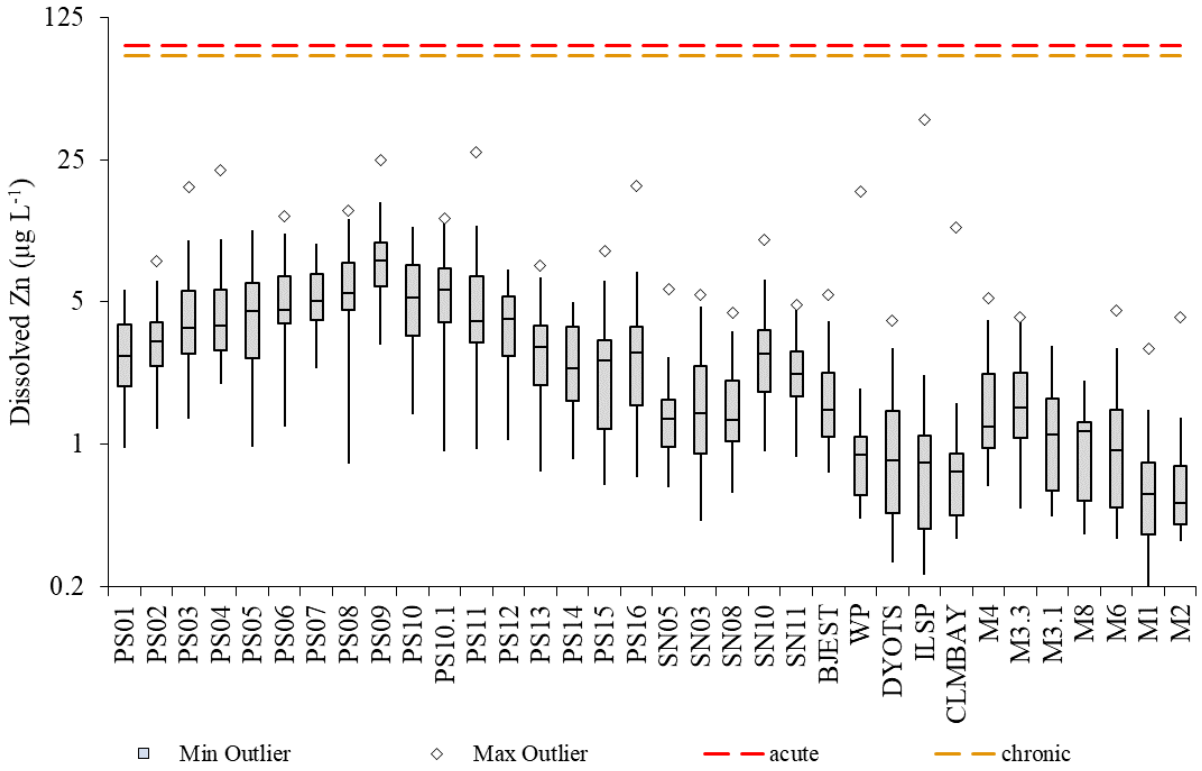

Figure 16. Zn_{diss} as the average of 29 sampling events over 10 years moving from the high to low impact zones of Sinclair and Dyes Inlets. Regulatory limits are those describe in WAC 173-201A-240 and 40 CFR 131.36 and provided in Table 2 of the current report; human health criteria for consumption of organisms is an order of magnitude greater than the data range.

Table 8. Tukey analysis of the differences between impact zones for Zn_{diss}.

Contrast	Difference (µg L^{-1})	Lower bound (95%)	Upper Bound (95%)	Significant ($\alpha = 0.05$)
PSNS Nearshore vs Sinclair/Dyes Marine	4.01	3.39	4.63	Yes
PSNS Nearshore vs Sinclair/Dyes Nearshore	3.31	2.75	3.86	Yes
PSNS Nearshore vs PSNS Barrier	2.15	1.40	2.90	Yes
PSNS Barrier vs Sinclair/Dyes Marine	1.86	1.03	2.68	Yes
PSNS Barrier vs Sinclair/Dyes Nearshore	1.16	0.380	1.94	Yes
Sinclair/Dyes Nearshore vs Sinclair/Dyes Marine	0.699	0.0409	1.36	Yes

C_{DGT} Zn trends are plotted in Figure 17 and ENVVEST is developing a C_{DGT} Zn CMC toward prospective use as an NPDES tool. C_{DGT} Zn is first presented as the 14-day baseline conditions for each station (Figure 17). The data are presented at this scale for fundamental interpretation of the comparison between PSNS stations and reference stations in Figure 18, which depicts 3-day deployment statistics for PSNS stations (3-day deployments were not conducted at reference points). Due to normally low ambient levels within the study area, the proximity of input of solid phase sources (e.g., sacrificial anodes, anti-foulant paint, galvanized products, etc.), diurnal fluctuations, and pH sensitive speciation combined with minimal kinetic limitation to lability (i.e., multiple diffusion rates that must come into equilibrium) when adsorbed to OC ligands — 3-day C_{DGT} Zn may over- or underestimate mixing-zone scale bioavailability (Strivens et al. 2018b). That is to say, multiple DGTs should be deployed and averaged for each receiving zone when

scaling to short durations and the preliminary single-sampler outliers in Figure 18 should not be interpreted within the current report to indicate toxic conditions (e.g., the average RPD of field duplicates at 3-day is 74%, n = 31).

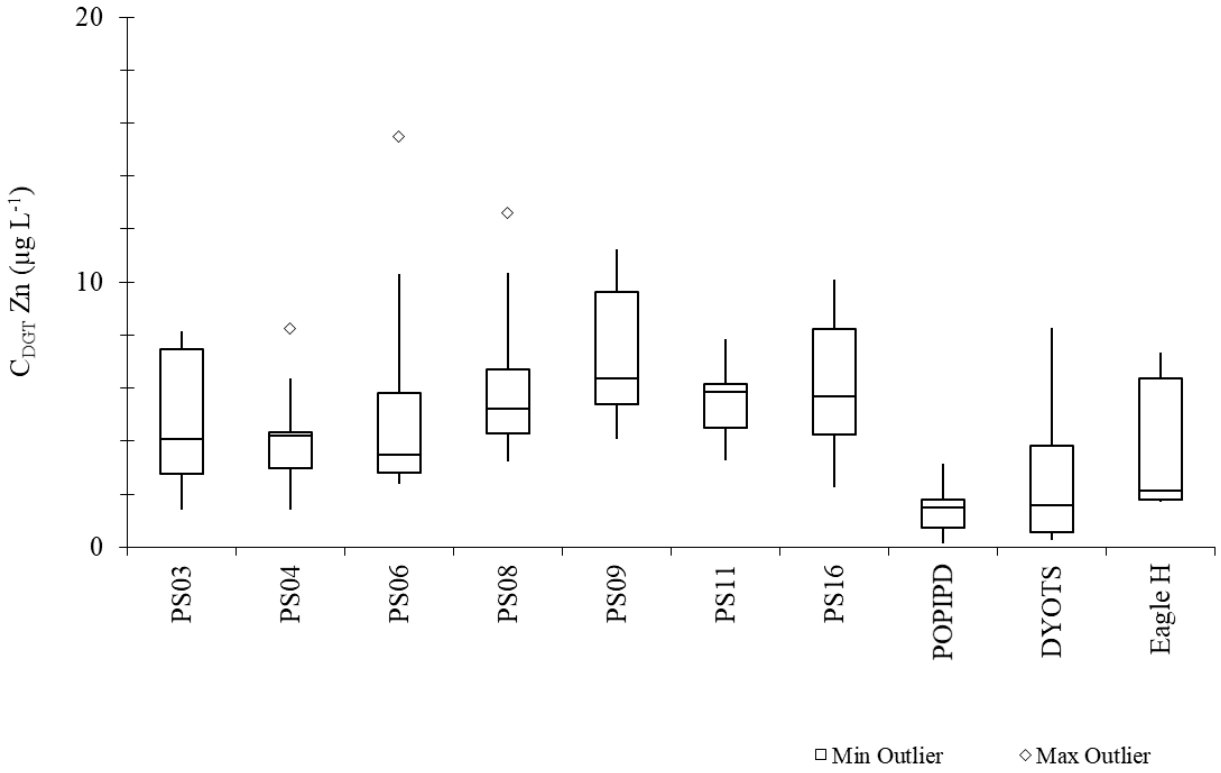

Figure 17. Long-term lability of Zn in the PSNS Nearshore and reference stations within the Kitsap Basin. The compiled data consist of 14-day DGT deployments (PSNS stations; n = 8/station) and 14-d deployments (reference locations; n = 5–8/station) between December 2016 and July 2019. Due to the speciation of Zn in seawater, C_{DGT} Zn will typically reflect the dissolved fraction, meaning the results in Figure 17 may be preliminarily considered to have a CCC equivalent to the dissolved fraction (i.e., 81 µg L^{-1}).

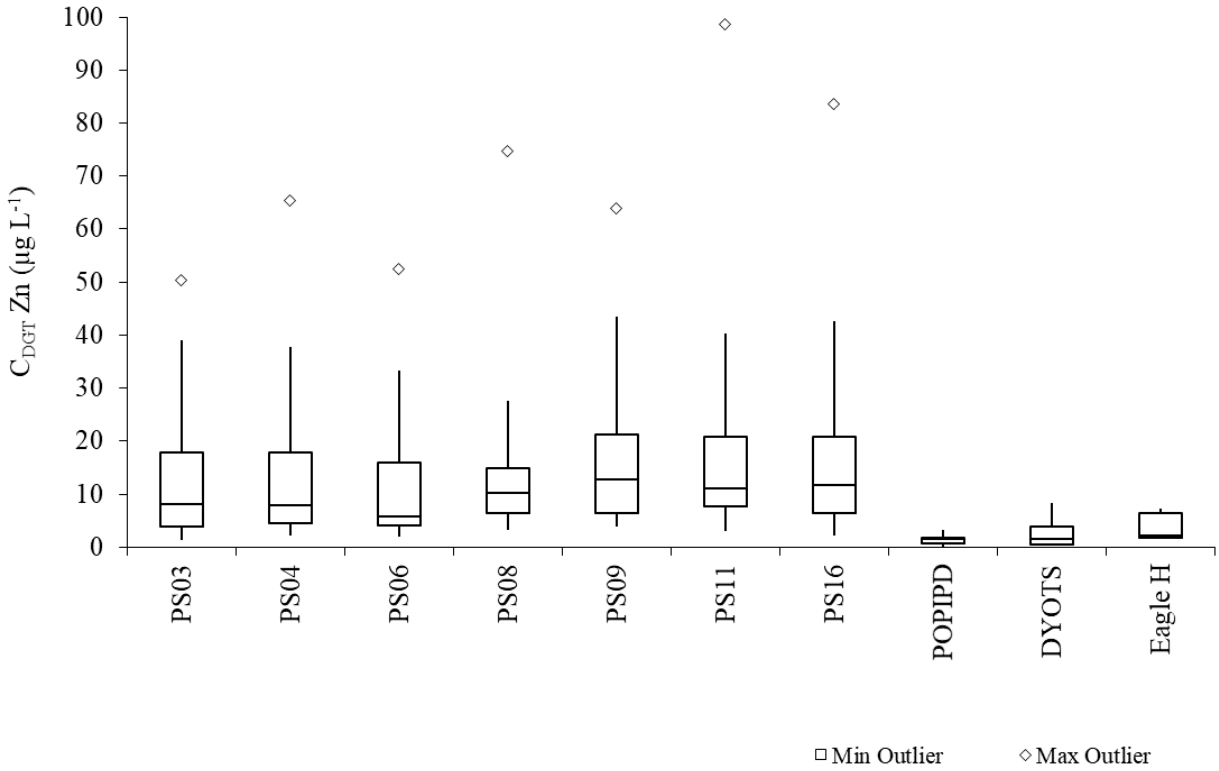

Figure 18. Long-term lability of Zn in the PSNS Nearshore and reference stations within the Kitsap Basin. The compiled data consist of 3-day DGT deployments (PSNS stations; n = 28/station) and 14-d deployments (reference locations; n = 5–8/station) between December 2016 and July 2019.

5.1.1.5 Ancillary Parameters

Table 9 provides physicochemical parameter summary statistics for each of the four marine water impact zones. The purpose of these data is to aid in interpreting the chemical concentrations; they are considered vital model input variables (complete datasets are given in Appendix E). There were no significant differences among impact zones for any ancillary parameter except TSS, where Sinclair/Dyes Nearshore stations had significantly higher levels than the PSNS Nearshore stations (mean difference of 1.99 mg L^{-1}: $p < 0.05$) likely due to the fact that many of these stations are in riparian flumes and are prone to dense algal and *Medusozoa* blooms. Other parameters given here track primary productivity potential. Additional ancillary parameters include dissolved oxygen, pH, temperature and turbidity and are recorded in the ENVVEST Fecal Coliform Monitoring Program reports (Johnston et al. 2018b), for which sampling is concurrent with the Ambient Water grab sampling subtasks (NIWC holds these records in EIM format – POC: Cheryl Ann Cooke ckurtz@spawar.navy.mil).

In brief,

- Salinity is a key component of marine habitat monitoring because it transforms trace metal chemistry interactions with biota via stratification and circulation patterns.
- Knowledge of OC levels is integral to modeling bioavailability of metals and organics due to protective effects provided by complexing ligands.

- Dissolved metals can attach to suspended particles, and thus an increase in TSS can often indicate potential pollution and enhanced bioavailability to filter-feeders. Increased TSS is also indicative of the development of harmful algal blooms.
- All species of nitrogen are biochemically interconvertible components of the biological nitrogen cycle. The presence of ammonia nitrogen in surface water can be indicative of sewage pollution (e.g., SN03).
- Phytoplankton productivity in marine waters can be limited by the availability of fixed inorganic nitrogen, nitrate being the principal form. Total inorganic nitrogen = NNN + AN.
- TKN has also been measured for select events when quantification of organic nitrogen was requested by PSNS (total organic nitrogen = TKN − AN)
- P, supplied naturally by continental weathering, is also monitored as a primary productivity-limiting nutrient due to the potential for introduction of excess levels by fertilizer runoff and sewage system leaks.
- HEM is monitored, primarily in outfall composites, due to a total petroleum hydrocarbon limit (15 mg L^{-1}) under the effectual NPDES regulations; an exceedance of this level has never been observed during an AMB event.

Table 9. Summary statistics of ancillary parameters by receiving water impact zone.

	Parameter	Salinity (ppt)	TOC (mg L^{-1})	DOC (mg L^{-1})	TSS (mg L^{-1})	AN (mg L^{-1})	NNN (mg L^{-1})	TKN (mg L^{-1})	TP (mg L^{-1})	HEM (mg L^{-1})
PSNS Nearshore	Mean	28.5	1.49	1.40	3.57	0.0630	0.203	1.19	0.0763	1.58
	Median	28.6	1.31	1.26	1.71	0.0543	0.137	1.09	0.0800	0.70
	Minimum	24.5	0.66	0.64	0.400	0.0030	0.009	0.057	0.0040	0.70
	Maximum	31.8	16.4	9.40	41.0	0.558	0.447	4.44	0.410	8.30
	1st Quartile	27.8	1.04	1.02	1.06	0.0390	0.055	0.770	0.0610	0.70
	3rd Quartile	29.2	1.70	1.51	3.51	0.0809	0.369	1.50	0.0900	1.70
	n	384	382	379	383	369	381	160	381	17
PSNS Barrier	Mean	28.9	1.59	1.47	4.15	0.0484	0.188	1.19	0.0708	1.77
	Median	28.9	1.39	1.26	1.75	0.0445	0.101	1.10	0.0750	2.20
	Minimum	26.6	0.70	0.80	0.300	0.0030	0.009	0.064	0.0040	0.70
	Maximum	31.6	7.70	5.40	78.0	0.332	0.442	2.30	0.183	2.80
	1st Quartile	28.3	1.05	1.02	1.10	0.0290	0.027	0.755	0.0563	1.00
	3rd Quartile	29.4	1.78	1.55	3.34	0.0600	0.365	1.80	0.0860	2.35
	n	115	115	112	115	110.0	114	47	114	7
Non-PSNS Nearshore	Mean	28.0	2.05	1.70	5.56	0.0511	0.183	1.46	0.0829	1.75
	Median	28.7	1.46	1.31	2.50	0.0370	0.123	1.18	0.0740	1.75
	Minimum	8.20	0.50	0.70	0.385	0.0030	0.009	0.030	0.0040	0.70
	Maximum	31.7	66.3	50.0	133	0.588	0.675	12.1	1.50	2.80
	1st Quartile	27.7	1.14	1.08	1.42	0.0163	0.023	0.923	0.0580	1.23
	3rd Quartile	29.3	1.91	1.60	5.09	0.0628	0.360	1.68	0.0860	2.28
	n	275	275	274	274	270	275	112	275	2

	Parameter	Salinity (ppt)	TOC (mg L^{-1})	DOC (mg L^{-1})	TSS (mg L^{-1})	AN (mg L^{-1})	NNN (mg L^{-1})	TKN (mg L^{-1})	TP (mg L^{-1})	HEM (mg L^{-1})
Marine	Mean	28.9	1.75	1.47	4.58	0.0384	0.182	1.45	0.0765	1.08
	Median	28.9	1.34	1.28	1.94	0.0310	0.109	1.10	0.0690	0.70
	Minimum	23.0	0.70	0.60	0.371	0.0030	0.009	0.046	0.0130	0.70
	Maximum	31.6	23.6	8.36	44.9	0.637	0.439	8.95	0.691	2.20
	1st Quartile	28.3	1.02	1.01	1.21	0.0130	0.020	0.900	0.0590	0.70
	3rd Quartile	29.6	1.80	1.52	3.89	0.0505	0.361	1.60	0.0830	1.08
	n	199	199	198	199	192	199	82	199	4

5.1.2 Temporal Comparison

Temporal analysis of receiving waters is provided as a means to illustrate the water quality trends of metals of concern in the four receiving water impact zones (PSNS Nearshore, PSNS Barrier, Sinclair/Dyes Nearshore, and Sinclair/Dyes Marine). Although no adjustments have been made in the following plots to the pre-2016 averages, it should be considered that improvements to analytical methodology result in ~ 17% and ~ 13% increases in dissolved Cu and Zn recovery, respectively (Strivens et al. 2019a). Within the Cu discussion, site-specific temporal Cu trends are given for areas of minor toxicological concern (i.e., PS06, PS08, and PS09). Additionally, reported in this section is a summary of precipitation effects on ambient dissolved-fraction metals concentrations for PSNS Nearshore stations.

5.1.2.1 Linear Time

Mercury

Dissolved Hg in surface water samples, by designated impact zone, have averaged (a) 0.705 ± 0.961 ng L^{-1} Hg_{diss} in the PSNS Nearshore (b) 0.313 ± 0.0537 ng L^{-1} Hg_{diss} at the PSNS Barrier, (c) 0.345 ± 0.139 ng L^{-1} Hg_{diss} in the Sinclair/Dyes Nearshore and (d) 0.307 ± 0.102 ng L^{-1} Hg_{diss} in the Sinclair/Dyes Marine zone (Figure 19). Average Hg_{diss} has remained an order of magnitude below the Toxics Substances Criteria for human health. The highest values within the PSNS (values > 3.75 ng L^{-1}) are from Station PS03, which drives the variability observed in Figure 19a.

Total Hg surface water samples, by designated impact zone, have averaged (a) 1.60 ± 1.96 ng L^{-1} Hg_{tot} in the PSNS Nearshore, (b) 0.755 ± 0.158 ng L^{-1} Hg_{tot} at the PSNS Barrier, (c) 0.982 ± 0.590 ng L^{-1} Hg_{tot} in the Sinclair/Dyes Nearshore, and (d) 0.740 ± 0.295 ng L^{-1} Hg_{tot} in the Sinclair/Dyes Marine zone (Figure 20). Average Hg_{tot} has breached the Toxics Substances Criteria for chronic toxicity twice. As with $Hg_{diss,}$ these elevated instances are associated with Station PS03. Hg in general shows neither a positive nor negative baseline trend over time, by impact delineated area.

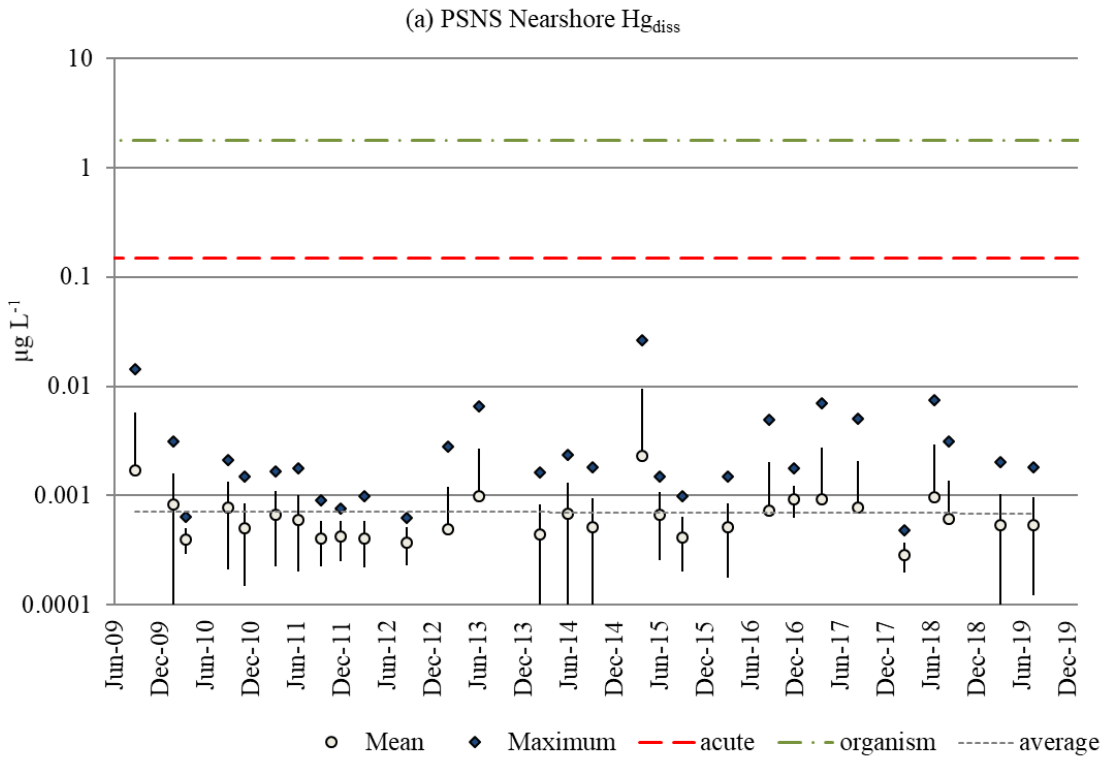

Figure 19 a–d. Hg$_{diss}$ trend over 10 years (29 sampling events) with stations divided in four areas: (a) PSNS Nearshore (n = 373), (b) the PSNS Barrier (n = 114), (c) the Sinclair/Dyes Nearshore (n = 275), and (d) the Sinclair/Dyes Marine (n = 192). Open circles are the mean values, diamonds are the maxima, and the trend line in linear.

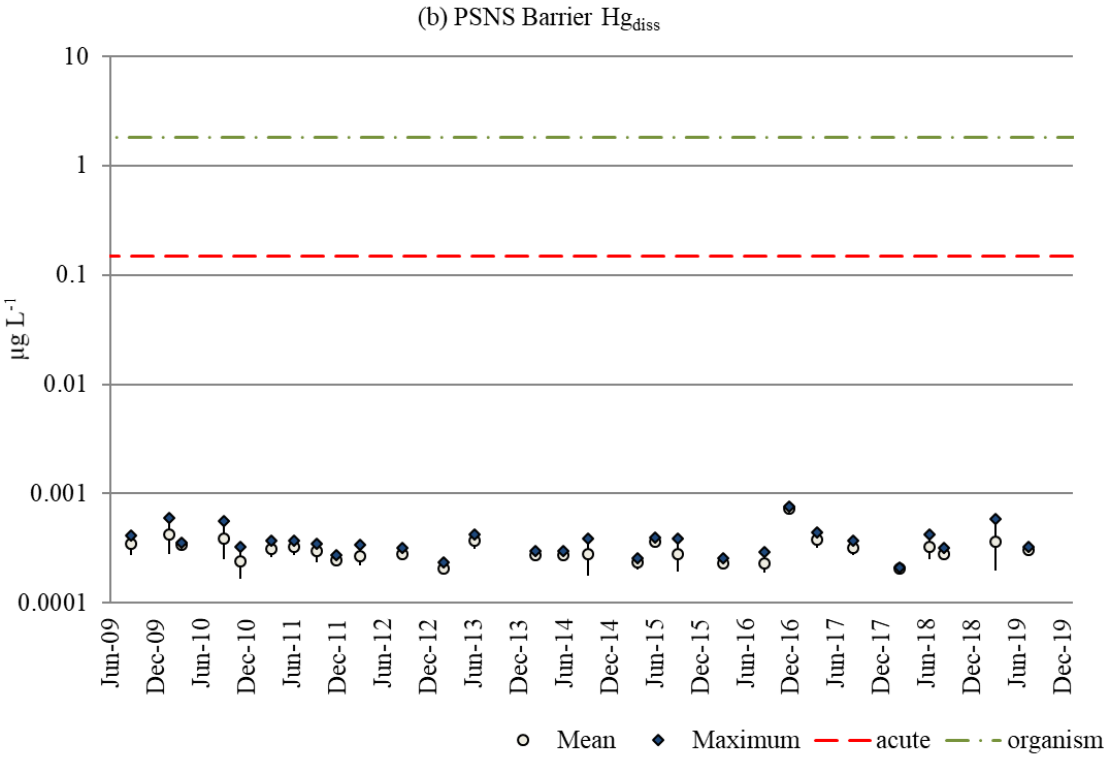

Figure 19. (Cont'd)

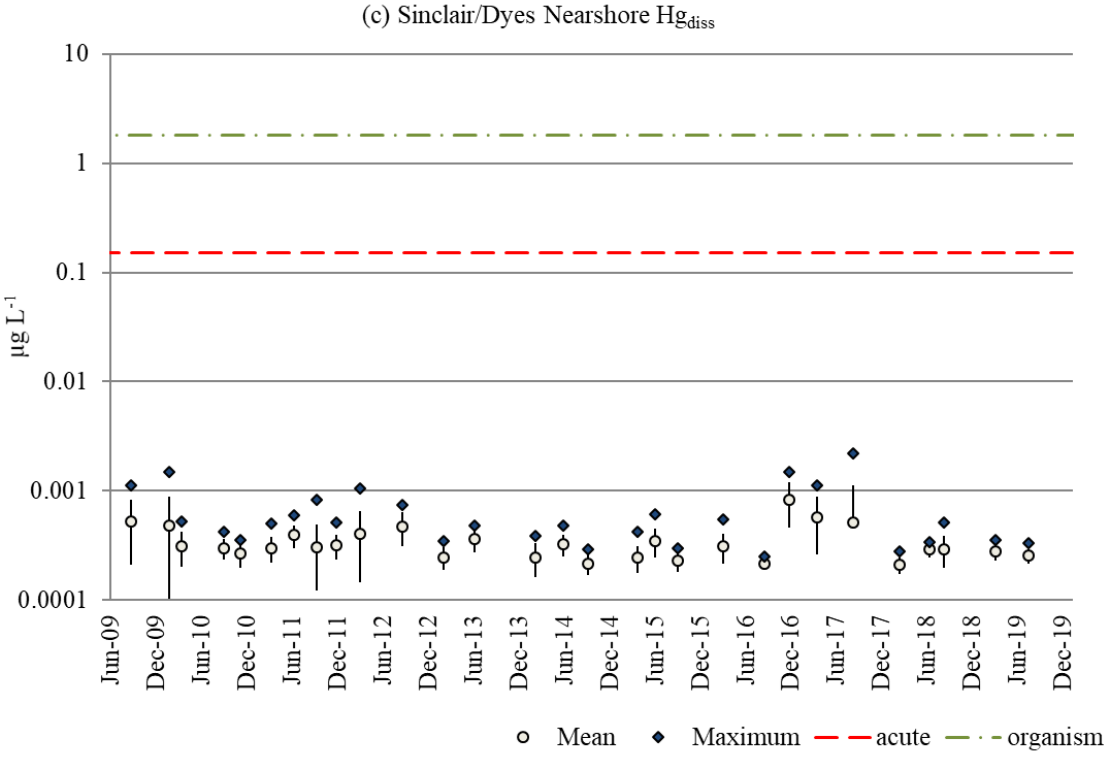

Figure 19. (Cont'd)

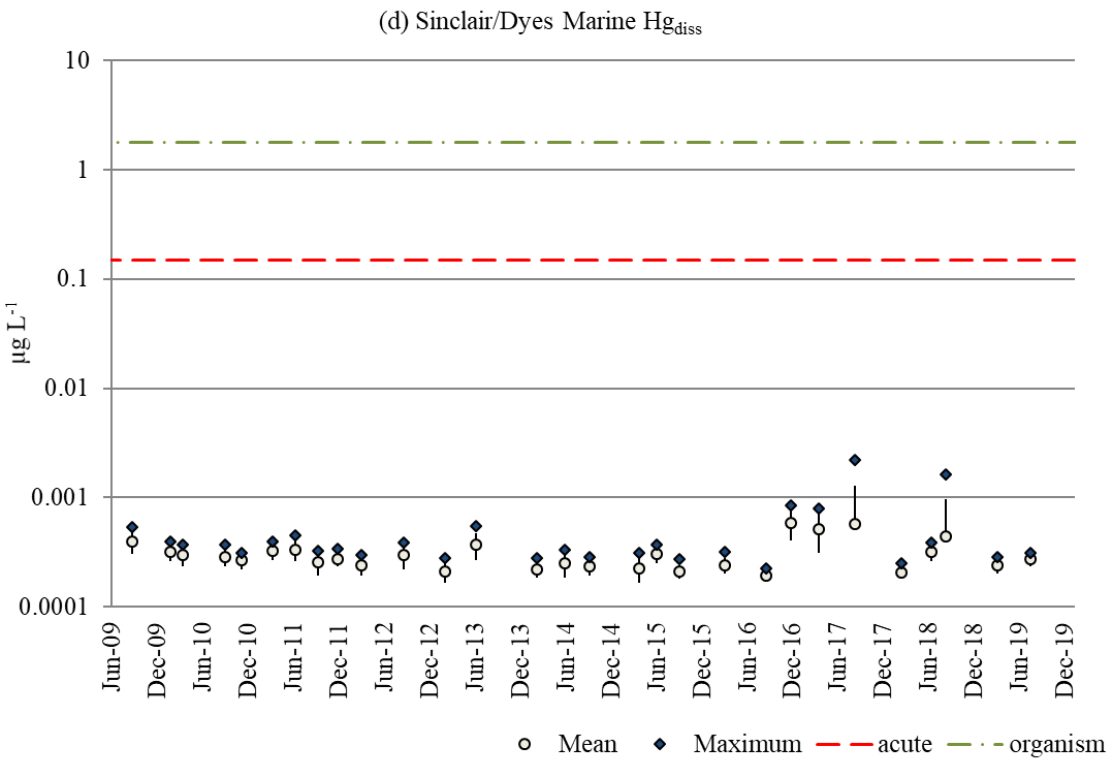

Figure 19. (Cont'd)

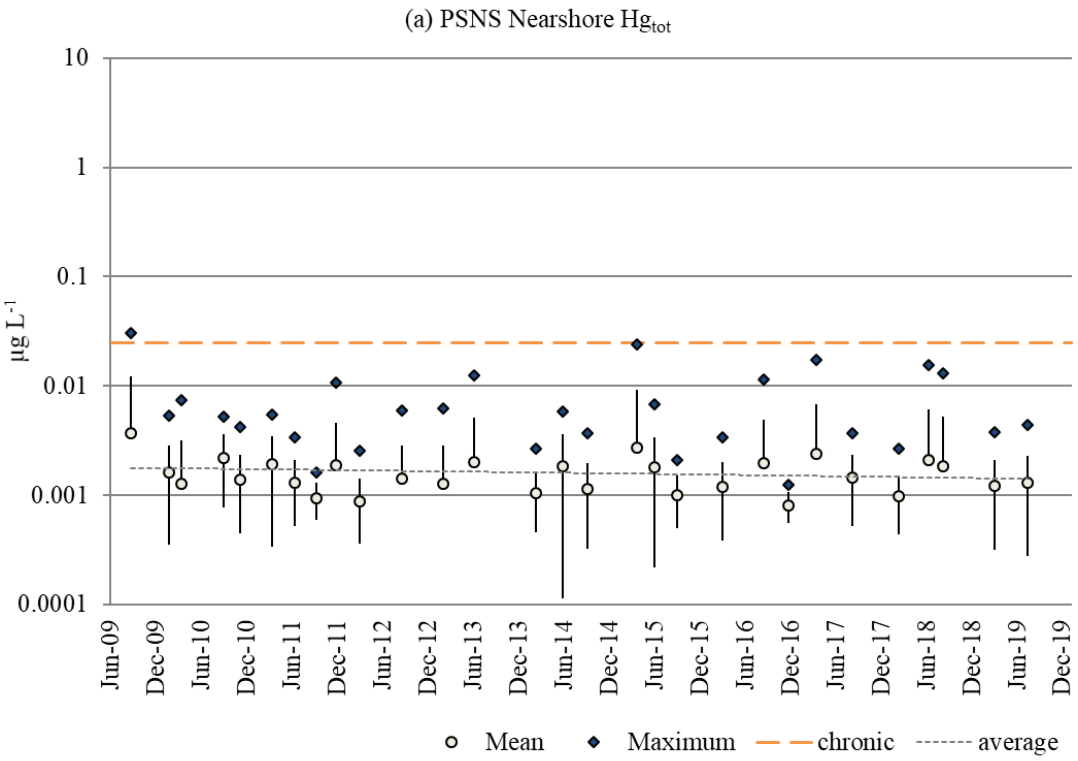

Figure 20 a–d. Hg_{tot} trend over 10 years (29 sampling events) with stations divided into four areas: (a) PSNS Nearshore (n = 373), (b) the PSNS Barrier (n = 114), (c) the Sinclair/Dyes Nearshore (n = 274), and (d) the Sinclair/Dyes Marine (n = 192). Open circles signify mean values, diamonds are the maxima, and the trend line is linear.

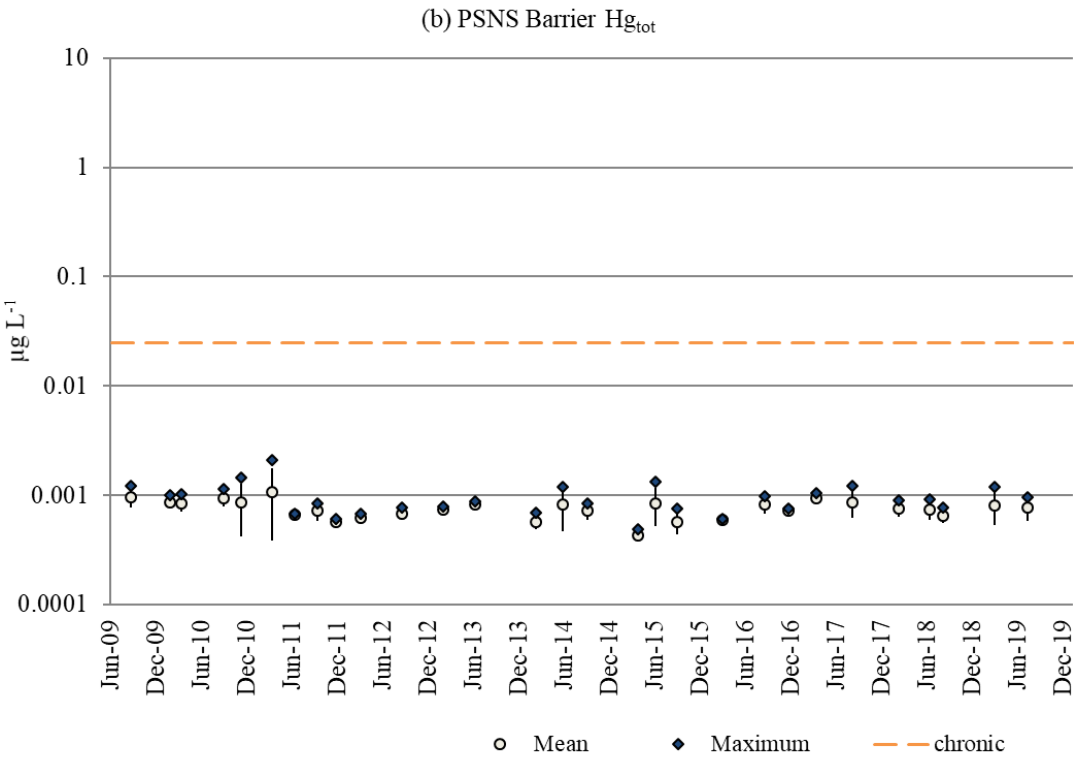

Figure 20. (Cont'd)

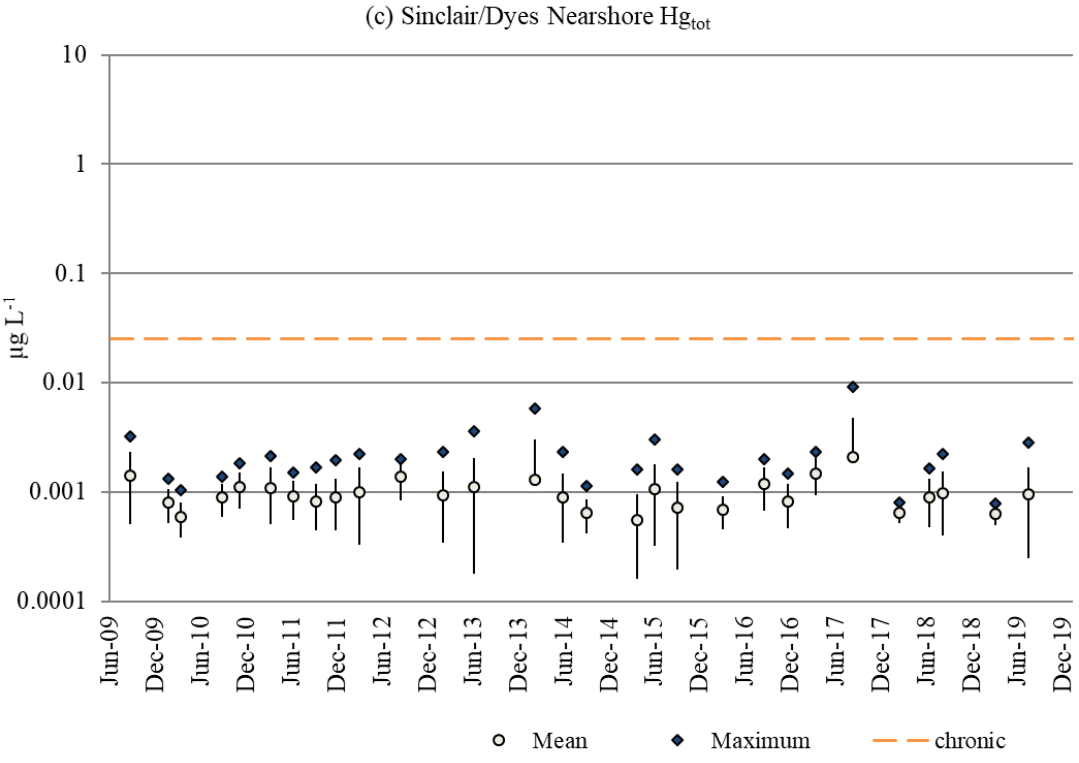

Figure 20. (Cont'd)

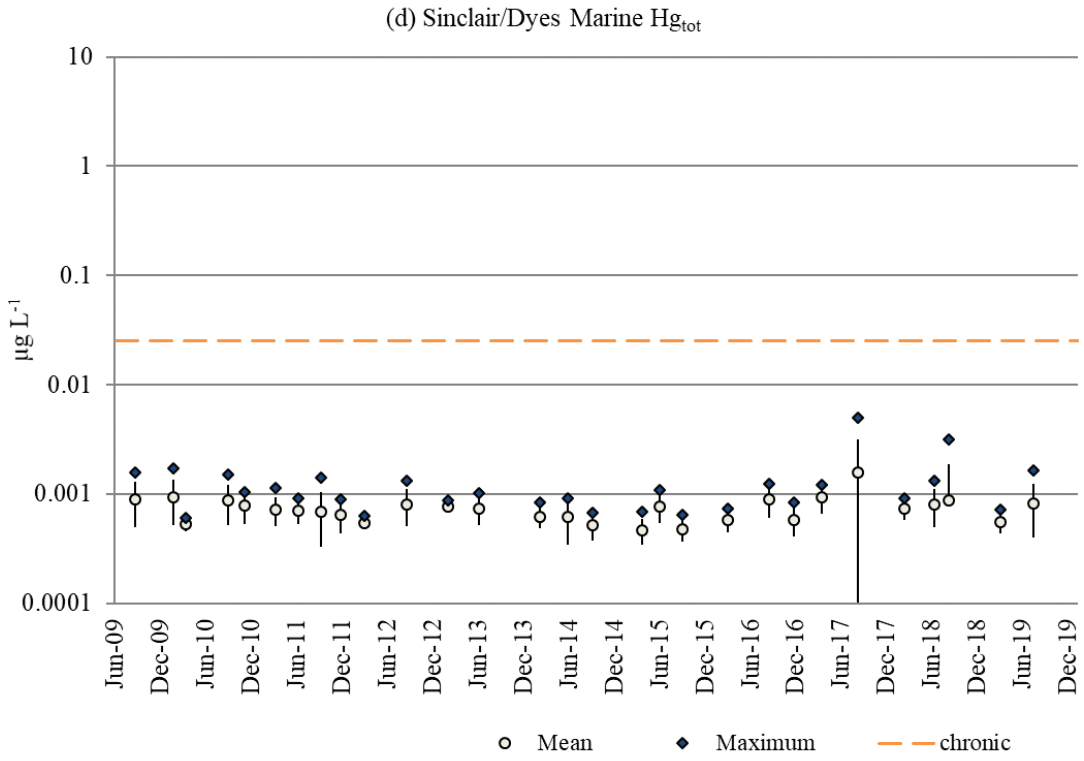

Figure 20. (Cont'd)

Copper

Dissolved Cu in surface water samples designated as PSNS Nearshore have averaged 1.25 ± 0.513 µg L^{-1} in the two-years proceeding the last AMB summary (2018–2019); the PSNS Barrier averaged 0.932 ± 0.301 µg L^{-1} Cu_{diss}, Sinclair/Dyes Nearshore 0.680 ± 0.268 µg L^{-1} Cu_{diss}, and Sinclair/Dyes Marine impact zone 0.543 ± 0.160 µg L^{-1} Cu_{diss} (Figure 21). Cu_{diss} has remained below the default Toxics Substances Criteria in areas outside of the PSNS. Samples within the PSNS breached the default chronic criterion at Stations PS06 and PS09 in August of 2018 (coinciding with both a docking event and the aforementioned sewage system failure [page 28]), however both points fall below the WER CCC of 4.8 µg L^{-1} and thus are not considered to show reasonable potential for chronic impairment effects in biota. In general, the frequency of values approaching toxicological concern is dropping (Figure 21a).

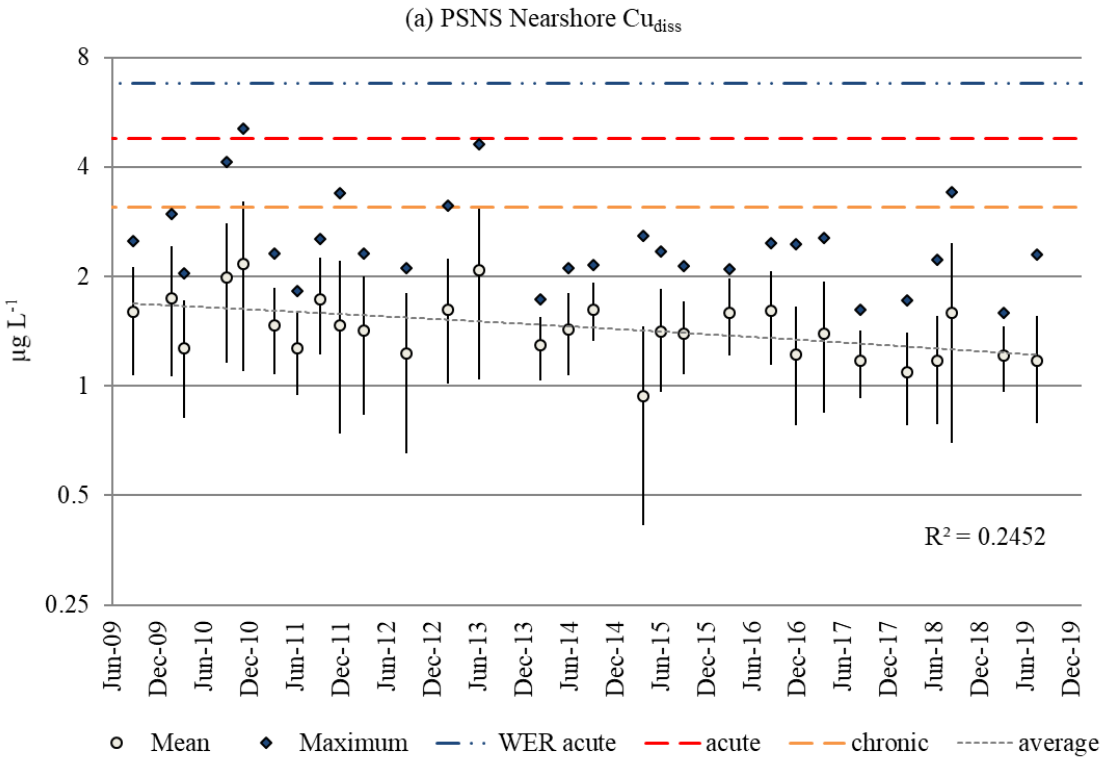

Figure 21 a-d. Cu$_{diss}$ trend over 10 years (29 sampling events) with stations divided in four areas: (a) PSNS Nearshore (*n* = 373), (b) the PSNS Barrier (*n* = 114), (c) the Sinclair/Dyes Nearshore (*n* = 275), and (d) the Sinclair/Dyes Marine (*n* = 192). Open circles are the mean values, diamonds are the maxima, and the trendline is linear.

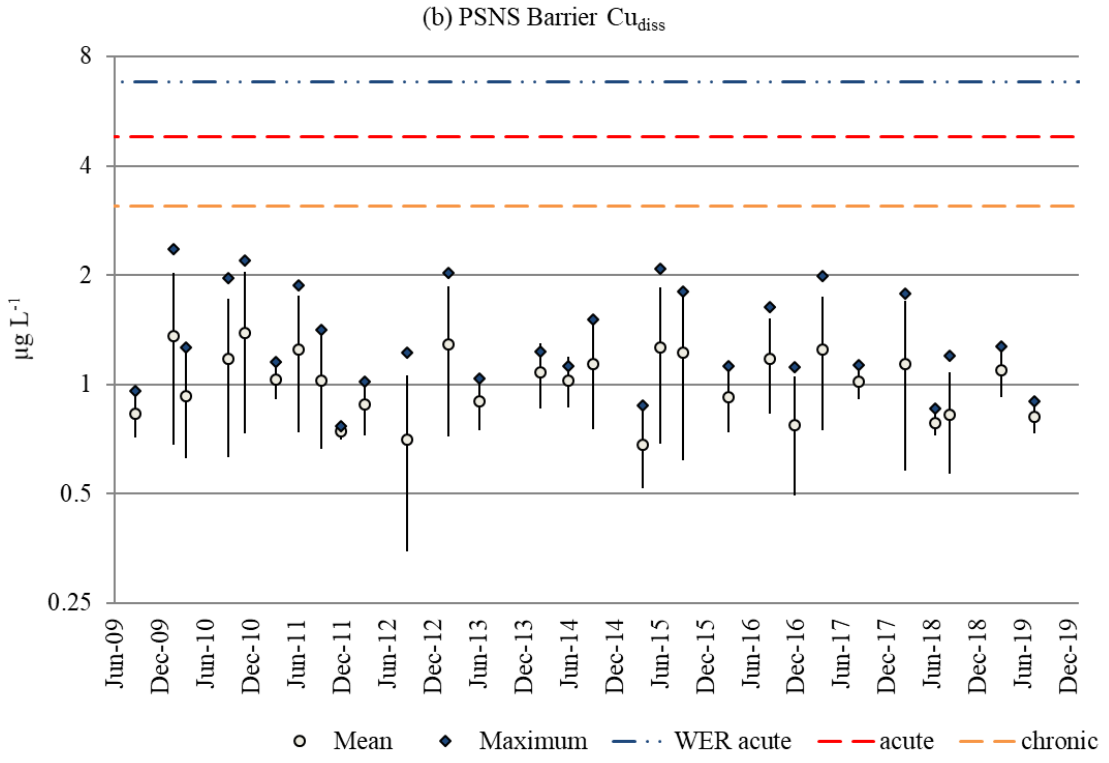

Figure 21. (Cont'd)

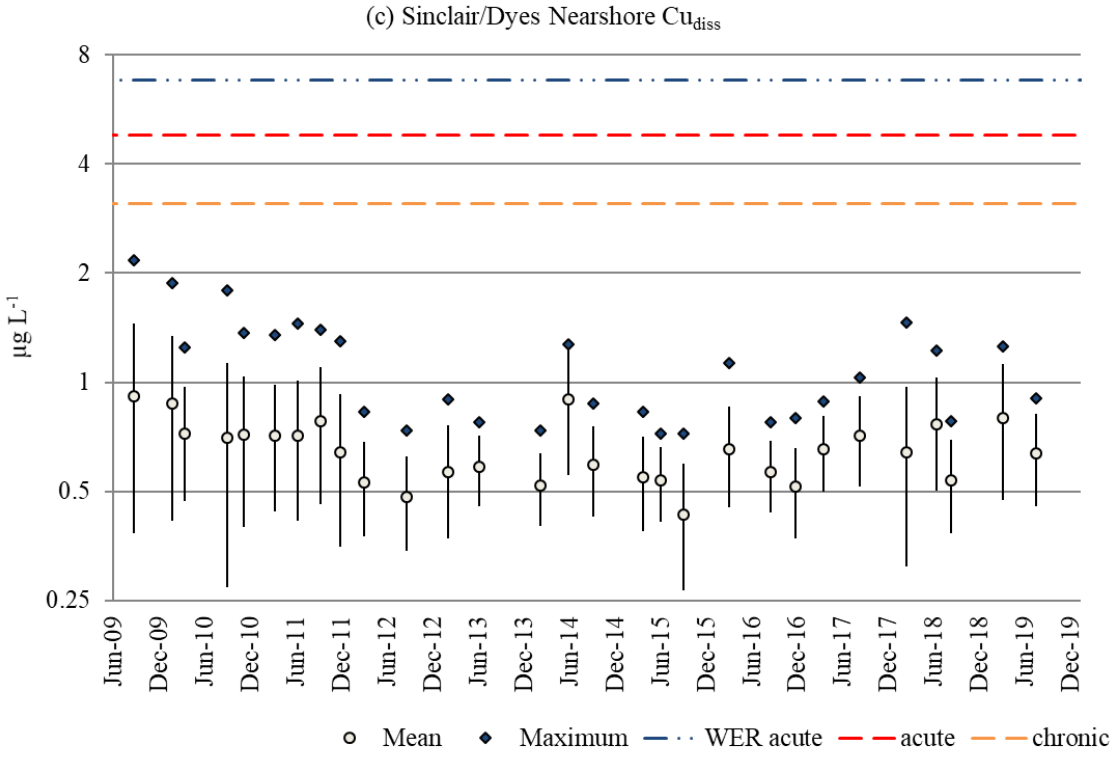

Figure 21. (Cont'd)

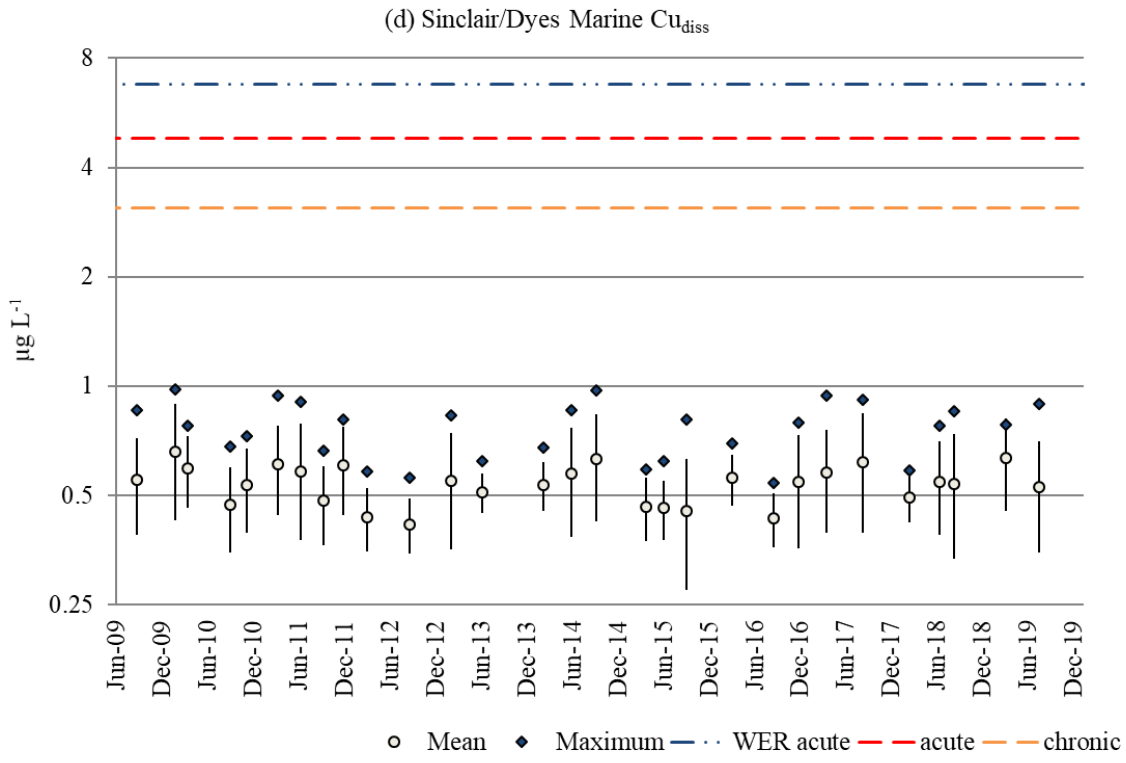

Figure 21. (Cont'd)

To comprehensively demonstrate the long-term status of surface water quality at industrial effluent mixing points (and a centrally affected location), the total, dissolved, and labile fractions of Cu are given for stations PS06 (Figure 22), PS08 (Figure 23), and PS09 (Figure 24). The results show a decade of environmental regulation compliance under the acute WER criterion. Exceedances of the chronic WER criterion highlight the environmental value of passive sampling, where without constant surveillance of a relevant period – substantive chronic effects are unknown. The long-term grab sample trends in PS08 indicate an improvement in water quality, while PS06 and PS09 appear arbitrary due to direct correlation with specific docking event and subsequent work phases that are occurring at the times of collection.

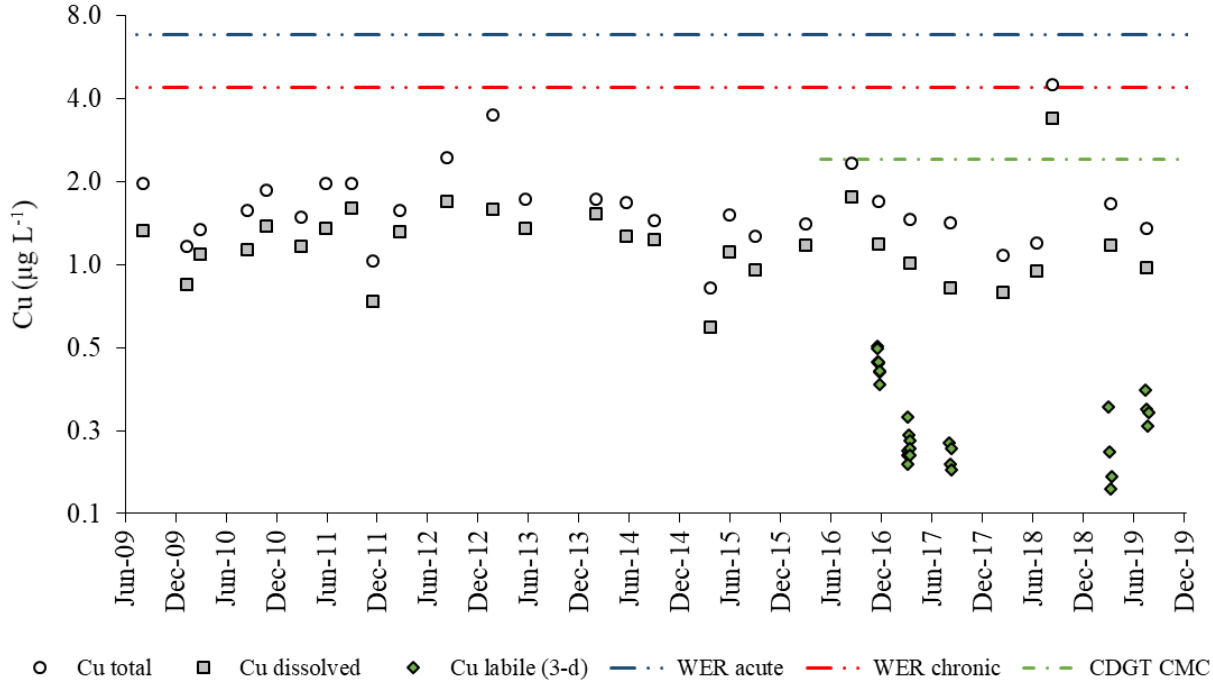

Figure 22. Long-term assessment of protection of beneficial uses from Cu exceedances at PS06. Total and dissolved Cu are plotted as single-point in time, while C_{DGT} Cu points represent 3-day averaging periods. Thresholds are depicted as acute criteria; however, it should also be understood that the C_{DGT} CMC is equivalent to C_{DGT} CCC (Strivens et al. 2020).

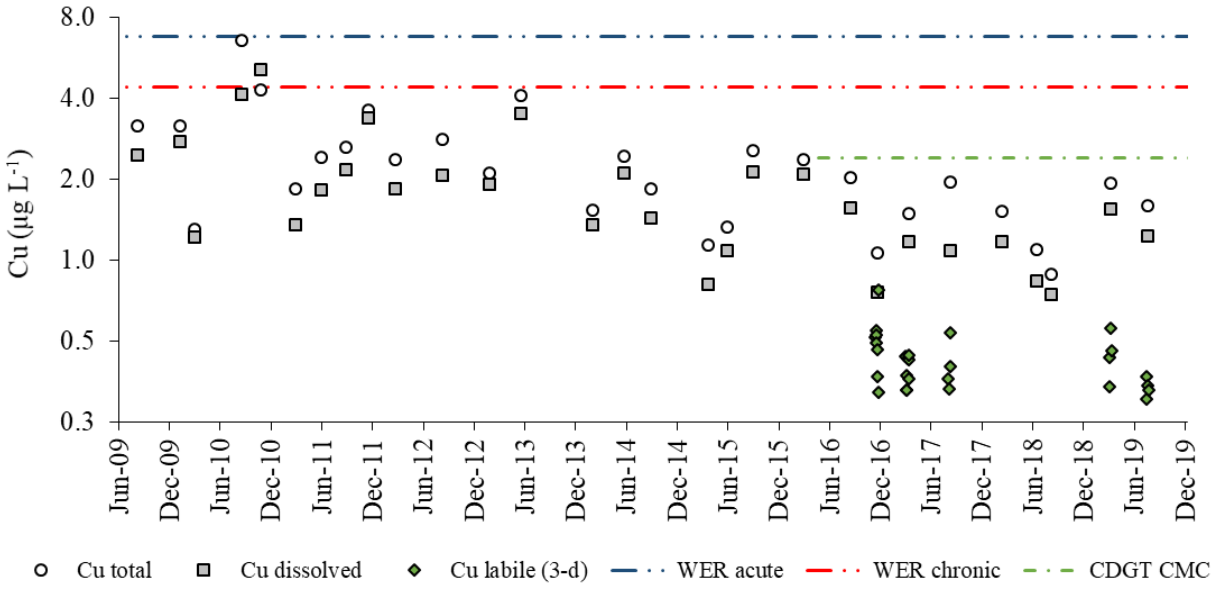

Figure 23. Long-term assessment of protection of beneficial uses from Cu exceedances at PS08. Total and dissolved Cu are plotted as single-point in time, while C_{DGT} Cu points represent 3-day averaging periods.

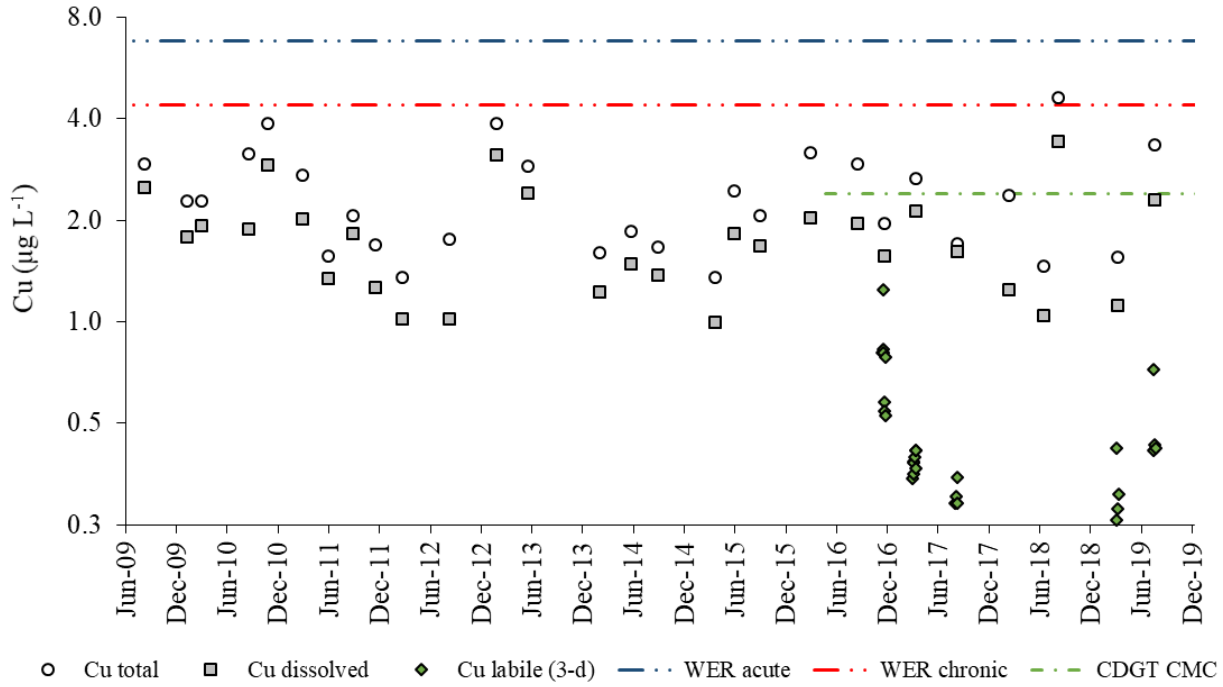

Figure 24. Long-term assessment of protection of beneficial uses from Cu exceedances at PS09. Total and dissolved Cu are plotted as single-point in time, while C_{DGT} Cu points represent 3-day averaging periods.

Lead

Over the decade (from 2009–2019) Pb_{diss} in surface water samples designated as PSNS Nearshore have averaged 0.0231 ± 0.0152 µg L^{-1}, PSNS Barrier 0.0175 ± 0.0100 µg L^{-1} Pb_{diss}, Sinclair/Dyes Nearshore 0.0171 ± 0.0116 µg L^{-1} Pb_{diss}, and Sinclair/Dyes Marine 0.0173 ± 0.0140 µg L^{-1} Pb_{diss} (Figure 25). Pb_{diss} has remained an order of magnitude below the marine Toxics Substances Criteria in all areas of Sinclair and Dyes Inlets and is not an imminent concern in surface waters.

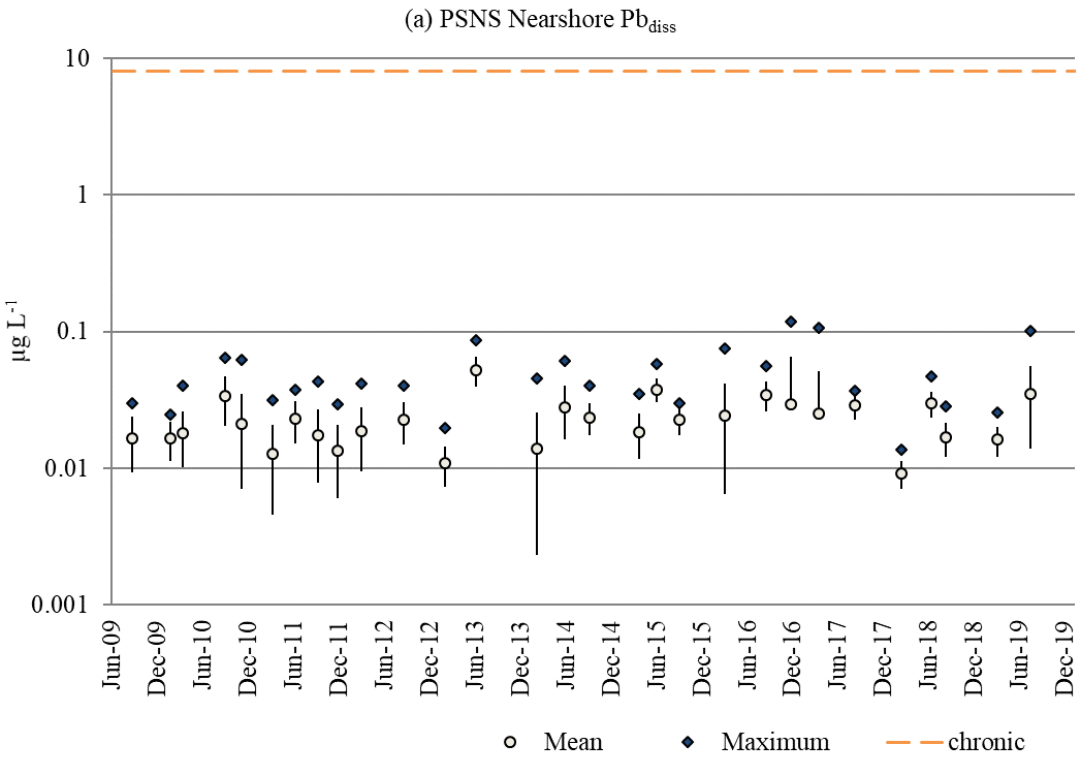

Figure 25 a-d. Pb_{diss} trend over 10 years (29 sampling events) with stations divided in four areas: (a) PSNS Nearshore (n = 373), (b) the PSNS Barrier (n = 114), (c) the Sinclair/Dyes Nearshore (n = 274), and (d) the Sinclair/Dyes Marine (n = 192). Open circles are the mean values, diamonds are the maxima, and the trendline is linear.

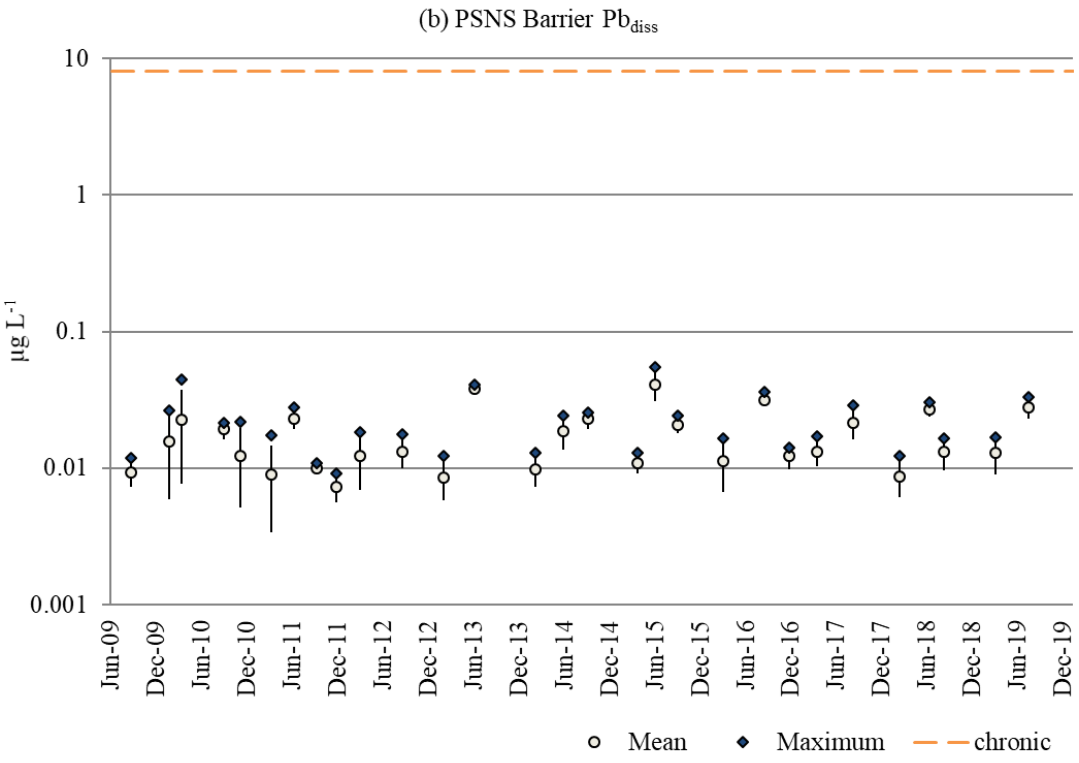

Figure 25. (Cont'd)

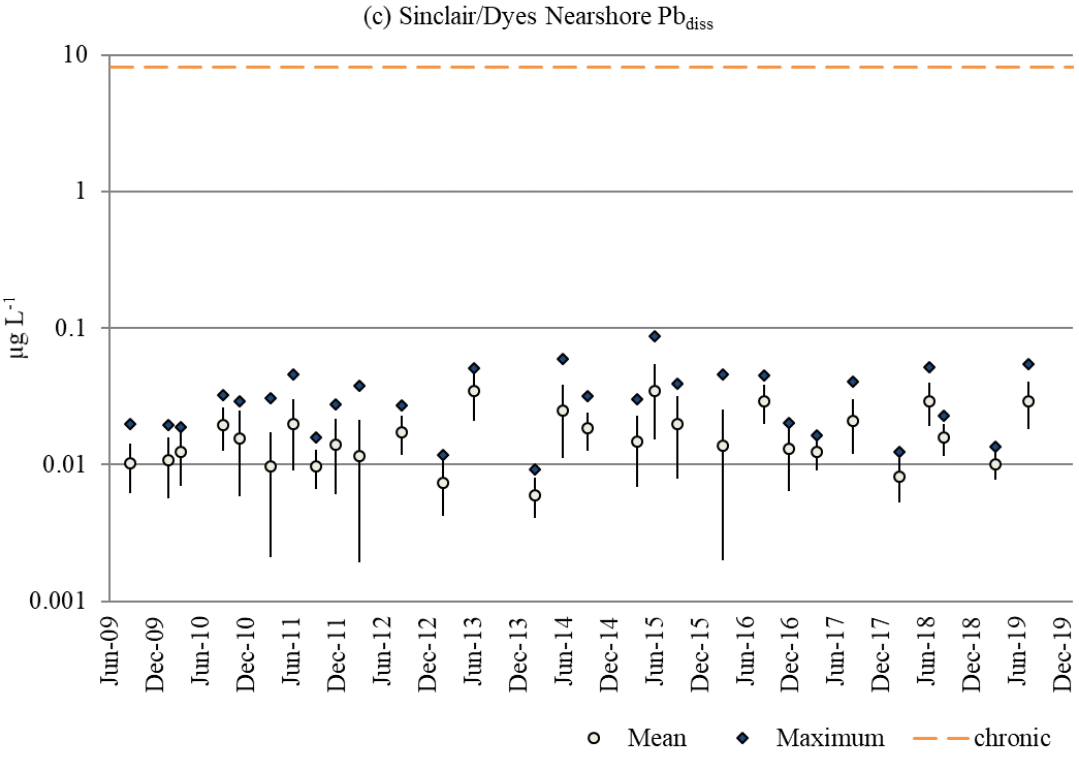

Figure 25. (Cont'd)

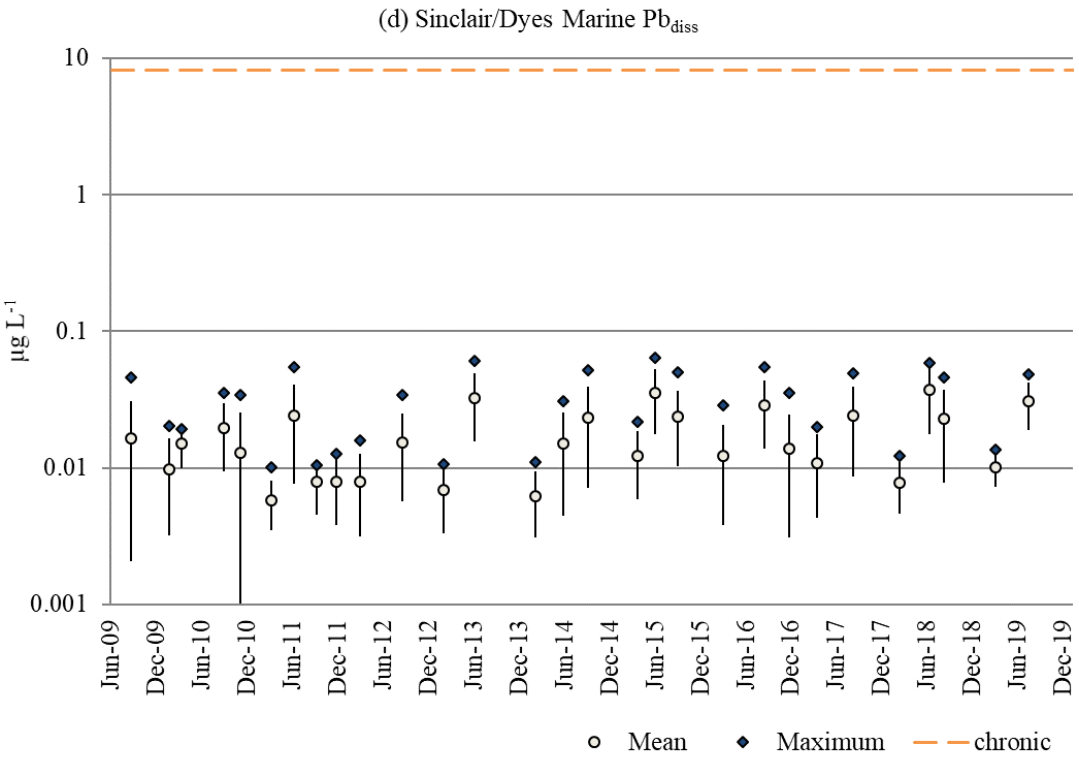

Figure 25. (Cont'd)

Zinc

Dissolved Zn surface water samples designated as PSNS Nearshore, from 2018–2019, averaged 4.57 ± 3.63 µg L^{-1}, the PSNS Barrier 2.99 ± 2.51 µg L^{-1} Zn$_{diss}$, Sinclair/Dyes Nearshore 1.90 ± 1.27 µg L^{-1} Zn$_{diss}$, and Sinclair/Dyes Marine 1.33 ± 0.107 µg L^{-1} Zn$_{diss}$ (Figure 26). Zn$_{diss}$ concentrations have remained well below the marine Toxics Substances Criteria in all areas of Sinclair and Dyes Inlets and are not an imminent concern toward surface water health.

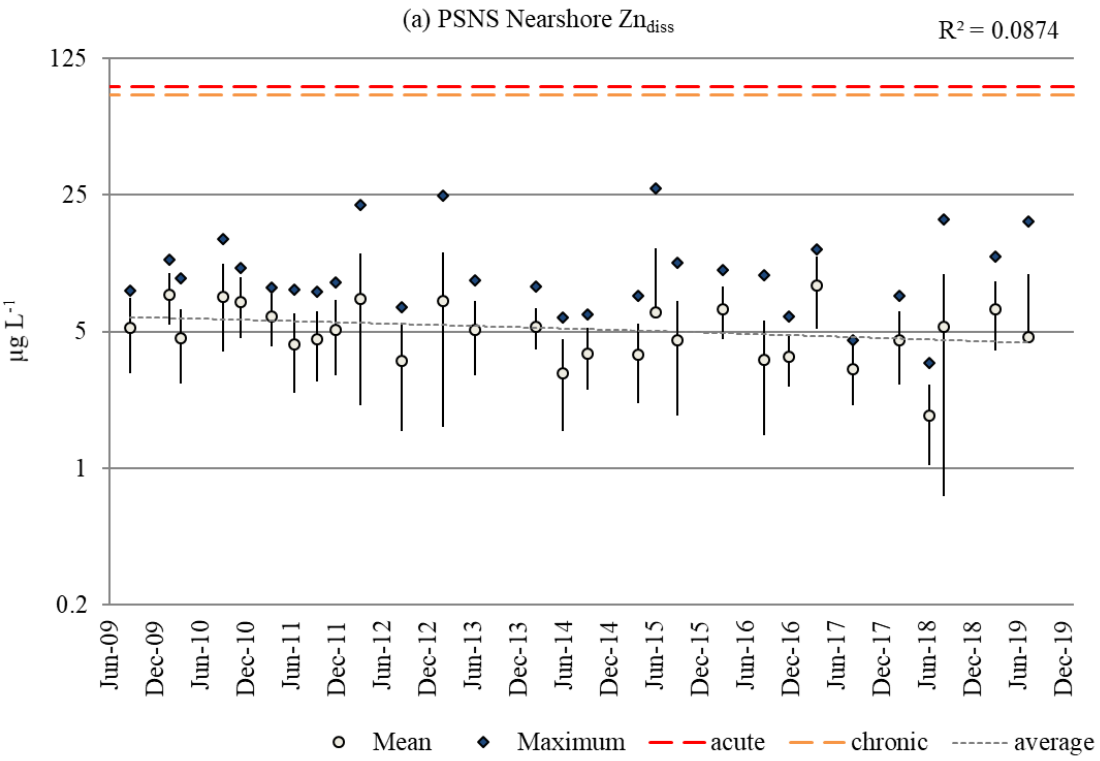

Figure 26 a-d. Zn_{diss} trend over 10 years (29 sampling events) with stations divided in four areas: (a) PSNS Nearshore (n = 373), (b) the PSNS Barrier (n = 114), (c) the Sinclair/Dyes Nearshore (n = 274), and (d) the Sinclair/Dyes Marine (n = 192). Open circles are the mean values, diamonds are the maxima, and the trendline is linear.

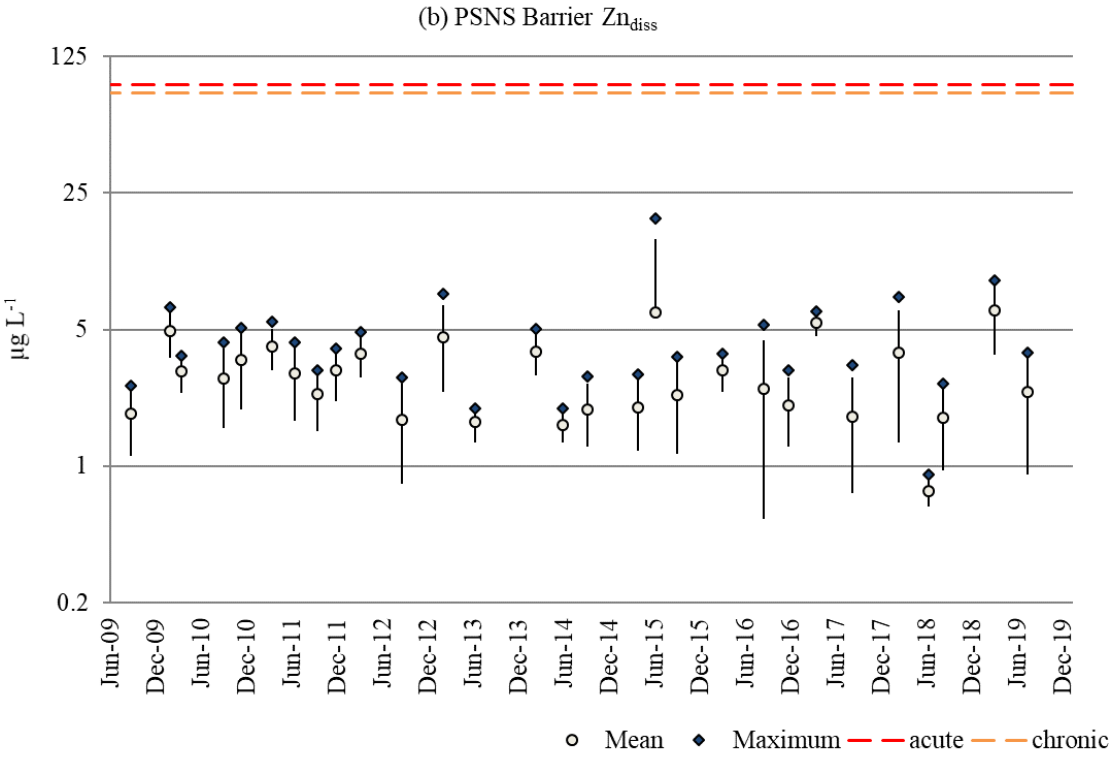

Figure 26. (Cont'd)

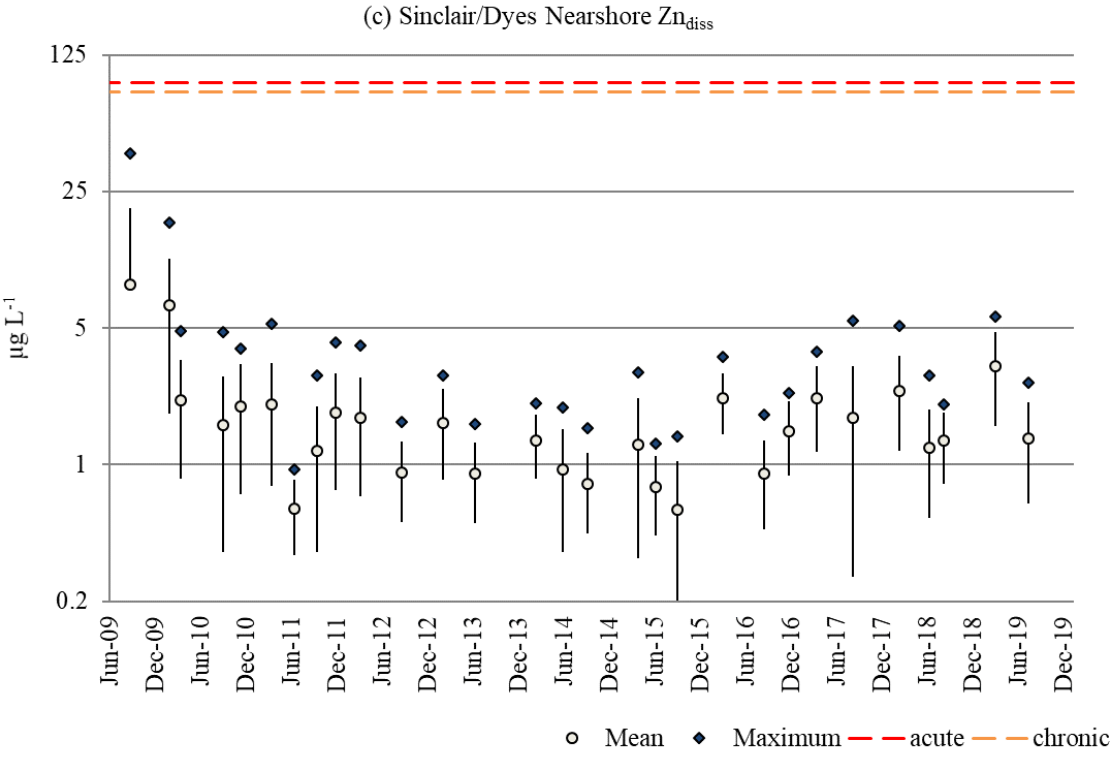

Figure 26. (Cont'd)

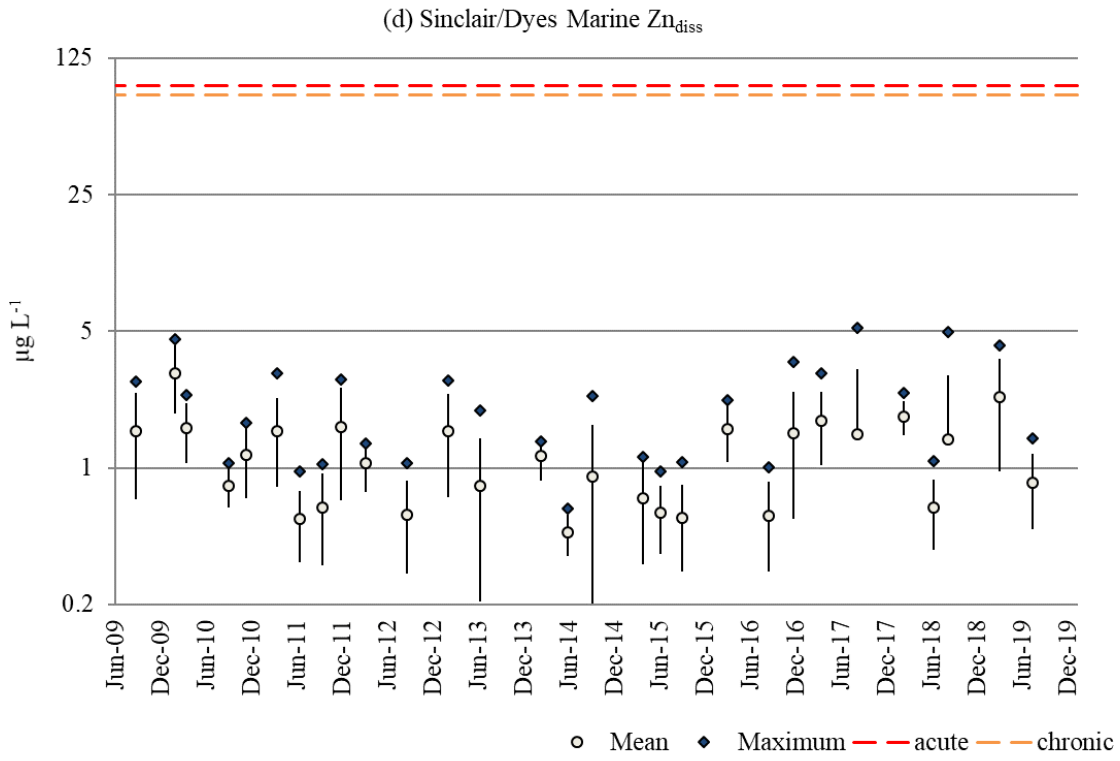

Figure 26. (Cont'd)

5.1.2.2 Seasonal

Marine water samples were categorized by preceding precipitation to elucidate observable effects. Each event was classified as a wet (November–April) or dry (May–October) period, and further codified as 1) wet weather base flow (WWBF): >72 hours after measurable precipitation >0.25 in./24hr; 2) wet weather storm event (WWSE): >0.25 in. of rain within a 24-h period, following a discernable period of no rainfall; 3) dry weather event (DWE): <0.25 in. of rain in the previous 72 hours; or 4) a dry weather storm event (DWSE): >0.25 in. of rain in the previous 72 hours. Discharge and receiving waters' concentrations of Hg, Cu, and Pb in the PSNS Nearshore Zone are mainly tied to concurrent industrial activities, BMP effectiveness, and biological processes; however, a significant difference was observed in ambient Cu_{diss} levels at PS03 between DWSEs (AMBs 04 and 08) and the WWBF (difference in means = 0.946 µg L^{-1}). Other observed differences were not of significant magnitude relative to the Toxics Substances Criteria; however, due tidal fluctuations the use of NPDES storm classifications toward receiving water monitoring in this manner will only highlight the most significant variations (for an in-depth site specific investigation, tidal conditions antecedent to each grab sample and in-water work records must be integrated).

5.2 Outfall Water

Temporal variance of metals regulated under the NPDES are plotted as total values and supplemented with dissolved values for visualization of partitioning. WA00206-2 limitations are depicted for reference. Summary trace metals and physicochemical parameters of composite samples are provided in Appendix B Table B.8.

Appendix C documents the calculations of reasonable potential evaluations, which are then applied to presentation of industrial effluent results herein. Reasonable potential analysis followed EPA (1991) guidance, with the assumption of no mixing zone, to provide conservative assessments. Briefly, the 10-year compilations of in-line sample results for OF018 (OF018A, OF018B and OF096) (n = 30) and OF019 (n = 25) were used to generate maximum projected effluent concentrations, which were then assessed against the Toxics Substances Criteria in WAC 173-201A-240. For OF018 and OF019 there was reasonable potential for exceedance of Cu (acute and chronic). OF018 has reasonable potential for chronic Zn exceedances and, while OF019 was calculated to potentially cause exceedances of acute and chronic Toxics Criteria, the acute potential of OF019 is driven by a single datapoint from 2009 (i.e., AKART implementation has successfully decreased the reasonable potential of Zn impairment from this source); additionally, the dataset presentations in Section 5.1.1 reflect the conservative nature of this assessment through long-term demonstration of receiving water health. Arsenic, Pb, and Hg did not show reasonable potential to cause impairment of the Sinclair Inlet surface waters.

5.2.1 Mercury

The previously published AMB01–24 OF018 Hg_{tot} averaged 0.0116 ± 0.00837 µg L^{-1} and Hg_{diss} averaged 0.00297 ± 0.00126 µg L^{-1} over the 8-year period. The fractional distribution of the 2-years of data joined by the current report averaged 0.00693 ± 0.00135 µg L^{-1} Hg_{tot} and 0.00256 ± 0.00113 µg L^{-1} Hg_{diss} (Figure 27). From 2009–2017, OF019 Hg_{tot} averaged 0.007599 ± 0.00518 µg L^{-1} post removal of an outlier during AMB11 (85 ng L^{-1}); this outlier was associated with particulates collected as a result of manual override of the pump for maintenance access (likely Inlet silt). Dissolved Hg averaged 0.00240 ± 0.00139 µg L^{-1}. From 2018–2019, Hg_{tot} averaged 0.00402 ± 0.00129 µg L^{-1} and Hg_{diss} averaged 0.00157 ± 0.000543 µg L^{-1}. Strivens et al. (2018) reported the variance associated with ship docking exercises (docking and undocking) at OF019 and demonstrated that shifts in effluent Hg_{tot} ranged from 24-h means of 0.00778 µg L^{-1} to 0.0192 µg L^{-1}, and had a maximum 1-h composite level of 0.0728 µg L^{-1} (3% of the maximum daily WQBEL suggested in EPA [2008a]). Those data are useful as bounds for interpretation of preceding and proceeding baseline variability over the 10-year dataset. The baseline slopes for both OF018 and 19 are trending downward.

The OF021, post AMB07, Hg_{tot} averaged 0.00221 ± 0.000417 µg L^{-1} and Hg_{diss} averaged 0.00195 ± 0.000340 µg L^{-1} (n = 22). Pre AMB07, Hg_{tot} averaged 0.0505 ± 0.0490 µg L^{-1} and Hg_{diss} averaged 0.0103 ± 0.0155 µg L^{-1} (n = 7). This shift reflects PSNS-implemented BMPs at the steam-plant facility (moving to a reverse osmosis method). No industrial NPDES limits are currently in place for this analyte.

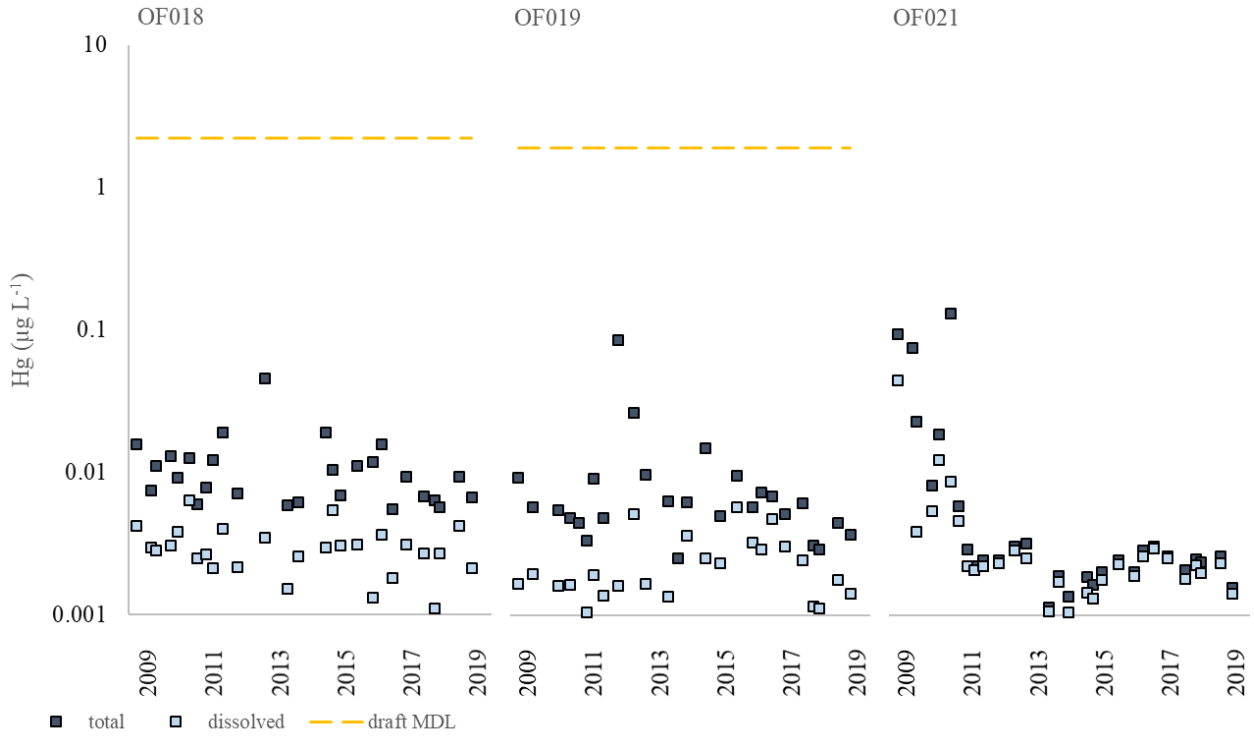

Figure 27. Hg_{diss} and Hg_{tot} at ENVVEST monitored outfalls over the course of 29 events spanning 10 years (n = 27, 26, and 29, respectively). The draft thresholds (EPA 2008a) are indicated as the maximum daily load (2.2 µg L^{-1} or 1.9 µg L^{-1}); corresponding draft AMLs are 1.1 and 0.9 µg L^{-1} for OF018 and OF019, respectively.

5.2.2 Copper

OF018 Cu_{tot} averaged 7.35 ± 5.94 µg L^{-1} and Cu_{diss} averaged 3.47 ± 1.88 µg L^{-1} over the 10 years captured in Figure 28. OF019 Cu_{tot} averaged 5.23 ± 5.01 µg L^{-1} post removal of an outlier during AMB11 (200 µg L^{-1} on 08/28/12); again, this outlier was associated with particulates collected as a result of manual override of the pump, which resulted in lower than normal water levels in the pump-well and is supported by the dissolved concentration. Dissolved Cu in OF019 discharges averaged 2.51 ± 2.18 µg L^{-1}. The OF021, post-AMB07, Cu_{tot} averaged 1.11 ± 0.460 µg L^{-1} and Cu_{diss} averaged 1.03 ± 0.410 µg L^{-1} (n = 22). Pre-AMB07, Cu_{tot} averaged 9.15 ± 3.89 µg L^{-1} and Cu_{diss} averaged 1.99 ± 2.35 µg L^{-1} (n = 7). This shift reflects PSNS–implemented BMPs at the steam-plant facility and boiler blow-down and facility industrial drains, which are now redirected to the sanitary sewer to eliminate the need for temperature compliance in the discharge. It is recommended that OF021 AKART efforts be considered successful and that monitoring at the Steam Plant Facility is removed from long-term ENVVEST supervision.

Demonstrating that other BMP's have been effective, Strivens et al. (2018) reported on the variance among 24-hour composites during all phases of carrier docking/undocking in DD06 and showed that shifts in effluent Cu_{tot} are expected to range from means of 1.88 µg L^{-1} to 4.43 µg L^{-1}, with a 1-hour maximum of 9.18 µg L^{-1}.

Toward developing the water quality-based effluent limits (WQBEL) for Cu loading into Sinclair and Dyes Inlets from PSNS, the Toxics Substances Criteria in WAC 173-201A-240 were used by EPA as the initial basis (EPA 2008b). A maximum daily load (MDL) of 5.8 µg L^{-1} and average monthly loads (AML) of 2.4 and 2.5 µg L^{-1} (for OF018 [OF018A, OF018B, OF096] and OF019, respectively) were drafted, for

consideration and improvement by Project ENVVEST, following guidance in the *Technical Support Document for Water Quality-Based Toxics Control* (TSD) (EPA 1991) and the MDL was also extended to cover stormwater. In that draft, the assumption of no mixing zone was used (i.e., the maximum projected effluent limit was set equal to the concentration of pollutant discharge for the edge of a mixing zone to calculate the maximum to projected receiving water concentration). The fractional translator used by EPA was the default guidance in *The Metals Translator: Guidance for Calculating A Total Recoverable Permit Limit from a Dissolved Criterion* (EPA 1996c), which under a no mixing zone assumption is multiplied by the maximum projected effluent concentration (C_e) in total recoverable form (TRM). The C_e was set as the 99th percentile of the lognormal distribution by multiplying the maximum reported effluent by a reasonable potential multiplier (RPM), which accounts for discharge variability, using a pre-2008 dataset (n = 85 or 53 for OF018 and OF019, respectively). The maximum discharge volumes used to draft the initial effluent limit were set to 7.11 and 13.64 mg d^{-1} for OF018 and OF019, respectively.

The initial response by ENVVEST, toward adoption of a site-specific Cu criteria, was to present Ecology with a water effects ratio (WER) for adoption by the State of Washington (subject to public involvement and intergovernmental coordination). The results in Rosen et al. (2009) demonstrated protection of aquatic life when adjusting the marine Toxics Substances Criteria for the Inlets to 6.8 µg L^{-1} (acute) and 4.4 µg L^{-1} (chronic). The adoption has yet to be realized and the WER is reincorporated into the current report for continued consideration.

In addition to the ENVVEST WER effort, the Project has developed Criterion Maximum Concentration (CMC) for Cu on a labile fraction basis using DGT (Strivens et al. 2020). The time integrated metals quantifications by DGT (C_{DGT}) better reflects free ion activity, represent metals integration over biologically relevant windows, and account for and dynamic receiving water mixing conditions (e.g. precipitation fluxes, tidal stages, etc.). Both methods are used in the current report to generate a pre-mixing zone WQBEL-range that accounts for the dominant protective effects afforded to sensitive life-stages by Cu-DOC kinetics; essentially meeting the goal of a biotic ligand model type approach (EPA 2016). This document concurrently serves to apply for C_{DGT} Cu to be recognized within the Washington State Standards as a legal endpoint for determining attainment of marine aquatic protection in receiving waters. Adoption of WER and C_{DGT} approaches will assist in fulfilling numerous objectives of the Project ENVVEST agreement (e.g., "Development of alternative or additional tools for the NPDES Program" [PSNS, EPA and Ecology 2000]) and make viable the use of these tools to other NPDES stakeholders.

Transport and fate, using the ENVVEST CH3D Model shall be used to further adjust the effluent thresholds, while also taking into strong consideration the Cu impairment indicators from the ENVVEST's multiple-lines-of-evidence approach, including surface water toxicological evaluations to account for synergism and effects within developed mixing zone isopleths (provided in the current report), sessile organism critical body residues for evaluation of overall biological integrity of the Inlets (e.g., food web distribution and effects to passing species) and human health protection (for consumers) (Strivens and Johnston 2019d), sediment lability by toxicological evaluation and acid-volatile-sulfide simultaneously extracted metals ratios (Johnston et al. 2019), and the Cu mass balance of the Inlets (Brandenberger et al. 2008). The final incorporation of ENVVEST's whole effluent, Cu-specific, and biological assessments shall then provide the most protective threshold for protection of beneficial uses.

The redrafting of WQBELs is comprehensively documented in Appendix C. PSNS Nearshore dataset (by which the toxicological buffering capacity reflects immediate end-of-pipe conditions) was first used for calculation of total → dissolved and total → labile translators. The site-specific total → dissolved translator for the PSNS nearshore zone is 0.773 ± 0.127 (n = 428); neither season (n = 221 dry and 207 wet) nor TSS were significant ($p > 0.05$) to correlation. The absence of a seasonally driven shift in F_Ds also suggests that Cu loading from collocated stormwater outfalls do not affect the toxicological buffering capacity, which is a significant consideration toward incorporation of that component to the NPDES permit. The site-specific

total → labile translator is 0.294 (n = 12 dry and 18 wet season pairs). The labile translator was adjusted, conservatively, upward within its range to bring the value > 4σ (from 2.0 to 2.9). The variability of the labile F_D is inherent in the comparison of grab sampling to 3-day accumulations of labile metals in a dynamic environment. This can be further seen when season is considered (i.e., F_D variation is significantly smaller during the dry season). Preliminary assessment of 1-day deployments in the ENVVEST datasets (n = 6, dry season) further demonstrates that the labile translator is conservative, there the average $F_D = 0.187 \pm 0.026$. Total–lability partitioning did not correlate with TSS (p = 0.08).

After the establishment of translators, waste load allocations (WLA) for Cu were calculated from (1) the Toxics Substances Criteria (WAC 173-201A-240; accessed on 06/06/2020), (2) the WER criteria (Rosen et al. 2009), and (3) the C_{DGT} CMC (Strivens et al 2020). WLAs were then used for calculation of MDLs and AMLs, which were then used to assess loading toward mass balance considerations (Table 10).

Use of the long-term ENVVEST dataset shifts the total recoverable (TRM) MDL from 5.8 (2008 draft suggestion) to 8.8 µg L^{-1}, for both outfalls, when the site-specific translator and the WER adjusted criterion are considered; AMLs become 3.9 and 3.6 µg L^{-1} for OF018 and OF019, respectively. C_{DGT} efforts are in agreement with WER results, producing a MDL of 8.2 µg L^{-1} as total recoverable Cu and AMLs of 3.6 and 3.3 µg L^{-1}. The mass export flux to the sediment (~ 88%) should be of primary consideration when finalizing these thresholds, toward maintaining a decreasing trend for the Inlets. The combined OF018/96 and OF019 WER or labile derived AMLs would contribute ~ 42– 46 kg y^{-1} to the Sinclair/Dyes system (using identical average loading in comparison to the 2008 draft permit derived effluent thresholds); positively, this mass range is below the load used in the Brandenberger et al. (2008) mass balance, indicating that remaining below the WER or C_{DGT} derived AML for industrial discharge points is anticipated to facilitate sediment recovery in the Inlets' natural depositional areas.

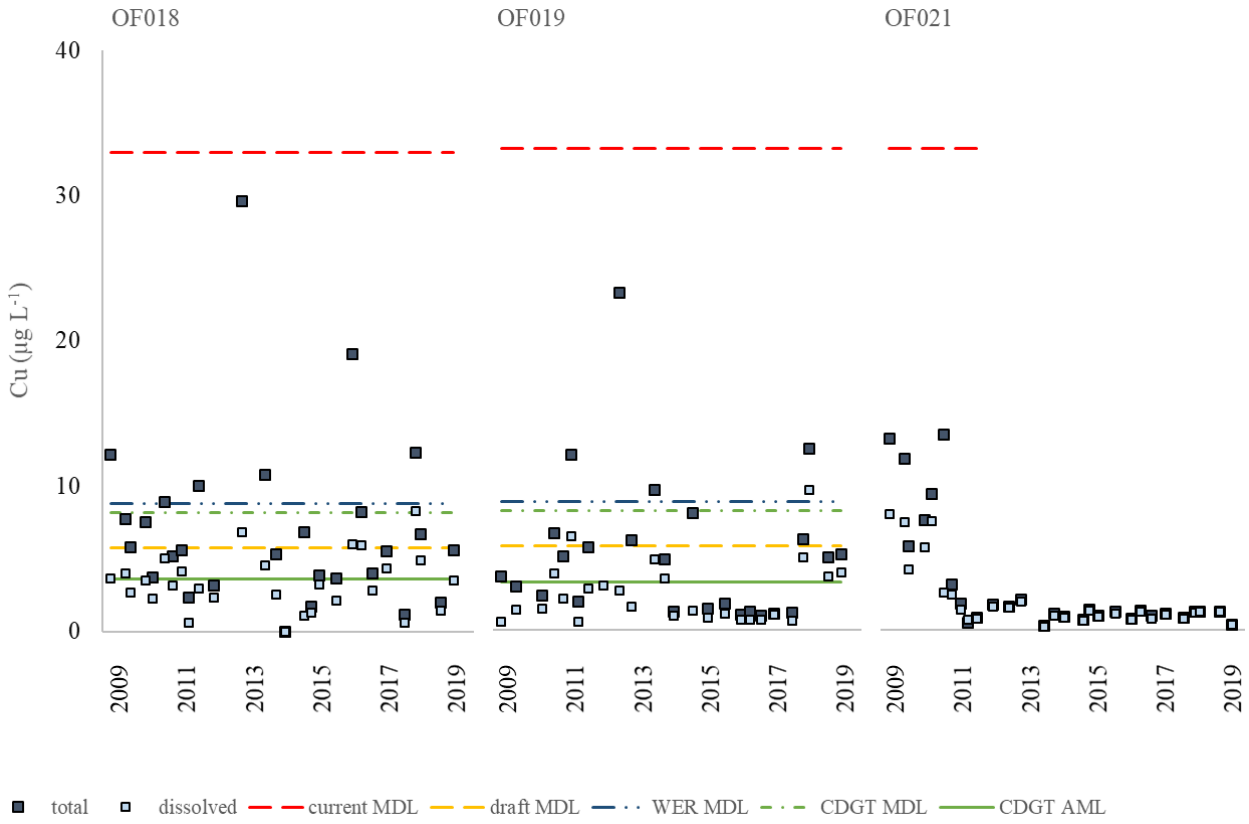

Figure 28. Cu_{diss} and Cu_{tot} at ENVVEST monitored industrial outfalls over the course of 29 events spanning 10 years. Protective thresholds are plotted as total fraction MDLs to reflect the drydock sampling scheme. The zone between the WER MDL and the C_{DGT} MDL is where the biologically relevant MDL falls prior to mixing zone consideration. The OF019 AMB11 outlier is not plotted.

Table 10. Draft mass balance contributions to the Sinclair/Dyes waterbody from PSNS industrial effluents, considering default and biologically adjusted toxics criteria.

Sum of OF018 and OF019:	Total Cu (kg y^{-1})	Total Zn (kg y^{-1})
Avg default mass balance contr.	30.0	606
Avg WER adjusted mass balance contr.	45.6	--
Avg C_{DGT} adjusted mass balance contr.	42.4	--

5.2.3 Lead

OF018 Pb_{tot} averaged 0.427 ± 0.564 µg L^{-1} and Pb_{diss} averaged 0.0175 ± 0.0135 µg L^{-1} over the 10 years captured in Figure 29. OF019 Pb_{tot} averaged 0.259 ± 0.339 µg L^{-1} after removal of the AMB11 outlier (9.06 ug L^{-1}). Dissolved Pb averaged 0.00111 ± 0.0131 µg L^{-1}. The OF021, post AMB07, Pb_{tot} averaged 0.0103 ± 0.00783 µg L^{-1} and Pb_{diss} averaged 0.00609 ± 0.00404 µg L^{-1} (n = 22). Pre AMB07, Pb_{tot} averaged 0.600 ± 0.373 µg L^{-1} and Pb_{diss} averaged 0.00551 ± 0.00314 µg L^{-1} (n = 7). As is the case for other metals, this shift reflects PSNS-implemented BMPs at the steam-plant facility. Strivens et al. (2018) reported that the maximum 1-h effluent during docking operations at DD06 was 1.13 µg L^{-1}. No NPDES limits are currently

in place for this analyte and reasonable potential assessment indicates that the draft WQBELs be removed from consideration for compliance monitoring.

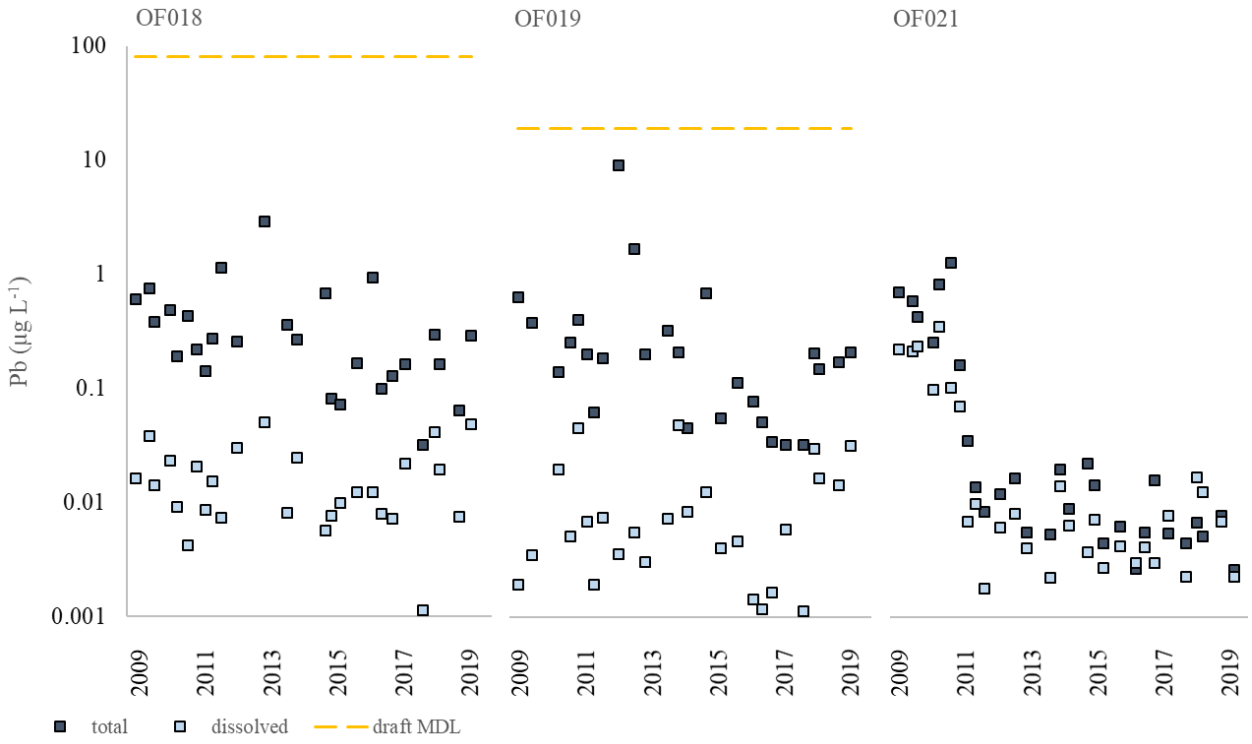

Figure 29. Pb_{diss} and Pb_{tot} at ENVVEST monitored outfalls over the course of 29 events spanning 10 years. The draft toxicological threshold (EPA 2008a) is given as the maximum daily load.

5.2.4 Zinc

OF018 Zn_{tot} averaged 36.8 ± 14.4 µg L^{-1} and Zn_{diss} averaged 30.4 ± 10.1 µg L^{-1} over the 10 years captured in Figure 30. OF019 Zn_{tot} averaged 22.0 ± 15.2 µg L^{-1} after removal of the outlier from AMB11 (365 ug L^{-1}); again, this outlier was associated with particulates (likely metals-enriched Inlet silt) collected as a result of manual override of the pump which resulted in lower than normal water levels in the pump-well and is supported by the dissolved fraction of analyte concentrations. Dissolved Zn concentrations from OF019 averaged 16.2 ± 6.03 µg L^{-1}. In-line OF021, post-AMB07, Zn_{tot} averaged 0.726 ± 0.417 µg L^{-1} and Zn_{diss} averaged 0.711 ± 0.390 µg L^{-1} (n = 22). Pre AMB07, Zn_{tot} averaged 7.48 ± 3.35 µg L^{-1} and Zn_{diss} averaged 1.91 ± 2.52 µg L^{-1} (n = 7). This shift reflects PSNS-implemented BMPs at the Steam-Plant facility. No NPDES exceedances were observed for this analyte, against the original effectual MDL, under the ENVVEST Ambient Monitoring Program's quarterly sampling and Strivens et al. (2018) reported that the maximum daily concentration expected during any phase of docking at OF019 was 37.4 µg L^{-1}. However, the 1-h maximum was 99.9 µg L^{-1} and the draft WQBMDL for both OF018 and OF019 is 95.1 µg L^{-1}; indicating that chronic mixing zone inclusion may be necessary for this analyte during limited windows and illustrating the effect on interpretation of health when relying on grab sampling versus auto-compositing of constant passive surveillance. While the effects of seasonality are significant and TSS insignificant toward a translator, no pre-mixing zone Zn WQBEL modifications are advised in the current report, and the default is conservatively protective.

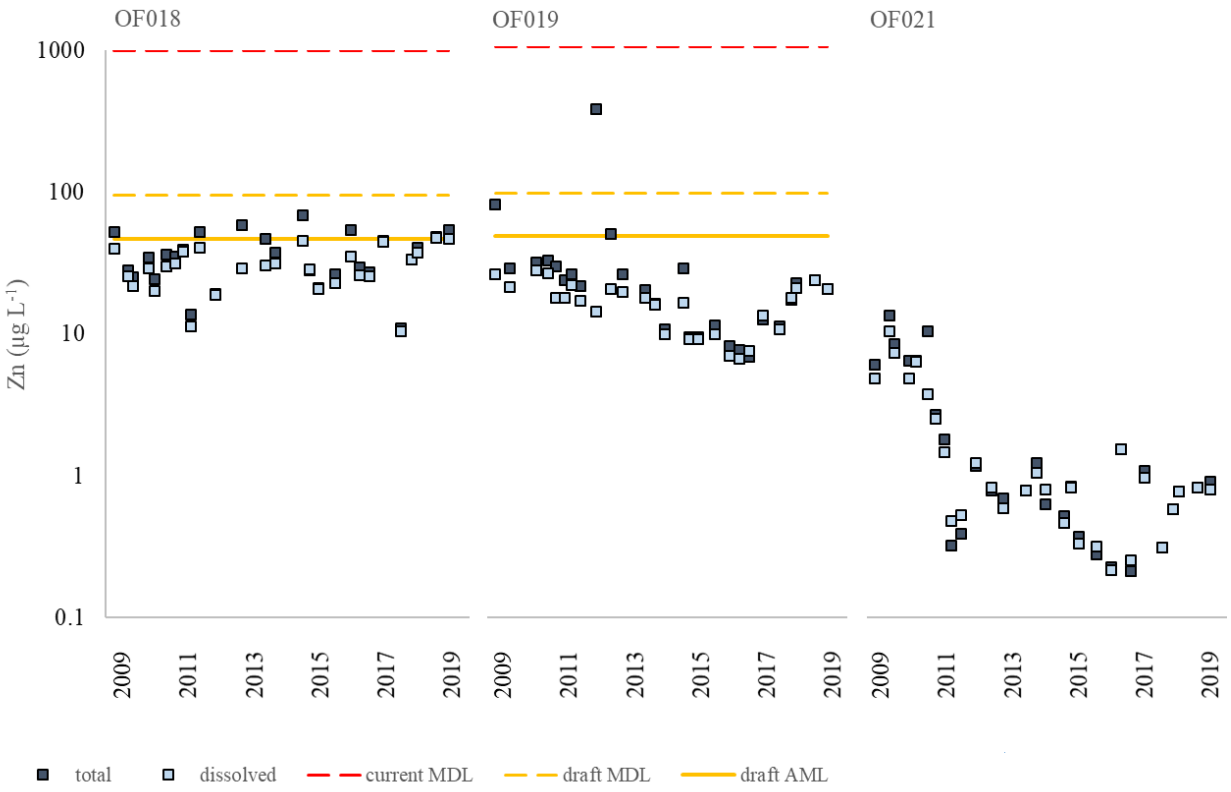

Figure 30. Zn_{diss} and Zn_{tot} at ENVVEST monitored outfalls over the course of 29 events spanning 10 years. Comparison of the total fraction to the draft MDL reflects the sampling scheme. The dissolved fraction and the draft AML threshold are provided for visualization of fractionation and the long-term accuracy of a mass flux estimation.

5.3 Toxicological Evaluations

5.3.1 Surface Waters

Near shore ambient seawater samples exhibited no to low toxicity throughout the monitoring events using either of the statistical methods described in section 4.3.3. Any harmful/toxic effects that were observed in these samples were attributed to natural harmful algal blooms by visual (microscopic) verification of the dinoflagellate *Gymnodimium splendens* (aka *G. sanguineum*) or of planktonic diatoms from the genus *Pseudo-nitzschia*. Both of these species are well known to produce toxins that can cause devastating effects to co-occurring aquatic life. *G. splendens* is known to produce a neurotoxin (saxitoxin) which is extremely toxic to some animals even at relatively low concentrations (Lalli and Parsons, 1993). Several *Pseudo-nitzchia* species are known to be toxic and can produce domoic acid. These harmful blooms were almost exclusively observed during AMB monitoring events conducted in late Summer months and on a fraction of the ambient samples.

For instance, during the AMB01 monitoring effort that occurred in September 2009, sub-samples from several near shore samples were collected and fixed with 10% buffered formalin to identify and enumerate the presence of these taxa in the samples. There was a significant, linear relationship between the densities of *G. splendens* and toxicity endpoints of all tested species including purple sea urchin embryo-larval development, mussel embryo-larval development, kelp germination and spore growth, dinoflagellate bioluminescence, and mysid shrimp survival (AMB01 Report in Appendix E). Densities of *G. splendens* in excess of ~300 cells/ml in water samples from Sinclair Inlet typically resulted in a toxic effect (Figure 31), which is comparable to previous reports regarding laboratory survival of oyster embryos in the presence of 200 cells/ml (Cardwell et al. 1979).

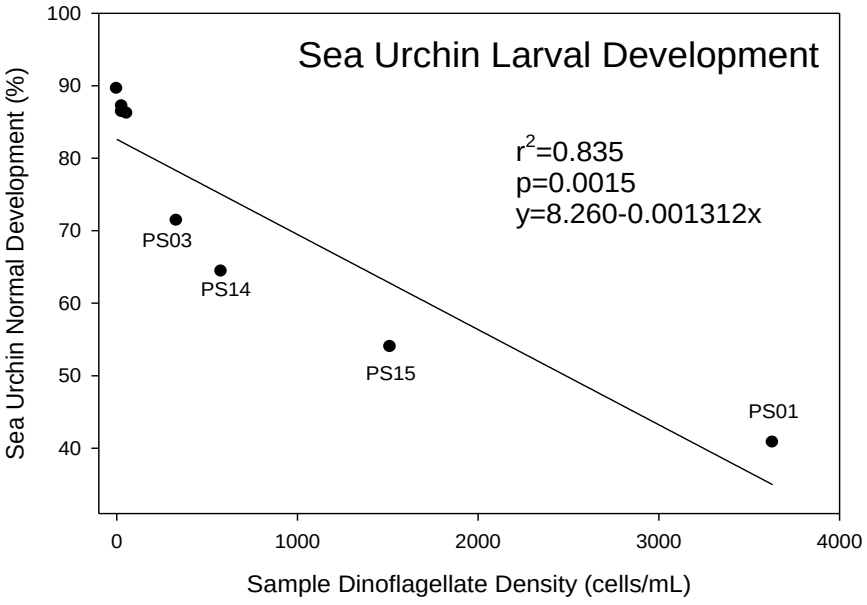

Figure 31. Relationship between sample toxic dinoflagellate (*Gymnodinium splendens*) density in nearshore area samples collected in September 2009 (AMB01) and sea urchin normal larval development (Appendix E.3).

For AMB21 (August 2016), *G. splendens* was only observed in the ambient sample M4 and at a much lower density (84 cells/ml). Unsurprisingly, there were no significant correlation with the distribution of

Gymnodinium across the four samples and their respective endpoints like that seen in Figure 31. Due to low sample size (n=4), these correlations are not very statistically powerful.

The other potentially toxic phytoplankton taxa present in ambient samples PS15, M4, and BJEST, from AMB21 (August 2016) was the chain-forming diatom *Pseudo-nitizchia* (especially associated with the BJEST sample). Several species of the genus are known to be toxigenic and are associated with domoic acid, responsible for amnesic shellfish poisoning (ASP; Lelong et al. 2012). While domoic acid production appears to be induced by the presence potential predators, such as copepods, the effectiveness of the toxin on these predators is inconclusive (Tammilehto et al. 2015). In addition, environmental factors certainly contribute to blooms of *Pseudo-nitzschia*, but the relationships appear to be complex and context dependent (Trainer et al. 2012). The lower threshold of density of *Pseudo-nitzschia* that result in toxic testing in Washington State with respect to human health concerns is 30 cells/mL (Trainer and Suddleson 2005). Ecological effects are likely to occur at lower concentrations with endpoints described herein that focus on larval development and survival. Table 12 shows that there is a significant correlation between mysid survival and densities of *Puesdo-nitzschia* sp. ($r = -0.960$, p-value < 0.05). Although domoic acid concentrations were not measured as part of this study, the presence and densities associated with specific samples suggest that their presence could have contributed to the observed toxicity.

Table 11. Summary of Phytoplankton Enumeration in Select Ambient Samples collected on August 30, 2016 (AMB21).

Sample ID	***Gymnodinium sp* (cells/mL)**	***Pseudo-nitzschia* (cells/mL)**	**Purple Sea Urchin Larval Dev. (% normal)**	**Mussel Larval Dev. (% normal)**	**Mussel Comb. Dev. (% normal survival)**	**QwikLite Biolum. (10^4 units)**	**Mysid Survival (%)**
BJEST	0	12	92.6	93.6	83.4	1.8	55
M3.1	0	0	98.6	98.4	84.8	1.8	100
M4	84	7.6	97	97.4	78.9	1.8	65
PS15	0	6	97.2	97.8	95.4	1.37	85

Table 12. Statistical Summary of Phytoplankton Enumeration in Select Ambient Samples collected on August 30, 2016 (AMB21).

R-values for correlation vs.	**Purple Sea Urchin Larval Dev. (% normal)**	**Mussel Larval Dev. (% normal)**	**Mussel Comb. Dev. (% normal survival)**	**QwikLite Biolum. (10^4 units)**	**Mysid Survival (%)**
Gymnodinium sp density	0.167	0.184	-0.641	0.333	-0.372
Pseudo-nitzschia sp density	-0.903	-0.861	-0.184	0.054	**-0.960[a]**

Values in bold indicate a statistically significant correlation coefficient.

Level of statistical significance: a - <0.05, b - <0.01, c - ≤0.001.

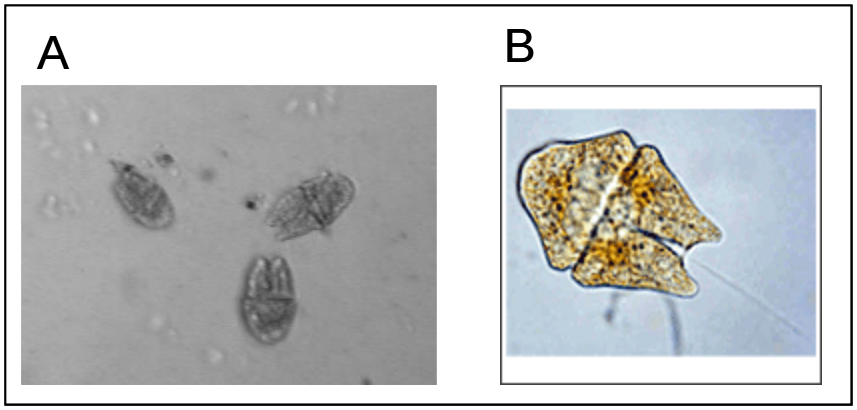

Figure 32. (A) Photograph of dinoflagellates (*Gymnodinium splendens*) observed in samples from the Cu WER study conducted in Sinclair and Dyes Inlets (B) Photograph *of G. splendens* from internet (with permission, Rosen et al. 2009). Actual cell sizes are 40-80 µm.

Figure 33. Photo of an unidentified species of *Pseudo-nitzschia* found in the BJEST sample from AMB 21 (August 2016) monitoring effort (left); a large celled toxigenic *Pseudo-nitzschia c.f. australis* (middle); and a small celled toxigenic *Pseudo-nitzschia c.f. delicatissima* (left) (Puget Sound Marine Monitoring Program).

5.3.2 Purple Sea Urchin Results

For the purple sea urchin (*Strongylocentrotus purpuratus*) chronic normal larval development endpoint (96 h), all samples were tested at a salinity of 34±2 ppt, adjusted using a hypersaline brine following standard procedures (EPA 1995). All data in Figure 34 represent the highest possible concentrations of the samples (typically >70%, but as low as 53%), as the hypersaline dilutes the full strength sample when used to adjust the salinity to meet test requirements (EPA 1995). The dotted line represents a 25% decrease from the control, which has been used to signify significant toxic effects, following the procedures outlined in the EPA TST (EPA 2010). The TST is designed to reduce false positive test reading due to low variability in replicate measurements. Following this procedure, OF021 has not been significantly toxic at any point over the 10-year testing period. OF018 and OF019 samples have resulted in some effects, which are discussed

below. Similar to the other toxicity tests described below, significant adverse effects have been sporadically detected in ambient samples, but these are primarily tied to red tide events (Figure 34).

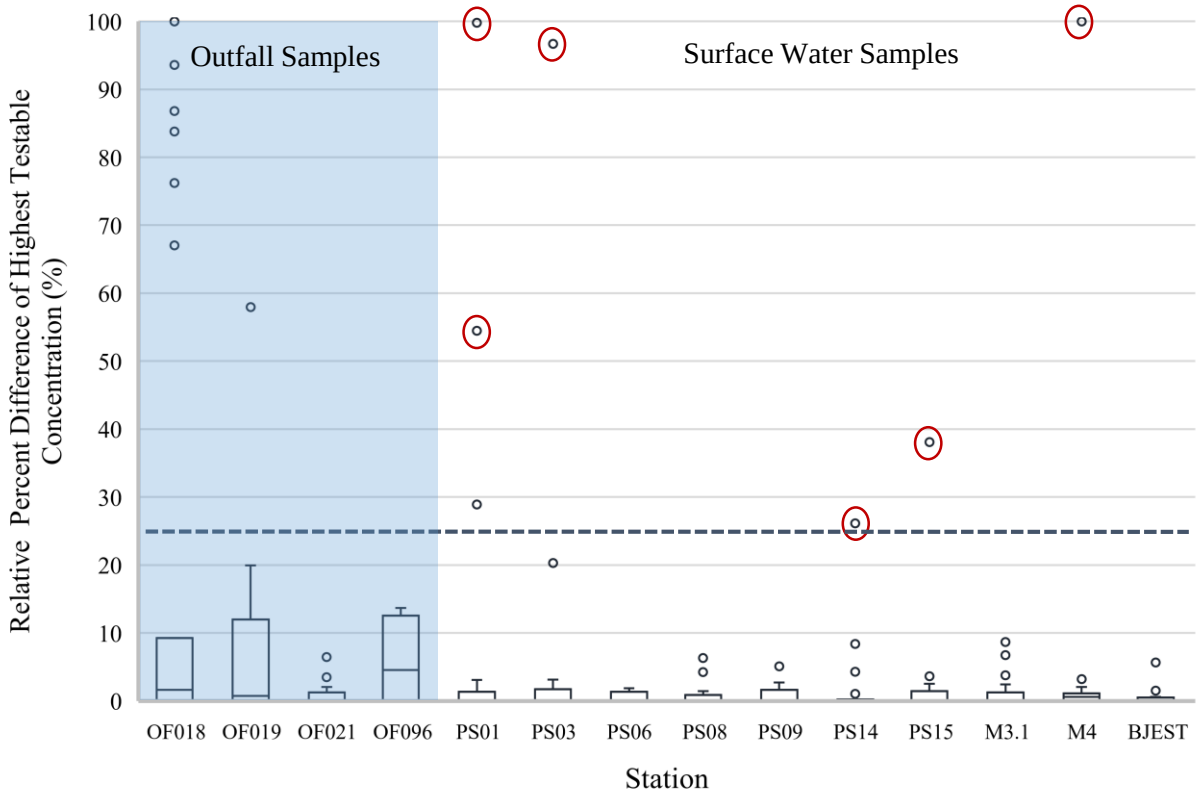

Figure 34. Box and whisker plot showing results of the 96-h echinoderm embryo-larval development bioassay as the relative percent difference from the control of the highest testable concentration (>50% depending on the salinity of the received sample) across stations. Higher values indicate toxicity. The dotted line represents a 25% effect, above which samples are considered toxic. The red circles represent significant toxic samples that were visually verified to naturally contain toxic algae associated with red tide events. Blue shaded area indicates outfall samples.

A time series of sea urchin response from OF018 (blue) and OF019 (orange) is presented in Figure 35. OF019 has generally not demonstrated significant toxicity, except during the monitoring event in February 2013 (AMB12). It is significant to note that neither PS09 (closest nearshore ambient station to OF018) nor PS06 (closest nearshore ambient station to OF019) have not demonstrated significant adverse effects, even when the outfall discharge does.

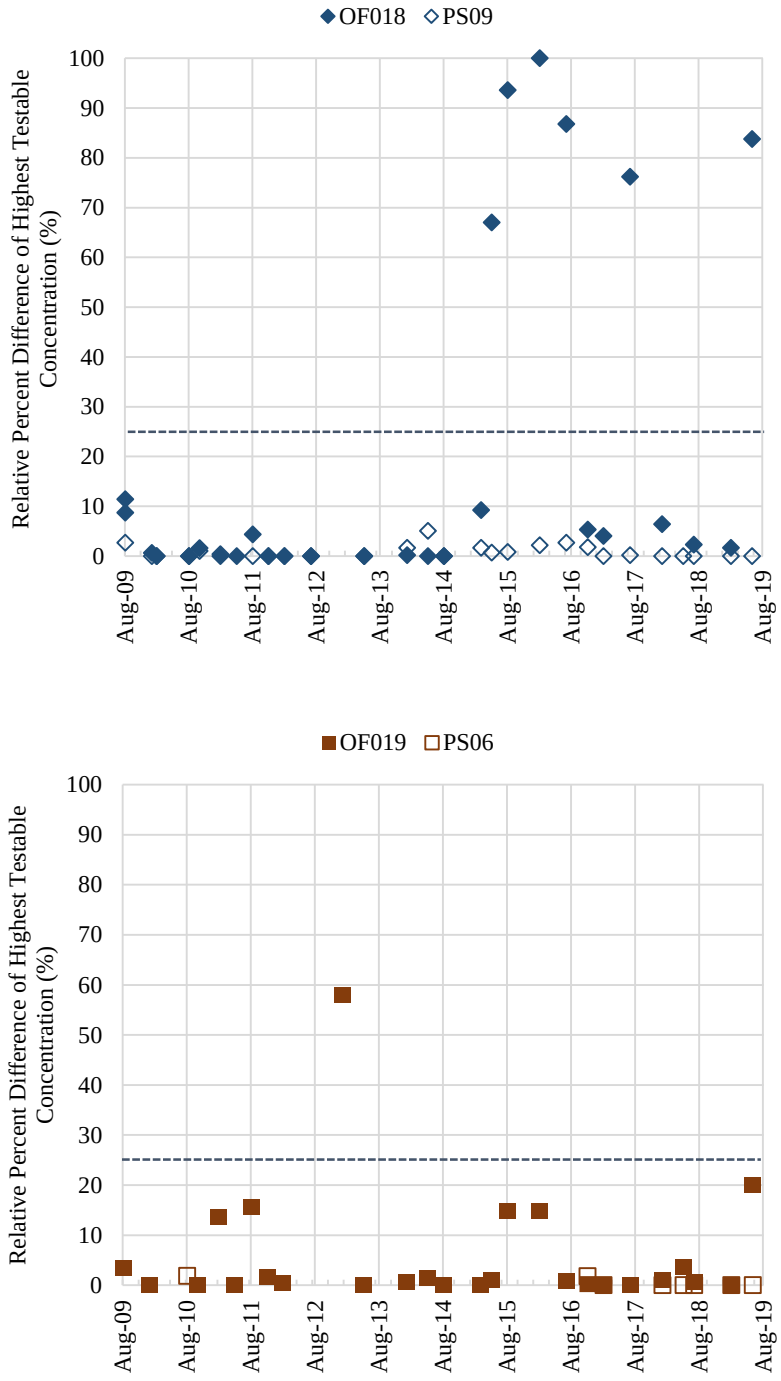

Figure 35. Time series showing the relative percent difference of highest testable concentration from OF018 and adjacent ambient site PS09 (top), and from OF019 and adjacent ambient site PS06 (bottom) following exposure to embryonic purple sea urchins (*S. purpuratus*). Dotted line represents a 25% effect, above which samples are considered toxic.

Table 13 provides detail of statistical results for each outfall. No observed effect concentrations (NOEC) and lowest observed effect concentration (LOEC) values for outfall samples are summarized in Table 13 for samples exhibiting toxicity. Table 14 shows NOEC and LOEC values for all outfall samples for each monitoring event. When interpreting these results, it is critical to remember that the highest testable concentration was never 100%, due to the addition of hypersaline brine. If the NOEC is the same as the highest testable concentration, no toxicity was observed.

Table 13. Summary of results of outfall (OF) samples deemed toxic[1] for the 96-h echinoderm embryo-larval development bioassay.

Sample Date	Outfall	Relative Percent Difference from Control	EPA 1995 Toxicity[1]	NOEC (%sample)[1]	LOEC (%sample)[1]	EC_{50} (%sample)[1]	TST Toxicity[2]
Sep-09	OF019	11.42	Toxic	50	76.4	NC	NA
Mar-11	OF019	13.65	Toxic	50	81.2	NC	NA
Sep-11	OF019	15.50	Toxic	25	50	NC	NA
Feb-13	OF019	57.95	Toxic	12.5	25	56.8	NA
Apr-15	OF018	9.27	Toxic	12.5	25	NC	NA
Jun-15	OF018	67.01	Toxic	12.5	25	40.3	Toxic
Sep-15	OF018	93.60	Toxic	6.25	12.5	23.8	Toxic
Sep-15	OF019	14.90	Toxic	50	82.2	NC	Non-Toxic
Sep-15	OF096	9.13	Toxic	50	91.5	NC	Non-Toxic
Mar-16	OF018	100.00	Toxic	6.25	12.5	67.9	Toxic
Aug-16	OF018	86.80	Toxic	6.25	12.5	54.8	Toxic
Dec-16	OF018	5.31	Toxic	50	79.7	NC	Non-Toxic
Mar-17	OF018	4.07	Toxic	50	76.9	NC	Non-Toxic
Aug-17	OF018	76.20	Toxic	50	76.4	70.2	Toxic
Jun-18	OF096	13.70	Toxic	25	50	NC	Non-Toxic
Jul-19	OF018	83.78	Toxic	50	83.9	66.3	Toxic
Jul-19	OF019	19.96	Toxic	50	82.3	NC	Toxic

1 - Toxicity as determined by EPA (1995) statistical procedures; 2 -Toxicity determined by TST (EPA 2010) statistical procedures; NC – EC50 not calculated; NA - not analyzed.

Table 14. Purple sea urchin 96-h normal development endpoint NOEC and LOEC values for all tested outfall samples.

Event	Sample Date	OF018			OF019			OF021			OF096		
		Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC
AMB01	Sep-09	77.3	77.3	>77.3	**76.4**	**50**	76.4	50.0	50.0	>50	--	--	--
AMB02	Feb-10	80.1	80.1	>80.1	86.2	86.2	>86.2	65.8	65.8	>65.8	--	--	--
AMB03	Mar-10	76.8	76.8	>76.8	--	--	--	66.2	66.2	>66.2	--	--	--
AMB04	Sep-10	74.2	74.2	>74.2	--	--	--	53.4	53.4	>53.4	--	--	--
AMB05	Nov-10	73.0	73.0	>73.0	83.4	83.4	>83.4	56.7	56.7	>56.7	--	--	--
AMB06	Mar-11	70.1	70.1	>70.1	**81.2**	**50.0**	81.2	54.9	54.9	>54.9	--	--	--
AMB07	Jun-11	85.6	85.6	>85.6	92.1	92.1	>92.1	66.3	66.3	>66.3	--	--	--
AMB08	Sep-11	83.1	83.1	>83.1	**90.0**	**25.0**	50.0	63.4	63.4	>63.4	--	--	--
AMB09	Dec-11	77.5	77.5	>77.5	77.5	77.5	>77.5	58.0	58.0	>58.0	--	--	--
AMB10	Mar-12	65.3	65.3	>65.3	77.4	77.4	>77.4	56.0	56.0	>56.0	--	--	--
AMB11	Aug-12	100	100	>100	--	--	--	--	--	--	--	--	--
AMB12	Feb-13	--	--	--	**79.3**	**12.5**	25	59.7	59.7	>59.7	--	--	--
AMB13	Jun-13	87.5	87.5	>87.5	76.5	76.5	>76.5	62.7	62.7	>62.7	--	--	--
AMB14	Feb-14	87.7	87.7	>87.7	90.7	90.7	>90.7	62.4	62.4	>62.4	--	--	--
AMB15	Jun-14	81.8	81.8	>81.8	86.7	86.7	>86.7	57.1	57.1	>57.1	--	--	--
AMB16	Sep-14	78.5	78.5	>78.5	75.8	75.8	>75.8	54.9	54.9	>54.9	--	--	--
AMB17	Apr-15	**79.8**	**12.5**	25.0	82.7	82.7	>82.7	61.2	61.2	>61.2	--	--	--
AMB18	Jun-15	**76.8**	**12.5**	25.0	77.6	77.6	>77.6	59.8	59.8	>59.8	87.8	87.8	>87.8
AMB19	Sep-15	**84.3**	**6.25**	12.5	**82.2**	**50.0**	82.2	66.0	66.0	>66.0	**91.5**	**50.0**	91.5
AMB20	Mar-16	**80.3**	**6.25**	12.5	75.0	75.0	>75.0	60.0	60.0	>60.0	--	--	--
AMB21	Aug-16	**81.1**	**12.5**	25.0	74.5	74.5	>74.5	61.0	61.0	>61.0	--	--	--
AMB22	Dec-16	**79.7**	**50.0**	79.7	74.3	74.3	>74.3	58.7	58.7	>58.7	--	--	--
AMB23	Mar-17	**76.9**	**50.0**	76.9	72.1	72.1	>72.1	58.5	58.5	>58.5	--	--	--
AMB24	Aug-17	**76.4**	**50.0**	76.4	72.6	72.6	>72.6	56.2	56.2	>56.2	--	--	--
AMB25	Feb-18	**76.7**	**50.0**	76.7	71.9	71.9	>71.9	57.6	57.6	>57.6	--	--	--
AMB26	Jun-18	--	--	--	81.9	81.9	>81.9	58.2	58.2	>58.2	**82.2**	**50.0**	82.2
AMB27	Aug-18	81.6	81.6	>81.6	84.1	84.1	>84.1	62.7	62.7	>62.7	--	--	--
AMB28	Mar-19	80.7	80.7	>80.7	82.7	82.7	>82.7	63.3	63.3	>63.3	72.1	72.1	>72.1
AMB29	Jul-19	**83.9**	**50.0**	83.9	**82.3**	**50.0**	82.3	61.3	61.3	>61.3	--	--	--

As *S. purpuratus* embryos are widely known to be sensitive both to copper and zinc, with reported EC50s at relatively low concentrations (14.3 µg/L; Rosen et al. 2008, and 97.4 µg/L; Phillips et al. 1998), it is conceivable that toxicity, when observed, was associated with these two metals. Dissolved copper averaged 3.47, 2.51, and 1.03 µg/L, while dissolved zinc averaged 30.4, 16.2, and 1.91 µg/L, for OF18, OF19, and OF21, respectively (Figure 28 and Figure 30) over the 10-year monitoring period, yet never exceeded EC50 levels for urchins. A simplistic toxic unit (TU) approach (Phillips et al. 2003; Figure 36) was employed herein to assess the likelihood that the combined Cu and Zn concentrations might contribute to toxicity. This was done by dividing the measured dissolved concentrations from the outfalls by their associated published EC50s and summing the Cu and Zn TUs from each AMB event. Using this approach a TU>1 would suggest that concentrations were high enough to elicit an EC50 assuming additivity between Cu and Zn in the mixture, while a TU somewhat less than 1 could also imply Cu and Zn as causal agents that resulted in significant differences relative to controls. It is noteworthy that the trend in terms of the frequency of toxicity was the same based on actual observed toxicity and the TU calculation in the order OF18>OF19>OF21>OF96. This said, the specific ability to predict observed toxicity using TU calculations was imperfect which could be associated with other factors including presence of other measured or unmeasured contaminants of potential concern and sample-specific water chemistry (e.g. dissolved organic carbon quality) that might alter metal bioavailability. It is possible that this disparity for such comparisons could be reduced as the development of Cu and Zn thresholds from DGT further develops.

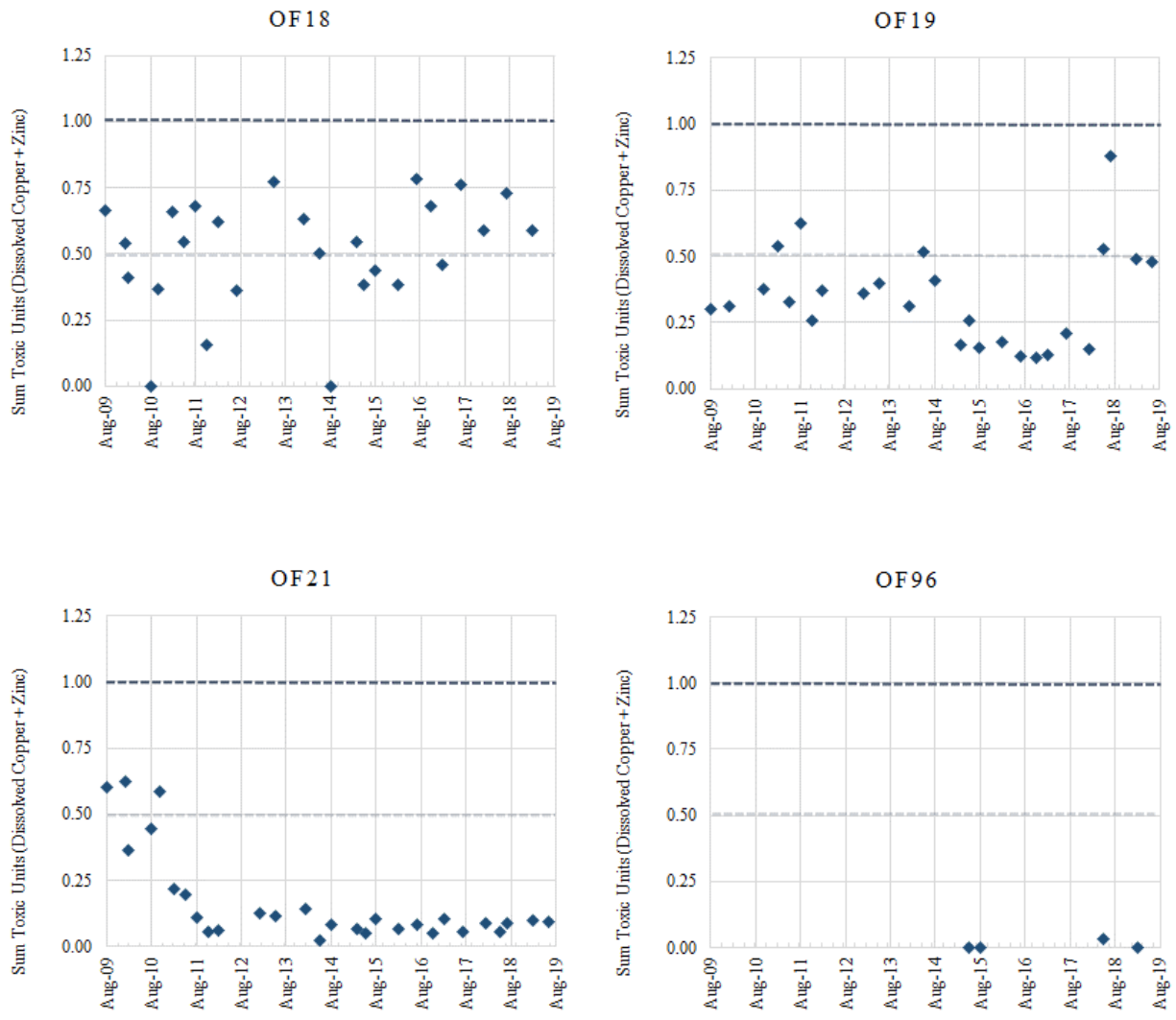

Figure 36. Sum toxic units (TU) of copper and zinc for sea urchins (*S. purpuratus*) calculated from outfalls from 10 years of monitoring using sample specific chemistry and species-specific EC50s. A TU of 0.5 to 1 could suggest the sample would be toxic due to copper and zinc, but may be dependent on various water chemistry parameters (e.g. dissolved organic carbon).

5.3.3 Mediterranean Mussel Results

Similar to the purple urchin, tests with the Mediterranean mussel (*Mytilus galloprovincialis*) 48hr chronic normal larval development endpoint (and the combined normal-alive endpoint) were conducted at a salinity of 34±2 ppt, adjusted using a hypersaline brine following standard procedures (EPA 1995). All data in Figure 37 represent the highest possible concentrations of the samples (typically >70%, but as low as 53%), as the brine dilutes the sample when used to adjust the salinity to meet test requirements. The dotted line represents a 25% decrease from the control, which has been used to signify significant toxic effects following procedures outlined in the EPA TST (EPA 2010). In general, both bivalve endpoints performed

similarly. OF018, OF019, and OF021 results are discussed in more detail below. OF096 did not demonstrate significant adverse effects when tested. Similar to the sea urchin tests, significant adverse effects in the ambient monitoring sites was uncommon and when they did occur, it was attributed to samples with evidence of naturally occurring red tide plankton species (Figure 37).

In a few instances, outfall samples (OF018, OF019, and OF021) demonstrated significant adverse effects relative to controls. OF019 and OF021 demonstrated a single instance of toxicity during the March 2011 (AMB06) sampling event. Samples from OF018 demonstrated toxicity twice in the last five years, one during the March 2016 (AMB20) event and one during the July 2019 (AMB29) event (Figure 38). Fewer adverse effects at OF018 were observed for the mussel test when compared to the sea urchin test for two possible reasons. First, due to failed spawning efforts that did not produce sufficient embryos for testing (a common problem especially during summer months which is outside the mussel's normal spawning period); there are fewer numbers of mussel embryo-larval development/survival tests relative to the number of sea urchin tests. Of the 29 monitoring events discussed herein, only 17 of these events were successful in producing viable mussel embryo-development results data. A second possibility is that sea urchin embryos can be more sensitive to certain contaminants, such as zinc (Phillips et al. 1998), resulting in decreased frequency of toxicity for the mussel tests relative to the sea urchin tests.

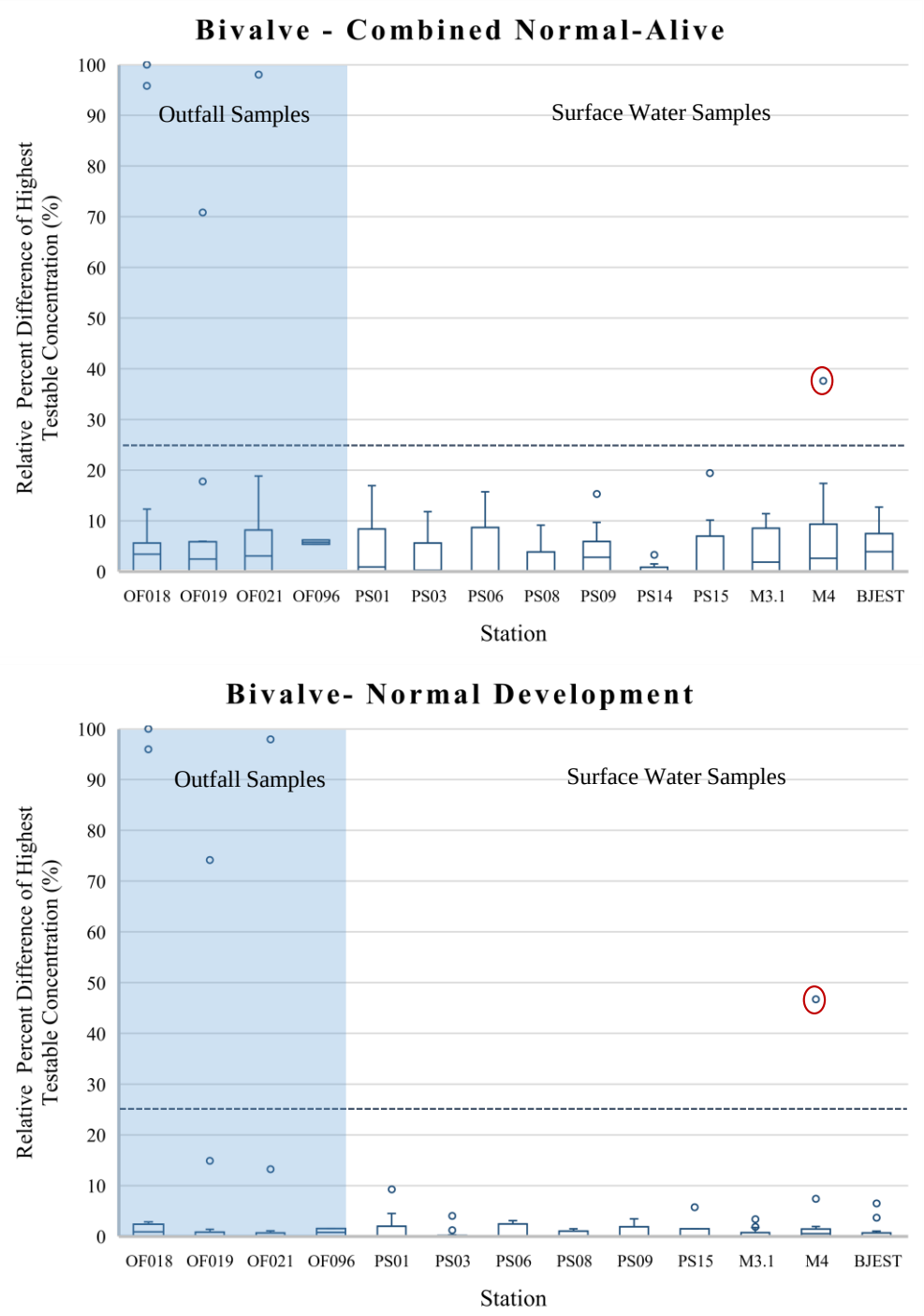

Figure 37. Box and whisker plot showing results of the 48-h bivalve embryo-larval development bioassay as the relative percent difference from the control of the highest testable concentration (>50% depending on the salinity of the received sample) across stations. (Top) combined percent normal alive; (bottom) percent normal development. Higher values indicate toxicity. The dotted line represents a 25% effect. The red circle represents significant toxic samples that were collected during red tide events. Blue shaded area indicates outfall samples.

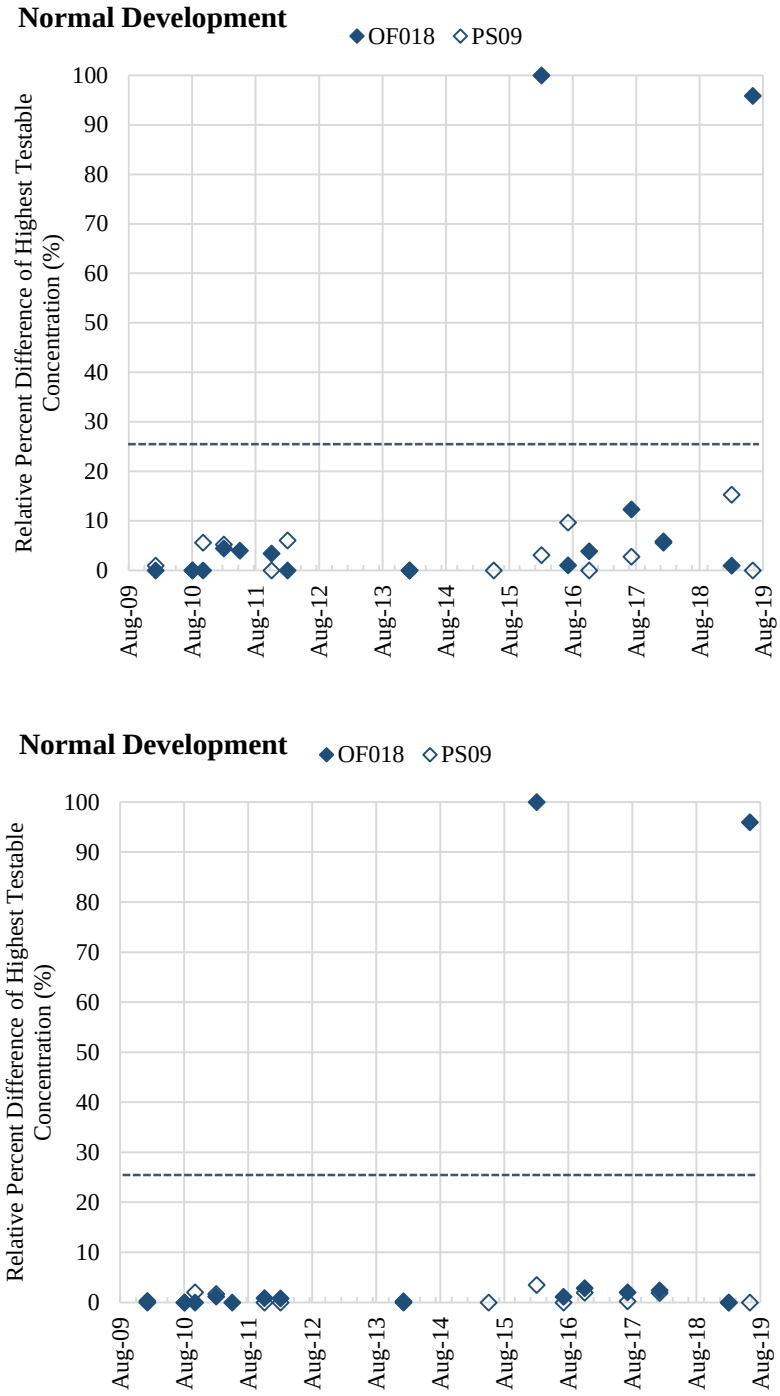

Figure 38 a–c. Time series showing the relative percent difference of highest testable concentration of effluent samples from the mussel bioassay for the combined normal-alive endpoint (top) and normal development endpoint (bottom) for (a) OF018 and adjacent ambient site PS09; (b) OF019 and adjacent ambient site PS06; and (c) OF021. Dotted line represents a 25% effect.

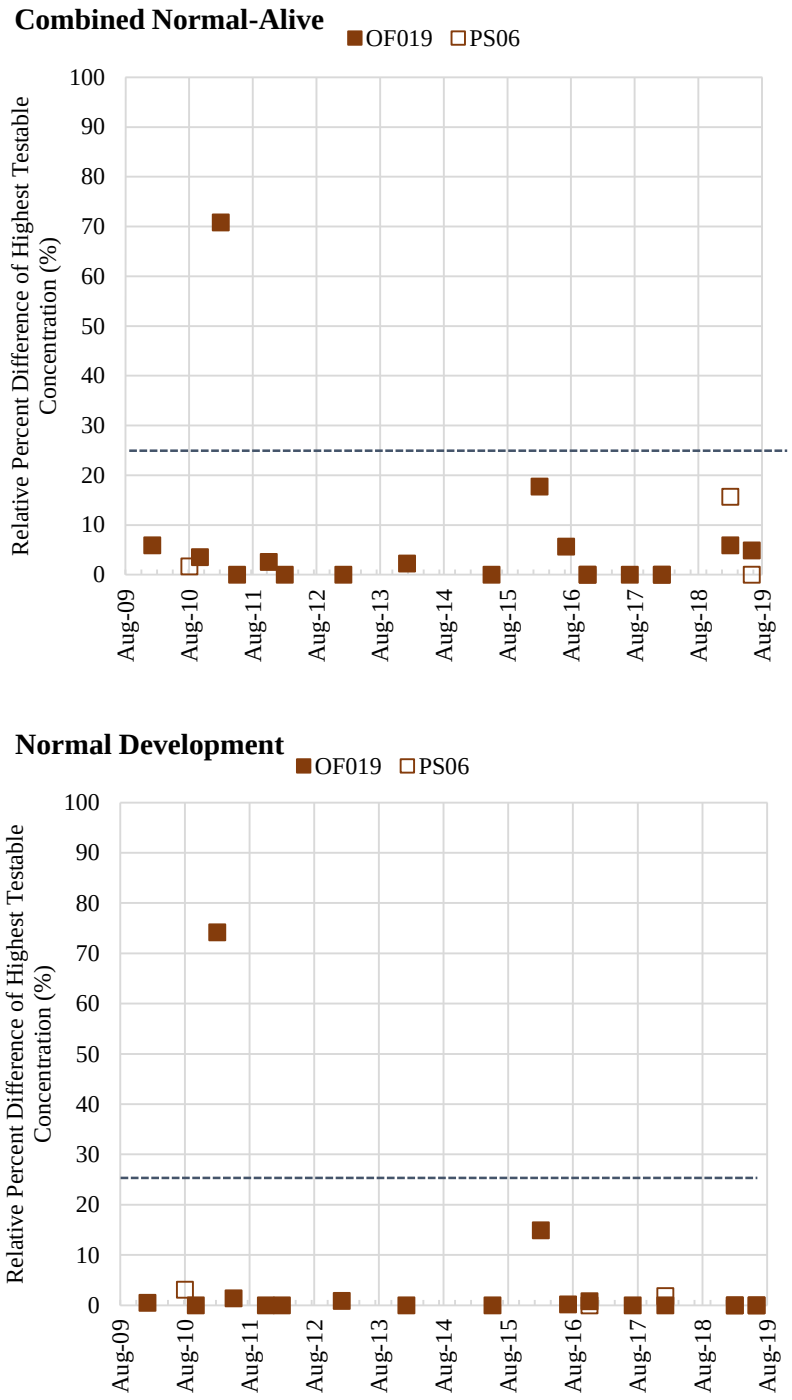

Figure 38. (Cont'd).

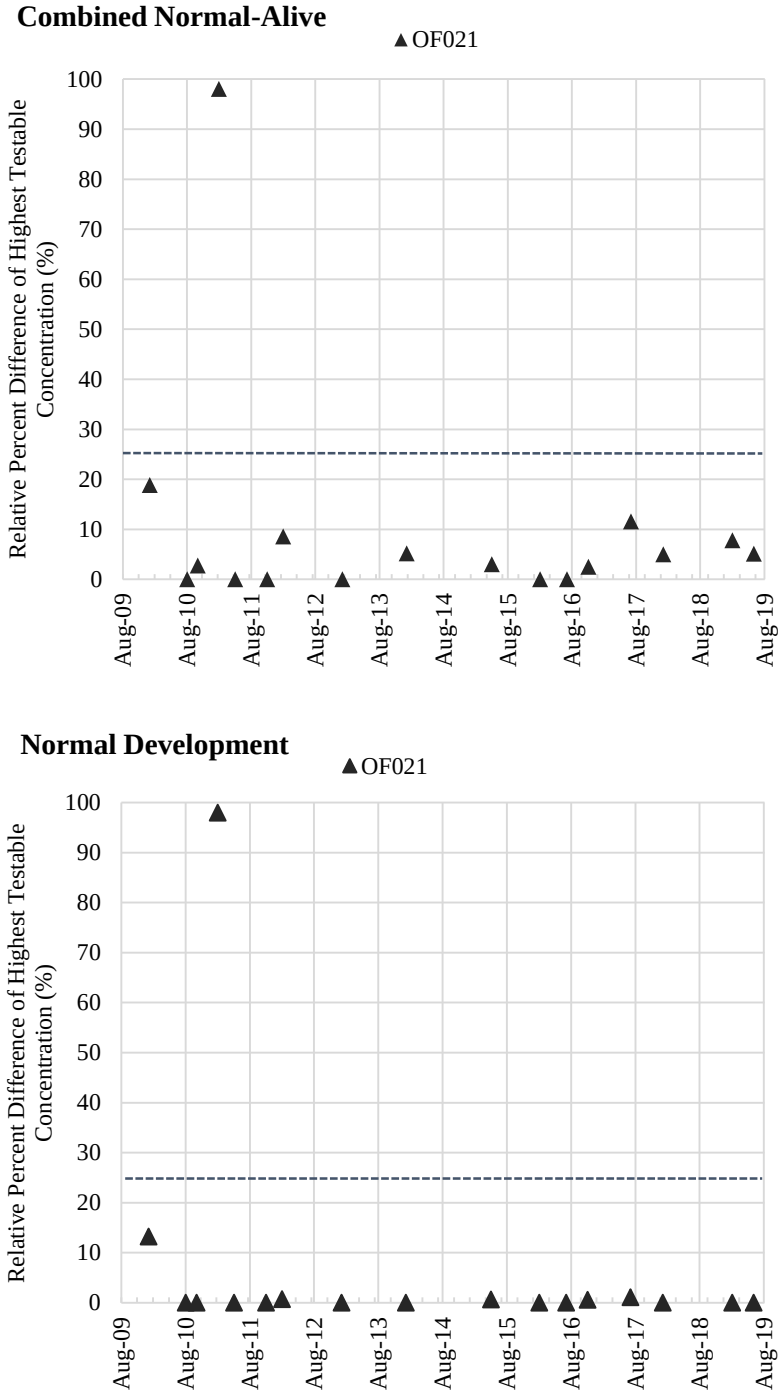

Figure 38. (Cont'd).

Table 15 provides finer detail of the toxicity results determined for the outfalls. No observed effect concentrations (NOEC) and lowest observed effect concentration (LOEC) values for outfall samples are summarized in Table 16 (normal development endpoint) and Table 17 (combined normal-alive endpoint) for all tests, and in Table 15 for just the toxic results. When interpreting these results, it is critical to

remember that the highest testable concentration was never 100%, due to the addition of hypersaline brine. If the NOEC is the same as the highest testable concentration, no toxicity was observed.

Table 15. Summary of results of outfall samples deemed toxic[1] for the 48-h mussel embryo-larval development bioassay.

Sample Date	Outfall	Relative Percent Difference from Control	Endpoint	EPA 1995 Toxicity[1]	NOEC (% sample)[1]	LOEC (% sample)[1]	EC50 (% sample)[1]	TST Toxicity[2]
Feb-10	OF021	18.84	Combined Normal Alive	Toxic	50	65.8	NC	NA
Feb-10	OF021	13.22	Normal Development	Toxic	50	65.8	NC	NA
Mar-11	OF019	70.82	Combined Normal Alive	Toxic	50	81.2	71.9	NA
Mar-11	OF019	74.15	Normal Development	Toxic	50	81.2	71	NA
Mar-11	OF021	98.06	Combined Normal Alive	Toxic	50	54.9	52.4	NA
Mar-11	OF021	97.96	Normal Development	Toxic	50	54.9	52.5	NA
Mar-16	OF018	100.00	Combined Normal Alive	Toxic	6.25	12.5	14.9	Toxic
Mar-16	OF018	100.00	Normal Development	Toxic	6.25	12.5	15.7	Toxic
Aug-17	OF018	2.00	Normal Development	Toxic	50	76.4	NC	Non-Toxic
Jul-19	OF018	95.85	Combined Normal Alive	Toxic	50	83.9	62.1	Toxic
Jul-19	OF018	95.98	Normal Development	Toxic	50	83.9	64.8	Toxic

1Toxicity as determined by EPA (1995) statistical procedures;

2Toxicity determined by TST (EPA 2010) statistical procedures; NC - EC50 not calculated; NA - not analyzed.

Table 16. Mediterranean mussel 48-h normal development endpoint NOEC and LOEC values for all tested outfall samples.

Event	Sample Date	OF018			OF019			OF021			OF096		
		Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC
AMB01	Sep-09	--	--	--	--	--	--	--	--	--	--	--	--
AMB02	Feb-10	80.1	80.1	>80.1	86.2	86.2	>86.2	**65.8**	**25.0**	65.8	--	--	--
AMB03	Mar-10	--	--	--	--	--	--	--	--	--	--	--	--
AMB04	Sep-10	74.2	74.2	>74.2	--	--	--	53.4	53.4	>53.4	--	--	--
AMB05	Nov-10	73.0	73.0	>73.0	83.4	83.4	>83.4	56.7	56.7	>56.7	--	--	--
AMB06	Mar-11	70.1	70.1	>70.1	**81.2**	**50.0**	81.2	**54.9**	**50**	54.9	--	--	--
AMB07	Jun-11	85.6	85.6	>85.6	92.1	92.1	>92.1	66.3	66.3	>66.3	--	--	--
AMB08	Sep-11	--	--	--	--	--	--	--	--	--	--	--	--
AMB09	Dec-11	77.5	77.5	>77.5	77.5	77.5	>77.5	58.0	58.0	>58.0	--	--	--
AMB10	Mar-12	65.3	65.3	>65.3	77.4	77.4	>77.4	56.0	56.0	>56.0	--	--	--
AMB11	Aug-12	--	--	--	--	--	--	--	--	--	--	--	--
AMB12	Feb-13	--	--	--	79.3	79.3	>79.3	59.7	59.7	>59.7	--	--	--
AMB13	Jun-13	--	--	--	--	--	--	--	--	--	--	--	--
AMB14	Feb-14	87.7	87.7	>87.7	90.7	90.7	>90.7	62.4	62.4	>62.4	--	--	--
AMB15	Jun-14	--	--	--	--	--	--	--	--	--	--	--	--
AMB16	Sep-14	--	--	--	--	--	--	--	--	--	--	--	--
AMB17	Apr-15	--	--	--	--	--	--	--	--	--	--	--	--
AMB18	Jun-15	--	--	--	77.6	77.6	>77.6	59.8	59.8	>59.8	87.8	87.8	>87.8
AMB19	Sep-15	--	--	--	--	--	--	--	--	--	--	--	--
AMB20	Mar-16	**80.3**	**6.25**	12.5	75.0	75.0	>75.0	60.0	60.0	>60.0	--	--	--
AMB21	Aug-16	81.1	81.1	>81.1	74.5	74.5	>74.5	61.0	61.0	>61.0	--	--	--
AMB22	Dec-16	79.7	79.7	>79.7	74.3	74.3	>74.3	58.7	58.7	>58.7	--	--	--
AMB23	Mar-17	--	--	--	--	--	--	--	--	--	--	--	--
AMB24	Aug-17	**76.4**	**50.0**	76.4	72.6	72.6	>72.6	56.2	56.2	>56.2	--	--	--
AMB25	Feb-18	76.7	76.7	>76.7	71.9	71.9	>71.9	57.6	57.6	>57.6	--	--	--
AMB26	Jun-18	--	--	--	--	--	--	--	--	--	--	--	--
AMB27	Aug-18	--	--	--	--	--	--	--	--	--	--	--	--
AMB28	Mar-19	80.7	80.7	>80.7	82.7	82.7	>82.7	63.3	63.3	>63.3	72.1	72.1	>72.1
AMB29	Jul-19	**83.9**	**50.0**	83.9	82.3	82.3	>82.3	61.3	61.3	>61.3	--	--	--

Table 17. Mediterranean mussel 48-h combined normal alive endpoint NOEC and LOEC values for all tested outfall samples.

Event	Sample Date	OF018			OF019			OF021			OF096		
		Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC	Highest Tested Concentration	NOEC	LOEC
AMB01	Sep-09	--	--	--	--	--	--	--	--	--	--	--	--
AMB02	Feb-10	80.1	80.1	>80.1	86.2	86.2	>86.2	65.8	25	65.8	--	--	--
AMB03	Mar-10	--	--	--	--	--	--	--	--	--	--	--	--
AMB04	Sep-10	74.2	74.2	>74.2	--	--	--	53.4	53.4	>53.4	--	--	--
AMB05	Nov-10	73.0	73.0	>73.0	83.4	83.4	>83.4	56.7	56.7	>56.7	--	--	--
AMB06	Mar-11	70.1	70.1	>70.1	81.2	50.0	81.2	54.9	50	54.9	--	--	--
AMB07	Jun-11	85.6	85.6	>85.6	92.1	92.1	>92.1	66.3	66.3	>66.3	--	--	--
AMB08	Sep-11	--	--	--	--	--	--	--	--	--	--	--	--
AMB09	Dec-11	77.5	77.5	>77.5	77.5	77.5	>77.5	58.0	58.0	>58.0	--	--	--
AMB10	Mar-12	65.3	65.3	>65.3	77.4	77.4	>77.4	56.0	56.0	>56.0	--	--	--
AMB11	Aug-12	--	--	--	--	--	--	--	--	--	--	--	--
AMB12	Feb-13	--	--	--	79.3	79.3	>79.3	59.7	59.7	>59.7	--	--	--
AMB13	Jun-13	--	--	--	--	--	--	--	--	--	--	--	--
AMB14	Feb-14	87.7	87.7	>87.7	90.7	90.7	>90.7	62.4	62.4	>62.4	--	--	--
AMB15	Jun-14	--	--	--	--	--	--	--	--	--	--	--	--
AMB16	Sep-14	--	--	--	--	--	--	--	--	--	--	--	--
AMB17	Apr-15	--	--	--	--	--	--	--	--	--	--	--	--
AMB18	Jun-15	--	--	--	77.6	77.6	>77.6	59.8	59.8	>59.8	87.8	87.8	>87.8
AMB19	Sep-15	--	--	--	--	--	--	--	--	--	--	--	--
AMB20	Mar-16	80.3	6.25	12.5	75.0	75.0	>75.0	60.0	60.0	>60.0	--	--	--
AMB21	Aug-16	81.1	81.1	>81.1	74.5	74.5	>74.5	61.0	61.0	>61.0	--	--	--
AMB22	Dec-16	79.7	79.7	>79.7	74.3	74.3	>74.3	58.7	58.7	>58.7	--	--	--
AMB23	Mar-17	--	--	--	--	--	--	--	--	--	--	--	--
AMB24	Aug-17	76.4	76.4	>76.4	72.6	72.6	>72.6	56.2	56.2	>56.2	--	--	--
AMB25	Feb-18	76.7	76.7	>76.7	71.9	71.9	>71.9	57.6	57.6	>57.6	--	--	--
AMB26	Jun-18	--	--	--	--	--	--	--	--	--	--	--	--
AMB27	Aug-18	--	--	--	--	--	--	--	--	--	--	--	--
AMB28	Mar-19	80.7	80.7	>80.7	82.7	82.7	>82.7	63.3	63.3	>63.3	72.1	72.1	>72.1
AMB29	Jul-19	83.9	50.0	83.9	82.3	82.3	>82.3	61.3	61.3	>61.3	--	--	--

5.3.4 Dinoflagellate Bioluminescence Results

For the 24-h bioluminescent test using *Pyrocystis lunula*, all samples were tested at a salinity of 34±2 ppt, adjusted using a hypersaline brine following standard procedures (EPA 1995). All data in Figure 39 represent the highest possible concentrations of the samples (typically >70%, but as low as 53%), as the hypersaline brine dilutes the sample when used to adjust the salinity to meet test requirements. While there is no specific acceptability criterion for the bioluminescence test, tests are typically deemed acceptable when controls exhibit light counts exceeding 5,000. This test was performed for 23 of the 29 monitoring events discussed herein. As can be seen in Figure 39, the bioluminescence test tends to have a greater amount of variability in the results than the other toxicity tests performed for the monitoring program. This has been our general overall observation with this test using the commercially available version of the QwikLite test unit. Prior work led by NIWC Pacific scientists dating back to the 1980s using a prototype test unit built and maintained by the Navy generally show lower variability (e.g. Lapota et al. 1994, Lapota et al. 1997, Rosen et al. 2008). We recommend using caution when making inferences with these data.

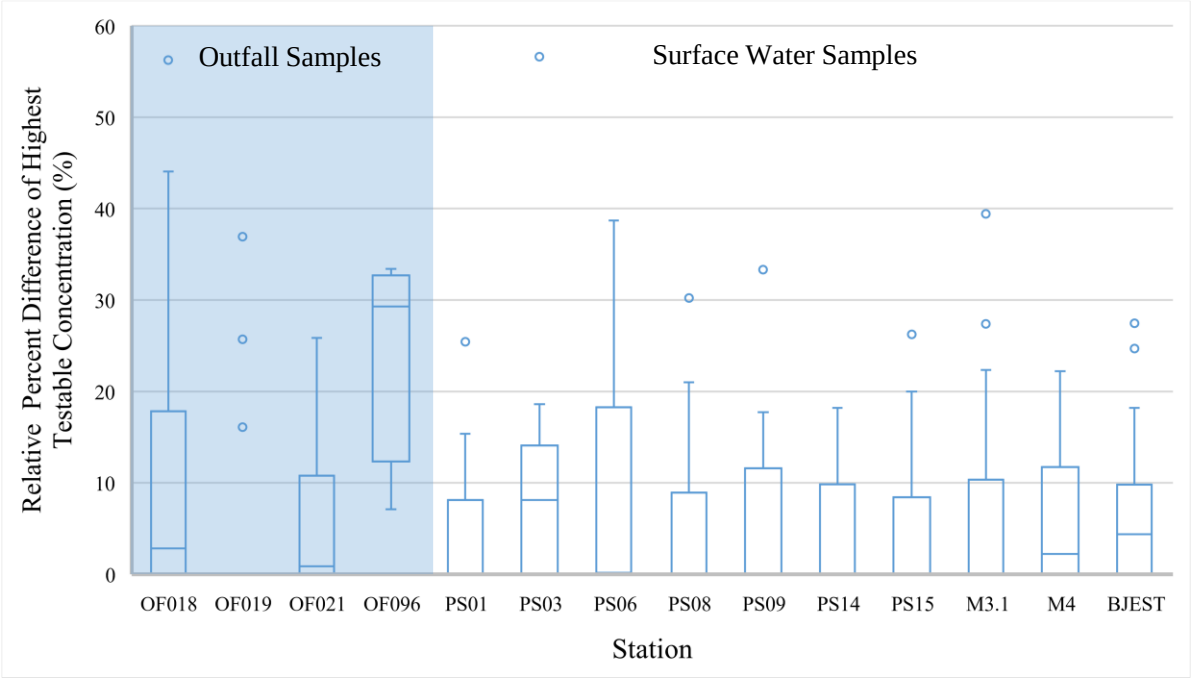

Figure 39. Box and whisker plot of results from the 24-h bioluminescent bioassay as the relative percent difference from the control of the highest testable concentration (>50% depending on the salinity of the received sample) across stations. Higher values indicate toxicity. Blue shaded areas indicate outfall samples.

In a few instances, outfall samples demonstrated significant adverse effects relative to concurrently performed controls. However, Figure 40 shows time series analyses of finer detail of the toxicity results determined for the outfalls and, where appropriate, the adjacent surface water sample. If toxicity was observed in an outfall water sample, there was no correlating toxicity in the adjacent surface water sample indicating that the discharges from the outfalls were not contributing to near-shore surface water toxicity.

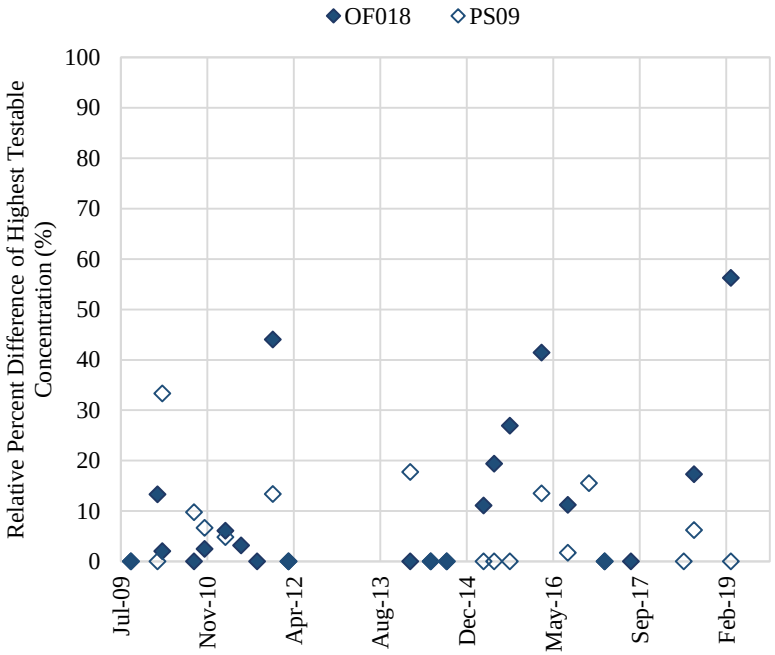

Figure 40 a-c. Time series showing the relative percent difference of highest testable concentration from the QwikLite bioluminescence bioassay for: (a) OF018 and adjacent ambient site PS09; (b) OF019 and adjacent ambient site PS06; and (c) OF021.

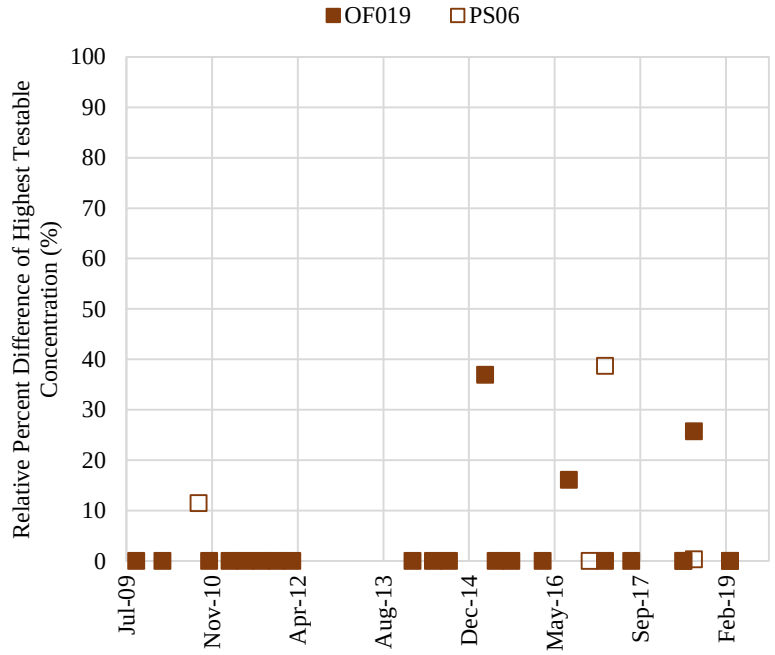

Figure 40. (Cont'd).

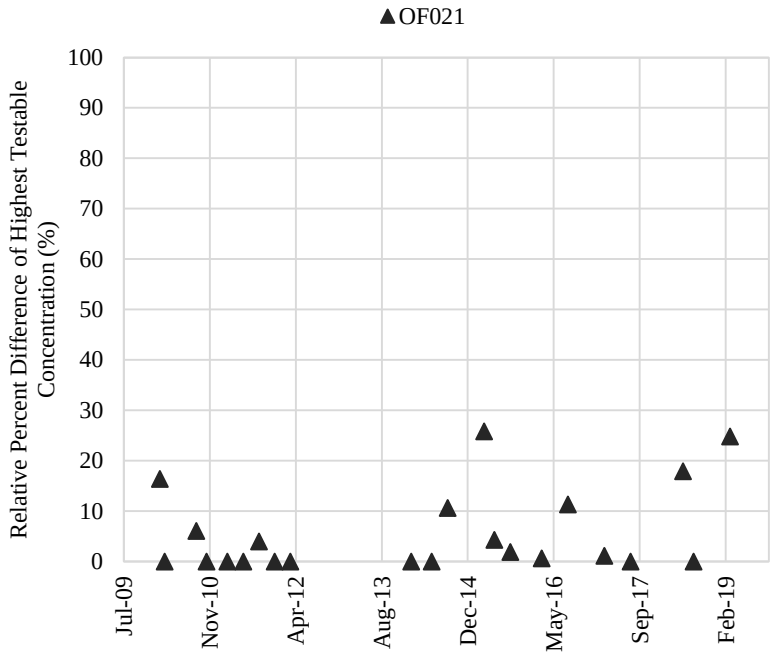

Figure 40. (Cont'd).

5.3.5 Mysid Shrimp Results

For the mysid shrimp (*Americamysis bahia*) acute survival endpoint (96-h), no adverse effects were detected at the outfall samples over the 10 years of data summarized in Figure 41. The dotted line represents a 20% decrease from the control, which has been used to represent meaningful adverse effects (toxicity), following the procedures outlined in the EPA Test for Significant Toxicity (TST) (EPA 2010). No observed effect concentrations (NOEC) and lowest observed effect concentration (LOEC) values were 100 and >100% concentrations, respectively, for all outfall samples tested. LOEC concentrations are estimated because the highest concentration tested was 100% and no toxicity was observed in the outfall samples.

Sporadic adverse effects are noted at surface water stations PS01 (August 2016), PS14 (August 2016), BJEST (August 2016), and M4 (August 2016, 2017, 2018) (Figure 41). As previously mentioned and shown in Figure 32 and Figure 33, these sampling events corresponded with significant red tide events, which included elevated densities of toxic phytoplankton, which seem likely responsible for the toxicity observed.

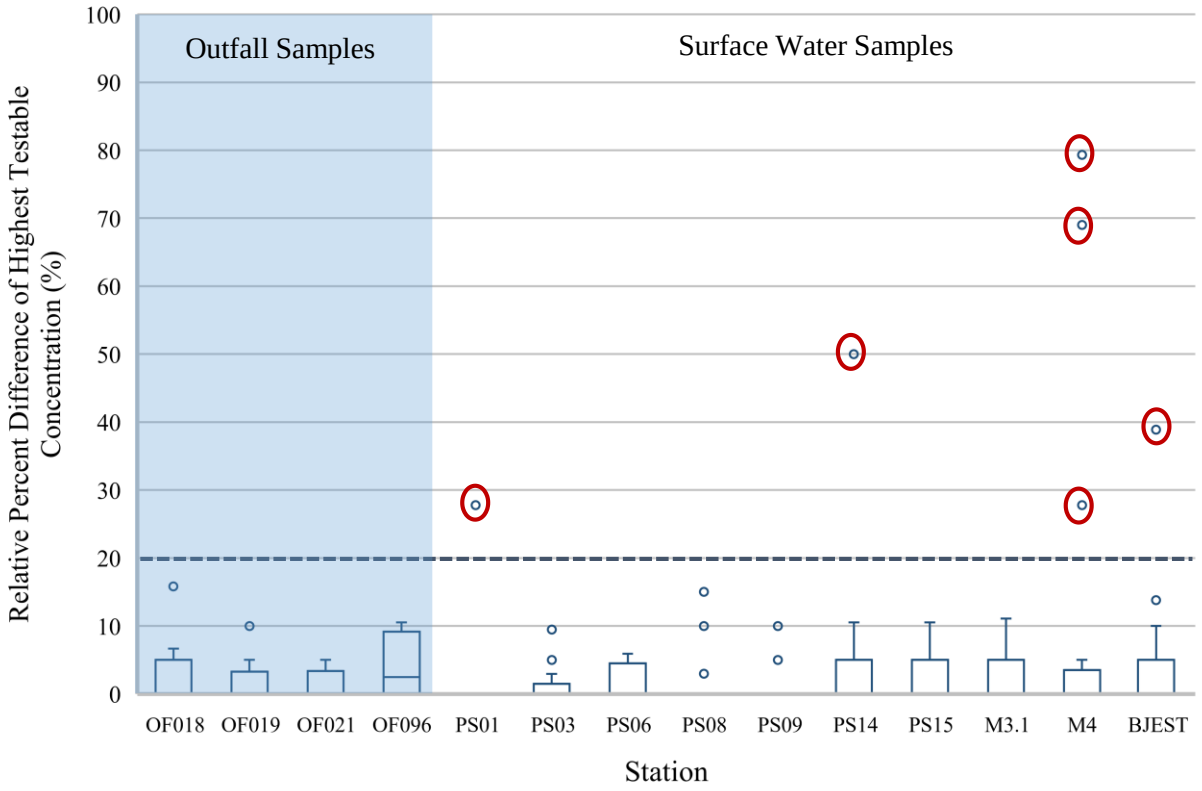

Figure 41. Box and whisker plot of results from the 96-h mysid survival bioassay as the relative percent difference from the control of the highest testable concentration (100% in this case) across stations. Higher values indicate toxicity. The dotted line represents a 20% effect. The red circle represents results from samples that were collected during red tide events. Blue shaded area indicates outfall samples.

5.3.6 Giant Kelp Results

The giant kelp spore (*Macrocystis pyrifera*) 48-h germination and growth test was performed on samples collected from September 2009 through March 2012 (AMB01 through AMB10) with tests performed at the Enthalpy Analytical Bioassay Laboratory in San Diego, CA (previously Nautilus Environmental, LLC.; ELAP Certificate No. 1802). Similar to the embryo-larval development tests with the purple urchin and Mediterranean mussel, all samples were tested at a salinity of 34±2 ppt adjusted using a hypersaline brine following standard procedures (EPA 1995). The dotted line in Figure 42 represents a 25% decrease from the control, which has been used to signify significant toxic effects, following the procedures outlined in the EPA TST (EPA 2010). The TST statistical analysis was not conducted on the giant kelp tests (the tests were conducted before NIWC began to employ TST in its reporting), but the effect level is shown for informational purposes. Through visual observation of data in Figure 42, none of the outfalls exhibited significant toxicity at any point over the 10 monitoring efforts conducted. One surface water sample, PS01, was above the 25% effect threshold for the kelp spore growth endpoint, however, the toxicity observed was attributed to the red tide event (with microscopic confirmation for that sample) that was occurring at the time of sample collection (AMB01).

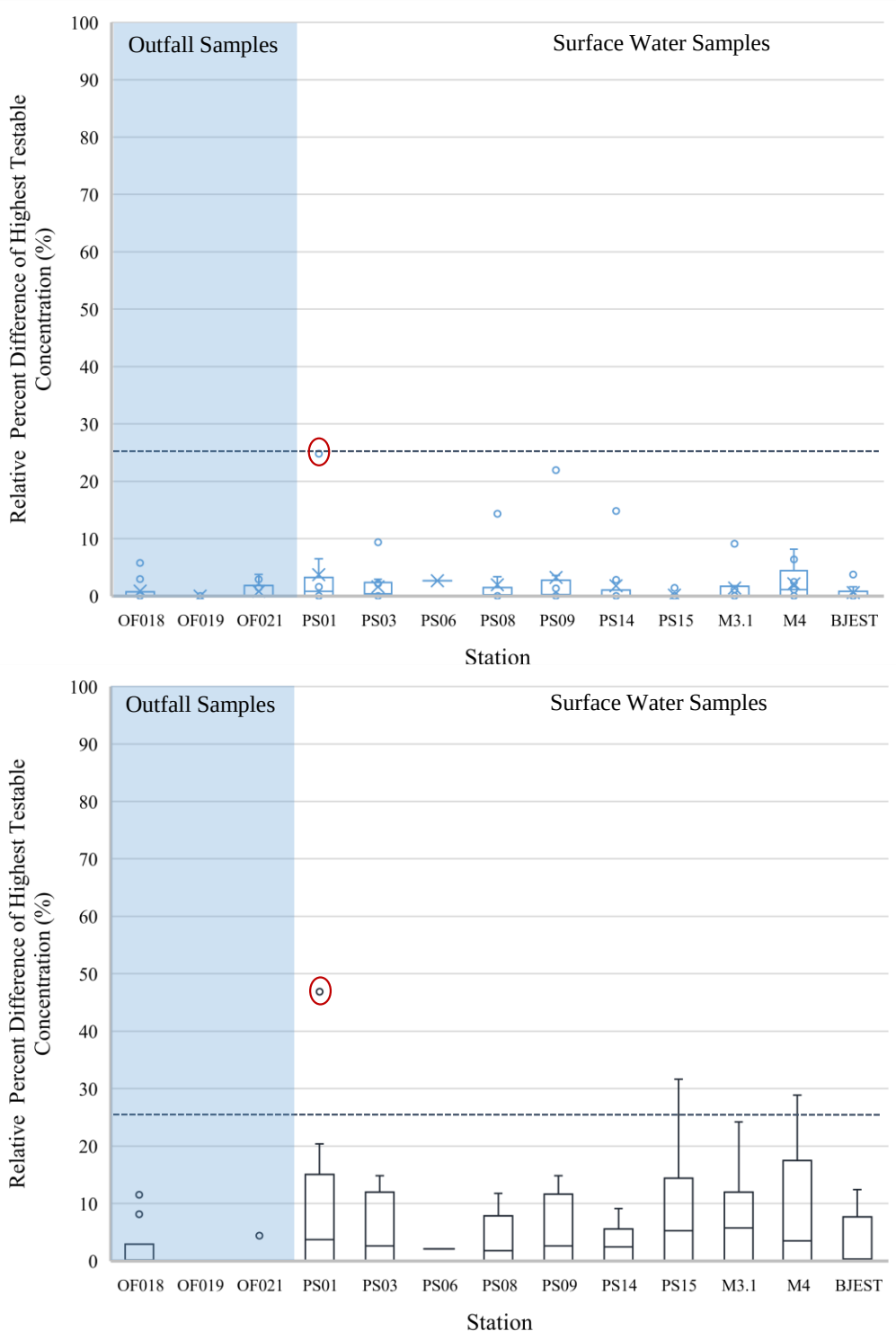

Figure 42. Box and whisker plot of results from the 48-h giant kelp spore germination (top) and growth survival (bottom) bioassay as the relative percent difference from the control of the highest testable concentration (>50% depending on the salinity of the received sample) across stations. Higher values indicate toxicity. The dotted line represents a 25% effect. The red circle represents results from samples that were collected during red tide events. Blue shaded area indicates outfall samples.

6.0 References

Angel BM, Simpson SL, Chariton AA, Stauber JL, Jolley DF. 2015. Time averaged copper concentrations from continuous exposures predicts pulsed exposure toxicity to the marine diatom, Phaeodactylum tricornutum: Importance of uptake and elimination. Aquat Toxicol 164:1–9.

APHA (American Public Health Association. Inc.). (1998). Standard methods for the examination of water and wastewater. Washington, D.C.

American Society for Testing and Materials (ASTM). 1997d. Standard guide for conducting toxicity tests with bioluminescent dinoflagellates, Method E 1924-97. ASTM, West Conshohocken, PA.

Battelle. 2003. SOP MSL-I-025-04, Methods of Sample Pre-concentration: Iron and Palladium/APDC Co-precipitation and Borohydride (Fe/Pd) Reductive Precipitation for Trace Metals Analysis in Water. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2009. SOP MSL-I-030-03, Determination of Metals in Aqueous and Digestate Samples by Hydride Generation Atomic Absorption (HGAA) with Flow Injection (FIAS). Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2011. SOP MSL-I-013-13, Total Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF). Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2012. SOP MSL-I-041-00, Total Suspended Solids Measures. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2013. SOP MSL-A-002-05, Sample Chain-of-Custody. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2014. SOP MSL-W-011, Determination of Total and Dissolved Organic Carbon in Seawater by high Temperature Catalytic Oxidation. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2016. SOP MSL-I-022-16, Determination of Elements in Aqueous and Digestate Samples by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2016b. SOP MSL-A-001-10, Sample Login Procedures. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2020a. SOP MSL-D-003-05, Archiving Documented Information. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2020b. SOP MSL-D-004-07, Data Reporting/Reduction and Information Backup/Archiving. Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2020c. SOP MSL-I-042-03, Automated Analysis of Total Mercury by Cold Vapor Atomic Fluorescence (CVAF). Marine Sciences Laboratory, Sequim, Washington.

Belzunce-Segarra J.M., Montero N., Rodríguez J.G., Menchaca I., Franco J., Larreta J., Amouroux I., Bersuder P., Bolam T., Caetano M.,…White B. 2019. MONITOOL: New tools for monitoring the Chemical

status in transitional and coastal waters under the Water Framework Directive. In Water Perspectives, Research, Management and Values of Water in Today's World. Dykinson. Madrid, Spain.

Burgess R.M., Driscoll K., Burton, A., Gschwend, P.M., Ghosh, U., Reible, D., Ahn, S. and Thompson, T. 2017. Laboratory, field, and analytical procedures for using passive sampling in the evaluation of contaminated sediments: User's manual. EPA/600/R-16/357.

Brandenberger J.M., Crecelius, E.C., and Johnston R.K. 2008. Draft: Contaminant Mass Balance for Sinclair and Dyes Inlets, Puget Sound, Washington. Prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility Project ENVVEST Bremerton, Washington under Contract DE-AC06-76RLO 1830, Pacific Northwest National Laboratory, Richland, Washington.

Brandenberger J.M., G.A. Gill, R.K. Johnston, J. Guerrero, J. Leather, G.H. Rosen, B. Beckwith, and J. Young. 2011. Sampling and Analysis Plan: Sediment Quality Verification Study and Baseline for Process Improvement for Puget Sound Naval Shipyard & Intermediate Maintenance Facility, Bremerton, WA. PNNL-29979, drafted for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Brandenberger J.M., D. Metallo, B. Rupert, R.K. Johnston, C. Gebhart, and J.E. Strivens. 2018. Non-Dry Dock Stormwater Monitoring Report for Puget Sound Naval Shipyard, Bremerton, Washington 2010-2013. PNNL-27900. Richland, WA: Pacific Northwest National Laboratory.

Cardwell, RD, Olsen S, Carr MI, Sanborn EW, 1979. Causes of oyster larvae mortality in South Puget Sound. NOAA Technical Memorandum ERL MESA-39. Marine Ecosystems Analysis Program, Boulder, CO. April 1979. P. 73.

Colvin M, Kowal K, Hayman N, Rosen G, Stransky C, VanVoorhis J, Carlson S. In prep. Refinement of Pulsed Exposure Toxicity Testing Methodology for Episodic Discharges.

Conn KE, Paulson AJ, Dinicola RS, DeWild JF. 2018. Tidal flushing of mercury from the Bremerton Naval Complex through the PSNS015 stormwater drain system to Sinclair Inlet, Kitsap County, Washington, 2011-12. Tacoma (WA): U.S. Geological Survey. Report No.: 2018-5087.

Crecelius E.A., R.K. Johnston, J. Leather, J. Guerrero, M.C. Miller, and J.M. Brandenberger. 2003. Contaminant Mass Balance for Sinclair and Dyes Inlets, Puget Sound, WA. In 2003 Georgia Basin/Puget Sound Research Conference Proceedings, Vancouver, BC, March 31 - April 3, 2003, edited by TW Droscher and DA Fraser. Olympia, Washington:Puget Sound Action Team. PNNL-SA-38523.

Davison W, ed. 2016. Diffusive Gradients in Thin-films for Environmental Measurements. Cambridge University Press, Cambridge, UK.

Dunn RJK, Teasdale PR, Warnken J, Jordan MA, Arthur JM. 2007. Evaluation of the in situ, time-integrated DGT technique by monitoring changes in heavy metal concentrations in estuarine waters. Environmental Pollution, 148(1), 213-220.

Eaton A.D., Clesceri L.S., Rice E.W., Greenberg A.E., Franson M.H. 2005. Total suspended solids dried at 103-105 C. Standard methods for the examination of water and wastewater, American Public Health Association. Inc., Washington. DC.

Ecology (Washington State Department of). 2016. Boatyard General Permit. Olympia, WA.

Ecology (Washington State Department of). 2019. Vessel Deconstruction General Permit. Olympia, WA.

EPA (U.S. Environmental Protection Agency). 1978. Method 365.3, Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Two Reagent). Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1983. US EPA. (1983). Method 365.4: Phosphorous, total (Colorimetric, automated, block digester AA II). Washington, D.C.

EPA (U.S. Environmental Protection Agency). (1986). Method 270.3 (Atomic Absorption, Gaseous Hydride). EPA 600/4-79-020. Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1991. Technical Support Document for Water Quality-Based Toxics Control. Office of Water, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1994. Interim guidance on determination and use of water-effect ratios for metals. EPA-823-B-94-001. Office of Water, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA/600/R-95/136.

EPA (U.S. Environmental Protection Agency). 1996a. Method 1669: Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels. Office of Water, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1996b. Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma – Mass Spectrometry. Office of Water, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1996c. The Metals Translator: Guidance for Calculating A Total Recoverable Permit Limit from a Dissolved Criterion. Office of Water, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1997. Method 1640: Determination of Trace Elements in Water by Pre-concentration and Inductively Coupled Plasma-Mass Spectrometry. Office of Water and Office of Science and Technology. Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1999. Method 1664 revision A: N-hexane extractable material (HEM; oil and grease) and silica gel treated N-hexane extractable material (SGT-HEM; non-polar material) by extraction and gravimetry. Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2000. Guidance for the Data Quality Objectives Process—Final. EPA QA/G-4. August 2000. Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2002. Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2002a. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. Fifth Edition. United States Environmental Protection Agency Office of Water, Washington D.C. EPA-821-R-02-012.

EPA (U.S. Environmental Protection Agency). 2008a. Draft Working NPDES Permit for the Puget Sound Naval Shipyard. Region 10, Olympia, Washington.

EPA (U.S. Environmental Protection Agency). 2008b. Draft Working NPDES Fact Sheet for Puget Sound Naval Shipyard. Region 10, Olympia, Washington.

EPA (U.S. Environmental Protection Agency). 2010. National Pollutant Discharge Elimination System Test of Significant Toxicity Implementation Document. Unites States Environmental Protection Agency, Office of Wastewater Management, EPA 833-R-10-003, June 2010.

EPA (U.S. Environmental Protection Agency). 2016. Draft aquatic life ambient estuarine/marine water quality criteria for copper. EPA 822-P-16-001. Office of Water, Washington, DC.

Garmo Ø. A., Røyset O., Steinnes E., Flaten T. P. (2003). Performance study of diffusive gradients in thin films for 55 elements. Analytical chemistry, 75(14), 3573-3580.

Hobbs W., McCall. M., Lanksbury J. 2018. Copper, Zinc, and Lead Concentrations at Five Puget Sound Marinas. Report, January 2018, prepared by Washington State Department of Ecology, Olympia, Washington.

Jabloner et al. 2009. All Known, Available, and Reasonable Methods of Treatment (AKART) Study for Puget Sound Naval Shipyard & IMF. Report prepared by Naval Facilities Engineering Command Northwest, Bremerton, Washington.

Johnston R.K. and Wang P.F. 2004. A Partnership for Modeling the Marine Environment of Puget Sound, Washington – Puget Sound Naval Shipyard Report. Progress Report for the National Ocean Partnership Program (NOPP), Office of Naval Research (ONR), Award Number: N00014-02-1-0502, Report date: Sept. 30, 2004.

Johnston R.K., G.H. Rosen, J.M. Brandenberger, V.S. Whitney, J.M. Wright. 2009a. Sampling and Analysis Plan for Ambient Monitoring and Toxicity Testing for Sinclair and Dyes Inlets, Puget Sound, Washington. U.S. Navy Project ENVVEST, Bremerton, Washington.

Johnston R.K., Wang P.F., Loy E.C., Blake A.C., Richter K.E., Brand M.C., Skahill B.E., May C.W., Cullinan V., Choi W., Whitney V.S., Leisle D.E., Beckwith B. 2009b. An Integrated Watershed and Receiving Water Model for Fecal Coliform Fate and Transport in Sinclair and Dyes Inlets, Puget Sound, WA. Technical Report 1977, Dec. 2, 2009, Space and Naval Warfare Systems Center, San Diego, http://mesodat.org/Public/TR1977/

Johnston R.K., Rosen G.H., Colvin M., Strivens J.E., Schlafer N., Brandenberger J.M., Aylward M., Caswell P. 2018a. Sampling and analysis plan for ambient monitoring and toxicity testing for Sinclair and Dyes Inlets, Puget Sound, Washington: water year 2018 update. Bremerton (WA): Puget Sound Naval Shipyard & Intermediate Facility. Prepared for project ENVVEST.

Johnston R.K., Aylward M., Casswell P., Hobgood C., Bunch D., and Brock B. 2018b. Fecal Coliform Monitoring, Assessment and Control Quality Assurance Project Plan: water year 2018 update. Bremerton (WA): Puget Sound Naval Shipyard & Intermediate Facility. Prepared for project ENVVEST.

Johnston R.K., Brandenberger J., Guerrero J., Rosen G., and Colvin M. 2019. Sediment Quality Verification Study and Baseline for Process Improvement at the Puget Sound Naval Shipyard and Intermediate Maintenance Facility, Bremerton, Washington. PNNL-29156, prepared for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Katz C.N., Noble P.L., Chadwick D.B., Davidson B., Gauthier R.D. 2004. Sinclair Inlet Water Quality Assessment: Water Quality Surveys Conducted September 1997, March 1998, and July 1998. Prepared for Puget Sound Naval Shipyard Project ENVVEST. Space and Naval Warfare Systems Center, San Diego, California, January 2004. http://www.ecy.wa.gov/programs/wq/tmdl/sinclair%2Ddyes%5Finlets/sinclair%5Fcd/Reports/ECOS_Survey_Rpt.htm

Kohn NP, Miller M, Brandenberger J, Johnston RK. 2004. Metals verification study for Sinclair and Dyes Inlet, Washington. Richland, WA: Prepared by Pacific Northwest National Laboratory for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST Report No.: PNNL-14872.

Kohn NP, Niewolny LA, Brandenberger JM, Johnston RK. 2006. Organics verification study for Sinclair and Dyes Inlets, Washington. Richland, WA: Prepared by: Pacific Northwest National Laboratory Prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility Project ENVVEST Bremerton, Washington under Contract DE-AC06-76RLO 1830-RS Report No.: PNNL-16070.

Kohn NP, Brandenberger JM, Johnston RK. 2008. Metals and PAH verification study—2008. Richland, WA: Prepared by Pacific Northwest National Laboratory for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST.

Kuo L-J., Farrell R.L., Liu Y., and Strivens J.E. 2019. LSND-AP o-DGT Trial: Screening of commercial o-DGT passive sampler for ability to quantify selected pharmaceuticals indicative of illicit aquatic discharges. PNNL-(29221), prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Lapota, D., Moskowitz, G.J., Rosenberger, D.E., Grovhoug, G.J., 1994. The use of stimulable bioluminescence from marine dinoflagellates as a means of detecting toxicity in the marine environment. In: Gorsuch, J.W., Dwyer, F.J., Ingersoll, C.G., LaPoint, T.W. (Eds.), Environmental Toxicology and Risk Assessment: 2nd Volume TP 1173, American Society for testing and Materials, Philadelphia, pp. 3–18

Lapota D, Robayo Osotrio A, Liao C, Bjorndal B, 2007. The use of bioluminescent dinoflagellates as an environmental risk assessment tool. Mar. Pollut. Bull. 54:1857-1867.

Lawrence S., Roberts M., Erickson K., Johnston R.K. 2012. Sinclair and Dyes Inlets Fecal Coliform Bacteria Total Maximum Daily Load: TMDL and Water Quality Implementation Plan. Washington State Department of Ecology, Publication number 11-10-051, Date Published April 2012, Date Revised June 2012. https://fortress.wa.gov/ecy/publications/summarypages/1110051.html

Lelong A, H Hégare, P Soudant, S Bates. 2012. *Pseudo-nitzschia* (Bacillariophyceae) species, domoic acid and amnesic shellfish poisoning: revisiting previous paradigms. Phycologi. 51(2):168-216.

May C.W. and Cullinan V.I. 2005. An Analysis of Microbial Pollution in the Sinclair-Dyes Inlet Watershed. PNNL-15373, Pacific Northwest National Laboratory (PNNL), Richland, Washington.

Noble M.A., Rosenberger K.J., Paulson A.J., Gartner A.L. 2013. Circulation exchange patterns in Sinclair Inlet, Washington (No. 2013-1117). U.S. Geological Survey.

O'Dell J.W. 1993. EPA Method 350.1 Determination of Ammonia Nitrogen by Semi-Automated Colorimetry. U.S. Environmental Protection Agency, Cincinnati, Ohio.

O'Dell, J.W. (1993b). Determination of nitrate-nitrite nitrogen by automated colorimetry. Methods for the determination of inorganic substances in environmental samples. US Environmental Protection Agency, Washington, D.C.

Paulson A.J. and Keys M.E.W. 2009. Mercury in the sediments of Sinclair Inlet, Puget Sound (1990–2007). Poster presented at the 2009 Puget Sound Georgia Basin Ecosystem Conference, Seattle, Washington, February 8–11, 2009. https://wa.water.usgs.gov/projects/sinclair/data/Paulson_Sediment-poster.pdf .

Paulson, A.J., Keys, M.E., and Scholting, K.L., 2010. Mercury in sediment, water, and biota of Sinclair Inlet, Puget Sound, Washington, 1989–2007: U.S. Geological Survey Open-File Report 2009-1285, 220 p. http://pubs.usgs.gov/of/2009/1285/

Phillips BM, Anderson BS, Hunt JW, 1998. Spatial and temporal variation in results of purple urchin (*Strongylocentrotus purpuratus*) toxicity tests with zinc. Environ. Toxicol. Chem. 17:453-459.

Phillips BM, Nicely PA, Hunt JW, Anderson BS, Tjeerdema RS, Palmer SE, Palmer FH, Puckett HM, 2003. Toxicity of cadmium-copper-nickel-zinc mixtures to larval purple sea urchins (*Strongylocentrotuts purpuratus*). Bull. Environ. Contam. Toxicol. 70:592-599.

Podger D., Toxics Cleanup Program/Aquatic Lands Cleanup Unit, Department of Ecology. 2010. Puget Sound Naval Shipyard (NPDES Permit WA-000206-2) NPDES Permit Review and Mixing Zone Request. Letter to EPA dated August 24, 2010.

Puget Sound Marine Monitoring Program; King County. Marine Life Photos. Accessed 1/30/2017. http://green2.kingcounty.gov/marine/Photo/Type/1

Puget Sound Naval Shipyard, U.S. Environmental Protection Agency, Washington State Dept of Ecology. 2000. Project ENVVEST Phase I final project agreement for Puget Sound Naval Shipyard. [cited 28 May 2020]. Available from https://archive.epa.gov/projectxl/web/pdf/fpasigned.pdf.

Rosen, G., Osorio-Robayo, A., Rivera-Duarte, I., and D. Lapota. 2008. Comparison of bioluminescent dinoflagellate (QwikLite) and bacterial (Microtox) rapid bioassays for the detection of metal and ammonia toxicity. *Archives of Environmental Contamination and. Toxicology* 54:606-611.

Rosen, G., I. Rivera-Duarte, D.B. Chadwick, A. Ryan, R.C. Santore, P.R. Paquin, 2008. Critical tissue copper residues for marine bivalve (*Mytilus galloprovincialis*) and echinoderm (*Strongylocentrotus purpuratus*) embryonic development: Conceptual, regulatory and environmental implications. *Mar. Environ. Res*. 66:327-336.

Rosen G., Rivera-Duarte I., Johnston R.K., Podegracz J. 2009. Sinclair and Dyes Inlets toxicity study: An assessment of copper bioavailability and toxicity in surface waters adjacent to the Puget Sound Naval Shipyard and Intermediate Maintenance Facility. SPAWAR/SCP-TR- 1985. Space and Naval Warfare Systems Center Pacific, San Diego, CA, USA.

Rosen G, Colvin M, Katz C, Munson-Decker J, Hayman, N. 2019. Pulsed exposure toxicity testing: Method Development and Initial Evaluation for Stormwater Compliance. Naval Information Warfare Center Pacific Technical Report #3393. https://search.dtic.mil/documents/rest/v1/download?caller=sni-user&id=/citation/TR/AD1082517.xml.

Schlueter A. 1977. Nitrate interference in total Kjeldahl nitrogen determinations and its removal by anion exchange resins. Available from the National Technical Information Service, Springfield VA 22161 as PB-267 285, Price codes: A 03 in paper copy, A 01 in microfiche. Report.

Sedar D. 2009. Control of Toxic Chemicals in Puget Sound: Identification and Evaluation of Water Column Data for Puget Sound and Its Ocean Boundary. Report, March 2008, prepared by Washington State Department of Ecology, Olympia, Washington.

Skahill B.E. and LaHatte C. 2006. Hydrological Simulation Program–Fortran Modeling of the Sinclair-Dyes Inlet Watershed for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility Environmental Investment Project–FY 2006 Report. Report to U.S. Navy Puget Sound Naval Shipyard and Intermediate Maintenance Facility Environmental Division by the U.S. Army Engineer Research and Development Center, Waterways Experiment Station, Vicksburg, Mississippi.

Skahill B.E. and LaHatte C. 2007. Hydrological Simulation Program–Fortran Modeling of the Sinclair-Dyes Inlet Watershed for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility Environmental Investment Project–FY 2007 Report. Report to the U.S. Navy Puget Sound Naval Shipyard and Intermediate Maintenance Facility Environmental Division by the U.S. Army Engineer Research and Development Center, Waterways Experiment Station, Vicksburg, Mississippi.

Sommers F, Mudrock E, Labenia J, Baldwin D, 2016. Effects of salinity on olfactory toxicity and behavioral responses of juvenile salmonids from copper. Aquat. Toxicol. 175:260-268.

Strivens J.E., G. Rosen, N.J. Schlafer, J.M. Brandenberger and R.K. Johnston. 2017. Laboratory Assessment of Diffusive Gradient Thin-Film Performance in Seawater Supported with Preliminary Field Data: Time Integrated Technique to Assess Bioavailable Trace Metals. PNNL-(Draft report provided to NESDI). Sequim, WA: Pacific Northwest National Laboratory.

Strivens J.E., R.K. Johnston, N.J. Schlafer, and J.M. Brandenberger. 2018a. ENVVEST Ambient Monitoring Program: In-Progress Summary 2009-2017. PNNL-28116. Sequim, WA: Pacific Northwest National Laboratory.

Strivens J.E., R.K. Johnston, G.H. Rosen, N.J. Schlafer, N. Hayman, J.M. Brandenberger, and R. Gauthier, et al. 2018b. Short-Term in situ Monitoring Response of Diffusive Gradients in Thin Films in Marine Waters for Pulse Capture of Cd, Cu, Ni, Pb, and Zn. Presented by J.E. Strivens at SETAC North America 39th Annual Meeting, Sacramento, California. PNNL-SA-138970.

Strivens J.E., J.M. Brandenberger, and R.K. Johnston. 2019a. Data Trend Shifts Induced by Method of Concentration for Trace Metals in Seawater: Automated Online Preconcentration vs Borohydride Reductive Coprecipitation of Nearshore Seawater Samples for Analysis of Ni, Cu, Zn, Cd, and Pb via ICP-MS. Limnology and Oceanography Methods 17, no. 4:266-276. PNNL-SA-140847. doi:10.1002/lom3.10311

Strivens J.E., R.K. Johnston, G.H. Rosen, N. Hayman, N.J. Schlafer, and J.M. Brandenberger. 2019b. Diffusive Gradient Thin-Films: Time Integrated Passive Sampling for Trace Metals in Receiving Waters of Puget Sound. 2018 Salish Sea Toxics Monitoring Review, Puget Sound Ecosystem Monitoring Program 2018. PNNL-SA-135681.

Strivens J.E., N. Hayman, R.K. Johnston, and G.H. Rosen. 2019c. Effects of Dissolved Organic Carbon on Copper Toxicity to Embryos of Mytilus galloprovincialis as Measured by Diffusive Gradient in Thin Films. Environmental Toxicology and Chemistry 38, no. 5:1029-1034. PNNL-SA-139169. doi:10.1002/etc.4404

Strivens, J.E. & Johnston R.K. 2019d. ENVVEST Mussel Watch Program In-Progress Summary 2010–2018. PNNL-29110, prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Strivens, J.E., and L-J. Kuo. 2019e. ENVVEST Mussel Watch: PBDE trends in select Sinclair Inlet stations 2010–2018. PNNL-28986, prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Strivens J.E., N. Hayman, G. Rosen, and A.N. Myers-Pigg. 2020a. Toward Validation of Toxicological Interpretation of Diffusive Gradients in Thin Films in Marine Waters Impacted by Copper. Environmental Toxicology and Chemistry 39, no. 4:873-881. PNNL-SA-150328. doi:10.1002/etc.4673

Strivens, J.E., Frew, J., Hayman, H., Rosen, G., Colvin, M., & Richardson, T. 2020b. ENVVEST Sediment Quality Confirmation Study: Sampling and Analysis Plan. PNNL-(DRAFT), prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the PNNL Marine Sciences Laboratory, Sequim, Washington.

Tammilehto A, TG Nielsen, B Krock, EF Møller, N Lundholm. 2015. Induction of domoic acid production in the toxic diatom *Pseudo-nitzschia* seriata by calanoid copepods. Aquatic Toxicology. 159: 52-61.

Tidepool Scientific Software. 2000-2012. CETIS Comprehensive Environmental Toxicity Information System Software, Version 1.9.2.8.

Trainer VL, SS Bates, NL Lundholm, AE Thessen, WP Cochlan, NG Adamns, CG Trick. 2012. *Psuedo-nitzschia* physiological ecology, phylogeny, toxicity, monitoring and impacts on ecosystem health. Harmful Algae. 14:271-300.

URS Group. 2008. Bremerton Naval Complex 5-yr Review. Prepared for Naval Facilities Engineering Command, Engineering Field Activity NW, Bangor, Washington.

U.S. Navy. 2012a. Third Five-Year Review, Bremerton Naval Complex, Bremerton, Washington. https://semspub.epa.gov/work/10/676795.pdf

U.S. Navy. 2012b. All Known, Available, and Reasonable Methods of Treatment Study for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Bremerton, Washington. Prepared by Naval Facilities Engineering Command Northwest and Puget Sound Naval Shipyard & IMF.

U.S. Navy. 2017. Fourth Five-Year Review Puget Sound Naval Shipyard (PSNS) Complex Superfund Site.Bangor, WA: Naval Facilities Engineering Command Northwest.

WAC 173-201A-240 (Washington Administrative Code). 2006. Chapter 173-201A, Water Quality Standards for Surface Waters of the State of Washington, Section 240, Toxic substances. Department of Ecology, Olympia, Washington.

Wang, P. F. and K. Richter (1999). A hydrodynamic modeling study using CH3D for Sinclair Inlet. San Diego, CA, SPAWAR Systems Center.

Wang P.F., Johnston R.K., Halkola H., Richter R.E., Davidson B. 2005. A Modeling Study of Combined Sewer Overflows in the Port Washington Narrows and Fecal Coliform Transport in Sinclair and Dyes Inlets, Washington. Final report prepared for Puget Sound Naval Shipyard & Intermediate Maintenance Facility

Project ENVVEST, prepared by the Space and Naval Warfare Systems Center, San Diego for, Final Report. http://www.ecy.wa.gov/biblio/0503042appf.html

Wang P.F., Choi W., Johnston R.K. 2011. A Modeling Study of Copper Loading in Sinclair and Dyes Inlets, Washington. Prepared for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST, prepared by the Space and Naval Warfare Systems Center Pacific, San Diego, California.

Zhang H, Davison W. 1995. Performance characteristics of diffusion gradients in thin-films for the in situ measurement of trace metals in aqueous solution. Anal Chem 67:3391–3400.

Appendix A – Ambient Monitoring QAPP Summary

Table A.1. Definitions, requirements, and frequency for typical quality control (QC) samples.

QC Sample	Definition	Frequency
Method or Procedural Blank (MB)	A combination of solvents, surrogates, and all reagents used during sample processing, processed concurrently with the field samples. Monitors purity of reagents and laboratory contamination.	1/sample batch of 20 A processing batch MB must be analyzed with each sequence.
Standard Reference Material (SRM)	An external reference sample that contains a certified level of target analytes; serves as a monitor of accuracy. Extracted and analyzed with samples of a like matrix (not available for all analytes).	1/batch of 20
Matrix Spike (MS)	A field sample spiked with the analytes of interest is processed concurrently with the field samples; monitors effectiveness of method on sample matrix; performed in duplicate.	1/sample batch of 20
Duplicate Sample	Second aliquot of a field sample processed and analyzed to monitor precision; each sample set should contain a duplicate.	1/sample batch of 20
Recovery Internal Standards (RIS)	All field and QC samples are spiked with recovery internal standards just prior to analysis; used to quantify surrogates to monitor extraction efficiency on a per sample basis.	Each sample analyzed for organic compounds

Table A.2**. Measurement quality criteria.**

QC Parameter	Acceptance Criteria	Corrective Action
Method Blank (MB)	MB<RL If MB>RL; sample values ≤10X MB, then perform corrective action	Perform corrective action re-process (extract, digest) sample batch. If batch cannot be re-processed, notify client and flag data.
Standard Reference Material (SRM)	Determined vs certified range. Analyte concentration must be 10xMDL to be used for DQO. Metals: ≤20% PD Method criteria for all other parameters	Review data to assess impact of matrix. Reanalyze sample and/or document corrective action. If other QC data are acceptable then flag associated data if sample is not reanalyzed.
Matrix Spike (MS)/MS Duplicate (MSD)	Metals: 70–130% recovery Method criteria for all other parameters	Review data to assess impact of matrix. If other QC data are acceptable and no spiking error occurred, then flag associated data. If QC data are not affected by matrix failure or spiking errors occurred, then re-process MS. If not possible, then notify client and flag associated data.
Laboratory Control Sample (LCS)	Metals: <30% RPD Method criteria for all other parameters	Perform corrective action. Reanalyze and/or re-process sample batch. If batch cannot be re-processed: notify client, flag data, discuss impact in report narrative.
Laboratory Duplicates (R2)	Metals: <30% RPD Method criteria for all other parameters	Review data to assess impact of matrix. If other QC data are acceptable, then flag associated data. If QC data are not affected by matrix failure, then re-process the duplicate. If not possible, then notify client and flag associated data.

Table A.3. Sample containers, sample size, preservative requirements, and holding times for analytical samples.

Parameter	Method	Sample Preservation	Holding Time
Total Suspended Solids (TSS)	MSL-I-041	4ºC	7 days
Total Organic Carbon (TOC)	MSL-W-011	-20°C, or HCl to pH <2	28 days or 7 days
Dissolved Organic Carbon (DOC)	MSL-W-011	-20°C, or HCl to pH <2	28 days or 7 days
Total/Dissolved Hg	MSL-I-013	HNO_3 pH<2.0	90 days
Total/Dissolved Al	MSl-I-022	HNO_3 pH<2.0	6 months
Total/Dissolved As	MSl-I-030	HNO_3 pH<2.0	6 months
Total/Dissolved Cd	MSl-I-022	HNO_3 pH<2.0	6 months
Total/Dissolved Cr	MSl-I-022	HNO_3 pH<2.0	6 months
Total//Dissolved Cu	MSl-I-022	HNO_3 pH<2.0	6 months
Total/Dissolved Pb	MSl-I-022	HNO_3 pH<2.0	6 months
Total/Dissolved Ag	MSl-I-022	HNO_3 pH<2.0	6 months
Total/Dissolved Zn	MSl-I-022	HNO_3 pH<2.0	6 months

Table A.4. Purple Sea Urchin Embryo-Larval Development Toxicity Test Specifications.

Test period	96hr
Test organism	*Strongylocentrotus purpuratus* (purple sea urchin)
Test organism source	Field collected off of Point Loma, San Diego, CA
Test endpoints	96 hr Embryo-Larval Development Success (Proportion Normal)
Test solution renewal	None
Feeding	None
Test chamber size/type	30 mL scintillation vial
Test solution volume	10 mL
Test temperature	15 ± 1 °C
Test salinity	34 ± 2 ppt
Light quality	Ambient laboratory illumination
Light intensity	10-20 µE/m^2/s (Ambient laboratory levels)
Photoperiod	16 hr light/ 8 hr dark
Aeration	None
No. of organisms per chamber	Approximately 250 embryos
No. of replicates	5
Control/dilution water	Filtered (0.45 µm) natural seawater collected from near the mouth of San Diego Bay at NIWC Pacific Laboratory
Additional control	Hypersaline brine
Sample manipulation	Hypersaline brine was used to increase the salinity of all samples to 34±2 ppt
Test concentrations (% of sample)	Effluent Samples: 100*, 50, 25, 12.5 & 6.25%, plus laboratory and brine controls Ambient Samples: 100*%, plus laboratory and brine controls
Test acceptability criteria	≥ 80% normal development in surviving controls; < 25% Minimum Significant Difference (MSD)
Reference toxicant	Copper sulfate
Test protocol	EPA 600/R-95/136 (EPA 1995)

* - Highest concentration possible to test likely <100% effluent, due to the addition of hypersaline brine

Table A.5. Mediterranean mussel Embryo-Larval Development Toxicity Test Specifications.

Test period	48hr
Test organism	*Mytilus galloprovincialis* (Mediterranean mussel)
Test organism source	Field collected in Mission Bay, San Diego, CA or Commercial supplier (varies on seasonal availability)
Test endpoints	48 hr Embryo-Larval Development Success (Proportion Normal) 48 hr Embryo-Larval Combined Development Rate (% Normal Alive)
Test solution renewal	None
Feeding	None
Test chamber size/type	30 mL scintillation vial
Test solution volume	10 mL
Test temperature	15 ± 1 °C
Test salinity	34 ± 2 ppt
Light quality	Ambient laboratory illumination
Light intensity	10-20 µE/m^2/s (Ambient laboratory levels)
Photoperiod	16 hr light/ 8 hr dark
Aeration	None
No. of organisms per chamber	Approximately 250 embryos
No. of replicates	5
Control/dilution water	Filtered (0.45 µm) natural seawater collected from near the mouth of San Diego Bay at NIWC Pacific Laboratory
Additional control	Hypersaline brine
Sample manipulation	Hypersaline brine was used to increase the salinity of all samples to 34 ± 2 ppt
Test concentrations (% of sample)	Effluent Samples: 100*, 50, 25, 12.5 & 6.25%, plus laboratory and brine controls Ambient Samples: 100*%, plus laboratory and brine controls
Test acceptability criteria	≥ 50% survival in controls; ≥ 90% normal shell development in surviving controls; < 25% Minimum Significant Difference (MSD)
Reference toxicant	Copper sulfate
Test protocol	EPA 600/R-95/136 (EPA 1995)

* - Highest concentration possible to test likely <100% effluent, due to the addition of hypersaline brine

Table A.6. Dinoflagellate Bioluminescent Toxicity Test Specifications.

Test period	24hr
Test organism	*Pyrocystis lunula* (bioluminescent dinoflagellate)
Test organism source	In-house culture
Test endpoints	24 hr bioluminescence
Test solution renewal	None
Feeding	None
Test chamber size/type	5 mL plastic cuvette
Test solution volume	2.0 mL sample and 0.5mL dinoflagellate culture (2.5mL total)
Test temperature	19 ± 2 °C
Test salinity	34 ± 2 ppt
Light quality	Ambient laboratory illumination
Light intensity	10-20 µE/m^2/s (Ambient laboratory levels)
Photoperiod	12 hr light/ 12 hr dark
Aeration	None
No. of organisms per chamber	Approximately 3,000 cells (0.5mL from stock culture density 6,000 cells/ml ± 1,000 cells)
No. of replicates	6
Control/dilution water	Filtered (0.45 µm) natural seawater collected from near the mouth of San Diego Bay at NIWC Pacific Laboratory
Additional control	Hypersaline brine
Sample manipulation	Hypersaline brine was used to increase the salinity of all samples to 34 ± 2 ppt
Test concentrations (% of sample)	Effluent Samples: 100*, 50, 25, & 12.5%, plus laboratory and brine controls Ambient Samples: 100*%, plus laboratory and brine controls
Test acceptability criteria	No standard; however, luminescence generally exceeds 5,000 light counts in controls with QwikLite 200 test unit
Reference toxicant	Copper sulfate
Test protocol	ASTM E1924-97 (ASTM 2004)

* - Highest concentration possible to test likely <100% effluent, due to the addition of hypersaline brine

Table A.7. Mysid Shrimp Acute Survival Toxicity Test Specifications.

Test period	96hr
Test organism	*Americamysis bahia* (mysid shrimp)
Test organism source	Aquatic Research Organisms, Hampton, NH
Test endpoints	96 hr survival
Test solution renewal	Once at 48 hr
Feeding	*Artemia*, twice a day
Test chamber size/type	400 mL plastic cup
Test solution volume	200 mL
Test temperature	20 ± 1 °C
Test salinity	30 ± 2 ppt
Light quality	Ambient laboratory illumination
Light intensity	10-20 µE/m^2/s (Ambient laboratory levels)
Photoperiod	16 hr light/ 8 hr dark
Aeration	None
No. of organisms per chamber	5
No. of replicates	6
Control/dilution water	Artificial seawater - DI water salted to 30 ppt with synthetic sea salts (Bioassay Grade Crystal Sea Marine Mix®)
Additional control	Filtered (0.45 µm) natural seawater collected from near the mouth of San Diego Bay at NIWC Pacific Laboratory diluted to 30 ppt with DI water
Sample manipulation	Effluent Samples: Sample salinity was increased to 30 ± 2 ppt by the addition of synthetic sea salts (Bioassay Grade Crystal Sea Marine Mix®)
Test concentrations (% of sample)	Effluent: 100%, plus laboratory and salt controls Ambient: 100%, plus laboratory and salt controls
Test acceptability criteria	≥ 90% survival in controls
Reference toxicant	Copper sulfate
Test protocol	EPA 821/R-02/012 (EPA 2002)

Table A.8. Giant Kelp Germination and Growth Toxicity Test Specifications.

Test period	48hr
Test organism	*Macrocystis pyrifera* (giant kelp)
Test organism source	Field collected
Test endpoints	48-hour spore germination and germ-tube length (growth)
Test solution renewal	None
Feeding	None
Test chamber size/type	100 mL petri dish
Test solution volume	30 mL
Test temperature	15 ± 1 °C
Test salinity	34 ± 2 ppt
Light quality	Cool white fluorescent lights
Light intensity	200 ± 40 foot candles
Photoperiod	16 hr light/ 8 hr dark
Aeration	None
No. of organisms per chamber	225,000 spores
No. of replicates	5
Control/dilution water	Natural laboratory seawater (Source: Scripps Institution of Oceanography intake)
Additional control	Hypersaline brine
Sample manipulation	Hypersaline brine was used to increase the salinity of all samples to 34 ± 2 ppt
Test concentrations (% of sample)	Effluent Samples: 100*, 50, 25, & 12.5%, plus laboratory and brine controls Ambient Samples: 100*%, plus laboratory and brine controls
Test acceptability criteria	≥ 70% germination, ≥ 10 µm growth, < 20% MSD for both endpoints, and <35 µg/L growth NOEC in the reference toxicant test
Reference toxicant	Copper chloride
Test protocol	EPA 600/R-95/136, 1995 West Coast Manual

* - Highest concentration possible to test likely <100% effluent, due to the addition of hypersaline brine

Appendix B – Supporting Data

Table B.1. Summary statistics of analytical accuracy and precision for analytes of interest in seawater.

	Cu	Pb	Zn	Hg
LCS Percent Recovery (%)				
n	167	165	162	334
Mean	96%	100%	95%	101%
Minimum	78%	85%	72%	88%
Maximum	114%	111%	114%	119%
STD	8%	6%	11%	4%
MS Percent Recovery (%)[(a)]				
n	339	340	323	601
Mean	97%	100%	95%	103%
Minimum	71%	41%	15%	75%
Maximum	119%	115%	175%	129%
STD	9%	8%	15%	5%
Laboratory Duplicates Relative Percent Difference (%)				
n	178	178	175	172
Mean	3%	4%	5%	7%
Minimum	0%	0%	0%	0%
Maximum	24%	76%	139%	58%
STD	3%	7%	12%	9%

(a) The appropriate fortification level to represent potential matrix interferences is 2–5x the native sample concentration. To assess matrix interference, the target fortification levels should be no greater than 10 times the native concentrations. When MS did not fall between 2–10x the native concentration data were not included in statistics.

Table B.2. Summary statistics of analytical accuracy and precision for ancillary trace metals in seawater.

	Ag	Al	As	Cd	Cr	Ni
LCS Percent Recovery (%)						
n	66	126	35	159	152	137
Mean	90%	101%	98%	98%	96%	99%
Minimum	80%	40%	90%	83%	81%	76%
Maximum	102%	272%	103%	117%	109%	119%
STD	4%	28%	3%	8%	5%	10%
MS Percent Recovery (%)[(a)]						
n	132	238	59	316	317	285
Mean	91%	101%	98%	97%	97%	97%
Minimum	81%	44%	89%	35%	75%	71%
Maximum	102%	259%	106%	118%	115%	129%
STD	4%	22%	4%	9%	6%	9%
Laboratory Duplicates Relative Percent Difference (%)						

	Ag	Al	As	Cd	Cr	Ni
n	8	140	36	172	162	145
Mean	12%	5%	2%	3%	7%	4%
Minimum	1%	0%	0%	0%	0%	0%
Maximum	30%	60%	11%	24%	131%	108%
STD	9%	7%	2%	4%	11%	10%

(a) The appropriate fortification level to represent potential matrix interferences is 2–5x the native sample concentration. To assess matrix interference, the target fortification levels should be no greater than 10 times the native concentrations. When MS did not fall between 2–10x the native concentration data were not included in statistics.

Table B.3. Summary statistics of analytical accuracy and precision for organic carbon and suspended solids.

	Salinity	TOC/DOC Method 1[(a)]	TOC/DOC Method 2[(b)]	TSS
Reference Material Percent Recovery (%)[(c, d, e)]				
n	182	69	357	180
Mean	99%	98%	96%	97%
Minimum	94%	92%	80%	82%
Maximum	101%	105%	131%	116%
STD	1%	3%	6%	5%
MS Percent Recovery (%)				
n	NA	55	NA	NA
Mean	NA	93%	NA	NA
Minimum	NA	62%	NA	NA
Maximum	NA	102%	NA	NA
STD	NA	8%	NA	NA
Laboratory Duplicates Relative Percent Difference (%)				
n	29	246	182	72
Mean	0%	8%	2%	13%
Minimum	0%	1%	0%	0%
Maximum	1%	62%	10%	128%
STD	0%	8%	2%	17%

(a) Persulfate-Ultraviolet or Heated-Persulfate Oxidation SM 5310 C
(b) MSL-W-011 Determination of Total and Dissolved Organic Carbon in Seawater by High Temperature Catalytic Oxidation
(c) Copenhagen standard
(d) MSL-W-011 Ref is DSR purchased from RSMAS Hansell Laboratory (http://yyy.rsmas.miami.edu/groups/biogeochem/CRM.html)
(e) Celite Standard, Aqua Solutions, Deer Park, TX.

Table B.4. Summary statistics of analytical accuracy and precision for nutrients.

	AN	NNN	TKN	TP	HEM
LCS Percent Recovery (%)					
n	97	100	37	97	56
Mean	98%	99%	103%	103%	91%
Minimum	87%	94%	86%	90%	79%
Maximum	110%	107%	120%	113%	100%
STD	5%	3%	7%	5%	5%
MS Percent Recovery (%)					
n	147	202	55	159	NA
Mean	101%	101%	103%	78%	NA
Minimum	85%	92%	61%	54%	NA
Maximum	113%	110%	161%	129%	NA
STD	5%	4%	17%	13%	NA
Laboratory Duplicates Relative Percent Difference (%)					
n	78	92	21	78	NA
Mean	11%	2%	7%	5%	NA
Minimum	1%	0%	1%	1%	NA
Maximum	80%	18%	17%	74%	NA
STD	15%	3%	5%	10%	NA

Table B.5. Replication of field duplicate samples as relative percent difference.

			Ag	Al	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Trace Metals	Total	Mean	6%	16%	4%	7%	17%	11%	16%	20%	15%	17%
		Median	0%	11%	2%	3%	12%	6%	11%	11%	11%	9%
		Min	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
		Max	76%	85%	29%	65%	110%	87%	63%	120%	66%	167%
		1st Quartile	0%	5%	1%	1%	5%	3%	4%	5%	4%	3%
		3rd Quartile	0%	22%	4%	6%	22%	14%	22%	28%	20%	23%
		n	42	99	33	99	99	102	102	86	102	102
	Dissolved	Mean	2%	13%	7%	6%	18%	12%	15%	18%	22%	19%
		Median	0%	5%	5%	3%	13%	6%	10%	8%	12%	12%
		Min	0%	0%	2%	0%	0%	0%	0%	0%	0%	0%
		Max	77%	89%	15%	53%	86%	114%	69%	101%	164%	169%
		1st Quartile	0%	0%	4%	1%	7%	2%	5%	4%	6%	6%
		3rd Quartile	0%	18%	10%	7%	28%	15%	18%	23%	23%	26%
		n	42	76	3	100	100	103	103	86	102	102

		SAL	TOC	DOC	TSS	AN	NNN	TKN	PT
Ancillary Parameters	Mean	1%	5%	7%	16%	25%	4%	30%	13%
	Median	0%	2%	4%	13%	14%	1%	33%	3%
	Min	0%	0%	0%	0%	0%	0%	0%	0%
	Max	22%	24%	79%	94%	125%	55%	69%	179%
	1st Quartile	0%	1%	2%	6%	6%	0%	17%	2%
	3rd Quartile	1%	6%	8%	21%	33%	3%	40%	8%
	n	73	76	76	77	70	73	17	73

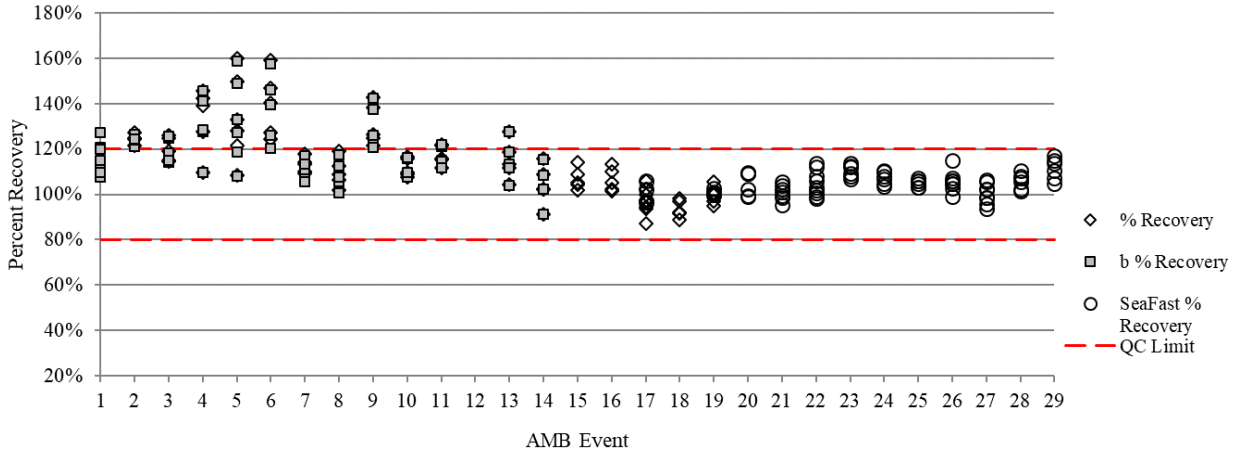

Figure B.1. Analytical recovery of CRM CASS for AMB events 1–29 Cd. Events 1–14 were analyzed after Fe-Pd preconcentration, and blank corrected post-analysis; events 15–19 were analyzed after Fe-Pd preconcentration, and blank corrected via inclusion of reagents in the calibration curve; events 20–29 were analyzed via online preconcentration and did not require blank correction. QC limits are defined by the ENVVEST QAPP and may be greater or smaller than the certified ranges.

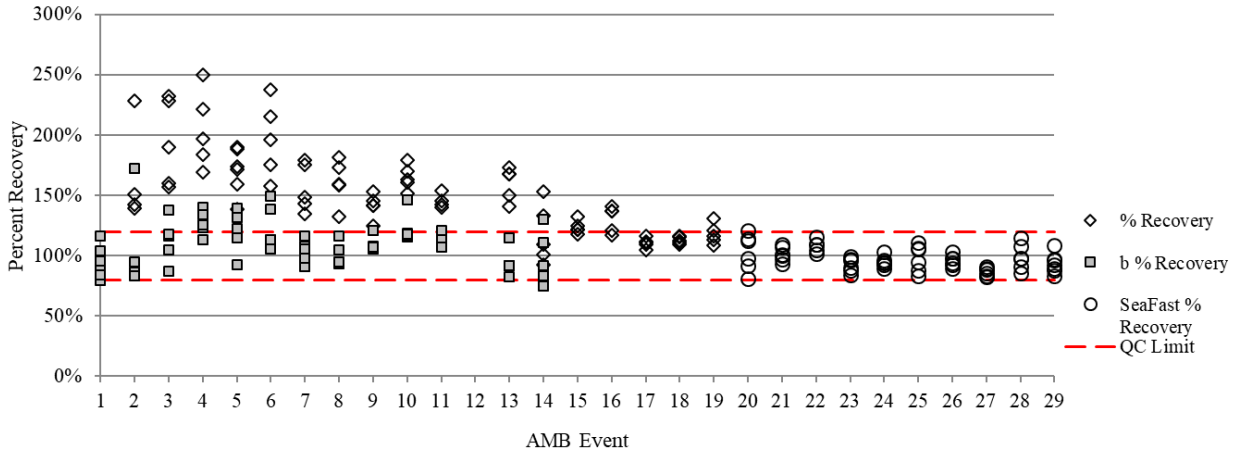

Figure B.2. Analytical recovery of CRM CASS for AMB events 1–29 Cr. Events 1–14 were analyzed after Fe-Pd preconcentration, and blank corrected post-analysis; events 15–19 were analyzed after Fe-Pd preconcentration, and blank corrected via inclusion of reagents in the calibration curve; events 20–29 were analyzed via online preconcentration and did not require blank correction. QC limits are defined by the ENVVEST QAPP and may be greater or smaller than the certified ranges.

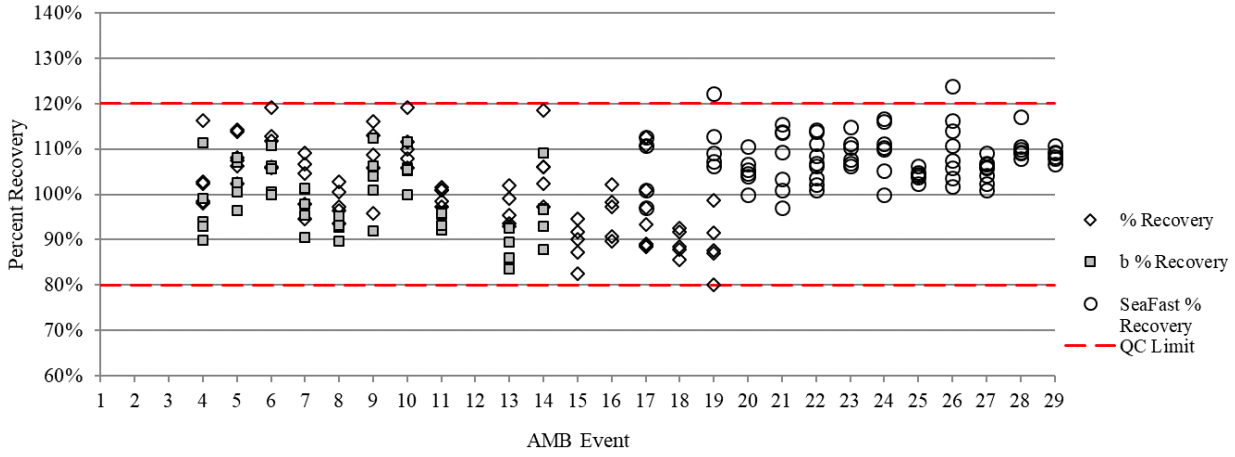

Figure B.3. Analytical recovery of CRM CASS for AMB events 1–29 Ni. Events 1–14 were analyzed after Fe-Pd preconcentration, and blank corrected post-analysis; events 15–19 were analyzed after Fe-Pd preconcentration, and blank corrected via inclusion of reagents in the calibration curve; events 20–29 were analyzed via online preconcentration and did not require blank correction. QC limits are defined by the ENVVEST QAPP and may be greater or smaller than the certified ranges.

Table B.6. Summary statistics of analytical accuracy and precision for passive samplers in seawater.

	Cd	**Cu**	**Ni**	**Pb**	**Zn**
CRM Percent Difference (%)					
n	43	43	43	43	44
Mean	2%	1%	2%	2%	3%
Minimum	0%	0%	0%	0%	0%
Maximum	13%	5%	6%	9%	20%
STD	2%	1%	1%	3%	3%
MS Percent Recovery (%)					
n	53	46	51	54	37
Mean	102%	98%	97%	95%	105%
Minimum	91%	81%	80%	86%	81%
Maximum	114%	109%	117%	113%	125%
STD	4%	6%	6%	7%	10%
Laboratory Duplicates Relative Percent Difference (%)					
n	37	38	38	38	38
Mean	2%	2%	2%	5%	1%
Minimum	0%	0%	0%	0%	0%
Maximum	7%	15%	11%	22%	6%
STD	2%	3%	2%	5%	1%

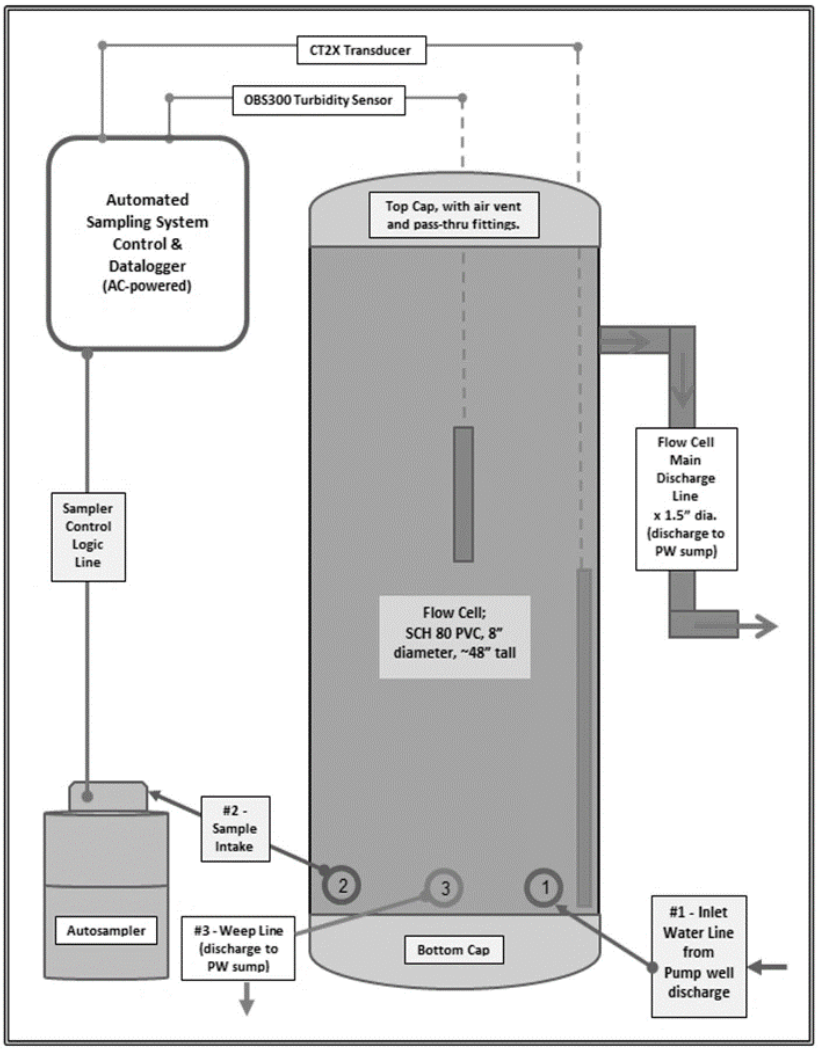

Figure B.4. Auto-sampler flow cell OF019.

Table B.7. Sampling frequency of ENVVEST AMB stations.

	Ancove	BJEST	BM01	CLMBAY	DY07	DYOTS	HRTP	ISLP	M1	M1 DEEP	M2	M2 DEEP	M3.1	M3.1 DEEP	M3.3	M3.3 DEEP	M4	M5	M6	M6 DEEP	M7	M7 DEEP	M8	OF018	OF019	OF021	OF096	POPIPD	PS01	PS02	PS03	PS04	PS05	PS06	PS07	PS08	PS09	PS10	PS10.1	PS11	PS12	PS13	PS14	PS15	PS16	PWNLP	SN03	SN05	SN08	SN10	SN11	WP
AMB01	x	x	x	x	x		x		x	x	x		x	x	x		x	x	x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x		x	x	x	x	x	x
AMB02		x		x					x		x	x	x		x		x		x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x
AMB03		x	x	x					x	x	x	x	x	x	x		x	x	x		x		x	x		x		x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x
AMB04		x	x	x		x			x	x	x	x	x	x	x		x		x		x		x	x		x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB05		x		x		x			x	x	x	x	x	x			x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB06		x	x	x		x			x	x	x	x	x	x	x		x		x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB07		x	x	x		x			x	x	x	x	x	x	x		x		x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB08		x	x	x		x			x	x	x	x	x	x	x		x		x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB09		x		x		x			x	x	x	x	x		x		x	x			x		x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x		x	x	x	x	x	x
AMB10		x	x	x		x			x	x	x		x	x	x		x		x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB11		x	x	x		x			x	x	x	x	x	x	x		x		x		x				x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB12		x		x		x			x	x	x	x	x	x	x		x		x		x		x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB13		x		x		x			x	x	x	x	x	x	x		x		x				x	x	x	x			x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB14		x		x		x		x	x	x	x	x	x		x	x	x		x				x	x	x	x			x	x	x	x	x	x	x	x	x	x	x		x	x	x		x	x	x	x		x
AMB15		x		x				x	x	x	x	x	x	x			x	x						x	x	x			x	x	x	x	x	x	x	x	x	x	x	x		x	x	x		x	x	x	x	x	x
AMB16		x		x		x		x	x	x	x	x	x	x	x		x		x	x				x	x	x			x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB17		x		x		x		x	x	x	x	x	x	x	x		x		x				x	x	x	x			x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB18		x		x		x		x	x	x	x	x	x	x	x		x		x				x	x		x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB19		x		x		x		x	x	x	x	x	x	x	x		x		x				x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x							x
AMB20		x		x		x		x	x	x	x	x	x	x	x		x		x				x	x	x	x			x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB21		x		x		x		x	x		x	x	x	x	x	x	x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB22		x		x		x		x	x	x	x	x	x		x	x	x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x		x
AMB23		x		x		x			x	x	x	x	x		x	x	x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x		x	x	x
AMB24		x		x		x		x	x	x	x	x	x		x	x	x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x					x	x	x
AMB25		x		x		x		x	x	x	x	x	x		x	x	x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x	x	x	x	x
AMB26		x		x		x		x	x	x	x	x	x		x		x	x	x		x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
AMB27		x		x		x			x	x	x	x	x		x		x		x		x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB28		x		x		x		x	x		x	x	x	x	x		x				x			x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
AMB29		x		x		x		x	x	x	x	x	x		x	x	x		x				x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
Sampling Frequency	3%	100%	28%	100%	3%	86%	3%	48%	100%	90%	100%	93%	100%	66%	93%	24%	100%	17%	90%	3%	48%	7%	86%	93%	90%	100%	14%	72%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	97%	93%	100%	100%	100%	31%	93%	97%	93%	97%	90%	100%

Table B.8. Station statistics.

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
BJEST	47.5436	-122.62754	*Total*	***n***	29.0	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	28	2
				Average	27.1	1.80	0.0039	68.7	1.19	0.0652	0.327	1.04	1.11	0.739	0.137	2.44	0.034	0.171	1.22	0.064	31560	5.23	1.8
				Median	27.9	1.73	0.0042	32.5	1.20	0.0616	0.230	1.01	0.94	0.617	0.116	2.35	0.025	0.075	1.24	0.071	31300	3.12	1.8
				1st Quartile	27.2	1.40	0.0042	20.8	1.16	0.0513	0.192	0.889	0.69	0.497	0.0628	1.71	0.012	0.020	0.888	0.051	31100	2.03	1.2
				3rd Quartile	28.9	2.17	0.0042	52.4	1.26	0.0810	0.300	1.13	1.35	0.783	0.170	2.98	0.053	0.358	1.70	0.080	32800	4.38	2.3
				Maximum	30.7	2.84	0.0042	472	1.31	0.0953	1.38	1.51	2.34	2.14	0.496	4.19	0.103	0.441	1.90	0.095	33700	32.0	2.8
				Minimum	16.0	0.900	0.0020	2.22	1.01	0.0348	0.113	0.725	0.43	0.434	0.0102	1.23	0.004	0.009	0.030	0.004	28900	0.58	0.7
			Dissolved	***n***		28	13	21	1	28	28	29	29	23	29	29							
				Average		1.52	0.0039	1.97	1.02	0.0594	0.160	0.781	0.32	0.523	0.0158	1.81							
				Median		1.44	0.0042	2.14		0.0530	0.141	0.737	0.29	0.475	0.0121	1.48							
				1st Quartile		1.19	0.0042	1.16		0.0486	0.113	0.690	0.27	0.417	0.0091	1.09							
				3rd Quartile		1.70	0.0042	2.14		0.0787	0.163	0.862	0.35	0.546	0.0203	2.26							
				Maximum		2.90	0.0042	4.60		0.0928	0.503	1.45	0.82	1.11	0.0353	5.39							
				Minimum		0.900	0.0020	0.352		0.0254	0.064	0.499	0.19	0.317	0.0059	0.726							
BM01	47.56478	-122.62037	*Total*	***n***	8	8	8	8	8	8	8	8	8	6	8	8	7	8	8	8	3	8	--
				Average	29.4	1.34	0.0042	17.2	1.19	0.0729	0.149	0.667	0.71	0.491	0.0779	2.76	0.030	0.200	1.03	0.078	33033	6.54	
				Median	29.6	1.36	0.0042	13.6	1.20	0.0707	0.148	0.648	0.77	0.484	0.0867	1.12	0.028	0.163	0.900	0.080	32500	3.22	
				1st Quartile	28.9	0.978	0.0042	10.6	1.12	0.0664	0.143	0.607	0.55	0.411	0.0562	1.06	0.015	0.102	0.785	0.075	32300	2.20	
				3rd Quartile	29.8	1.73	0.0042	18.8	1.24	0.0806	0.166	0.726	0.83	0.505	0.0902	1.70	0.043	0.330	1.26	0.084	33500	6.75	
				Maximum	30.8	2.00	0.0042	39.2	1.35	0.0866	0.190	0.810	0.89	0.704	0.118	12.9	0.060	0.366	1.60	0.088	34500	27.0	
				Minimum	28.1	0.600	0.0042	8.45	1.10	0.0595	0.095	0.521	0.51	0.374	0.0438	0.888	0.003	0.031	0.640	0.063	32100	0.62	
			Dissolved	***n***		7	8	6	1	8	8	8	8	6	8	8							
				Average		1.40	0.0042	2.14	1.18	0.0680	0.105	0.519	0.27	0.381	0.0145	2.74							
				Median		1.40	0.0042	2.14	1.18	0.0661	0.113	0.481	0.25	0.383	0.0163	0.963							
				1st Quartile		1.21	0.0042	2.14	1.18	0.0596	0.093	0.449	0.23	0.369	0.0076	0.813							
				3rd Quartile		1.65	0.0042	2.14	1.18	0.0761	0.116	0.547	0.31	0.403	0.0198	1.52							
				Maximum		1.80	0.0042	2.14	1.18	0.0859	0.126	0.744	0.36	0.409	0.0236	13.8							
				Minimum		0.884	0.0042	2.14	1.18	0.0527	0.077	0.413	0.21	0.337	0.0045	0.763							
CLMBAY	47.57133	-122.5495	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	29.0	1.23	0.0039	40.9	1.24	0.0738	0.820	0.593	0.73	0.678	0.0788	1.77	0.028	0.232	1.10	0.072	32600	5.70	
				Median	29.2	1.21	0.0042	25.9	1.25	0.0728	0.187	0.549	0.58	0.517	0.0608	0.785	0.026	0.187	1.11	0.075	33300	2.32	
				1st Quartile	28.8	1.10	0.0042	15.9	1.21	0.0698	0.146	0.482	0.48	0.477	0.0463	0.676	0.011	0.124	0.913	0.063	32000	1.27	
				3rd Quartile	29.9	1.33	0.0042	37.2	1.30	0.0783	0.240	0.624	0.79	0.682	0.0808	1.07	0.040	0.365	1.33	0.080	33600	3.62	
				Maximum	31.7	2.00	0.0042	241	1.35	0.0887	17.3	1.19	1.81	1.91	0.303	17.7	0.080	0.465	1.90	0.093	33600	45.0	
				Minimum	23.2	0.800	0.0020	9.12	1.07	0.0627	0.101	0.378	0.29	0.397	0.0281	0.401	0.005	0.024	0.075	0.049	30500	0.65	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.23	0.0039	2.20	1.28	0.0707	0.124	0.419	0.27	0.453	0.0092	1.15							
				Median		1.13	0.0042	2.14		0.0690	0.113	0.405	0.25	0.429	0.0094	0.740							
				1st Quartile		1.00	0.0042	0.821		0.0656	0.098	0.377	0.21	0.404	0.0042	0.450							
				3rd Quartile		1.40	0.0042	2.14		0.0777	0.135	0.469	0.33	0.490	0.0123	0.908							
				Maximum		1.90	0.0042	7.48		0.0822	0.319	0.539	0.58	0.690	0.0221	11.6							
				Minimum		0.800	0.0020	0.200		0.0597	0.082	0.313	0.17	0.358	0.0019	0.346							
DYOTS	47.64193	-122.69395	*Total*	***n***	25	25	10	24	8	24	24	25	25	22	25	25	24	25	9	25	2	25	--
				Average	27.5	2.00	0.0038	31.0	1.12	0.0660	0.238	0.661	0.85	0.658	0.106	1.47	0.048	0.157	1.28	0.071	32950	4.11	
				Median	28.4	1.60	0.0042	20.7	1.15	0.0629	0.167	0.611	0.69	0.555	0.0782	1.21	0.043	0.046	1.10	0.068	32950	1.80	
				1st Quartile	27.8	1.24	0.0042	10.6	1.00	0.0533	0.157	0.578	0.64	0.445	0.0634	0.805	0.023	0.020	0.810	0.054	32925	1.42	
				3rd Quartile	29.2	1.89	0.0042	30.4	1.23	0.0743	0.203	0.683	0.86	0.600	0.114	1.71	0.060	0.323	1.90	0.078	32975	3.54	
				Maximum	30.9	12.1	0.0042	154	1.27	0.138	0.964	1.17	2.23	1.78	0.490	5.72	0.161	0.420	2.40	0.192	33000	34.5	
				Minimum	14.7	0.904	0.0020	3.62	0.910	0.0429	0.118	0.413	0.29	0.396	0.0264	0.420	0.003	0.009	0.081	0.019	32900	0.69	
			Dissolved	***n***		25	10	19	--	24	24	25	25	22	25	25							
				Average		1.59	0.0038	3.24		0.0564	0.140	0.501	0.38	0.506	0.0202	1.15							
				Median		1.43	0.0042	2.14		0.0550	0.124	0.494	0.30	0.486	0.0161	0.840							
				1st Quartile		1.24	0.0042	1.19		0.0441	0.103	0.425	0.24	0.452	0.0122	0.462							

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
DYOTS cont.				**3rd Quartile**		1.80	0.0042	2.14		0.0674	0.148	0.542	0.38	0.569	0.0324	1.46							
				Maximum		4.18	0.0042	16.4		0.0828	0.445	0.747	1.04	0.734	0.0389	4.06							
				Minimum		0.968	0.0020	0.454		0.0189	0.089	0.351	0.18	0.367	0.0038	0.263							
ILSP	47.60046	-122.59414	*Total*	***n***	26	26	12	25	10	25	25	26	26	21	26	26	25	26	11	26	4	26	--
				Average	29.2	1.39	0.0038	13.0	1.19	0.0718	0.156	0.529	0.46	0.531	0.0447	2.59	0.031	0.193	1.44	0.068	31725	4.10	
				Median	29.1	1.15	0.0042	11.4	1.21	0.0731	0.140	0.526	0.46	0.478	0.0452	0.829	0.024	0.139	1.30	0.072	31600	1.31	
				1st Quartile	28.8	1.01	0.0042	8.26	1.13	0.0614	0.127	0.487	0.38	0.442	0.0341	0.538	0.010	0.032	0.980	0.053	30175	1.06	
				3rd Quartile	29.7	1.57	0.0042	18.3	1.24	0.0815	0.168	0.571	0.50	0.605	0.0540	1.12	0.035	0.363	1.69	0.080	33150	3.72	
				Maximum	31.5	3.57	0.0042	26.5	1.38	0.0948	0.328	0.659	0.70	0.806	0.0705	38.8	0.156	0.431	3.39	0.104	33900	32.5	
				Minimum	26.3	0.500	0.0020	4.14	1.01	0.0497	0.106	0.435	0.30	0.377	0.0193	0.395	0.003	0.009	0.074	0.037	29800	0.60	
			Dissolved	***n***		26	12	20	1	25	25	26	26	21	26	26							
				Average		1.24	0.0038	1.37	1.22	0.0684	0.168	0.453	0.22	0.610	0.0138	2.57							
				Median		1.11	0.0042	1.26		0.0707	0.112	0.414	0.22	0.435	0.0113	0.816							
				1st Quartile		1.03	0.0042	0.508		0.0560	0.097	0.383	0.19	0.381	0.0067	0.388							
				3rd Quartile		1.27	0.0042	2.14		0.0799	0.130	0.454	0.26	0.462	0.0167	1.11							
				Maximum		2.40	0.0042	3.66		0.0883	1.34	1.40	0.34	0.806	0.0458	39.1							
				Minimum		0.771	0.0020	0.200		0.0456	0.064	0.349	0.16	0.336	0.0028	0.229							
M1	47.63276	-122.58203	*Total*	***n***	28	28	13	27	11	27	27	28	28	22	28	28	27	28	12	28	5	28	--
				Average	29.1	1.56	0.0039	11.7	1.17	0.0694	0.167	0.531	0.44	0.553	0.0400	0.962	0.028	0.165	1.26	0.063	31520	3.80	
				Median	28.9	1.37	0.0042	9.07	1.17	0.0696	0.145	0.520	0.45	0.514	0.0359	0.820	0.021	0.096	1.22	0.065	32300	1.78	
				1st Quartile	28.6	1.05	0.0042	6.17	1.13	0.0600	0.118	0.479	0.37	0.438	0.0300	0.564	0.006	0.020	0.808	0.049	30200	1.10	
				3rd Quartile	29.7	1.66	0.0042	17.6	1.24	0.0811	0.175	0.563	0.49	0.571	0.0475	1.11	0.048	0.343	1.52	0.076	32600	3.68	
				Maximum	31.5	3.48	0.0042	26.9	1.32	0.0884	0.461	0.719	0.63	1.21	0.0996	3.5	0.074	0.429	2.90	0.105	33700	32.5	
				Minimum	26.5	0.700	0.0020	3.45	0.981	0.0455	0.096	0.427	0.30	0.390	0.0217	0.382	0.003	0.009	0.046	0.013	28800	0.60	
			Dissolved	***n***		28	13	20	1	27	27	28	28	22	28	28							
				Average		1.28	0.0039	1.40	1.09	0.0646	0.155	0.447	0.23	0.463	0.0093	0.697							
				Median		1.16	0.0042	2.13		0.0661	0.112	0.429	0.22	0.418	0.0093	0.571							
				1st Quartile		1.03	0.0042	0.458		0.0516	0.087	0.382	0.18	0.380	0.0050	0.364							
				3rd Quartile		1.42	0.0042	2.14		0.0782	0.119	0.475	0.26	0.473	0.0125	0.813							
				Maximum		3.00	0.0042	2.41		0.0870	1.24	0.983	0.35	1.08	0.0176	2.96							
				Minimum		0.600	0.0020	0.200		0.0434	0.078	0.323	0.16	0.342	0.0021	0.202							
M1 DEEP¶	47.63276	-122.58203	*Total*	***n***	26	26	12	25	10	25	25	26	26	21	26	26	25	26	11	26	4	26	--
				Average	29.3	1.23	0.0038	12.7	1.21	0.0725	0.154	0.535	0.54	0.595	0.0474	0.827	0.036	0.205	0.966	0.072	32900	2.51	
				Median	29.3	1.22	0.0042	11.6	1.20	0.0709	0.153	0.516	0.51	0.504	0.0465	0.788	0.030	0.142	1.00	0.074	32800	1.26	
				1st Quartile	28.8	0.964	0.0042	7.87	1.18	0.0634	0.120	0.485	0.44	0.441	0.0376	0.620	0.013	0.116	0.865	0.060	32425	0.83	
				3rd Quartile	29.9	1.47	0.0042	16.0	1.25	0.0808	0.173	0.573	0.57	0.581	0.0554	1.00	0.052	0.349	1.10	0.083	33275	2.62	
				Maximum	31.5	2.00	0.0042	34.1	1.36	0.0963	0.274	0.733	1.43	1.50	0.0886	1.34	0.134	0.432	1.76	0.093	34400	10.5	
				Minimum	27.2	0.600	0.0020	2.76	1.08	0.0596	0.098	0.391	0.32	0.389	0.0245	0.431	0.003	0.044	0.086	0.052	31600	0.54	
			Dissolved	***n***		26	12	18	1	25	25	26	26	21	26	26							
				Average		1.25	0.0038	1.39	1.23	0.0665	0.119	0.428	0.25	0.489	0.0112	0.746							
				Median		1.13	0.0042	1.73		0.0639	0.112	0.396	0.21	0.450	0.0091	0.656							
				1st Quartile		0.992	0.0042	0.589		0.0605	0.090	0.362	0.19	0.388	0.0065	0.509							
				3rd Quartile		1.53	0.0042	2.14		0.0746	0.123	0.477	0.27	0.506	0.0143	0.881							
				Maximum		2.00	0.0042	2.14		0.0856	0.318	0.764	0.49	1.25	0.0316	2.42							
				Minimum		0.800	0.0020	0.200		0.0493	0.077	0.316	0.17	0.357	0.0025	0.311							
M2	47.57424	-122.53654	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	29.3	1.10	0.0039	18.8	1.27	0.0759	0.183	0.544	0.54	0.566	0.0570	0.874	0.030	0.256	1.24	0.072	32620	2.93	
				Median	29.3	1.08	0.0042	20.6	1.25	0.0731	0.162	0.527	0.53	0.485	0.0470	0.666	0.025	0.239	1.01	0.074	32900	1.65	
				1st Quartile	28.8	0.900	0.0042	10.6	1.22	0.0694	0.135	0.473	0.43	0.458	0.0424	0.626	0.009	0.159	0.938	0.063	31200	1.06	
				3rd Quartile	29.9	1.22	0.0042	22.7	1.29	0.0826	0.179	0.554	0.61	0.571	0.0643	0.883	0.044	0.367	1.45	0.080	34000	3.12	
				Maximum	31.6	1.70	0.0042	35.6	1.41	0.102	0.679	1.19	0.91	1.52	0.227	2.91	0.112	0.439	3.55	0.104	34200	15.0	
				Minimum	26.6	0.700	0.0020	3.46	1.14	0.0660	0.087	0.371	0.31	0.384	0.0250	0.409	0.003	0.064	0.067	0.038	30800	0.52	

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
M2 cont.			*Dissolved*	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.17	0.0039	1.49	1.32	0.0716	0.140	0.400	0.26	0.435	0.0085	0.811							
				Median		1.05	0.0042	1.45		0.0709	0.108	0.399	0.24	0.426	0.0052	0.518							
				1st Quartile		0.923	0.0042	0.595		0.0656	0.095	0.371	0.20	0.390	0.0031	0.405							
				3rd Quartile		1.40	0.0042	2.14		0.0768	0.127	0.416	0.29	0.455	0.0121	0.782							
				Maximum		1.90	0.0042	4.32		0.0861	0.884	0.475	0.78	0.663	0.0540	4.22							
				Minimum		0.748	0.0020	0.200		0.0585	0.079	0.340	0.16	0.343	0.0019	0.335							
M2 DEEP¶	47.57424	-122.53654	*Total*	***n***	27	27	11	26	9	26	26	27	27	22	27	27	26	27	10	27	4	27	--
				Average	29.4	1.10	0.0038	18.7	1.28	0.0744	0.185	0.537	0.52	0.626	0.0505	0.831	0.031	0.259	1.01	0.072	32475	3.38	
				Median	29.4	1.11	0.0042	18.5	1.27	0.0744	0.161	0.532	0.51	0.565	0.0506	0.720	0.025	0.224	1.02	0.073	32550	1.39	
				1st Quartile	28.9	0.939	0.0042	12.0	1.21	0.0680	0.134	0.480	0.41	0.476	0.0390	0.552	0.009	0.162	0.713	0.060	31925	0.87	
				3rd Quartile	29.9	1.20	0.0042	21.8	1.31	0.0795	0.201	0.575	0.60	0.624	0.0601	1.00	0.045	0.372	1.25	0.081	33100	1.95	
				Maximum	31.6	1.80	0.0042	37.1	1.45	0.0900	0.539	0.783	0.82	1.65	0.0787	1.81	0.080	0.438	1.82	0.106	33400	38.0	
				Minimum	27.3	0.500	0.0020	7.38	1.15	0.0628	0.117	0.394	0.26	0.397	0.0241	0.399	0.003	0.065	0.072	0.051	31400	0.42	
			Dissolved	***n***		27	11	20	--	26	26	27	27	22	27	27							
				Average		1.17	0.0038	1.52		0.0703	0.154	0.412	0.25	0.525	0.0089	0.798							
				Median		1.03	0.0042	0.976		0.0706	0.109	0.390	0.22	0.442	0.0077	0.664							
				1st Quartile		0.936	0.0042	0.587		0.0630	0.097	0.368	0.20	0.409	0.0037	0.456							
				3rd Quartile		1.26	0.0042	2.14		0.0762	0.142	0.425	0.27	0.528	0.0131	0.843							
				Maximum		2.70	0.0042	6.51		0.0857	0.754	0.643	0.50	1.28	0.0220	2.41							
				Minimum		0.800	0.0020	0.200		0.0568	0.072	0.272	0.15	0.348	0.0015	0.285							
M3.1	47.55978	-122.61121	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	1
				Average	29.0	1.32	0.0039	19.9	1.21	0.0684	0.525	0.741	0.73	0.624	0.0801	1.76	0.034	0.194	1.24	0.068	32260	4.39	0.7
				Median	29.0	1.32	0.0042	18.7	1.20	0.0665	0.158	0.700	0.69	0.529	0.0734	1.36	0.029	0.109	1.10	0.067	32100	1.83	
				1st Quartile	28.4	1.00	0.0042	11.4	1.15	0.0602	0.143	0.623	0.55	0.450	0.0584	0.879	0.020	0.044	0.848	0.060	31600	1.36	
				3rd Quartile	29.5	1.60	0.0042	27.9	1.24	0.0813	0.213	0.815	0.80	0.579	0.0932	2.14	0.044	0.368	1.66	0.084	32200	2.88	
				Maximum	31.5	1.96	0.0042	37.5	1.39	0.0929	9.802	1.16	1.73	2.04	0.161	7.46	0.111	0.431	2.70	0.096	34600	36.0	
				Minimum	27.2	0.800	0.0020	2.14	1.03	0.0334	0.049	0.438	0.45	0.385	0.0379	0.504	0.003	0.009	0.052	0.035	30800	0.61	
			Dissolved	***n***		28	13	21	1	28	28	29	29	23	29	29							
				Average		1.42	0.0039	1.56	1.01	0.0646	0.119	0.575	0.27	0.514	0.0168	1.24							
				Median		1.25	0.0042	2.14		0.0634	0.113	0.547	0.26	0.450	0.0124	1.12							
				1st Quartile		1.01	0.0042	0.810		0.0544	0.097	0.466	0.23	0.410	0.0075	0.596							
				3rd Quartile		1.57	0.0042	2.14		0.0779	0.130	0.673	0.30	0.484	0.0218	1.67							
				Maximum		3.30	0.0042	3.45		0.0867	0.263	0.907	0.43	1.92	0.0456	3.05							
				Minimum		0.800	0.0020	0.375		0.0287	0.039	0.351	0.16	0.323	0.0036	0.443							
M3.1 DEEP¶	47.55978	-122.61121	*Total*	***n***	19	19	10	18	9	18	18	19	19	14	19	19	17	18	10	18	4	19	1
				Average	29.2	1.35	0.0040	17.3	1.24	0.0720	0.171	0.735	0.72	0.551	0.0752	1.27	0.035	0.203	1.10	0.069	32450	3.95	1.4
				Median	29.1	1.29	0.0042	16.0	1.22	0.0729	0.164	0.635	0.65	0.510	0.0719	1.30	0.033	0.124	1.13	0.071	32250	1.91	
				1st Quartile	28.6	1.01	0.0042	10.7	1.17	0.0644	0.143	0.572	0.60	0.455	0.0583	0.932	0.024	0.111	0.850	0.061	32050	1.51	
				3rd Quartile	29.7	1.44	0.0042	21.4	1.31	0.0785	0.190	0.758	0.76	0.581	0.0890	1.62	0.051	0.350	1.55	0.078	32650	2.80	
				Maximum	31.5	3.40	0.0042	36.5	1.38	0.0872	0.263	2.27	1.58	0.917	0.151	2.19	0.061	0.439	1.70	0.092	33700	29.0	
				Minimum	27.7	0.896	0.0020	8.13	1.11	0.0574	0.110	0.398	0.46	0.397	0.0383	0.620	0.003	0.037	0.057	0.042	31600	0.49	
			Dissolved	***n***		18	10	15	1	18	18	19	19	14	19	19							
				Average		1.34	0.0040	1.42	1.29	0.0663	0.122	0.489	0.27	0.424	0.0151	1.08							
				Median		1.22	0.0042	2.14		0.0633	0.125	0.505	0.23	0.408	0.0132	0.95							
				1st Quartile		1.06	0.0042	0.491		0.0609	0.108	0.431	0.21	0.387	0.0085	0.663							
				3rd Quartile		1.57	0.0042	2.14		0.0727	0.132	0.550	0.31	0.432	0.0180	1.41							
				Maximum		2.30	0.0042	2.14		0.0916	0.170	0.661	0.52	0.598	0.0337	1.99							
				Minimum		0.865	0.0020	0.200		0.0528	0.085	0.340	0.18	0.349	0.0052	0.546							
M3.3	47.54958	-122.64303	*Total*	***n***	28	28	12	27	10	27	27	28	28	23	28	28	27	28	11	28	4	28	--
				Average	28.5	1.66	0.0038	16.4	1.13	0.0700	0.185	0.902	0.76	0.611	0.0810	1.98	0.052	0.157	1.16	0.065	32050	4.09	
				Median	28.5	1.40	0.0042	13.2	1.15	0.0619	0.160	0.946	0.68	0.535	0.0836	1.74	0.034	0.049	1.10	0.069	31400	2.04	

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
M3.3 cont.				**1st Quartile**	28.1	1.04	0.0042	9.33	1.08	0.0554	0.137	0.746	0.63	0.475	0.0698	1.29	0.009	0.020	0.800	0.043	30625	1.25	
				3rd Quartile	29.3	2.21	0.0042	23.0	1.19	0.0794	0.209	1.03	0.84	0.587	0.0913	2.44	0.045	0.347	1.25	0.079	32825	4.23	
				Maximum	31.3	4.00	0.0042	35.2	1.31	0.198	0.520	1.28	2.06	1.74	0.134	3.94	0.637	0.429	3.24	0.103	35000	33.0	
				Minimum	23.0	0.701	0.0020	2.83	0.967	0.0414	0.099	0.544	0.41	0.366	0.0316	0.786	0.003	0.009	0.098	0.021	30400	0.52	
			Dissolved	***n***		28	12	20	1	27	27	28	28	23	28	28							
				Average		1.34	0.0038	1.67	1.00	0.0622	0.167	0.723	0.31	0.514	0.0151	1.71							
				Median		1.27	0.0042	2.01		0.0603	0.117	0.742	0.28	0.460	0.0119	1.48							
				1st Quartile		1.02	0.0042	0.859		0.0510	0.098	0.613	0.23	0.439	0.0092	1.08							
				3rd Quartile		1.41	0.0042	2.14		0.0767	0.140	0.822	0.32	0.527	0.0219	2.21							
				Maximum		3.70	0.0042	5.48		0.0911	1.19	0.971	0.64	1.10	0.0353	4.19							
				Minimum		0.719	0.0020	0.200		0.0303	0.087	0.401	0.19	0.380	0.0051	0.487							
M3.3 DEEP¶	47.54958	-122.64303	*Total*	***n***	7	7	1	7	--	7	7	7	7	7	7	7	7	7	--	7	--	7	--
				Average	28.6	1.58	0.0020	25.0		0.0716	0.183	0.824	0.86	0.628	0.1043	1.72	0.064	0.234		0.080		2.38	
				Median	28.7	0.986		23.5		0.0731	0.141	0.752	0.83	0.518	0.0967	1.61	0.049	0.272		0.084		2.01	
				1st Quartile	28.0	0.971		19.6		0.0636	0.136	0.732	0.75	0.492	0.0845	1.45	0.021	0.063		0.070		0.94	
				3rd Quartile	29.4	2.16		25.3		0.0779	0.174	0.887	0.89	0.548	0.1120	1.94	0.083	0.399		0.089		3.67	
				Maximum	29.7	2.89		47.0		0.0842	0.401	1.12	1.33	1.32	0.1816	2.34	0.191	0.432		0.095		4.63	
				Minimum	27.3	0.939		14.7		0.0608	0.122	0.656	0.58	0.485	0.0587	1.32	0.003	0.009		0.065		0.77	
			Dissolved	***n***		7	1	4	--	7	7	7	7	7	7	7							
				Average		1.06	0.0020	1.10		0.0660	0.094	0.582	0.23	0.512	0.0183	1.50							
				Median		1.04		1.14		0.0683	0.090	0.569	0.19	0.463	0.0128	1.45							
				1st Quartile		1.00		0.863		0.0534	0.087	0.542	0.18	0.458	0.0103	1.01							
				3rd Quartile		1.15		1.37		0.0801	0.094	0.646	0.26	0.521	0.0224	1.85							
				Maximum		1.18		1.42		0.0845	0.124	0.692	0.35	0.736	0.0436	2.59							
				Minimum		0.937		0.685		0.0424	0.082	0.438	0.16	0.426	0.0062	0.738							
M4	47.54487	-122.66686	*Total*	***n***	30	30	14	29	12	29	29	30	30	23	30	30	29	30	13	30	6	30	3
				Average	28.6	3.25	0.0039	22.7	1.20	0.0996	0.191	0.896	1.05	0.557	0.0960	2.39	0.045	0.162	1.79	0.123	32067	6.05	1.2
				Median	28.7	1.83	0.0042	23.4	1.18	0.0734	0.186	0.857	0.82	0.529	0.0941	1.93	0.041	0.060	1.28	0.081	32300	2.68	0.7
				1st Quartile	28.0	1.10	0.0042	13.9	1.16	0.0554	0.144	0.787	0.72	0.487	0.0711	1.38	0.023	0.020	1.10	0.065	31275	1.61	0.7
				3rd Quartile	29.3	2.59	0.0042	31.8	1.25	0.0842	0.231	0.993	1.01	0.567	0.120	2.41	0.063	0.353	1.94	0.094	33025	4.93	1.5
				Maximum	31.3	23.6	0.0042	44.6	1.34	0.493	0.302	1.47	5.04	1.21	0.182	8.35	0.101	0.423	5.95	0.691	33900	44.9	2.2
				Minimum	25.4	0.939	0.0020	3.67	1.07	0.0479	0.110	0.602	0.36	0.417	0.0360	1.00	0.003	0.009	0.084	0.030	29700	0.37	0.7
			Dissolved	***n***		30	14	22	1	29	29	30	30	23	30	30							
				Average		2.05	0.0039	1.98	1.10	0.0752	0.134	0.659	0.41	0.438	0.0162	1.73							
				Median		1.39	0.0042	2.14		0.0715	0.115	0.643	0.31	0.441	0.0132	1.27							
				1st Quartile		1.10	0.0042	0.784		0.0493	0.110	0.565	0.23	0.401	0.0093	0.966							
				3rd Quartile		2.33	0.0042	2.14		0.0814	0.134	0.734	0.38	0.471	0.0190	2.10							
				Maximum		8.36	0.0042	10.2		0.221	0.441	0.918	2.19	0.546	0.0476	5.22							
				Minimum		0.800	0.0020	0.284		0.0430	0.083	0.452	0.18	0.347	0.0061	0.621							
M5	47.61044	-122.66637	*Total*	***n***	6	6	3	6	3	6	6	6	6	4	6	6	6	6	4	6	2	6	--
				Average	28.7	1.95	0.0042	19.5	1.17	0.0804	0.167	0.629	0.83	0.579	0.0906	1.37	0.032	0.188	1.58	0.079	31600	5.48	
				Median	28.9	1.41	0.0042	17.5	1.17	0.0826	0.151	0.623	0.80	0.590	0.0859	1.42	0.031	0.178	1.91	0.073	31600	2.96	
				1st Quartile	28.5	1.14	0.0042	10.2	1.15	0.0649	0.146	0.608	0.77	0.525	0.0769	0.975	0.019	0.021	1.33	0.067	31200	2.49	
				3rd Quartile	29.0	2.27	0.0042	22.0	1.19	0.0864	0.184	0.630	0.87	0.644	0.111	1.71	0.048	0.360	2.16	0.090	32000	7.15	
				Maximum	29.8	4.60	0.0042	48.5	1.21	0.115	0.225	0.685	1.43	0.700	0.148	2.06	0.056	0.374	2.50	0.107	32400	15.0	
				Minimum	27.4	0.700	0.0042	2.14	1.13	0.0554	0.138	0.604	0.31	0.435	0.0318	0.675	0.003	0.009	0.020	0.062	30800	1.08	
			Dissolved	***n***		6	3	2	1	6	6	6	6	4	6	6							
				Average		1.75	0.0057	1.30	1.07	0.0670	0.120	0.497	0.50	0.473	0.0219	1.03							
				Median		1.34	0.0042	1.30		0.0673	0.105	0.485	0.33	0.472	0.0152	1.03							
				1st Quartile		1.22	0.0042	0.873		0.0560	0.101	0.464	0.29	0.445	0.0143	0.746							
				3rd Quartile		2.08	0.0065	1.72		0.0808	0.117	0.512	0.34	0.500	0.0211	1.38							
				Maximum		3.50	0.0087	2.14		0.0867	0.195	0.593	1.49	0.514	0.0498	1.49							

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
M5 cont.				**Minimum**		0.800	0.0042	0.450		0.0433	0.092	0.438	0.24	0.432	0.0139	0.514							
M6	47.59767	-122.68472	*Total*	***n***	26	26	12	25	10	25	25	26	26	20	26	26	25	26	11	26	5	26	--
				Average	28.9	1.50	0.0038	22.7	1.16	0.0651	0.173	0.602	0.80	0.589	0.102	1.21	0.041	0.168	1.84	0.066	33000	4.89	
				Median	29.0	1.46	0.0042	23.6	1.14	0.0611	0.156	0.600	0.73	0.530	0.0865	1.19	0.032	0.054	1.10	0.067	33100	1.87	
				1st Quartile	28.3	1.08	0.0042	11.2	1.12	0.0533	0.136	0.563	0.60	0.481	0.0653	0.682	0.017	0.022	0.915	0.057	31800	1.34	
				3rd Quartile	29.6	1.60	0.0042	32.3	1.16	0.0810	0.183	0.659	0.99	0.604	0.130	1.61	0.057	0.333	1.30	0.076	33100	3.55	
				Maximum	31.5	3.10	0.0042	41.9	1.29	0.0917	0.381	0.807	1.32	1.38	0.219	2.51	0.143	0.415	8.95	0.097	36200	33.0	
				Minimum	25.5	0.96	0.0020	3.52	1.03	0.0419	0.093	0.404	0.39	0.393	0.0453	0.431	0.003	0.009	0.092	0.021	30800	0.62	
			Dissolved	***n***		26	12	18	1	25	25	26	26	20	26	26							
				Average		1.44	0.0038	1.82	1.12	0.0599	0.223	0.469	0.31	0.464	0.0284	1.11							
				Median		1.31	0.0042	2.07		0.0529	0.110	0.463	0.29	0.460	0.0296	0.936							
				1st Quartile		1.15	0.0042	0.875		0.0447	0.095	0.418	0.25	0.396	0.0112	0.490							
				3rd Quartile		1.48	0.0042	2.14		0.0783	0.127	0.513	0.32	0.511	0.0413	1.48							
				Maximum		3.30	0.0042	6.07		0.0922	2.97	0.675	0.80	0.745	0.0591	4.54							
				Minimum		0.893	0.0020	0.200		0.0301	0.067	0.351	0.16	0.325	0.0056	0.346							
M7	47.62447	-122.69194	*Total*	***n***	14	14	10	14	10	13	13	14	14	10	14	14	14	14	10	14	4	14	--
				Average	28.7	1.75	0.0042	14.6	1.13	0.0719	0.279	0.686	0.62	0.530	0.0629	1.61	0.024	0.177	1.43	0.070	31900	5.97	
				Median	28.8	1.71	0.0042	10.6	1.14	0.0796	0.137	0.560	0.62	0.514	0.0510	1.37	0.018	0.142	1.36	0.069	32000	2.84	
				1st Quartile	28.6	1.13	0.0042	8.47	1.07	0.0587	0.126	0.547	0.51	0.460	0.0424	1.17	0.005	0.025	1.00	0.055	31150	1.47	
				3rd Quartile	29.5	2.18	0.0042	17.8	1.18	0.0825	0.194	0.639	0.67	0.583	0.0643	1.81	0.030	0.352	1.76	0.082	32750	7.64	
				Maximum	30.2	3.86	0.0042	50.3	1.30	0.0967	1.78	2.13	1.01	0.765	0.146	4.42	0.111	0.411	2.40	0.094	34100	26.0	
				Minimum	25.3	0.700	0.0042	2.19	1.01	0.0474	0.093	0.494	0.39	0.392	0.0331	0.448	0.003	0.009	0.660	0.046	29500	0.98	
			Dissolved	***n***		14	10	10	1	13	13	14	14	10	14	14							
				Average		1.52	0.0042	2.30	1.06	0.0714	0.187	0.482	0.33	0.460	0.0133	1.32							
				Median		1.48	0.0042	2.14		0.0802	0.120	0.476	0.30	0.467	0.0115	1.30							
				1st Quartile		1.22	0.0042	2.14		0.0481	0.108	0.458	0.25	0.445	0.0068	0.586							
				3rd Quartile		1.75	0.0042	2.14		0.0850	0.140	0.505	0.35	0.500	0.0191	1.51							
				Maximum		2.60	0.0042	4.65		0.114	0.986	0.680	0.64	0.530	0.0286	4.12							
				Minimum		0.700	0.0042	0.711		0.0437	0.078	0.364	0.17	0.345	0.0042	0.351							
M7 DEEP¶	47.62447	-122.69194	*Total*	***n***	2	2	--	2	--	2	2	2	2	2	2	2	2	2	--	2	--	2	--
				Average	29.3	1.51		16.0		0.0569	0.126	0.576	0.69	0.687	0.0957	0.862	0.029	0.049		0.068		1.67	
				Median	29.3	1.51		16.0		0.0569	0.126	0.576	0.69	0.687	0.0957	0.862	0.029	0.049		0.068		1.67	
				1st Quartile	29.2	1.51		15.1		0.0546	0.121	0.554	0.66	0.673	0.0875	0.814	0.026	0.035		0.067		1.61	
				3rd Quartile	29.4	1.51		17.0		0.0591	0.130	0.599	0.71	0.700	0.104	0.911	0.033	0.064		0.069		1.73	
				Maximum	29.6	1.51		18.0		0.0614	0.135	0.622	0.73	0.714	0.112	0.959	0.036	0.078		0.070		1.79	
				Minimum	29.0	1.51		14.1		0.0523	0.116	0.531	0.64	0.660	0.0793	0.765	0.022	0.020		0.066		1.56	
			Dissolved	***n***		2	--	--	--	2	2	2	2	2	2	2							
				Average		1.23				0.0478	0.082	0.393	0.23	0.464	0.0355	0.674							
				Median		1.23				0.0478	0.082	0.393	0.23	0.464	0.0355	0.674							
				1st Quartile		1.20				0.0459	0.078	0.379	0.22	0.461	0.0347	0.653							
				3rd Quartile		1.27				0.0498	0.086	0.407	0.24	0.468	0.0362	0.696							
				Maximum		1.31				0.0517	0.090	0.421	0.24	0.472	0.0369	0.717							
				Minimum		1.16				0.0440	0.074	0.364	0.22	0.457	0.0340	0.632							
M8	47.57256	-122.67512	*Total*	***n***	24	24	11	23	9	23	23	24	24	19	24	24	23	24	10	24	4	24	--
				Average	28.5	1.76	0.0038	28.2	1.15	0.0725	0.195	0.643	0.95	0.616	0.133	1.33	0.041	0.177	1.50	0.075	32125	6.17	
				Median	28.7	1.58	0.0042	25.8	1.15	0.0742	0.167	0.662	0.92	0.544	0.126	1.48	0.036	0.062	1.12	0.068	32450	1.83	
				1st Quartile	27.9	1.08	0.0042	19.5	1.12	0.0521	0.149	0.584	0.69	0.492	0.0970	0.859	0.012	0.020	0.925	0.061	31700	1.40	
				3rd Quartile	29.0	2.14	0.0042	33.6	1.18	0.0857	0.220	0.729	1.05	0.654	0.156	1.61	0.056	0.369	1.65	0.083	32875	4.08	
				Maximum	31.2	5.40	0.0042	79.4	1.29	0.140	0.426	0.829	1.63	1.15	0.255	2.23	0.119	0.405	5.10	0.165	34000	43.0	
				Minimum	25.3	0.800	0.0020	12.0	1.06	0.0394	0.118	0.411	0.48	0.411	0.0600	0.518	0.003	0.009	0.092	0.018	29600	0.90	
			Dissolved	***n***		24	11	16	1	23	23	24	24	19	24	24							
				Average		1.54	0.0038	1.57	1.07	0.0606	0.113	0.466	0.28	0.467	0.0299	0.978							

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
M8 cont.				**Median**		1.41	0.0042	2.00		0.0606	0.117	0.458	0.29	0.467	0.0217	1.16							
				1st Quartile		1.01	0.0042	1.04		0.0438	0.098	0.415	0.22	0.394	0.0149	0.532							
				3rd Quartile		1.68	0.0042	2.14		0.0787	0.125	0.511	0.34	0.542	0.0433	1.29							
				Maximum		4.00	0.0042	2.14		0.0879	0.183	0.593	0.44	0.636	0.0639	2.05							
				Minimum		0.800	0.0020	0.200		0.0323	0.069	0.349	0.17	0.321	0.0100	0.361							
OF018	47.560071	-122.636556	*Total*	***n***	21	24	13	25	11	26	26	26	26	21	26	26	11	11	8	11	4	26	21
				Average	22.3	1.45	0.0282	31.5	1.76	0.108	1.60	7.31	11.4	3.80	0.433	37.7	0.191	0.624	1.14	0.151	21425	3.46	1.8
				Median	22.9	1.10	0.0218	16.0	1.85	0.103	0.702	5.57	9.30	2.89	0.260	35.5	0.164	0.593	0.935	0.158	21100	1.72	1.2
				1st Quartile	21.7	1.00	0.0173	9.71	1.49	0.092	0.466	3.87	6.75	2.42	0.145	27.5	0.151	0.492	0.778	0.129	19900	0.90	0.7
				3rd Quartile	23.5	1.34	0.0347	25.7	1.99	0.127	1.47	8.09	12.4	4.19	0.471	48.0	0.235	0.641	1.07	0.178	22625	4.66	1.8
				Maximum	25.5	7.03	0.0618	207	2.20	0.152	8.15	29.6	45.5	10.5	2.89	68.7	0.286	1.520	3.03	0.310	23600	14.2	9.4
				Minimum	16.7	0.713	0.0135	1.99	1.35	0.0762	0.323	1.69	5.53	1.37	0.0604	13.7	0.106	0.327	0.550	0.004	19900	0.42	0.7
			Dissolved	***n***		24	13	19	1	26	26	26	26	21	26	26							
				Average		1.54	0.0131	1.85	1.80	0.102	0.355	3.42	3.09	3.01	0.0167	31.1							
				Median		1.06	0.0107	2.14		0.0969	0.355	3.37	2.97	2.25	0.0124	30.4							
				1st Quartile		0.904	0.0082	0.812		0.0876	0.294	2.40	2.50	1.67	0.0077	25.6							
				3rd Quartile		1.75	0.0151	2.14		0.117	0.387	4.28	3.62	3.70	0.0215	37.8							
				Maximum		6.32	0.0339	7.85		0.156	0.647	6.82	6.34	8.50	0.0503	47.4							
				Minimum		0.500	0.0042	0.200		0.0619	0.208	0.586	1.31	0.882	0.0042	11.3							
OF019	47.553212	-122.642148	*Total*	***n***	21	25	11	25	9	25	25	26	26	21	26	26	14	14	8	14	3	26	21
				Average	21.8	1.31	0.0235	62.2	2.10	0.0923	5.05	12.7	9.88	8.44	0.598	35.6	0.234	0.335	1.01	0.191	25667	7.34	1.3
				Median	21.1	1.05	0.0187	17.7	1.51	0.0828	3.31	4.90	5.73	2.20	0.192	21.5	0.208	0.313	0.840	0.157	26200	1.94	0.7
				1st Quartile	18.7	1.00	0.0139	7.37	1.40	0.0749	0.332	1.52	4.53	1.63	0.0657	11.4	0.187	0.195	0.730	0.137	24650	0.62	0.7
				3rd Quartile	24.6	1.21	0.0280	43.9	1.61	0.0970	5.73	6.53	8.61	10.2	0.303	28.0	0.264	0.380	1.26	0.212	26950	4.82	1.2
				Maximum	29.5	3.29	0.0651	844	6.78	0.273	31.8	200	85.0	61.6	9.06	365	0.558	0.691	1.66	0.509	27700	108	3.6
				Minimum	16.3	0.696	0.0090	2.69	1.29	0.0623	0.194	0.949	2.52	1.26	0.0320	6.67	0.047	0.095	0.610	0.074	23100	0.27	0.7
			Dissolved	***n***		25	11	19	1	25	25	26	26	21	26	26							
				Average		1.27	0.0065	1.72	1.05	0.0800	0.456	2.51	2.24	4.28	0.0111	16.4							
				Median		1.02	0.0072	1.21		0.0794	0.185	1.52	1.71	2.13	0.0056	17.4							
				1st Quartile		0.901	0.0047	0.491		0.0725	0.171	0.879	1.38	1.49	0.0031	11.2							
				3rd Quartile		1.19	0.0077	2.14		0.0859	0.976	3.63	2.78	6.74	0.0137	20.3							
				Maximum		3.60	0.0126	9.00		0.101	1.30	9.62	5.69	12.7	0.0477	27.0							
				Minimum		0.604	0.0022	0.360		0.0571	0.031	0.581	0.65	1.2	0.0011	6.50							
OF021	47.552083	-122.653844	*Total*	***n***	22	23	13	28	11	28	28	29	29	23	29	29	13	13	8	13	2	25	20
				Average	0.2	2.66	0.0048	12.9	1.15	0.0079	1.61	3.05	13.9	1.15	0.153	2.34	0.016	0.509	1.05	0.309	743	0.95	1.2
				Median	0.2	2.60	0.0032	8.27	1.05	0.0040	1.28	1.26	2.45	0.764	0.0120	0.811	0.020	0.488	0.730	0.288	743	0.49	0.7
				1st Quartile	0.1	1.94	0.0032	6.83	0.586	0.0025	0.951	0.913	2.01	0.580	0.0055	0.449	0.003	0.224	0.595	0.091	696	0.42	0.7
				3rd Quartile	0.2	3.63	0.0053	15.1	1.54	0.0067	1.61	2.06	3.19	1.4	0.0350	1.77	0.026	0.612	1.28	0.434	789	0.56	1.3
				Maximum	0.6	4.55	0.0110	49.5	2.62	0.0522	8.11	13.4	130	3.18	1.26	13.0	0.033	1.51	2.64	0.843	835	5.00	3.9
				Minimum	0.1	0.320	0.0020	3.03	0.117	0.0006	0.262	0.269	1.13	0.264	0.0026	0.209	0.003	0.176	0.440	0.033	650	0.12	0.7
			Dissolved	***n***		24	13	24	1	28	28	29	28	23.0	29	29							
				Average		2.71	0.0032	9.33	0.357	0.0067	1.53	2.08	4.39	1.05	0.0487	1.88							
				Median		2.61	0.0032	7.30		0.0040	1.30	1.23	2.26	0.877	0.0069	0.804							
				1st Quartile		1.71	0.0032	5.91		0.0029	0.979	0.773	1.79	0.547	0.0037	0.515							
				3rd Quartile		3.78	0.0032	9.18		0.0065	1.61	1.96	2.86	1.27	0.0166	1.50							
				Maximum		5.37	0.0042	48.3		0.0502	5.89	7.94	44.1	3.07	0.345	10.1							
				Minimum		0.300	0.0020	4.08		0.0006	0.261	0.234	1.04	0.128	0.0018	0.214							
OF096	47.560715	-122.632414	*Total*	***n***	4	4	--	3	--	4	4	4	4	3	4	4	1	1	--	1	--	4	4
				Average	24.1	1.01		9.36		0.0790	0.524	6.56	7.37	3.44	0.268	33.3	0.234	0.274		0.122		0.92	1.5
				Median	27.1	1.06		7.11		0.0748	0.285	5.61	5.67	3.82	0.227	33.8						0.83	1.2
				1st Quartile	23.1	0.967		4.54		0.0704	0.239	4.80	4.87	2.47	0.158	30.1						0.65	0.7
				3rd Quartile	28.1	1.10		13.1		0.0834	0.570	7.37	8.17	4.59	0.338	36.9						1.10	2.0
				Maximum	29.5	1.11		19.0		0.101	1.29	12.3	13.8	5.37	0.465	44.5						1.47	2.8

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
OF096 cont.				**Minimum**	12.5	0.808		1.97		0.0654	0.234	2.72	4.33	1.12	0.154	20.9						0.56	0.7
			Dissolved	***n***		4	--	2	--	4	4	4	4	3	4	4							
				Average		0.960		0.648		0.0532	0.119	3.61	1.32	3.72	0.0289	23.3							
				Median		0.994		0.648		0.0673	0.120	2.92	1.35	4.31	0.0305	26.3							
				1st Quartile		0.910		0.553		0.0505	0.104	1.40	1.20	2.68	0.0243	17.0							
				3rd Quartile		1.04		0.744		0.0700	0.134	5.12	1.46	5.05	0.0351	32.6							
				Maximum		1.06		0.840		0.0747	0.158	8.28	1.47	5.79	0.0409	33.6							
				Minimum		0.791		0.457		0.0035	0.078	0.331	1.10	1.05	0.0138	6.93							
POPIPD	47.61295	-122.5948	*Total*	***n***	11	11	1	11	1	11	11	11	11	10	11	11	11	11	1	11	1	11	--
				Average	28.7	1.31	0.0042	36.7	1.38	0.0685	0.199	0.579	0.61	0.630	0.0724	1.24	0.041	0.185	0.970	0.059	33400	2.84	
				Median	28.9	1.09		23.4		0.0702	0.167	0.561	0.56	0.554	0.0677	1.03	0.039	0.192		0.049		2.74	
				1st Quartile	28.3	1.03		18.8		0.0628	0.142	0.537	0.46	0.529	0.0533	0.674	0.016	0.071		0.048		1.63	
				3rd Quartile	29.7	1.55		47.6		0.0752	0.218	0.624	0.69	0.651	0.0831	1.37	0.068	0.273		0.071		3.45	
				Maximum	30.6	2.05		111		0.0855	0.448	0.683	1.00	1.08	0.138	3.97	0.080	0.429		0.089		5.63	
				Minimum	25.7	0.900		7.87		0.0501	0.122	0.494	0.40	0.474	0.0362	0.507	0.003	0.009		0.041		1.22	
			Dissolved	***n***		11	1	5	--	11	11	11	11	10	11	11							
				Average		1.14	0.0042	1.00		0.0656	0.100	0.422	0.24	0.487	0.0123	1.00							
				Median		1.12		0.799		0.0657	0.107	0.415	0.21	0.462	0.0132	0.868							
				1st Quartile		0.990		0.684		0.0549	0.084	0.389	0.19	0.438	0.0067	0.496							
				3rd Quartile		1.23		0.819		0.0762	0.109	0.470	0.23	0.530	0.0161	1.33							
				Maximum		1.51		2.14		0.0876	0.139	0.498	0.50	0.655	0.0224	2.43							
				Minimum		0.947		0.555		0.0443	0.076	0.321	0.15	0.372	0.0041	0.329							
PS01	47.55401	-122.65725	*Total*	***n***	30	30	14	29	12	29	29	30	30	23	30	30	29	30	13	30	6	30	4
				Average	28.1	2.15	0.0065	26.3	1.36	0.0739	0.250	1.45	1.64	0.634	0.178	3.64	0.065	0.213	1.43	0.093	31050	4.21	2.9
				Median	28.1	1.42	0.0042	15.8	1.36	0.0757	0.199	1.28	1.15	0.570	0.100	3.03	0.067	0.152	1.03	0.084	30550	2.33	1.4
				1st Quartile	27.5	1.12	0.0042	11.1	1.22	0.0631	0.155	1.08	0.84	0.527	0.0839	2.27	0.040	0.065	0.880	0.066	30100	1.40	0.7
				3rd Quartile	28.6	1.80	0.0062	21.2	1.38	0.0829	0.266	1.72	1.70	0.737	0.134	4.62	0.084	0.367	1.84	0.095	32275	4.90	3.6
				Maximum	30.8	16.4	0.0191	112	1.96	0.105	0.618	3.04	5.83	1.09	0.697	8.47	0.164	0.444	4.44	0.410	33200	25.0	8.3
				Minimum	24.8	0.700	0.0020	2.14	1.07	0.0423	0.113	0.690	0.38	0.434	0.0407	1.55	0.003	0.009	0.123	0.004	29200	0.49	0.7
			Dissolved	***n***		29	14	22	1	29	29	30	30	23	30	30							
				Average		1.76	0.0044	2.26	1.03	0.0681	0.251	1.03	0.65	0.609	0.0260	3.03							
				Median		1.32	0.0042	2.14		0.0707	0.177	0.973	0.55	0.550	0.0180	2.84							
				1st Quartile		1.11	0.0042	1.04		0.0549	0.123	0.856	0.37	0.487	0.0139	1.93							
				3rd Quartile		1.86	0.0042	2.17		0.0817	0.226	1.19	0.70	0.632	0.0314	4.08							
				Maximum		9.40	0.0081	7.76		0.0920	2.28	1.68	2.10	1.32	0.0860	5.75							
				Minimum		0.866	0.0020	0.462		0.0376	0.086	0.588	0.13	0.397	0.0097	0.961							
PS02	47.55456	-122.65452	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	28.1	1.50	0.0039	17.1	1.32	0.0727	0.217	1.79	1.60	0.606	0.121	3.99	0.052	0.207	1.06	0.075	30440	4.26	
				Median	28.1	1.43	0.0042	13.5	1.30	0.0744	0.192	1.67	1.18	0.604	0.0992	3.66	0.048	0.134	1.02	0.081	30900	1.84	
				1st Quartile	27.4	1.05	0.0042	9.55	1.26	0.0614	0.160	1.36	0.96	0.530	0.0794	2.96	0.038	0.059	0.835	0.062	29300	1.31	
				3rd Quartile	28.9	1.66	0.0042	20.4	1.38	0.0840	0.252	2.11	1.72	0.655	0.110	5.00	0.065	0.382	1.22	0.088	31900	4.09	
				Maximum	31.2	3.77	0.0044	83.2	1.60	0.103	0.500	2.96	5.35	0.854	0.583	7.43	0.148	0.447	2.10	0.121	31900	31.0	
				Minimum	24.5	0.800	0.0020	5.12	1.12	0.0366	0.129	0.969	0.68	0.440	0.0513	1.87	0.004	0.009	0.148	0.018	28200	0.70	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.51	0.0039	1.71	1.29	0.0676	0.172	1.32	0.72	0.599	0.0226	3.46							
				Median		1.30	0.0042	2.14		0.0633	0.152	1.22	0.57	0.509	0.0195	3.19							
				1st Quartile		1.03	0.0042	0.872		0.0576	0.132	1.02	0.38	0.441	0.0130	2.43							
				3rd Quartile		1.70	0.0042	2.14		0.0804	0.176	1.62	0.80	0.562	0.0288	4.00							
				Maximum		5.90	0.0042	4.69		0.101	0.450	2.15	3.16	2.08	0.0540	7.91							
				Minimum		0.800	0.0020	0.422		0.0343	0.083	0.695	0.21	0.389	0.0094	1.19							
PS03	47.55592	-122.65182	*Total*	***n***	58	58	23	57	17	56	56	58	58	51	58	58	55	56	18	56	5	57	4
				Average	28.3	1.73	0.0046	16.2	1.24	0.0707	0.204	2.05	6.38	0.615	0.157	5.14	0.068	0.175	1.42	0.073	31120	2.94	1.4
				Median	28.4	1.60	0.0042	11.8	1.23	0.0678	0.185	1.88	3.41	0.549	0.103	4.20	0.059	0.087	1.25	0.073	31400	1.81	1.1

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
PS03 cont.				**1st Quartile**	27.5	1.20	0.0042	7.39	1.18	0.0573	0.157	1.63	1.86	0.509	0.0764	2.82	0.035	0.027	0.858	0.055	31000	0.99	0.7
				3rd Quartile	29.2	1.99	0.0042	14.9	1.26	0.0817	0.222	2.19	6.16	0.676	0.141	5.43	0.085	0.369	1.90	0.092	31500	3.00	1.7
				Maximum	31.0	5.81	0.0187	158	1.43	0.118	0.696	4.48	46.6	1.12	1.88	48.5	0.558	0.454	4.00	0.201	32300	16.5	2.7
				Minimum	25.6	0.700	0.0020	2.64	1.15	0.0384	0.132	1.06	0.64	0.402	0.0310	1.85	0.003	0.009	0.137	0.020	29400	0.45	0.7
			Dissolved	***n***		58	23	46	1	56	56	58	58	51	58	58							
				Average		1.39	0.0037	1.74	1.17	0.0653	0.160	1.56	2.88	0.573	0.0279	4.66							
				Median		1.28	0.0042	1.14		0.0622	0.151	1.48	1.51	0.510	0.0236	3.59							
				1st Quartile		1.05	0.0039	0.758		0.0541	0.129	1.26	0.73	0.451	0.0151	2.37							
				3rd Quartile		1.53	0.0042	2.14		0.0799	0.172	1.78	2.90	0.596	0.0332	5.32							
				Maximum		2.70	0.0042	13.6		0.0995	0.539	2.55	26.4	1.87	0.106	49.5							
				Minimum		0.700	0.0020	0.379		0.0376	0.069	0.792	0.31	0.374	0.0073	1.11							
PS04	47.55458	-122.64752	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	28.7	1.43	0.0039	10.5	1.24	0.0666	0.170	2.01	0.92	0.528	0.0835	5.39	0.054	0.186	1.31	0.069	31900	2.74	
				Median	28.6	1.40	0.0042	9.91	1.22	0.0651	0.140	2.04	0.82	0.545	0.0707	4.31	0.052	0.098	1.04	0.077	32300	1.50	
				1st Quartile	28.2	1.09	0.0042	6.41	1.19	0.0547	0.122	1.58	0.73	0.467	0.0640	3.24	0.038	0.030	0.720	0.057	31200	0.85	
				3rd Quartile	29.4	1.71	0.0042	15.5	1.30	0.0806	0.175	2.42	1.07	0.566	0.0996	6.50	0.064	0.368	1.51	0.086	32400	2.59	
				Maximum	31.1	2.38	0.0042	20.7	1.34	0.0990	0.717	3.06	1.87	0.757	0.176	23.1	0.143	0.432	3.30	0.097	32400	15.0	
				Minimum	26.9	0.899	0.0020	2.14	1.12	0.0376	0.071	1.03	0.56	0.388	0.0286	1.78	0.003	0.009	0.057	0.018	31200	0.40	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.38	0.0041	1.64	1.09	0.0653	0.134	1.69	0.39	0.481	0.0232	5.04							
				Median		1.31	0.0042	2.14		0.0631	0.126	1.68	0.38	0.453	0.0206	3.81							
				1st Quartile		1.05	0.0042	0.729		0.0527	0.111	1.34	0.31	0.422	0.0141	2.89							
				3rd Quartile		1.50	0.0042	2.14		0.0773	0.148	2.01	0.43	0.527	0.0295	5.78							
				Maximum		2.30	0.0068	3.98		0.0958	0.352	2.59	0.67	0.859	0.0757	22.3							
				Minimum		0.904	0.0020	0.325		0.0309	0.084	0.858	0.21	0.362	0.0042	1.98							
PS05	47.55606	-122.64491	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	28.8	1.44	0.0039	13.5	1.23	0.0678	0.162	1.85	0.91	0.545	0.0982	5.20	0.054	0.188	1.08	0.070	31940	2.46	
				Median	28.7	1.36	0.0042	13.4	1.22	0.0688	0.144	1.76	0.83	0.530	0.0787	4.52	0.053	0.096	1.08	0.072	32000	1.41	
				1st Quartile	28.1	1.10	0.0042	7.85	1.17	0.0543	0.131	1.52	0.73	0.477	0.0676	3.34	0.035	0.020	0.813	0.055	30400	0.75	
				3rd Quartile	29.6	1.62	0.0042	17.2	1.31	0.0809	0.171	1.98	1.02	0.573	0.104	6.70	0.064	0.370	1.45	0.084	32900	2.98	
				Maximum	30.8	2.86	0.0042	31.8	1.38	0.102	0.383	3.43	2.12	0.782	0.263	13.5	0.137	0.435	1.70	0.114	34600	11.0	
				Minimum	26.5	0.898	0.0020	2.56	1.07	0.0366	0.098	1.06	0.58	0.434	0.0500	1.46	0.003	0.009	0.062	0.036	29800	0.42	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.35	0.0039	1.61	1.13	0.0659	0.136	1.44	0.36	0.461	0.0203	4.73							
				Median		1.31	0.0042	2.14		0.0636	0.114	1.38	0.37	0.459	0.0169	4.50							
				1st Quartile		1.08	0.0042	0.908		0.0539	0.101	1.17	0.30	0.427	0.0140	2.66							
				3rd Quartile		1.50	0.0042	2.14		0.0799	0.135	1.59	0.42	0.489	0.0262	6.17							
				Maximum		2.20	0.0042	3.68		0.0949	0.647	2.29	0.61	0.570	0.0454	11.3							
				Minimum		0.800	0.0020	0.295		0.0327	0.077	0.879	0.19	0.370	0.0053	0.974							
PS06	47.5531	-122.64225	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	1
				Average	28.1	1.29	0.0039	16.6	1.26	0.0705	0.186	1.72	1.25	0.655	0.110	5.72	0.088	0.208	1.20	0.082	30780	2.50	0.7
				Median	28.2	1.21	0.0042	15.0	1.26	0.0690	0.149	1.57	1.08	0.593	0.0982	4.81	0.083	0.153	1.27	0.086	30400	1.50	
				1st Quartile	27.2	0.984	0.0042	11.0	1.21	0.0603	0.138	1.35	0.92	0.559	0.0679	4.29	0.063	0.073	0.870	0.072	29900	1.09	
				3rd Quartile	29.0	1.44	0.0042	18.9	1.32	0.0790	0.195	1.85	1.43	0.727	0.117	7.22	0.104	0.367	1.65	0.093	31500	2.98	
				Maximum	31.1	2.60	0.0046	42.2	1.38	0.0964	0.552	4.47	2.55	1.03	0.342	14.6	0.189	0.425	1.90	0.107	32900	9.50	
				Minimum	25.1	0.859	0.0020	5.23	1.16	0.0519	0.102	0.824	0.59	0.482	0.0535	2.06	0.014	0.020	0.132	0.016	29200	0.50	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.43	0.0039	1.63	1.32	0.0688	0.117	1.26	0.52	0.566	0.0227	5.28							
				Median		1.19	0.0042	1.77		0.0673	0.111	1.17	0.45	0.533	0.0189	4.55							
				1st Quartile		0.994	0.0042	0.841		0.0587	0.100	0.975	0.34	0.480	0.0134	3.93							
				3rd Quartile		1.50	0.0042	2.14		0.0800	0.129	1.35	0.62	0.581	0.0266	6.67							
				Maximum		4.20	0.0042	5.50		0.0947	0.170	3.38	1.26	0.988	0.101	13.2							
				Minimum		0.800	0.0020	0.336		0.0444	0.077	0.593	0.28	0.419	0.0062	1.23							

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
PS07	47.55598	-122.64134	*Total*	***n***	50	49	18	47	16	49	49	50	50	40	50	50	46	49	18	49	8	50	--
				Average	28.5	1.46	0.0041	14.2	1.26	0.0734	0.226	1.87	1.16	0.683	0.108	6.92	0.080	0.209	0.945	0.076	30900	3.43	
				Median	28.7	1.28	0.0042	13.1	1.23	0.0746	0.153	1.49	1.00	0.632	0.0963	5.17	0.076	0.136	0.925	0.083	31550	1.43	
				1st Quartile	27.7	1.00	0.0042	8.45	1.20	0.0654	0.134	1.28	0.81	0.579	0.0697	4.17	0.053	0.089	0.783	0.069	31075	0.93	
				3rd Quartile	29.3	1.60	0.0042	17.5	1.32	0.0800	0.193	2.15	1.24	0.684	0.125	6.84	0.102	0.364	1.28	0.089	31925	2.52	
				Maximum	31.3	3.92	0.0075	34.1	1.41	0.0949	2.81	5.47	6.82	1.50	0.2950	56.5	0.188	0.427	1.63	0.131	33600	40.0	
				Minimum	24.5	0.800	0.0020	2.14	1.11	0.0498	0.109	0.748	0.52	0.447	0.0435	1.65	0.003	0.009	0.097	0.004	24700	0.49	
			Dissolved	***n***		50	18	32	2	49	49	50	50	40	50	50							
				Average		1.39	0.0040	1.67	1.17	0.0707	0.122	1.48	0.52	0.597	0.0250	6.24							
				Median		1.22	0.0042	1.99	1.17	0.0710	0.107	1.21	0.46	0.559	0.0203	4.78							
				1st Quartile		1.02	0.0042	0.884	1.16	0.0617	0.099	0.985	0.37	0.510	0.0145	3.90							
				3rd Quartile		1.40	0.0042	2.14	1.18	0.0782	0.144	1.65	0.56	0.640	0.0315	6.59							
				Maximum		4.04	0.0042	5.96	1.19	0.0993	0.271	4.64	3.75	0.897	0.0700	54.8							
				Minimum		0.842	0.0020	0.327	1.15	0.0463	0.077	0.546	0.17	0.403	0.0077	1.11							
PS08	47.55784	-122.6388	*Total*	***n***	30	30	14	29	12	29	29	30	30	23	30	30	29	30	13	30	6	30	4
				Average	28.7	1.42	0.0041	15.1	1.25	0.0705	0.168	2.38	0.83	0.599	0.102	6.42	0.054	0.203	1.22	0.073	30800	2.96	1.4
				Median	28.8	1.41	0.0042	11.6	1.27	0.0724	0.151	2.08	0.70	0.570	0.0682	6.20	0.053	0.127	1.10	0.076	31750	1.99	1.2
				1st Quartile	27.9	1.02	0.0042	7.65	1.22	0.0593	0.136	1.53	0.59	0.507	0.0598	4.84	0.030	0.056	0.890	0.059	29700	1.09	0.7
				3rd Quartile	29.3	1.70	0.0042	15.2	1.30	0.0800	0.177	2.77	0.83	0.671	0.109	8.02	0.071	0.366	1.50	0.087	32225	3.44	1.9
				Maximum	31.3	2.84	0.0068	70.7	1.37	0.0947	0.358	6.60	2.69	0.868	0.497	15.9	0.136	0.429	2.61	0.100	32700	14.0	2.6
				Minimum	26.2	0.855	0.0020	2.14	1.11	0.0316	0.055	0.886	0.42	0.457	0.0468	1.70	0.003	0.009	0.093	0.023	27200	0.50	0.7
			Dissolved	***n***		29	14	22	1	29	29	30	30	23	30	30							
				Average		1.32	0.0044	1.70	1.12	0.0694	0.133	2.00	0.32	0.590	0.0197	6.05							
				Median		1.31	0.0042	2.02		0.0694	0.120	1.70	0.30	0.565	0.0176	5.68							
				1st Quartile		1.01	0.0042	0.788		0.0578	0.102	1.18	0.23	0.479	0.0113	4.58							
				3rd Quartile		1.50	0.0042	2.14		0.0831	0.156	2.16	0.36	0.687	0.0234	7.86							
				Maximum		2.20	0.0119	6.81		0.0964	0.304	6.86	0.74	0.886	0.0516	14.0							
				Minimum		0.856	0.0020	0.339		0.0272	0.068	0.745	0.17	0.399	0.0053	0.802							
PS09	47.55996	-122.63626	*Total*	***n***	31	31	14	30	12	30	30	31	31	24	31	31	29	30	13	30	6	31	4
				Average	27.9	1.40	0.0041	15.0	1.29	0.0743	0.188	2.44	1.46	0.766	0.122	9.48	0.076	0.231	1.20	0.078	30033	3.86	0.8
				Median	28.0	1.20	0.0042	12.9	1.31	0.0763	0.163	2.27	1.35	0.732	0.106	8.87	0.077	0.219	1.00	0.077	29800	1.66	0.7
				1st Quartile	27.3	1.00	0.0042	8.52	1.19	0.0611	0.138	1.70	0.95	0.566	0.0776	6.38	0.049	0.105	0.800	0.064	29525	0.96	0.7
				3rd Quartile	28.8	1.58	0.0042	20.6	1.38	0.0837	0.218	2.94	1.85	0.897	0.145	11.4	0.097	0.378	1.40	0.095	30000	3.20	0.8
				Maximum	30.0	3.60	0.0055	37.8	1.43	0.102	0.466	5.10	3.99	1.64	0.418	25.9	0.181	0.441	3.00	0.112	31700	30.5	1.2
				Minimum	25.4	0.656	0.0020	3.02	1.14	0.0553	0.121	1.35	0.54	0.458	0.0480	4.20	0.026	0.009	0.121	0.021	29400	0.41	0.7
			Dissolved	***n***		31	14	22	1	30	30	31	31	24	31	31							
				Average		1.31	0.0039	1.61	1.09	0.0713	0.160	1.84	0.48	0.653	0.0225	8.81							
				Median		1.22	0.0042	1.94		0.0716	0.136	1.79	0.41	0.611	0.0188	8.21							
				1st Quartile		0.982	0.0042	0.715		0.0597	0.108	1.30	0.31	0.504	0.0127	6.08							
				3rd Quartile		1.38	0.0042	2.14		0.0803	0.153	2.03	0.59	0.707	0.0294	9.86							
				Maximum		2.70	0.0046	5.24		0.0991	0.968	3.85	1.11	1.16	0.0614	24.7							
				Minimum		0.644	0.0020	0.245		0.0505	0.080	1.00	0.19	0.396	0.0064	3.08							
PS10	47.56046	-122.63322	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	28.7	1.38	0.0056	13.9	1.24	0.0720	0.181	2.22	1.23	0.675	0.115	6.26	0.065	0.209	1.27	0.074	30700	3.65	
				Median	28.3	1.28	0.0042	10.7	1.23	0.0696	0.154	1.92	0.78	0.556	0.0816	5.51	0.050	0.131	1.11	0.075	31300	1.54	
				1st Quartile	28.1	1.03	0.0042	6.75	1.20	0.0602	0.130	1.65	0.67	0.490	0.0718	3.74	0.040	0.068	0.578	0.060	29300	1.01	
				3rd Quartile	29.1	1.70	0.0042	17.8	1.31	0.0844	0.169	2.42	1.07	0.642	0.0990	8.63	0.082	0.375	1.90	0.089	31500	2.68	
				Maximum	31.2	2.40	0.0272	50.3	1.47	0.102	0.601	7.25	10.7	1.89	0.839	14.5	0.287	0.443	2.93	0.123	32100	37.0	
				Minimum	27.3	0.800	0.0020	4.40	1.00	0.0467	0.096	0.816	0.50	0.399	0.0462	2.22	0.011	0.009	0.070	0.004	29300	0.49	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.27	0.0039	1.61	0.940	0.0688	0.181	1.57	0.39	0.531	0.0208	5.61							
				Median		1.22	0.0042	2.12		0.0658	0.115	1.47	0.34	0.497	0.0193	5.25							
				1st Quartile		1.00	0.0042	0.889		0.0577	0.101	1.20	0.30	0.432	0.0134	3.41							

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
PS10 cont.				**3rd Quartile**		1.37	0.0042	2.14		0.0819	0.142	1.90	0.41	0.572	0.0250	7.62							
				Maximum		2.40	0.0042	3.52		0.0968	1.80	2.97	1.35	1.27	0.0454	11.7							
				Minimum		0.700	0.0020	0.353		0.0451	0.067	0.630	0.19	0.379	0.0065	1.40							
PS10.1	47.56123	-122.63132	*Total*	***n***	26	26	10	25	8	25	25	26	26	23	26	26	25	26	9	26	2	26	--
				Average	28.9	1.39	0.0038	12.4	1.22	0.0684	0.159	1.89	0.86	0.564	0.0876	6.70	0.048	0.188	0.895	0.074	32400	3.32	
				Median	28.7	1.31	0.0042	11.7	1.22	0.0653	0.150	1.87	0.75	0.563	0.0830	6.01	0.046	0.109	0.890	0.074	32400	1.77	
				1st Quartile	28.3	1.01	0.0042	7.81	1.16	0.0581	0.137	1.56	0.68	0.505	0.0697	4.70	0.026	0.040	0.570	0.056	32250	1.00	
				3rd Quartile	29.3	1.67	0.0042	15.8	1.29	0.0805	0.177	2.18	0.90	0.607	0.0968	7.65	0.053	0.365	1.16	0.082	32550	2.57	
				Maximum	31.3	2.68	0.0042	22.8	1.39	0.0929	0.275	3.86	2.32	0.818	0.198	12.9	0.143	0.440	1.50	0.137	32700	38.5	
				Minimum	27.4	0.900	0.0020	4.23	1.10	0.0487	0.101	0.692	0.50	0.399	0.0505	1.27	0.013	0.009	0.121	0.037	32100	0.49	
			Dissolved	***n***		25	10	20	0	25	25	26	26	23	26	26							
				Average		1.23	0.0040	1.65		0.0652	0.124	1.45	0.31	0.537	0.0193	6.12							
				Median		1.17	0.0042	2.14		0.0617	0.120	1.42	0.29	0.498	0.0193	5.73							
				1st Quartile		0.966	0.0042	0.955		0.0528	0.103	1.19	0.26	0.443	0.0124	3.98							
				3rd Quartile		1.31	0.0042	2.14		0.0784	0.144	1.74	0.35	0.563	0.0245	7.29							
				Maximum		2.40	0.0045	3.25		0.0877	0.188	2.59	0.55	0.923	0.0463	12.8							
				Minimum		0.700	0.0020	0.480		0.0434	0.076	0.528	0.18	0.351	0.0052	0.925							
PS11	47.56048	-122.62986	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	29.0	1.34	0.0039	15.4	1.21	0.0721	0.162	1.71	1.09	0.558	0.118	6.67	0.050	0.204	0.984	0.075	32100	4.24	
				Median	29.0	1.26	0.0042	12.2	1.21	0.0710	0.148	1.67	0.85	0.536	0.0986	5.50	0.046	0.143	0.850	0.081	32200	1.51	
				1st Quartile	28.4	1.05	0.0042	9.88	1.15	0.0618	0.125	1.36	0.68	0.466	0.0647	3.78	0.031	0.058	0.660	0.063	32000	1.11	
				3rd Quartile	29.3	1.48	0.0042	19.6	1.30	0.0834	0.173	1.95	1.24	0.592	0.132	8.02	0.066	0.369	1.24	0.089	32200	3.20	
				Maximum	31.8	2.60	0.0042	44.4	1.32	0.0945	0.331	3.15	3.72	1.04	0.371	26.9	0.134	0.433	2.30	0.108	33500	41.0	
				Minimum	27.3	0.800	0.0020	4.86	1.07	0.0516	0.082	0.591	0.52	0.403	0.0514	1.14	0.003	0.009	0.110	0.037	30600	0.51	
			Dissolved	***n***		28	13	21	1	28	28	29	29	23	29	29							
				Average		1.28	0.0039	1.65	1.04	0.0687	0.127	1.31	0.32	0.534	0.0219	5.85							
				Median		1.18	0.0042	1.90		0.0705	0.111	1.19	0.29	0.500	0.0177	4.03							
				1st Quartile		1.00	0.0042	0.874		0.0568	0.096	0.937	0.24	0.432	0.0129	3.18							
				3rd Quartile		1.32	0.0042	2.14		0.0797	0.132	1.60	0.38	0.567	0.0285	6.66							
				Maximum		2.60	0.0042	6.24		0.0956	0.354	2.36	0.71	0.971	0.0618	27.0							
				Minimum		0.848	0.0020	0.344		0.0448	0.061	0.454	0.15	0.347	0.0071	0.948							
PS12	47.56052	-122.62836	*Total*	***n***	29	28	13	28	12	28	28	29	29	22	29	29	28	28	12	28	6	28	--
				Average	29.0	1.30	0.0042	21.4	1.24	0.0727	0.253	1.51	1.17	0.636	0.152	4.88	0.051	0.205	1.27	0.073	32483	3.79	
				Median	28.9	1.26	0.0042	15.8	1.21	0.0740	0.167	1.39	0.99	0.570	0.106	4.74	0.046	0.156	1.27	0.077	32300	2.16	
				1st Quartile	28.6	1.02	0.0042	9.79	1.20	0.0619	0.147	1.21	0.71	0.527	0.0883	3.61	0.027	0.060	1.08	0.062	32050	1.30	
				3rd Quartile	29.5	1.60	0.0042	19.8	1.32	0.0834	0.211	1.62	1.19	0.648	0.133	5.92	0.067	0.364	1.53	0.087	32475	3.56	
				Maximum	31.3	1.80	0.0059	153	1.35	0.103	2.09	3.15	5.44	1.39	0.9500	10.1	0.120	0.434	1.82	0.105	34100	23.0	
				Minimum	27.4	0.800	0.0020	5.98	1.12	0.0428	0.108	0.964	0.56	0.394	0.0472	1.66	0.004	0.009	0.600	0.004	31700	0.54	
			Dissolved	***n***		28	13	21	1	28	28	29	29	22	29	29							
				Average		1.39	0.0040	1.61	1.20	0.0667	0.156	1.06	0.32	0.513	0.0219	4.13							
				Median		1.22	0.0042	2.14		0.0664	0.119	1.06	0.31	0.506	0.0210	4.20							
				1st Quartile		1.06	0.0042	0.792		0.0557	0.108	0.909	0.27	0.420	0.0131	2.75							
				3rd Quartile		1.39	0.0042	2.14		0.0800	0.130	1.14	0.35	0.550	0.0278	5.26							
				Maximum		3.40	0.0042	4.26		0.0912	1.07	1.64	0.79	0.792	0.0453	7.26							
				Minimum		0.800	0.0020	0.200		0.0342	0.081	0.571	0.17	0.323	0.0049	1.06							
PS13	47.55199	-122.65407	*Total*	***n***	27	27	12	26	10	26	26	27	27	21	27	27	26	27	11	27	5	27	1
				Average	28.7	1.79	0.0039	13.1	1.16	0.0703	0.169	1.64	0.79	0.555	0.0838	3.65	0.055	0.180	1.20	0.078	31560	5.08	2.4
				Median	28.5	1.56	0.0042	11.9	1.22	0.0689	0.150	1.61	0.76	0.518	0.0796	3.44	0.055	0.073	1.20	0.080	31500	1.87	
				1st Quartile	28.0	1.13	0.0042	8.62	1.14	0.0571	0.128	1.29	0.64	0.459	0.0576	2.18	0.040	0.026	0.960	0.059	31300	1.13	
				3rd Quartile	29.4	1.80	0.0042	16.5	1.24	0.0836	0.183	1.84	0.89	0.569	0.0951	4.39	0.076	0.356	1.60	0.095	32000	4.15	
				Maximum	31.0	6.14	0.0049	29.4	1.33	0.0998	0.439	2.94	1.45	1.38	0.208	7.56	0.115	0.442	1.90	0.183	32200	42.5	
				Minimum	26.6	0.959	0.0020	3.93	0.648	0.0367	0.109	0.873	0.44	0.402	0.0373	1.46	0.004	0.009	0.090	0.035	30800	0.52	
			Dissolved	***n***		27	12	19	1	26	26	27	27	21	27	27							

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
PS13 cont.				**Average**		1.63	0.0043	1.72	0.620	0.0646	0.136	1.31	0.32	0.520	0.0195	3.23							
				Median		1.29	0.0042	2.14		0.0600	0.114	1.22	0.32	0.455	0.0170	3.02							
				1st Quartile		1.08	0.0042	0.928		0.0507	0.100	1.03	0.26	0.430	0.0117	1.96							
				3rd Quartile		1.75	0.0042	2.14		0.0808	0.135	1.47	0.37	0.501	0.0271	3.82							
				Maximum		4.80	0.0093	4.21		0.0888	0.499	2.36	0.47	1.63	0.0448	7.58							
				Minimum		0.900	0.0020	0.421		0.0325	0.081	0.632	0.17	0.383	0.0058	0.733							
PS14	47.55241	-122.64371	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	3
				Average	28.8	1.49	0.0039	13.9	1.22	0.0662	0.166	1.30	0.76	0.659	0.0777	3.02	0.054	0.183	1.14	0.063	31360	2.85	1.4
				Median	29.0	1.37	0.0042	12.8	1.24	0.0654	0.142	1.26	0.78	0.515	0.0732	2.72	0.046	0.092	1.14	0.076	31500	1.61	1.3
				1st Quartile	28.2	1.10	0.0042	8.90	1.18	0.0563	0.120	1.04	0.66	0.478	0.0610	2.18	0.029	0.026	0.743	0.055	31000	0.92	1.0
				3rd Quartile	29.4	1.70	0.0042	19.1	1.31	0.0775	0.202	1.43	0.86	0.622	0.0903	3.70	0.061	0.364	1.45	0.083	31800	3.00	1.8
				Maximum	31.1	3.03	0.0050	26.5	1.36	0.0943	0.338	2.02	1.19	2.30	0.159	5.15	0.332	0.431	2.30	0.096	32900	16.0	2.2
				Minimum	27.0	0.878	0.0020	5.03	0.930	0.0267	0.106	0.576	0.44	0.406	0.0372	0.890	0.003	0.009	0.090	0.004	29600	0.30	0.7
			Dissolved	***n***		28	13	21	1	28	28	29	29	23	29	29							
				Average		1.37	0.0039	1.52	0.885	0.0637	0.120	1.02	0.31	0.507	0.0172	2.70							
				Median		1.27	0.0042	2.14		0.0606	0.119	0.960	0.31	0.494	0.0155	2.38							
				1st Quartile		1.08	0.0042	0.788		0.0529	0.099	0.857	0.27	0.454	0.0098	1.63							
				3rd Quartile		1.52	0.0042	2.14		0.0759	0.137	1.15	0.34	0.530	0.0219	3.79							
				Maximum		2.80	0.0042	2.80		0.0966	0.193	1.68	0.56	0.748	0.0404	4.97							
				Minimum		0.800	0.0020	0.312		0.0226	0.072	0.460	0.18	0.373	0.0062	0.849							
PS15	47.55562	-122.63658	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	3
				Average	28.9	1.64	0.0039	13.3	1.21	0.0711	0.166	1.14	0.72	0.608	0.0737	2.99	0.045	0.189	1.19	0.071	31060	5.69	1.9
				Median	28.9	1.37	0.0042	12.2	1.22	0.0672	0.147	1.07	0.71	0.522	0.0723	2.71	0.040	0.120	1.12	0.074	31300	1.76	2.3
				1st Quartile	28.3	1.00	0.0042	8.71	1.17	0.0559	0.134	0.930	0.57	0.473	0.0621	1.63	0.031	0.020	0.663	0.054	30500	1.06	1.5
				3rd Quartile	29.3	1.60	0.0042	17.5	1.31	0.0806	0.182	1.21	0.77	0.557	0.0835	3.62	0.055	0.365	1.82	0.086	31500	3.22	2.6
				Maximum	31.3	7.70	0.0053	23.9	1.35	0.213	0.412	2.76	1.22	1.82	0.111	9.08	0.094	0.432	2.10	0.177	32200	78.0	2.8
				Minimum	27.1	0.868	0.0020	2.14	0.850	0.0288	0.077	0.724	0.45	0.395	0.0334	1.28	0.003	0.009	0.064	0.016	29800	0.50	0.7
			Dissolved	***n***		28	13	21	1	28	28	29	29	23	29	29							
				Average		1.41	0.0039	1.70	0.833	0.0661	0.211	0.901	0.30	0.526	0.0167	2.68							
				Median		1.24	0.0042	2.00		0.0641	0.111	0.802	0.28	0.493	0.0137	2.57							
				1st Quartile		1.00	0.0042	0.900		0.0529	0.096	0.733	0.23	0.410	0.0094	1.19							
				3rd Quartile		1.41	0.0042	2.14		0.0797	0.126	1.09	0.33	0.587	0.0213	3.25							
				Maximum		5.40	0.0042	5.23		0.119	2.82	2.20	0.60	0.833	0.0553	8.92							
				Minimum		0.800	0.0020	0.271		0.0244	0.058	0.474	0.15	0.314	0.0057	0.631							
PS16	47.55872	-122.62844	*Total*	***n***	30	30	13	29	11	29	29	30	30	24	30	30	28	29	12	29	5	30	--
				Average	29.1	1.46	0.0039	15.5	1.21	0.0713	0.191	1.18	0.77	0.626	0.0835	4.31	0.041	0.199	1.22	0.071	31900	3.09	
				Median	29.2	1.30	0.0042	13.2	1.22	0.0698	0.154	1.01	0.68	0.554	0.0773	2.98	0.042	0.102	0.955	0.071	32100	1.77	
				1st Quartile	28.5	0.978	0.0042	8.80	1.17	0.0595	0.132	0.934	0.59	0.478	0.0602	1.93	0.025	0.047	0.738	0.061	31100	1.16	
				3rd Quartile	29.5	1.72	0.0042	18.0	1.25	0.0815	0.177	1.26	0.83	0.691	0.0872	5.69	0.053	0.366	1.85	0.084	32500	3.41	
				Maximum	31.6	2.93	0.0042	64.4	1.38	0.0910	1.16	2.77	2.08	1.69	0.332	19.3	0.093	0.431	2.22	0.097	32800	13.0	
				Minimum	26.9	0.700	0.0020	2.29	1.01	0.0545	0.087	0.610	0.36	0.383	0.0296	1.37	0.003	0.009	0.092	0.007	31000	0.66	
			Dissolved	***n***		29	13	21	1	29	29	30	30	24	30	30							
				Average		1.47	0.0039	1.53	0.979	0.0672	0.129	0.904	0.26	0.520	0.0165	3.66							
				Median		1.26	0.0042	1.98		0.0641	0.113	0.820	0.25	0.497	0.0144	2.96							
				1st Quartile		0.968	0.0042	0.839		0.0565	0.103	0.709	0.22	0.411	0.0091	1.61							
				3rd Quartile		1.45	0.0042	2.14		0.0804	0.148	1.01	0.29	0.554	0.0229	3.95							
				Maximum		4.10	0.0042	3.11		0.0892	0.406	2.08	0.55	1.21	0.0386	18.6							
				Minimum		0.853	0.0020	0.305		0.0420	0.054	0.479	0.16	0.354	0.0049	0.693							
PWNLP	47.58426	-122.64405	*Total*	***n***	8	8	7	8	7	8	8	8	8	5	8	8	8	8	7	8	4	8	--
				Average	29.4	1.50	0.0042	19.6	1.20	0.0736	0.223	0.647	0.72	0.630	0.0843	1.66	0.032	0.226	1.16	0.077	31900	4.92	
				Median	29.1	1.50	0.0042	17.7	1.21	0.0723	0.171	0.645	0.68	0.462	0.0818	1.00	0.024	0.229	1.11	0.074	31750	4.63	
				1st Quartile	28.9	1.33	0.0042	15.2	1.16	0.0638	0.130	0.562	0.59	0.425	0.0669	0.765	0.019	0.101	0.905	0.069	31025	2.25	
				3rd Quartile	29.8	1.83	0.0042	21.9	1.25	0.0820	0.217	0.706	0.84	0.809	0.0980	1.50	0.042	0.341	1.35	0.083	32625	6.88	

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
PWNLP cont.				**Maximum**	30.6	2.03	0.0042	38.6	1.34	0.0918	0.599	0.810	0.92	1.07	0.146	5.66	0.061	0.410	1.98	0.100	33900	10.0	
				Minimum	28.8	0.800	0.0042	9.13	1.06	0.0616	0.124	0.534	0.56	0.387	0.0369	0.603	0.011	0.021	0.520	0.060	30200	0.62	
			Dissolved	***n***		8	7	6	--	8	8	8	8	5	8	8							
				Average		1.47	0.0042	2.43		0.0690	0.833	0.464	0.33	0.404	0.0148	1.96							
				Median		1.50	0.0042	2.14		0.0693	0.110	0.457	0.28	0.416	0.0101	0.830							
				1st Quartile		1.22	0.0042	2.14		0.0596	0.101	0.439	0.23	0.372	0.0083	0.677							
				3rd Quartile		1.65	0.0042	2.14		0.0772	0.114	0.477	0.35	0.439	0.0204	1.27							
				Maximum		2.00	0.0042	3.90		0.0864	5.93	0.553	0.70	0.445	0.0309	9.50							
				Minimum		0.918	0.0042	2.14		0.0528	0.084	0.413	0.21	0.350	0.0069	0.435							
SN03	47.54658	-122.67124	*Total*	***n***	27	27	13	27	11	26	26	27	27	22	27	27	27	27	11	27	5	27	--
				Average	28.1	5.03	0.0039	22.7	1.13	0.134	0.211	0.965	1.65	0.673	0.110	2.95	0.146	0.193	2.29	0.170	30640	8.66	
				Median	28.6	1.60	0.0042	18.9	1.18	0.0667	0.185	0.886	1.06	0.589	0.0980	1.91	0.110	0.134	1.20	0.090	30300	2.27	
				1st Quartile	27.9	1.28	0.0042	11.3	1.14	0.0576	0.150	0.816	0.75	0.490	0.0721	1.41	0.055	0.048	1.06	0.068	30100	1.37	
				3rd Quartile	29.3	1.86	0.0042	35.2	1.23	0.0814	0.229	1.00	1.71	0.682	0.146	2.42	0.204	0.358	1.59	0.111	32000	5.40	
				Maximum	30.0	66.3	0.0042	49.3	1.34	1.38	0.517	2.07	9.24	1.69	0.248	19.8	0.588	0.451	12.1	1.50	33000	133	
				Minimum	18.3	1.00	0.0020	4.83	0.446	0.0486	0.092	0.602	0.51	0.423	0.0426	1.03	0.015	0.009	0.780	0.032	27800	0.62	
			Dissolved	***n***		27	13	20	1	26	26	27	27	22	27	27							
				Average		3.68	0.0039	1.90	0.470	0.0749	0.151	0.687	0.47	0.523	0.0181	1.85							
				Median		1.40	0.0042	2.14		0.0639	0.125	0.680	0.30	0.496	0.0138	1.42							
				1st Quartile		1.08	0.0042	0.834		0.0510	0.108	0.534	0.24	0.437	0.0117	0.908							
				3rd Quartile		1.70	0.0042	2.14		0.0785	0.164	0.787	0.41	0.550	0.0232	2.44							
				Maximum		50.0	0.0042	6.44		0.273	0.556	1.03	2.19	1.08	0.0453	5.42							
				Minimum		0.800	0.0020	0.200		0.0422	0.074	0.399	0.16	0.358	0.0065	0.424							
SN05	47.53143	-122.68687	*Total*	***n***	28	28	13	28	11	27	27	28	28	23	28	28	28	28	11	28	5	28	--
				Average	26.0	1.78	0.0043	94.8	1.01	0.0675	0.451	0.972	1.74	0.758	0.229	2.07	0.060	0.193	1.90	0.084	28680	7.56	
				Median	28.1	1.62	0.0042	87.7	0.993	0.0666	0.406	0.967	1.52	0.752	0.218	1.92	0.048	0.105	1.20	0.081	30000	5.46	
				1st Quartile	25.3	1.29	0.0042	33.6	0.882	0.0500	0.307	0.783	1.14	0.587	0.109	1.58	0.026	0.031	1.05	0.067	25900	3.44	
				3rd Quartile	28.6	1.99	0.0042	119.6	1.15	0.0765	0.552	1.17	2.17	0.858	0.302	2.22	0.088	0.365	2.49	0.098	32900	7.50	
				Maximum	30.1	4.20	0.0056	259.0	1.25	0.152	1.15	1.38	3.94	1.44	0.517	4.99	0.176	0.675	5.80	0.172	33500	35.0	
				Minimum	8.2	1.04	0.0020	17.8	0.777	0.0420	0.141	0.642	0.57	0.427	0.0586	1.20	0.003	0.009	0.700	0.026	21100	1.01	
			Dissolved	***n***		28	13	21	1	27	27	28	28	23	28	28							
				Average		1.52	0.0039	2.82	1.1	0.0602	0.213	0.588	0.39	0.505	0.0259	1.65							
				Median		1.38	0.0042	2.14		0.0607	0.161	0.557	0.36	0.487	0.0193	1.33							
				1st Quartile		1.17	0.0042	1.79		0.0449	0.117	0.473	0.30	0.417	0.0105	0.972							
				3rd Quartile		1.69	0.0042	3.30		0.0728	0.203	0.679	0.47	0.531	0.0325	1.66							
				Maximum		3.00	0.0042	8.99		0.116	0.845	1.21	0.82	0.999	0.0876	5.75							
				Minimum		0.973	0.0020	0.545		0.0328	0.063	0.350	0.22	0.393	0.0068	0.617							
SN08	47.54008	-122.66242	*Total*	***n***	27	27	13	27	11	26	26	27	27	22	27	27	27	27	11	27	5	27	--
				Average	27.9	2.41	0.0039	30.3	1.15	0.0724	0.240	0.948	1.04	0.578	0.120	2.16	0.042	0.163	1.68	0.090	31760	6.90	
				Median	28.1	1.55	0.0042	28.6	1.17	0.0691	0.229	0.926	1.01	0.555	0.114	1.99	0.037	0.055	1.36	0.076	31700	2.36	
				1st Quartile	27.0	1.22	0.0042	19.4	1.13	0.0538	0.196	0.782	0.73	0.493	0.0820	1.41	0.019	0.021	1.00	0.055	30400	1.67	
				3rd Quartile	29.2	2.38	0.0042	38.7	1.22	0.0825	0.253	1.11	1.22	0.624	0.151	2.50	0.060	0.341	2.15	0.101	32800	6.34	
				Maximum	30.0	14.8	0.0048	74.2	1.30	0.219	0.443	1.40	2.60	0.857	0.208	5.93	0.101	0.428	3.75	0.420	33500	69.0	
				Minimum	24.6	0.900	0.0020	13.4	0.922	0.0387	0.110	0.634	0.54	0.449	0.0554	0.970	0.003	0.009	0.660	0.021	30400	0.62	
			Dissolved	***n***		27	13	21	1	26	26	27	27	22	27	27							
				Average		1.97	0.0039	1.91	0.894	0.0612	0.161	0.702	0.32	0.503	0.0187	1.58							
				Median		1.37	0.0042	2.14		0.0560	0.125	0.684	0.27	0.465	0.0174	1.32							
				1st Quartile		1.11	0.0042	0.974		0.0478	0.105	0.568	0.23	0.399	0.0093	1.04							
				3rd Quartile		1.62	0.0042	2.14		0.0769	0.179	0.854	0.35	0.510	0.0254	2.06							
				Maximum		9.70	0.0042	6.82		0.0875	0.515	1.05	1.12	1.46	0.0421	4.44							
				Minimum		0.700	0.0020	0.309		0.0350	0.067	0.478	0.16	0.346	0.0069	0.578							
SN10	47.54095	-122.64264	*Total*	***n***	28	28	13	28	11	27	27	28	28	23	28	28	28	28	11	28	5	28	--
				Average	28.4	1.89	0.0039	18.9	1.12	0.0737	0.199	1.40	0.81	0.608	0.0973	3.80	0.045	0.162	1.42	0.074	31440	4.61	

Site Code	Latitude*(W)	Longitude (N)	Fraction	Statistic	Salinity (ppt)	TOC/DOC (mg/L)	Ag† (µg/L)	Al (µg/L)	As‡ (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	AN (mg/L)	NNN (mg/L)	TKN‡ (mg/L)	TP (mg/L)	TS§ (mg/L)	TSS (mg/L)	HEM‖ (mg/L)
SN10 cont.				**Median**	28.5	1.52	0.0042	16.5	1.12	0.0748	0.168	1.24	0.72	0.527	0.0885	3.06	0.040	0.052	1.00	0.078	32400	2.90	
				1st Quartile	27.3	1.06	0.0042	13.6	1.06	0.0589	0.151	1.09	0.60	0.479	0.0720	2.41	0.014	0.020	0.915	0.055	29800	1.55	
				3rd Quartile	29.3	2.30	0.0042	21.2	1.18	0.0821	0.221	1.49	0.90	0.606	0.106	4.16	0.065	0.352	1.64	0.090	33000	5.02	
				Maximum	30.0	4.98	0.0042	77.4	1.32	0.127	0.448	2.93	1.62	1.61	0.282	14.1	0.117	0.437	3.56	0.122	33100	40.0	
				Minimum	26.3	0.600	0.0020	2.14	0.923	0.0467	0.103	0.873	0.50	0.420	0.0401	1.47	0.003	0.009	0.660	0.025	28900	0.39	
			Dissolved	***n***		28	13	21	1	27	27	28	28	23	28	28							
				Average		1.51	0.0039	1.71	0.932	0.0656	0.140	1.07	0.30	0.451	0.0186	3.17							
				Median		1.37	0.0042	2.14		0.0665	0.117	0.893	0.28	0.442	0.0174	2.80							
				1st Quartile		1.17	0.0042	0.829		0.0516	0.102	0.781	0.24	0.408	0.0112	1.81							
				3rd Quartile		1.60	0.0042	2.14		0.0797	0.165	1.27	0.33	0.495	0.0224	3.65							
				Maximum		3.10	0.0042	4.22		0.0896	0.429	2.17	0.67	0.549	0.0400	10.1							
				Minimum		0.800	0.0020	0.200		0.0449	0.083	0.654	0.19	0.362	0.0062	0.931							
SN11	47.54338	-122.63549	*Total*	***n***	26	26	12	26	11	25	25	26	26	21	26	26	26	26	11	26	5	26	--
				Average	27.6	1.86	0.0040	17.9	1.16	0.0656	0.221	1.14	0.75	0.705	0.0833	2.81	0.040	0.150	1.24	0.068	31420	4.00	
				Median	28.6	1.72	0.0042	13.7	1.14	0.0639	0.180	1.07	0.71	0.556	0.0759	2.57	0.035	0.046	1.10	0.067	32200	2.85	
				1st Quartile	27.4	1.33	0.0042	8.46	1.09	0.0516	0.138	0.933	0.58	0.484	0.0630	2.19	0.011	0.020	0.955	0.056	31600	1.47	
				3rd Quartile	29.2	2.30	0.0042	20.9	1.21	0.0817	0.246	1.33	0.85	0.680	0.0959	3.02	0.054	0.352	1.48	0.078	32500	4.87	
				Maximum	30.3	4.00	0.0042	51.5	1.35	0.0946	0.699	1.58	1.68	3.09	0.248	5.65	0.139	0.433	2.00	0.122	34200	25.0	
				Minimum	20.0	0.900	0.0020	2.14	1.03	0.0260	0.094	0.843	0.33	0.377	0.0253	1.08	0.003	0.009	0.520	0.028	26600	0.55	
			Dissolved	***n***		26	12	20	1	25	25	26	26	21	26	26							
				Average		1.54	0.0040	2.46	0.987	0.0614	0.171	0.870	0.29	0.464	0.0160	2.46							
				Median		1.47	0.0042	2.14		0.0600	0.138	0.795	0.28	0.463	0.0126	2.22							
				1st Quartile		1.24	0.0042	0.634		0.0482	0.099	0.688	0.22	0.412	0.0093	1.73							
				3rd Quartile		1.96	0.0042	2.47		0.0778	0.170	1.11	0.33	0.518	0.0187	2.86							
				Maximum		2.60	0.0042	9.25		0.0881	0.593	1.27	0.47	0.598	0.0426	4.86							
				Minimum		0.841	0.0020	0.200		0.0379	0.074	0.630	0.18	0.350	0.0065	0.874							
WP	47.58397	-122.57182	*Total*	***n***	29	29	13	28	11	28	28	29	29	23	29	29	28	29	12	29	5	29	--
				Average	29.1	1.28	0.0039	21.4	1.22	0.0709	0.192	0.636	0.69	0.621	0.0774	1.44	0.037	0.206	1.10	0.070	32320	4.57	
				Median	29.1	1.25	0.0042	21.2	1.20	0.0676	0.163	0.628	0.69	0.541	0.0729	1.00	0.035	0.126	1.05	0.072	32100	1.88	
				1st Quartile	28.7	1.00	0.0042	15.7	1.19	0.0631	0.141	0.577	0.57	0.487	0.0568	0.827	0.016	0.074	0.988	0.058	32000	1.16	
				3rd Quartile	29.6	1.43	0.0042	25.5	1.23	0.0776	0.195	0.665	0.79	0.692	0.0921	1.41	0.052	0.365	1.32	0.080	32500	2.67	
				Maximum	31.2	2.02	0.0042	36.0	1.37	0.0914	0.716	0.938	1.16	1.66	0.157	7.74	0.150	0.431	2.10	0.117	34100	35.0	
				Minimum	27.3	0.700	0.0020	7.91	1.08	0.0574	0.110	0.428	0.37	0.376	0.0287	0.548	0.003	0.009	0.078	0.011	30900	0.62	
			Dissolved	***n***		29	13	21	1	28	28	29	29	23	29	29							
				Average		1.27	0.0039	1.53	1.13	0.0673	0.625	0.495	0.28	0.628	0.0151	1.53							
				Median		1.16	0.0042	2.10		0.0648	0.114	0.470	0.26	0.441	0.0147	0.886							
				1st Quartile		0.981	0.0042	0.638		0.0588	0.091	0.443	0.22	0.410	0.0075	0.565							
				3rd Quartile		1.55	0.0042	2.14		0.0785	0.132	0.533	0.28	0.534	0.0232	1.09							
				Maximum		2.78	0.0042	4.79		0.0859	13.9	0.670	0.61	2.59	0.0279	17.4							
				Minimum		0.700	0.0020	0.200		0.0458	0.069	0.381	0.17	0.333	0.0033	0.434							

* Coordinates are listed as target locations

† Analyte not sampled post-AMB14; determined to be non-concern

‡ Analyte not sampled post-AMB11; determined to be non-concern

§ Parameter not sampled post-AMB05; determined to be non-concern

‖ Parameter not sampled in receiving waters post-AMB22; determined to be non-concern

¶ Collected below seasonal thermocline

☞ Non-detects are included as method detection limits

Appendix C– WQBEL Calculations

Table C.1. OF018 pre-mixing WQBEL drafts.

OF018	Collection Date	Total As (µg L^{-1})	Total Cu (µg L^{-1})	Total Hg (ng L^{-1})	Total Pb (µg L^{-1})	Total Zn (µg L^{-1})
AMB01	08/31/09	2.09	12.2	15.7	0.599	52.2
AMB02	02/02/10	1.37	7.71	7.44	0.743	28.0
AMB03	03/23/10	1.45	5.78	11.1	0.381	25.0
AMB04	09/08/10	2.01	7.52	13.0	0.484	34.5
AMB05	11/16/10	1.86	3.73	9.14	0.190	24.5
AMB06	03/22/11	1.52	8.90	12.5	0.431	36.1
AMB07	06/21/11	1.35	5.16	6.00	0.218	34.9
AMB08	09/20/11	1.97	5.56	7.82	0.140	39.2
AMB09	12/06/11	2.20	2.33	12.2	0.270	13.7
AMB10	03/13/12	1.85	10.0	19.1	1.14	52.0
AMB11	08/28/12	1.65	3.16	7.07	0.255	19.3
AMB13	06/18/13	--	29.6	45.5	2.89	58.8
AMB14	02/19/14	--	10.8	5.90	0.357	47.2
AMB15	06/09/14	--	5.29	6.12	0.265	37.6
AMB17	04/07/15	--	6.83	19.1	0.680	68.7
AMB18	06/16/15	--	1.69	10.3	0.0816	28.0
AMB18[a]	06/16/15	--	2.72	5.05	0.159	34.4
AMB19	09/15/15	--	3.83	6.87	0.0724	21.0
AMB19[a]	09/15/15	--	5.72	4.33	0.154	20.9
AMB20	03/15/16	--	3.65	11.1	0.167	26.2
AMB21	08/30/16	--	19.1	11.8	0.933	54.3
AMB22	12/06/16	--	8.22	15.8	0.0992	29.5
AMB23	03/28/17	--	4.00	5.53	0.129	27.4
AMB24	08/22/17	--	5.50	9.36	0.163	45.7
AMB25	02/27/18	--	5.25	6.71	0.0604	32.9
AMB26[a]	06/26/18	--	12.3	6.30	0.296	33.2
AMB27	08/22/18	--	6.71	5.72	0.161	40.8
AMB28	03/19/19	--	2.01	9.24	0.0639	48.3
AMB28[a]	03/19/19	--	5.49	13.8	0.465	44.5
AMB29	07/30/19	--	5.59	6.70	0.287	54.3
	mean	1.76	7.21	10.9	0.411	37.1
	stdev	0.302	5.61	7.70	0.538	13.2
	n	11	30	30	30	30
	CV	0.172	0.778	0.708	1.31	0.356
	Pn	0.658	0.858	0.858	0.858	0.858
	acute σ^2	0.0292	0.473	0.406	0.998	0.119
	chronic σ^2	0.00739	0.141	0.118	0.356	0.0312

OF018	Collection Date	Total As (µg L^{-1})	Total Cu (µg L^{-1})	Total Hg (ng L^{-1})	Total Pb (µg L^{-1})	Total Zn (µg L^{-1})
	C_{99}	1.47	3.91	3.59	6.20	2.10
	C_{95}	1.31	2.45	2.33	3.14	1.66
	RPM	1.12	1.60	1.54	1.97	1.27
	C_e	2.47	47.3	70.2	5.71	86.9
	dissolved translator[b]	1	0.83	0.85	0.951	0.946
	dissolved C_D	2.47	39.3	59.7	5.43	82.2
	> CMC	no	yes	no	no	no
	> CCC	no	yes	--	no	yes
	WER criterion$_{acute}$[c]	--	6.8	--	--	--
	WER criterion$_{chronic}$[c]	--	4.4	--	--	--
	C_{DGT} criterion$_{acute}$[d]	--	2.4	--	--	pending
	WLA_{acute}	--	5.78	--	--	95.1
	$WLA_{chronic}$	--	3.73	--	--	85.6
	PSNS dissolved translator	--	0.773	--	--	agree
	WER WLA_{acute}	--	8.79	--	--	--
	WER $WLA_{chronic}$	--	5.69	--	--	--
	C_{DGT} translator	--	0.294	--	--	--
	C_{DGT} WLA_{acute}	--	8.2	--	--	--
	LTA_{acute}	--	1.48	--	--	45.2
	$LTA_{chronic}$	--	1.67	--	--	58.1
	acute < chronic	--	yes	--	--	yes
	MDL (µg L^{-1})	--	**5.78**	--	--	**95.1**
	AML (µg L^{-1})	--	**2.56**	--	--	**59.2**
	WER LTA_{acute}	--	2.25	--	--	--
	WER $LTA_{chronic}$	--	2.55	--	--	--
	acute < chronic	--	yes	--	--	--
	WER MDL (µg L^{-1})	--	**8.79**	--	--	--
	WER AML (µg L^{-1})	--	**3.89**	--	--	--
	C_{DGT} LTA_{acute}	--	2.09	--	--	--
	C_{DGT} $LTA_{chronic}$	--	3.67	--	--	--
	acute < chronic	--	yes	--	--	--
	C_{DGT} MDL (µg L^{-1})	--	**8.2**	--	--	--
	C_{DGT} AML (µg L^{-1})	--	**3.61**	--	--	--
	avg discharge volume (mg d^{-1})	--	3.10	--	--	3.10
	avg mass balance contribution (kg y^{-1})	--	10.9	--	--	253
	avg WER mass balance contr. (kg y^{-1})	--	16.6	--	--	--
	avg C_{DGT} mass balance contr, (kg y^{-1})	--	15.5	--	--	--

[a] collected at OF096

OF018	Collection Date	Total As (µg L^{-1})	Total Cu (µg L^{-1})	Total Hg (ng L^{-1})	Total Pb (µg L^{-1})	Total Zn (µg L^{-1})

[b] soucre: (EPA 2008b), conversion factor for Hg is applicable to acute criteria only

[c] Rosen et al. 2009

[d] Strivens et al. 2020

Table C.2. OF019 pre-mixing WQBEL drafts.

OF019	Collection Date	Total As (µg L^{-1})	Total Cu (µg L^{-1})	Total Hg (ng L^{-1})	Total Pb (µg L^{-1})	Total Zn (µg L^{-1})
AMB01	08/31/09	1.91	3.64	9.20	0.633	79.0
AMB02	02/02/10	1.52	2.99	5.72	0.380	27.9
AMB05	11/16/10	1.51	2.33	5.41	0.139	30.6
AMB06	03/22/11	1.39	6.63	4.81	0.253	32.0
AMB07	06/21/11	1.29	5.03	4.44	0.398	28.8
AMB08	09/20/11	1.48	12.0	3.35	0.200	23.3
AMB09	12/06/11	1.61	1.97	9.09	0.0620	25.3
AMB10	03/13/12	1.40	5.70	4.83	0.185	21.0
AMB11	08/28/12	--	--	--	--	--
AMB12	02/12/13	--	23.1	26.2	1.66	48.9
AMB13	06/18/13	--	6.18	9.71	0.199	25.5
AMB14	02/19/14	--	9.58	6.29	0.319	19.7
AMB15	06/09/14	--	4.8	2.52	0.207	15.8
AMB16	09/16/14	--	1.28	6.21	0.0446	10.4
AMB 17	04/07/15	--	8.02	14.8	0.689	28.0
AMB 19	09/15/15	--	1.43	4.92	0.0546	9.2
AMB20	03/15/16	--	1.79	9.46	0.112	11.1
AMB21	08/30/16	--	1.03	5.73	0.0767	7.95
AMB22	12/06/16	--	1.23	7.19	0.0502	7.47
AMB23	03/28/17	--	0.949	6.77	0.0343	6.67
AMB24	08/22/17	--	1.11	5.09	0.0320	12.3
AMB25	02/27/18	--	1.19	6.05	0.0320	11.0
AMB26	06/26/18	--	6.22	3.07	0.202	16.9
AMB27	08/22/18	--	12.4	2.85	0.147	22.0
AMB28	03/19/19	--	4.97	4.43	0.169	22.8
AMB29	07/30/19	--	5.16	3.67	0.207	17.6
	mean	1.51	5.23	6.87	0.259	22.4
	stdev	0.186	5.01	4.86	0.339	15.3
	n	8	25	25	25	25
	CV	0.123	0.957	0.708	1.31	0.684
	Pn	0.562	0.832	0.832	0.832	0.832
	acute σ^2	0.0150	0.650	0.406	0.997	0.383

OF019	Collection Date	Total As (µg L^{-1})	Total Cu (µg L^{-1})	Total Hg (ng L^{-1})	Total Pb (µg L^{-1})	Total Zn (µg L^{-1})
	chronic σ^2	0.00377	0.206	0.118	0.356	0.1105
	C_{99}	1.32	4.71	3.59	6.19	3.49
	C_{95}	1.21	2.72	2.33	3.14	2.29
	RPM	1.09	1.73	1.54	1.97	1.52
	C_e	2.07	40.0	40.4	3.28	120.4
	dissolved translator[b]	1	0.83	0.85	0.951	0.946
	dissolved C_D	2.07	33.2	34.4	3.12	113.9
	> CMC	no	yes	no	no	yes
	> CCC	no	yes	--	no	yes
	WER $criterion_{acute}$[c]	--	6.8	--	--	--
	WER $criterion_{chronic}$[c]	--	4.4	--	--	--
	C_{DGT} $criterion_{acute}$[d]	--	2.4	--	--	pending
	WLA_{acute}	--	5.78	--	--	95.1
	$WLA_{chronic}$	--	3.73	--	--	85.6
	PSNS dissolved translator	--	0.773	--	--	agree
	WER WLA_{acute}	--	8.79	--	--	--
	WER $WLA_{chronic}$	--	5.69	--	--	--
	C_{DGT} translator	--	0.294	--	--	--
	C_{DGT} WLA_{acute}	--	8.2	--	--	--
	LTA_{acute}	--	1.23	--	--	27.3
	$LTA_{chronic}$	--	1.44	--	--	43.7
	acute < chronic	--	yes	--	--	yes
	MDL (µg L^{-1})	--	**5.78**	--	--	**95.1**
	AML (µg L^{-1})	--	**2.34**	--	--	**43.3**
	WER LTA_{acute}	--	1.87	--	--	--
	WER $LTA_{chronic}$	--	2.19	--	--	--
	acute < chronic	--	yes	--	--	--
	WER MDL (µg L^{-1})	--	**8.79**	--	--	--
	WER AML (µg L^{-1})	--	**3.55**	--	--	--
	C_{DGT} LTA_{acute}	--	1.73	--	--	--
	C_{DGT} $LTA_{chronic}$	--	3.15	--	--	--
	acute < chronic	--	yes	--	--	--
	C_{DGT} MDL (µg L^{-1})	--	**8.2**	--	--	--
	C_{DGT} AML (µg L^{-1})	--	**3.30**	--	--	--
	avg discharge volume (mg d^{-1})	--	5.90	--	--	5.90
	avg mass balance contribution (kg y^{-1})	--	19.0	--	--	352
	avg WER mass balance contr. (kg y^{-1})	--	28.9	--	--	--
	avg C_{DGT} mass balance contr, (kg y^{-1})	--	26.9	--	--	--

OF019	Collection Date	Total As (µg L^{-1})	Total Cu (µg L^{-1})	Total Hg (ng L^{-1})	Total Pb (µg L^{-1})	Total Zn (µg L^{-1})

[b] source: (EPA 2008b), conversion factor for Hg is applicable to acute criteria only

[c] Rosen et al. 2009

[d] Strivens et al. 2020

Table C.3. PSNS Nearshore Total:Dissolved Cu Translator

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB01	PS01	08/31/09	Dry	1.370	1.030	25.000	0.752
AMB01	PS02	08/31/09	Dry	2.140	1.680	24.000	0.785
AMB01	PS03	08/31/09	Dry	2.900	2.170	15.000	0.748
AMB01	PS04	08/31/09	Dry	1.820	1.320	15.000	0.725
AMB01	PS05	08/31/09	Dry	1.980	1.690	11.000	0.854
AMB01	PS06	08/31/09	Dry	1.960	1.330	7.000	0.679
AMB01	PS07	08/31/09	Dry	1.740	1.400	15.000	0.805
AMB01	PS08	08/31/09	Dry	3.180	2.460	14.000	0.774
AMB01	PS09	08/31/09	Dry	2.930	2.500	15.000	0.853
AMB01	PS10	08/31/09	Dry	1.920	1.470	14.000	0.766
AMB01	PS11	08/31/09	Dry	1.570	1.170	18.000	0.745
AMB01	PS07	09/01/09	Dry	1.480	1.040	25.000	0.703
AMB01	PS12	09/01/09	Dry	1.150	0.940	23.000	0.817
AMB04	PS01	09/08/10	Dry	2.889	1.671	12.500	0.578
AMB04	PS02	09/08/10	Dry	2.108	1.593	31.000	0.756
AMB04	PS03	09/08/10	Dry	2.957	2.212	7.000	0.748
AMB04	PS04	09/08/10	Dry	2.355	1.884	8.500	0.800
AMB04	PS05	09/08/10	Dry	1.239	0.978	5.000	0.789
AMB04	PS06	09/08/10	Dry	1.567	1.135	5.000	0.724
AMB04	PS07	09/08/10	Dry	4.425	3.685	6.000	0.833
AMB04	PS08	09/08/10	Dry	6.598	4.134	7.500	0.627
AMB04	PS09	09/08/10	Dry	3.143	1.882	30.500	0.599
AMB04	PS10	09/08/10	Dry	3.416	2.539	37.000	0.743
AMB04	PS10.1	09/08/10	Dry	1.860	1.420	38.500	0.763
AMB04	PS11	09/08/10	Dry	3.151	2.361	41.000	0.749
AMB04	PS07	09/09/10	Dry	1.903	1.503	40.000	0.790
AMB04	PS12	09/09/10	Dry	1.794	1.394	7.000	0.777
AMB07	PS01	06/21/11	Dry	1.370	1.120	1.380	0.818
AMB07	PS02	06/21/11	Dry	1.760	1.470	1.320	0.835
AMB07	PS03	06/21/11	Dry	2.080	1.430	3.910	0.688
AMB07	PS04	06/21/11	Dry	1.410	1.050	2.250	0.745
AMB07	PS05	06/21/11	Dry	2.050	1.450	2.980	0.707
AMB07	PS06	06/21/11	Dry	1.960	1.350	1.820	0.689
AMB07	PS07	06/21/11	Dry	2.250	1.680	1.430	0.747

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB07	PS08	06/21/11	Dry	2.410	1.830	2.310	0.759
AMB07	PS09	06/21/11	Dry	1.570	1.340	3.100	0.854
AMB07	PS10	06/21/11	Dry	1.580	0.672	1.590	0.425
AMB07	PS10.1	06/21/11	Dry	1.660	1.260	4.590	0.759
AMB07	PS11	06/21/11	Dry	1.220	0.937	1.400	0.768
AMB07	PS12	06/21/11	Dry	1.380	0.914	1.200	0.662
AMB08	PS01	09/20/11	Dry	1.080	0.908	3.070	0.841
AMB08	PS02	09/20/11	Dry	2.000	1.620	5.090	0.810
AMB08	PS03	09/20/11	Dry	3.000	2.500	4.130	0.833
AMB08	PS04	09/20/11	Dry	2.170	1.680	3.780	0.774
AMB08	PS05	09/20/11	Dry	2.970	2.290	3.750	0.771
AMB08	PS06	09/20/11	Dry	1.960	1.600	6.010	0.816
AMB08	PS07	09/20/11	Dry	2.610	2.020	3.650	0.774
AMB08	PS08	09/20/11	Dry	2.630	2.170	2.900	0.825
AMB08	PS09	09/20/11	Dry	2.070	1.820	2.430	0.879
AMB08	PS10	09/20/11	Dry	2.130	1.630	3.630	0.765
AMB08	PS10.1	09/20/11	Dry	1.540	1.230	1.970	0.799
AMB08	PS11	09/20/11	Dry	1.830	1.460	3.200	0.798
AMB08	PS12	09/20/11	Dry	1.530	1.130	3.080	0.739
AMB08	PS07	09/21/11	Dry	4.030	3.070	2.530	0.762
AMB11	PS01	08/28/12	Dry	0.982	0.703	2.450	0.716
AMB11	PS02	08/28/12	Dry	1.240	0.922	1.540	0.744
AMB11	PS03	08/28/12	Dry	4.480	0.792	5.140	0.177
AMB11	PS03	08/28/12	Dry	1.480	1.240	1.890	0.838
AMB11	PS04	08/28/12	Dry	2.090	1.570	1.700	0.751
AMB11	PS05	08/28/12	Dry	3.430	2.110	1.410	0.615
AMB11	PS06	08/28/12	Dry	2.440	1.700	1.030	0.697
AMB11	PS07	08/28/12	Dry	2.180	1.670	0.927	0.766
AMB11	PS08	08/28/12	Dry	2.820	2.070	2.270	0.734
AMB11	PS09	08/28/12	Dry	1.760	1.020	0.899	0.580
AMB11	PS10	08/28/12	Dry	1.880	1.400	1.720	0.745
AMB11	PS10.1	08/28/12	Dry	0.692	0.528	0.778	0.763
AMB11	PS11	08/28/12	Dry	0.591	0.454	2.180	0.768
AMB11	PS12	08/28/12	Dry	1.090	0.571	2.480	0.524
AMB11	PS03	08/29/12	Dry	1.850	1.490	1.270	0.805
AMB11	PS03	08/29/12	Dry	2.200	1.750	1.420	0.795
AMB13	PS01	06/18/13	Dry	2.036	1.661	1.170	0.816
AMB13	PS02	06/18/13	Dry	2.693	2.148	1.110	0.798
AMB13	PS03	06/18/13	Dry	3.002	2.429	1.180	0.809
AMB13	PS03	06/18/13	Dry	2.662	2.532	1.000	0.951
AMB13	PS04	06/18/13	Dry	2.418	2.011	0.590	0.832
AMB13	PS05	06/18/13	Dry	2.297	2.031	0.700	0.884
AMB13	PS06	06/18/13	Dry	1.724	1.347	0.800	0.781

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB13	PS07	06/18/13	Dry	5.474	4.635	0.570	0.847
AMB13	PS08	06/18/13	Dry	4.121	3.506	0.900	0.851
AMB13	PS09	06/18/13	Dry	2.893	2.413	0.900	0.834
AMB13	PS10	06/18/13	Dry	1.652	1.403	1.010	0.849
AMB13	PS10.1	06/18/13	Dry	2.131	1.612	1.080	0.756
AMB13	PS11	06/18/13	Dry	1.035	0.769	1.070	0.743
AMB13	PS12	06/18/13	Dry	1.519	1.079	0.990	0.710
AMB13	PS03	06/19/13	Dry	2.953	2.490	0.510	0.843
AMB15	PS01	06/10/14	Dry	3.040	1.210	3.671	0.398
AMB15	PS02	06/10/14	Dry	2.550	1.220	4.086	0.478
AMB15	PS03	06/10/14	Dry	1.570	1.190	10.099	0.758
AMB15	PS03	06/10/14	Dry	1.510	1.310	1.898	0.868
AMB15	PS03	06/10/14	Dry	1.620	1.290	2.995	0.796
AMB15	PS04	06/10/14	Dry	1.230	1.090	2.180	0.886
AMB15	PS05	06/10/14	Dry	1.140	1.030	4.112	0.904
AMB15	PS06	06/10/14	Dry	1.680	1.260	1.857	0.750
AMB15	PS07	06/10/14	Dry	1.980	1.570	2.075	0.793
AMB15	PS08	06/10/14	Dry	2.430	2.110	4.289	0.868
AMB15	PS09	06/10/14	Dry	1.850	1.480	2.350	0.800
AMB15	PS10	06/10/14	Dry	2.610	2.060	1.671	0.789
AMB15	PS10.1	06/10/14	Dry	2.350	1.860	1.854	0.791
AMB15	PS11	06/10/14	Dry	1.360	1.130	1.448	0.831
AMB15	PS12	06/10/14	Dry	1.780	1.380	2.389	0.775
AMB15	PS03	06/11/14	Dry	1.360	1.220	3.226	0.897
AMB16	PS01	09/16/14	Dry	1.720	1.340	3.310	0.779
AMB16	PS02	09/16/14	Dry	1.780	1.500	1.980	0.843
AMB16	PS03	09/16/14	Dry	2.090	1.850	1.630	0.885
AMB16	PS03	09/16/14	Dry	1.570	1.180	2.930	0.752
AMB16	PS04	09/16/14	Dry	2.040	1.900	1.600	0.931
AMB16	PS05	09/16/14	Dry	2.340	1.590	1.560	0.679
AMB16	PS06	09/16/14	Dry	1.440	1.230	1.130	0.854
AMB16	PS07	09/16/14	Dry	2.450	2.150	1.360	0.878
AMB16	PS08	09/16/14	Dry	1.850	1.440	1.580	0.778
AMB16	PS09	09/16/14	Dry	1.670	1.370	1.470	0.820
AMB16	PS10	09/16/14	Dry	2.200	1.900	0.975	0.864
AMB16	PS10.1	09/16/14	Dry	2.380	2.050	1.460	0.861
AMB16	PS11	09/16/14	Dry	1.950	1.520	1.510	0.779
AMB16	PS12	09/16/14	Dry	1.690	1.360	1.360	0.805
AMB16	PS03	09/17/14	Dry	2.760	2.340	0.985	0.848
AMB18	PS01	06/16/15	Dry	1.180	0.974	1.450	0.825
AMB18	PS02	06/16/15	Dry	2.350	1.920	1.090	0.817
AMB18	PS03	06/16/15	Dry	1.620	1.400	1.070	0.864
AMB18	PS04	06/16/15	Dry	1.680	1.500	0.803	0.893
AMB18	PS05	06/16/15	Dry	1.570	1.380	0.420	0.879
AMB18	PS06	06/16/15	Dry	1.510	1.110	1.500	0.735

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB18	PS07	06/16/15	Dry	1.430	1.160	1.650	0.811
AMB18	PS07	06/16/15	Dry	1.470	1.160	1.110	0.789
AMB18	PS08	06/16/15	Dry	1.330	1.090	1.610	0.820
AMB18	PS09	06/16/15	Dry	2.450	1.830	0.788	0.747
AMB18	PS10	06/16/15	Dry	1.920	1.520	1.100	0.792
AMB18	PS10.1	06/16/15	Dry	1.920	1.510	2.420	0.786
AMB18	PS11	06/16/15	Dry	2.860	2.340	0.985	0.818
AMB18	PS12	06/16/15	Dry	0.964	0.721	2.360	0.748
AMB18	PS07	06/17/15	Dry	0.897	0.723	2.700	0.806
AMB19	PS01	09/15/15	Dry	1.120	0.957	2.190	0.854
AMB19	PS02	09/15/15	Dry	1.490	1.300	2.260	0.872
AMB19	PS03	09/15/15	Dry	1.770	1.470	0.630	0.831
AMB19	PS04	09/15/15	Dry	1.580	1.300	1.500	0.823
AMB19	PS05	09/15/15	Dry	1.850	1.340	0.750	0.724
AMB19	PS06	09/15/15	Dry	1.260	0.957	1.330	0.760
AMB19	PS07	09/15/15	Dry	2.150	1.810	0.600	0.842
AMB19	PS08	09/15/15	Dry	2.560	2.140	1.180	0.836
AMB19	PS09	09/15/15	Dry	2.070	1.680	0.690	0.812
AMB19	PS10	09/15/15	Dry	1.890	1.540	0.490	0.815
AMB19	PS12	09/15/15	Dry	1.370	1.100	1.000	0.803
AMB19	PS07	09/16/15	Dry	1.210	1.020	0.490	0.843
AMB19	PS07	09/16/15	Dry	1.210	1.050	0.640	0.868
AMB19	PS10.1	09/16/15	Dry	1.880	1.520	0.530	0.809
AMB19	PS11	09/16/15	Dry	1.730	1.470	1.390	0.850
AMB21	PS01	08/30/16	Dry	1.850	0.887	4.990	0.479
AMB21	PS02	08/30/16	Dry	2.460	1.740	2.910	0.707
AMB21	PS03	08/30/16	Dry	2.930	2.010	2.120	0.686
AMB21	PS04	08/30/16	Dry	2.670	2.120	2.020	0.794
AMB21	PS05	08/30/16	Dry	1.680	1.310	2.600	0.780
AMB21	PS06	08/30/16	Dry	2.320	1.760	1.920	0.759
AMB21	PS07	08/30/16	Dry	2.140	1.460	1.830	0.682
AMB21	PS07	08/30/16	Dry	3.360	2.660	1.760	0.792
AMB21	PS08	08/30/16	Dry	2.040	1.560	2.620	0.765
AMB21	PS09	08/30/16	Dry	2.940	1.960	2.390	0.667
AMB21	PS10	08/30/16	Dry	1.480	1.060	3.130	0.716
AMB21	PS10.1	08/30/16	Dry	1.430	1.110	3.770	0.776
AMB21	PS11	08/30/16	Dry	1.810	1.260	3.000	0.696
AMB21	PS12	08/30/16	Dry	2.300	1.640	1.570	0.713
AMB21	PS07	08/31/16	Dry	4.210	3.290	2.090	0.781
AMB24	PS01	08/22/17	Dry	1.130	0.851	1.980	0.753
AMB24	PS02	08/22/17	Dry	2.960	1.020	1.400	0.345
AMB24	PS03	08/22/17	Dry	1.600	1.440	1.570	0.900
AMB24	PS03	08/22/17	Dry	1.830	1.590	2.440	0.869
AMB24	PS04	08/22/17	Dry	1.800	1.570	1.450	0.872

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB24	PS05	08/22/17	Dry	1.500	1.170	1.150	0.780
AMB24	PS06	08/22/17	Dry	1.410	0.822	1.840	0.583
AMB24	PS07	08/22/17	Dry	1.250	0.960	1.720	0.768
AMB24	PS08	08/22/17	Dry	1.960	1.090	2.800	0.556
AMB24	PS09	08/22/17	Dry	1.700	1.620	1.660	0.953
AMB24	PS10	08/22/17	Dry	1.310	1.210	1.530	0.924
AMB24	PS10.1	08/22/17	Dry	1.600	1.190	3.140	0.744
AMB24	PS11	08/22/17	Dry	1.910	1.190	3.130	0.623
AMB24	PS12	08/22/17	Dry	1.420	1.130	1.460	0.796
AMB24	PS03	08/23/17	Dry	1.700	1.430	2.890	0.841
AMB26	PS01	06/26/18	Dry	1.120	1.030	3.677	0.920
AMB26	PS02	06/26/18	Dry	1.606	1.079	2.770	0.672
AMB26	PS03	06/26/18	Dry	1.829	1.280	2.075	0.700
AMB26	PS03	06/26/18	Dry	2.000	1.450	2.899	0.725
AMB26	PS04	06/26/18	Dry	2.658	2.230	3.348	0.839
AMB26	PS05	06/26/18	Dry	1.840	1.230	2.477	0.668
AMB26	PS06	06/26/18	Dry	1.197	0.943	2.980	0.788
AMB26	PS07	06/26/18	Dry	1.767	1.370	2.665	0.775
AMB26	PS08	06/26/18	Dry	1.093	0.838	3.513	0.767
AMB26	PS09	06/26/18	Dry	1.456	1.040	3.137	0.714
AMB26	PS10	06/26/18	Dry	1.754	1.200	2.658	0.684
AMB26	PS10.1	06/26/18	Dry	1.140	0.809	2.619	0.709
AMB26	PS11	06/26/18	Dry	1.139	0.845	2.575	0.742
AMB26	PS12	06/26/18	Dry	1.394	1.060	2.559	0.761
AMB26	PS03	06/27/18	Dry	2.136	1.580	2.170	0.740
AMB27	PS01	08/22/18	Dry	0.975	0.777	13.421	0.798
AMB27	PS02	08/22/18	Dry	1.685	1.193	8.158	0.708
AMB27	PS03	08/22/18	Dry	1.886	1.366	16.487	0.725
AMB27	PS03	08/22/18	Dry	2.099	1.630	7.404	0.777
AMB27	PS04	08/22/18	Dry	1.430	1.143	1.901	0.799
AMB27	PS05	08/22/18	Dry	1.405	1.134	1.930	0.807
AMB27	PS06	08/22/18	Dry	4.472	3.384	3.298	0.757
AMB27	PS07	08/22/18	Dry	2.315	1.655	4.251	0.715
AMB27	PS08	08/22/18	Dry	0.886	0.745	2.391	0.841
AMB27	PS09	08/22/18	Dry	4.606	3.411	11.172	0.741
AMB27	PS10	08/22/18	Dry	2.422	1.990	2.685	0.822
AMB27	PS10.1	08/22/18	Dry	2.081	1.632	3.094	0.784
AMB27	PS11	08/22/18	Dry	1.562	1.019	5.291	0.653
AMB27	PS12	08/22/18	Dry	1.067	0.909	2.412	0.852
AMB27	PS03	08/23/18	Dry	1.644	1.253	5.051	0.762
AMB29	PS01	07/30/19	Dry	1.191	0.872	4.617	0.732
AMB29	PS02	07/30/19	Dry	1.479	1.109	1.946	0.750
AMB29	PS03	07/30/19	Dry	1.596	1.205	1.809	0.755

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB29	PS03	07/30/19	Dry	1.875	1.491	2.492	0.795
AMB29	PS04	07/30/19	Dry	1.735	1.366	1.226	0.787
AMB29	PS05	07/30/19	Dry	1.352	1.059	2.162	0.783
AMB29	PS06	07/30/19	Dry	1.346	0.975	2.750	0.724
AMB29	PS07	07/30/19	Dry	1.729	1.300	2.393	0.752
AMB29	PS08	07/30/19	Dry	1.601	1.228	3.224	0.767
AMB29	PS09	07/30/19	Dry	3.334	2.297	3.260	0.689
AMB29	PS10	07/30/19	Dry	1.172	0.956	2.058	0.815
AMB29	PS10.1	07/30/19	Dry	1.240	0.942	2.288	0.760
AMB29	PS11	07/30/19	Dry	1.501	1.105	3.134	0.736
AMB29	PS12	07/30/19	Dry	1.021	0.759	3.086	0.743
AMB29	PS03	07/31/19	Dry	1.721	1.229	0.990	0.714
AMB02	PS01	02/02/10	Wet	1.089	0.933	6.000	0.856
AMB02	PS02	02/02/10	Wet	2.045	1.795	6.500	0.878
AMB02	PS03	02/02/10	Wet	2.092	1.760	8.500	0.841
AMB02	PS04	02/02/10	Wet	2.633	2.073	8.500	0.787
AMB02	PS05	02/02/10	Wet	1.973	1.410	9.000	0.715
AMB02	PS06	02/02/10	Wet	1.162	0.844	9.500	0.726
AMB02	PS07	02/02/10	Wet	1.825	1.632	7.500	0.894
AMB02	PS08	02/02/10	Wet	3.160	2.754	7.000	0.872
AMB02	PS09	02/02/10	Wet	2.276	1.786	8.000	0.785
AMB02	PS10	02/02/10	Wet	3.439	2.970	7.000	0.864
AMB02	PS11	02/02/10	Wet	2.336	2.049	6.500	0.877
AMB02	PS12	02/03/10	Wet	1.011	0.872	10.500	0.862
AMB03	PS01	03/23/10	Wet	0.891	0.819	6.500	0.919
AMB03	PS02	03/23/10	Wet	1.331	1.087	5.000	0.817
AMB03	PS03	03/23/10	Wet	2.004	0.830	11.500	0.414
AMB03	PS04	03/23/10	Wet	1.739	1.525	7.000	0.877
AMB03	PS05	03/23/10	Wet	2.538	2.047	6.000	0.807
AMB03	PS06	03/23/10	Wet	1.340	1.087	6.500	0.811
AMB03	PS07	03/23/10	Wet	1.347	1.206	6.000	0.895
AMB03	PS08	03/23/10	Wet	1.297	1.213	8.000	0.935
AMB03	PS09	03/23/10	Wet	2.272	1.926	8.000	0.848
AMB03	PS10	03/23/10	Wet	2.401	1.834	5.500	0.764
AMB03	PS11	03/23/10	Wet	0.825	0.759	7.500	0.919
AMB03	PS12	03/23/10	Wet	1.159	0.910	7.500	0.785
AMB05	PS01	11/16/10	Wet	2.310	1.680	5.000	0.727
AMB05	PS02	11/16/10	Wet	2.800	2.100	5.500	0.750
AMB05	PS03	11/16/10	Wet	2.190	1.790	5.500	0.817
AMB05	PS04	11/16/10	Wet	2.420	1.720	5.000	0.711
AMB05	PS05	11/16/10	Wet	1.820	1.130	5.000	0.621
AMB05	PS06	11/16/10	Wet	1.850	1.380	5.000	0.746
AMB05	PS07	11/16/10	Wet	2.350	1.790	0.490	0.762
AMB05	PS08	11/16/10	Wet	4.000	3.380	5.000	0.845

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB05	PS09	11/16/10	Wet	2.610	1.970	5.000	0.755
AMB05	PS10	11/16/10	Wet	3.370	2.920	5.000	0.866
AMB05	PS10.1	11/16/10	Wet	2.600	2.030	5.000	0.781
AMB05	PS11	11/16/10	Wet	2.270	1.860	5.000	0.819
AMB05	PS12	11/16/10	Wet	1.620	1.250	5.000	0.772
AMB05	PS01	11/18/10	Wet	1.770	0.891	9.500	0.503
AMB05	PS07	11/18/10	Wet	4.100	3.070	7.000	0.749
AMB05	PS08	11/18/10	Wet	4.300	6.860	5.000	1.595
AMB05	PS09	11/18/10	Wet	5.100	3.850	5.000	0.755
AMB05	PS12	11/18/10	Wet	2.320	1.550	5.000	0.668
AMB06	PS01	03/22/11	Wet	2.210	1.070	1.820	0.484
AMB06	PS02	03/22/11	Wet	1.490	1.040	1.840	0.698
AMB06	PS03	03/22/11	Wet	1.650	1.320	2.150	0.800
AMB06	PS04	03/22/11	Wet	2.850	2.310	0.847	0.811
AMB06	PS05	03/22/11	Wet	1.760	1.410	0.927	0.801
AMB06	PS06	03/22/11	Wet	1.490	1.160	1.230	0.779
AMB06	PS07	03/22/11	Wet	1.620	1.210	2.390	0.747
AMB06	PS07	03/22/11	Wet	2.010	1.330	2.490	0.662
AMB06	PS08	03/22/11	Wet	1.850	1.360	1.200	0.735
AMB06	PS09	03/22/11	Wet	2.710	2.010	1.110	0.742
AMB06	PS10	03/22/11	Wet	2.320	1.900	0.924	0.819
AMB06	PS10.1	03/22/11	Wet	1.870	1.490	1.850	0.797
AMB06	PS11	03/22/11	Wet	2.140	1.670	1.480	0.780
AMB06	PS12	03/22/11	Wet	3.150	1.110	12.900	0.352
AMB09	PS01	12/06/11	Wet	1.420	1.110	0.500	0.782
AMB09	PS02	12/06/11	Wet	1.480	1.200	0.700	0.811
AMB09	PS03	12/06/11	Wet	1.400	1.040	0.500	0.743
AMB09	PS03	12/06/11	Wet	2.500	1.940	0.500	0.776
AMB09	PS04	12/06/11	Wet	1.210	2.590	0.540	2.140
AMB09	PS05	12/06/11	Wet	1.060	0.879	0.500	0.829
AMB09	PS06	12/06/11	Wet	1.030	0.734	0.500	0.713
AMB09	PS07	12/06/11	Wet	1.510	1.340	0.500	0.887
AMB09	PS08	12/06/11	Wet	3.620	3.400	0.500	0.939
AMB09	PS09	12/06/11	Wet	1.690	1.260	0.500	0.746
AMB09	PS10	12/06/11	Wet	7.250	1.050	2.580	0.145
AMB09	PS10.1	12/06/11	Wet	2.710	1.190	1.690	0.439
AMB09	PS11	12/06/11	Wet	2.480	1.640	0.780	0.661
AMB09	PS12	12/06/11	Wet	2.310	1.270	0.500	0.550
AMB10	PS01	03/13/12	Wet	0.690	0.588	2.200	0.852
AMB10	PS02	03/13/12	Wet	0.969	0.695	1.140	0.717
AMB10	PS03	03/13/12	Wet	2.130	1.570	1.480	0.737
AMB10	PS04	03/13/12	Wet	2.750	2.270	1.270	0.825
AMB10	PS05	03/13/12	Wet	1.760	1.450	0.620	0.824
AMB10	PS06	03/13/12	Wet	1.570	1.310	0.620	0.834

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB10	PS07	03/13/12	Wet	1.330	0.963	1.560	0.724
AMB10	PS08	03/13/12	Wet	2.370	1.840	0.880	0.776
AMB10	PS09	03/13/12	Wet	1.350	1.020	0.620	0.756
AMB10	PS10	03/13/12	Wet	3.020	2.310	0.620	0.765
AMB10	PS10.1	03/13/12	Wet	2.570	2.110	0.790	0.821
AMB10	PS11	03/13/12	Wet	1.930	1.600	0.720	0.829
AMB10	PS03	03/14/12	Wet	1.610	0.989	2.140	0.614
AMB10	PS12	03/14/12	Wet	1.210	0.897	0.620	0.741
AMB10	PS03	03/16/12	Wet	1.800	1.570	0.620	0.872
AMB12	PS01	02/12/13	Wet	1.520	1.200	0.730	0.789
AMB12	PS02	02/12/13	Wet	1.670	1.300	0.710	0.778
AMB12	PS03	02/12/13	Wet	2.700	2.270	0.600	0.841
AMB12	PS04	02/12/13	Wet	1.870	1.490	0.400	0.797
AMB12	PS05	02/12/13	Wet	2.780	2.240	0.800	0.806
AMB12	PS06	02/12/13	Wet	3.490	1.580	1.480	0.453
AMB12	PS07	02/12/13	Wet	1.240	0.923	0.640	0.744
AMB12	PS08	02/12/13	Wet	2.110	1.920	0.610	0.910
AMB12	PS09	02/12/13	Wet	3.860	3.130	0.410	0.811
AMB12	PS10	02/12/13	Wet	1.800	1.450	0.600	0.806
AMB12	PS10.1	02/12/13	Wet	2.200	1.780	0.490	0.809
AMB12	PS11	02/12/13	Wet	1.240	0.930	1.120	0.750
AMB12	PS12	02/12/13	Wet	1.570	1.140	0.910	0.726
AMB12	PS03	02/13/13	Wet	2.190	1.780	0.970	0.813
AMB14	PS01	02/19/14	Wet	1.650	1.460	0.490	0.885
AMB14	PS02	02/19/14	Wet	1.630	1.340	1.770	0.822
AMB14	PS03	02/19/14	Wet	1.840	1.590	0.720	0.864
AMB14	PS03	02/19/14	Wet	1.600	1.300	0.620	0.813
AMB14	PS04	02/19/14	Wet	2.150	1.730	0.690	0.805
AMB14	PS05	02/19/14	Wet	1.560	1.470	0.810	0.942
AMB14	PS06	02/19/14	Wet	1.720	1.530	1.250	0.890
AMB14	PS07	02/19/14	Wet	1.370	1.110	0.860	0.810
AMB14	PS08	02/19/14	Wet	1.530	1.360	1.080	0.889
AMB14	PS09	02/19/14	Wet	1.600	1.230	0.800	0.769
AMB14	PS10	02/19/14	Wet	1.490	1.120	0.970	0.752
AMB14	PS10.1	02/19/14	Wet	1.220	0.894	1.340	0.733
AMB14	PS11	02/19/14	Wet	1.050	0.862	0.620	0.821
AMB14	PS03	02/20/14	Wet	1.680	1.340	0.670	0.798
AMB17	PS01	04/07/15	Wet	0.865	0.626	1.190	0.724
AMB17	PS02	04/07/15	Wet	1.240	0.939	1.680	0.757
AMB17	PS03	04/07/15	Wet	1.510	1.150	1.350	0.762
AMB17	PS04	04/07/15	Wet	1.030	0.858	1.070	0.833

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB17	PS05	04/07/15	Wet	1.180	0.912	1.560	0.773
AMB17	PS06	04/07/15	Wet	0.824	0.593	1.090	0.720
AMB17	PS07	04/07/15	Wet	0.748	0.546	1.350	0.730
AMB17	PS07	04/07/15	Wet	0.923	0.626	2.180	0.678
AMB17	PS08	04/07/15	Wet	1.140	0.811	1.100	0.711
AMB17	PS09	04/07/15	Wet	1.350	1.000	1.350	0.741
AMB17	PS10	04/07/15	Wet	0.816	0.630	1.530	0.772
AMB17	PS10.1	04/07/15	Wet	3.860	2.590	2.400	0.671
AMB17	PS11	04/07/15	Wet	1.560	0.929	4.680	0.596
AMB17	PS12	04/07/15	Wet	1.400	0.598	1.960	0.427
AMB17	PS03	04/08/15	Wet	1.060	0.894	0.453	0.843
AMB17	PS07	04/08/15	Wet	0.910	0.828	2.890	0.910
AMB20	PS01	03/15/16	Wet	1.330	1.150	0.574	0.865
AMB20	PS02	03/15/16	Wet	2.070	1.800	0.762	0.870
AMB20	PS03	03/15/16	Wet	2.280	1.950	0.557	0.855
AMB20	PS04	03/15/16	Wet	2.190	1.820	1.070	0.831
AMB20	PS05	03/15/16	Wet	1.520	1.320	0.925	0.868
AMB20	PS06	03/15/16	Wet	1.400	1.170	0.928	0.836
AMB20	PS07	03/15/16	Wet	1.310	1.150	0.857	0.878
AMB20	PS07	03/15/16	Wet	1.500	1.320	0.911	0.880
AMB20	PS08	03/15/16	Wet	2.370	2.100	0.747	0.886
AMB20	PS09	03/15/16	Wet	3.160	2.040	1.870	0.646
AMB20	PS10	03/15/16	Wet	2.420	1.860	1.410	0.769
AMB20	PS10.1	03/15/16	Wet	1.940	1.780	0.665	0.918
AMB20	PS11	03/15/16	Wet	1.670	1.450	0.506	0.868
AMB20	PS12	03/15/16	Wet	1.240	1.030	0.724	0.831
AMB20	PS07	03/16/16	Wet	1.280	1.020	0.652	0.797
AMB20	PS07	03/16/16	Wet	1.670	1.430	0.678	0.856
AMB22	PS01	12/06/16	Wet	1.707	1.266	0.759	0.741
AMB22	PS02	12/06/16	Wet	1.277	0.964	1.110	0.755
AMB22	PS03	12/06/16	Wet	1.390	1.038	0.650	0.747
AMB22	PS04	12/06/16	Wet	3.064	2.453	0.645	0.801
AMB22	PS05	12/06/16	Wet	1.565	1.221	0.515	0.780
AMB22	PS06	12/06/16	Wet	1.691	1.190	0.794	0.704
AMB22	PS07	12/06/16	Wet	1.028	0.706	1.290	0.687
AMB22	PS07	12/06/16	Wet	0.885	0.830	1.020	0.938
AMB22	PS08	12/06/16	Wet	1.068	0.762	1.160	0.714
AMB22	PS09	12/06/16	Wet	1.961	1.564	1.270	0.798
AMB22	PS10	12/06/16	Wet	2.006	1.466	1.040	0.731
AMB22	PS10.1	12/06/16	Wet	1.226	0.947	0.969	0.773
AMB22	PS11	12/06/16	Wet	1.379	0.963	1.110	0.699

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB22	PS12	12/06/16	Wet	1.262	0.864	1.330	0.685
AMB22	PS07	12/07/16	Wet	1.426	0.954	1.130	0.669
AMB22	PS07	12/07/16	Wet	1.294	0.917	1.080	0.709
AMB23	PS01	03/28/17	Wet	0.843	0.624	1.990	0.740
AMB23	PS02	03/28/17	Wet	1.151	0.871	1.590	0.757
AMB23	PS03	03/28/17	Wet	4.050	2.554	1.030	0.631
AMB23	PS04	03/28/17	Wet	2.402	1.981	1.210	0.825
AMB23	PS05	03/28/17	Wet	1.925	1.632	1.250	0.848
AMB23	PS06	03/28/17	Wet	1.460	1.015	1.150	0.695
AMB23	PS07	03/28/17	Wet	1.470	1.022	0.939	0.695
AMB23	PS07	03/28/17	Wet	1.176	0.973	1.300	0.828
AMB23	PS08	03/28/17	Wet	1.491	1.169	1.710	0.784
AMB23	PS09	03/28/17	Wet	2.235	1.784	1.270	0.798
AMB23	PS10	03/28/17	Wet	1.658	1.397	1.130	0.843
AMB23	PS10.1	03/28/17	Wet	1.716	1.410	1.240	0.822
AMB23	PS11	03/28/17	Wet	1.666	1.259	1.550	0.756
AMB23	PS12	03/28/17	Wet	1.353	1.036	1.470	0.766
AMB23	PS07	03/29/17	Wet	1.365	1.057	0.988	0.775
AMB23	PS09	04/05/17	Wet	3.093	2.460	2.640	0.795
AMB25	PS01	02/27/18	Wet	0.870	0.645	2.570	0.742
AMB25	PS02	02/27/18	Wet	0.978	0.723	1.310	0.739
AMB25	PS03	02/27/18	Wet	1.655	1.225	1.190	0.740
AMB25	PS03	02/27/18	Wet	1.713	1.266	0.636	0.739
AMB25	PS04	02/27/18	Wet	1.346	0.982	0.660	0.730
AMB25	PS05	02/27/18	Wet	1.580	1.192	0.660	0.755
AMB25	PS06	02/27/18	Wet	1.084	0.791	0.640	0.730
AMB25	PS07	02/27/18	Wet	0.975	0.711	1.420	0.730
AMB25	PS08	02/27/18	Wet	1.525	1.173	0.860	0.769
AMB25	PS09	02/27/18	Wet	2.373	1.235	1.010	0.521
AMB25	PS10	02/27/18	Wet	1.697	1.290	0.760	0.760
AMB25	PS10.1	02/27/18	Wet	1.778	1.403	0.670	0.789
AMB25	PS11	02/27/18	Wet	2.174	1.718	1.260	0.791
AMB25	PS12	02/27/18	Wet	1.470	1.121	0.540	0.763
AMB25	PS03	02/28/18	Wet	1.915	1.565	0.638	0.817
AMB28	PS01	03/19/19	Wet	1.225	0.972	1.489	0.793
AMB28	PS02	03/19/19	Wet	1.361	0.953	3.206	0.700
AMB28	PS03	03/19/19	Wet	1.944	1.602	2.148	0.824
AMB28	PS03	03/19/19	Wet	1.896	1.503	3.234	0.793
AMB28	PS04	03/19/19	Wet	1.564	1.344	2.592	0.859
AMB28	PS05	03/19/19	Wet	1.947	1.580	0.699	0.811
AMB28	PS06	03/19/19	Wet	1.660	1.170	1.650	0.705

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Dissolved Cu (µg L^{-1})	TSS	Dissolved/ Total
AMB28	PS07	03/19/19	Wet	1.333	1.102	0.975	0.827
AMB28	PS08	03/19/19	Wet	1.943	1.548	0.992	0.797
AMB28	PS09	03/19/19	Wet	1.552	1.113	1.156	0.717
AMB28	PS10	03/19/19	Wet	1.410	0.921	1.545	0.653
AMB28	PS10.1	03/19/19	Wet	1.630	1.310	1.175	0.804
AMB28	PS11	03/19/19	Wet	1.576	1.173	0.893	0.744
AMB28	PS12	03/19/19	Wet	1.317	0.955	1.739	0.725
AMB28	PS03	03/20/19	Wet	2.070	1.668	1.436	0.806
				Total:		*n*	428
						average	**0.773**
						σ	0.127
						avg/σ	6.11
						TSS Correlation	-0.0805
						p	0.0964
				Dry Season:		*n*	221
						average	0.767
						σ	0.0966
						avg/σ	7.94
						TSS Correlation	-0.103
						p	0.127
				Wet Season:		*n*	207
						average	0.779
						σ	0.152
						avg/σ	5.12
						TSS Correlation	-0.0741
						p	0.290
				season t-test:		*p*	0.33747

Table C.4. PSNS Nearshore Total:Labile Cu Translator

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Deployment Time	Deploy Time (d)	C_{DGT} Cu (µg L^{-1})	TSS	Labile/ Total
AMB24	PS03	08/22/17	Dry	1.71	8/18/17 10:58	4.0	0.293	1.6	0.171
AMB24	PS04	08/22/17	Dry	1.80	8/18/17 10:41	4.0	0.303	1.5	0.168
AMB24	PS06	08/22/17	Dry	1.41	8/18/17 10:17	3.9	0.188	1.8	0.133
AMB24	PS08	08/22/17	Dry	1.96	8/18/17 10:07	4.0	0.331	2.8	0.169
AMB24	PS09	08/22/17	Dry	1.70	8/18/17 9:53	4.0	0.303	1.7	0.178

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Deployment Time	Deploy Time (d)	C_{DGT} Cu (µg L^{-1})	TSS	Labile/ Total
AMB24	PS11	08/22/17	Dry	1.91	8/18/17 9:40	4.0	0.239	3.1	0.125
AMB29	PS03	07/30/19	Dry	1.73	7/29/19 12:26	2.9	0.449	1.8	0.260
AMB29	PS04	07/30/19	Dry	1.74	7/29/19 11:57	2.9	0.336	1.2	0.193
AMB29	PS06	07/30/19	Dry	1.35	7/29/19 11:25	2.9	0.300	2.8	0.223
AMB29	PS08	07/30/19	Dry	1.60	7/29/19 10:50	3.0	0.304	3.2	0.190
AMB29	PS09	07/30/19	Dry	3.33	7/29/19 10:22	3.0	0.415	3.3	0.124
AMB29	PS11	07/30/19	Dry	1.50	7/29/19 9:40	3.0	0.201	3.1	0.134
AMB22	PS03	12/06/16	Wet	1.39	12/5/16 14:28	2.8	0.180	0.7	0.130
AMB22	PS04	12/06/16	Wet	3.06	12/5/16 14:42	2.8	0.644	0.6	0.210
AMB22	PS06	12/06/16	Wet	1.69	12/5/16 15:01	2.7	0.441	0.8	0.261
AMB22	PS08	12/06/16	Wet	1.07	12/5/16 15:26	2.7	0.466	1.2	0.436
AMB22	PS09	12/06/16	Wet	1.96	12/5/16 12:50	2.8	0.579	1.3	0.295
AMB22	PS11	12/06/16	Wet	1.38	12/5/16 15:57	2.7	0.437	1.1	0.317
AMB23	PS03	03/28/17	Wet	4.05	3/27/17 13:22	2.8	0.396	1.0	0.0978
AMB23	PS04	03/28/17	Wet	2.40	3/27/17 13:10	2.8	0.568	1.2	0.236
AMB23	PS06	03/28/17	Wet	1.46	3/27/17 12:17	2.9	0.215	1.2	0.147
AMB23	PS08	03/28/17	Wet	1.49	3/27/17 12:30	2.9	0.444	1.7	0.298
AMB23	PS09	03/28/17	Wet	2.66	3/27/17 12:42	2.8	0.415	1.3	0.156
AMB23	PS11	03/28/17	Wet	1.67	3/27/17 11:53	2.9	0.327	1.6	0.196
AMB28	PS03	03/19/19	Wet	1.97	3/18/19 12:11	3.0	0.307	2.1	0.156
AMB28	PS04	03/19/19	Wet	1.56	3/18/19 11:56	3.0	0.295	2.6	0.188
AMB28	PS06	03/19/19	Wet	1.66	3/18/19 11:28	3.0	0.210	1.7	0.127
AMB28	PS08	03/19/19	Wet	1.94	3/18/19 10:58	3.0	0.339	1.0	0.174
AMB28	PS09	03/19/19	Wet	1.55	3/18/19 10:38	3.0	0.421	1.2	0.271
AMB28	PS11	03/19/19	Wet	1.58	3/18/19 9:57	3.0	0.386	0.9	0.245

Total:	*n*		30
	average		0.200
	adj average		**0.294**
	σ		0.0734
	avg/σ		4.00
	TSS Correlation		-0.316
	p		0.0885
Dry Season:	*n*		12
	average		0.172
	σ		0.0410
	avg/σ		4.21
	TSS Correlation		-0.357
	p		0.255

Event	Site Code	Collection Date	Season	Total Cu (µg L^{-1})	Deployment Time	Deploy Time (d)	C_{DGT} Cu (µg L^{-1})	TSS	Labile/ Total
						Wet Season:		*n*	18
								average	0.219
								σ	0.0848
								avg/σ	2.58
								TSS Correlation	-0.0939
								p	0.460
						season t-test:		*p*	0.0552

Table C.5. PSNS Nearshore Total:Dissolved Zn Translator

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB01	PS01	08/31/09	Dry	3.670	2.360	25.000	0.643
AMB01	PS02	08/31/09	Dry	4.710	4.000	24.000	0.849
AMB01	PS03	08/31/09	Dry	7.500	5.680	15.000	0.757
AMB01	PS04	08/31/09	Dry	1.780	3.480	15.000	1.955
AMB01	PS05	08/31/09	Dry	8.940	8.120	11.000	0.908
AMB01	PS06	08/31/09	Dry	8.700	8.000	7.000	0.920
AMB01	PS07	08/31/09	Dry	4.860	5.190	15.000	1.068
AMB01	PS08	08/31/09	Dry	8.080	7.820	14.000	0.968
AMB01	PS09	08/31/09	Dry	6.320	6.450	15.000	1.021
AMB01	PS10	08/31/09	Dry	3.740	3.100	14.000	0.829
AMB01	PS11	08/31/09	Dry	7.890	6.660	18.000	0.844
AMB01	PS07	09/01/09	Dry	56.500	54.800	25.000	0.970
AMB01	PS12	09/01/09	Dry	8.130	2.290	23.000	0.282
AMB04	PS01	09/08/10	Dry	7.964	5.752	12.500	0.722
AMB04	PS02	09/08/10	Dry	5.772	5.586	31.000	0.968
AMB04	PS03	09/08/10	Dry	4.229	3.730	7.000	0.882
AMB04	PS04	09/08/10	Dry	6.999	6.719	8.500	0.960
AMB04	PS05	09/08/10	Dry	4.331	4.274	5.000	0.987
AMB04	PS06	09/08/10	Dry	4.532	4.263	5.000	0.941
AMB04	PS07	09/08/10	Dry	11.639	10.909	6.000	0.937
AMB04	PS08	09/08/10	Dry	15.939	14.029	7.500	0.880
AMB04	PS09	09/08/10	Dry	8.931	7.652	30.500	0.857
AMB04	PS10	09/08/10	Dry	8.889	8.157	37.000	0.918
AMB04	PS10.1	09/08/10	Dry	10.421	9.770	38.500	0.938
AMB04	PS11	09/08/10	Dry	15.711	14.961	41.000	0.952
AMB04	PS07	09/09/10	Dry	4.670	4.400	40.000	0.942
AMB04	PS12	09/09/10	Dry	5.207	5.257	7.000	1.010
AMB07	PS01	06/21/11	Dry	2.490	1.920	1.380	0.771
AMB07	PS02	06/21/11	Dry	2.950	2.670	1.320	0.905
AMB07	PS03	06/21/11	Dry	4.400	3.210	3.910	0.730
AMB07	PS04	06/21/11	Dry	3.360	2.790	2.250	0.830

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB07	PS05	06/21/11	Dry	6.700	5.690	2.980	0.849
AMB07	PS06	06/21/11	Dry	5.550	4.810	1.820	0.867
AMB07	PS07	06/21/11	Dry	6.150	5.640	1.430	0.917
AMB07	PS08	06/21/11	Dry	6.400	5.540	2.310	0.866
AMB07	PS09	06/21/11	Dry	8.760	8.210	3.100	0.937
AMB07	PS10	06/21/11	Dry	5.160	4.120	1.590	0.798
AMB07	PS10.1	06/21/11	Dry	6.630	6.150	4.590	0.928
AMB07	PS11	06/21/11	Dry	2.830	2.490	1.400	0.880
AMB07	PS12	06/21/11	Dry	3.180	2.750	1.200	0.865
AMB08	PS01	09/20/11	Dry	1.800	1.500	3.070	0.833
AMB08	PS02	09/20/11	Dry	3.210	2.610	5.090	0.813
AMB08	PS03	09/20/11	Dry	4.830	4.760	4.130	0.986
AMB08	PS04	09/20/11	Dry	4.310	3.660	3.780	0.849
AMB08	PS05	09/20/11	Dry	6.270	5.990	3.750	0.955
AMB08	PS06	09/20/11	Dry	4.810	4.650	6.010	0.967
AMB08	PS07	09/20/11	Dry	5.190	4.670	3.650	0.900
AMB08	PS08	09/20/11	Dry	6.970	6.790	2.900	0.974
AMB08	PS09	09/20/11	Dry	7.210	7.980	2.430	1.107
AMB08	PS10	09/20/11	Dry	5.510	5.250	3.630	0.953
AMB08	PS10.1	09/20/11	Dry	4.470	3.950	1.970	0.884
AMB08	PS11	09/20/11	Dry	4.280	3.890	3.200	0.909
AMB08	PS12	09/20/11	Dry	3.230	2.660	3.080	0.824
AMB08	PS07	09/21/11	Dry	8.010	6.650	2.530	0.830
AMB11	PS01	08/28/12	Dry	1.550	1.330	2.450	0.858
AMB11	PS02	08/28/12	Dry	1.980	1.800	1.540	0.909
AMB11	PS03	08/28/12	Dry	6.190	2.100	5.140	0.339
AMB11	PS03	08/28/12	Dry	2.830	2.850	1.890	1.007
AMB11	PS04	08/28/12	Dry	4.400	4.020	1.700	0.914
AMB11	PS05	08/28/12	Dry	7.570	5.840	1.410	0.771
AMB11	PS06	08/28/12	Dry	7.320	6.670	1.030	0.911
AMB11	PS07	08/28/12	Dry	5.780	5.060	0.927	0.875
AMB11	PS08	08/28/12	Dry	6.090	5.340	2.270	0.877
AMB11	PS09	08/28/12	Dry	6.430	5.750	0.899	0.894
AMB11	PS10	08/28/12	Dry	2.940	2.890	1.720	0.983
AMB11	PS10.1	08/28/12	Dry	1.270	1.060	0.778	0.835
AMB11	PS11	08/28/12	Dry	1.140	0.948	2.180	0.832
AMB11	PS12	08/28/12	Dry	3.090	2.650	2.480	0.858
AMB11	PS03	08/29/12	Dry	3.610	3.240	1.270	0.898
AMB11	PS03	08/29/12	Dry	4.080	3.940	1.420	0.966
AMB13	PS01	06/18/13	Dry	5.228	4.311	1.170	0.825
AMB13	PS02	06/18/13	Dry	5.116	4.622	1.110	0.903
AMB13	PS03	06/18/13	Dry	6.160	5.589	1.180	0.907
AMB13	PS03	06/18/13	Dry	5.565	5.363	1.000	0.964
AMB13	PS04	06/18/13	Dry	5.020	4.795	0.590	0.955
AMB13	PS05	06/18/13	Dry	4.525	4.612	0.700	1.019
AMB13	PS06	06/18/13	Dry	4.287	3.934	0.800	0.918
AMB13	PS07	06/18/13	Dry	8.278	7.054	0.570	0.852
AMB13	PS08	06/18/13	Dry	8.753	8.689	0.900	0.993

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB13	PS09	06/18/13	Dry	9.491	9.170	0.900	0.966
AMB13	PS10	06/18/13	Dry	3.367	3.406	1.010	1.012
AMB13	PS10.1	06/18/13	Dry	4.420	4.065	1.080	0.920
AMB13	PS11	06/18/13	Dry	2.033	1.693	1.070	0.833
AMB13	PS12	06/18/13	Dry	4.511	4.203	0.990	0.932
AMB13	PS03	06/19/13	Dry	5.946	5.449	0.510	0.916
AMB15	PS01	06/10/14	Dry	8.470	3.360	3.671	0.397
AMB15	PS02	06/10/14	Dry	5.000	1.190	4.086	0.238
AMB15	PS03	06/10/14	Dry	2.240	1.530	10.099	0.683
AMB15	PS03	06/10/14	Dry	2.060	1.420	1.898	0.689
AMB15	PS03	06/10/14	Dry	2.760	1.300	2.995	0.471
AMB15	PS04	06/10/14	Dry	7.180	1.980	2.180	0.276
AMB15	PS05	06/10/14	Dry	1.460	0.974	4.112	0.667
AMB15	PS06	06/10/14	Dry	5.980	5.370	1.857	0.898
AMB15	PS07	06/10/14	Dry	4.810	4.230	2.075	0.879
AMB15	PS08	06/10/14	Dry	6.330	5.920	4.289	0.935
AMB15	PS09	06/10/14	Dry	4.260	3.080	2.350	0.723
AMB15	PS10	06/10/14	Dry	4.330	3.330	1.671	0.769
AMB15	PS10.1	06/10/14	Dry	4.590	3.610	1.854	0.786
AMB15	PS11	06/10/14	Dry	2.940	2.310	1.448	0.786
AMB15	PS12	06/10/14	Dry	4.130	3.230	2.389	0.782
AMB15	PS03	06/11/14	Dry	1.850	1.110	3.226	0.600
AMB16	PS01	09/16/14	Dry	2.580	2.030	3.310	0.787
AMB16	PS02	09/16/14	Dry	2.910	2.430	1.980	0.835
AMB16	PS03	09/16/14	Dry	2.810	2.340	1.630	0.833
AMB16	PS03	09/16/14	Dry	2.580	1.460	2.930	0.566
AMB16	PS04	09/16/14	Dry	3.100	2.930	1.600	0.945
AMB16	PS05	09/16/14	Dry	2.680	2.210	1.560	0.825
AMB16	PS06	09/16/14	Dry	4.500	4.500	1.130	1.000
AMB16	PS07	09/16/14	Dry	4.540	4.820	1.360	1.062
AMB16	PS08	09/16/14	Dry	5.220	4.780	1.580	0.916
AMB16	PS09	09/16/14	Dry	5.980	6.150	1.470	1.028
AMB16	PS10	09/16/14	Dry	5.450	5.190	0.975	0.952
AMB16	PS10.1	09/16/14	Dry	5.540	5.250	1.460	0.948
AMB16	PS11	09/16/14	Dry	4.350	3.860	1.510	0.887
AMB16	PS12	09/16/14	Dry	4.050	3.890	1.360	0.960
AMB16	PS03	09/17/14	Dry	3.750	3.330	0.985	0.888
AMB18	PS01	06/16/15	Dry	2.110	1.790	1.450	0.848
AMB18	PS02	06/16/15	Dry	3.660	3.190	1.090	0.872
AMB18	PS03	06/16/15	Dry	2.790	2.320	1.070	0.832
AMB18	PS04	06/16/15	Dry	3.280	3.210	0.803	0.979
AMB18	PS05	06/16/15	Dry	3.340	2.980	0.420	0.892
AMB18	PS06	06/16/15	Dry	5.020	4.520	1.500	0.900
AMB18	PS07	06/16/15	Dry	4.620	4.430	1.650	0.959
AMB18	PS07	06/16/15	Dry	4.130	3.790	1.110	0.918
AMB18	PS08	06/16/15	Dry	3.150	2.850	1.610	0.905
AMB18	PS09	06/16/15	Dry	11.800	11.800	0.788	1.000

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB18	PS10	06/16/15	Dry	5.720	5.260	1.100	0.920
AMB18	PS10.1	06/16/15	Dry	12.800	12.100	2.420	0.945
AMB18	PS11	06/16/15	Dry	26.900	27.000	0.985	1.004
AMB18	PS12	06/16/15	Dry	1.890	1.480	2.360	0.783
AMB18	PS07	06/17/15	Dry	1.650	1.110	2.700	0.673
AMB19	PS01	09/15/15	Dry	1.960	3.800	2.190	1.939
AMB19	PS02	09/15/15	Dry	2.650	2.330	2.260	0.879
AMB19	PS03	09/15/15	Dry	2.280	1.910	0.630	0.838
AMB19	PS04	09/15/15	Dry	2.390	2.080	1.500	0.870
AMB19	PS05	09/15/15	Dry	13.500	11.300	0.750	0.837
AMB19	PS06	09/15/15	Dry	3.020	2.860	1.330	0.947
AMB19	PS07	09/15/15	Dry	3.030	2.830	0.600	0.934
AMB19	PS08	09/15/15	Dry	6.300	5.940	1.180	0.943
AMB19	PS09	09/15/15	Dry	8.270	7.790	0.690	0.942
AMB19	PS10	09/15/15	Dry	5.160	4.540	0.490	0.880
AMB19	PS12	09/15/15	Dry	3.650	3.450	1.000	0.945
AMB19	PS07	09/16/15	Dry	2.580	2.500	0.490	0.969
AMB19	PS07	09/16/15	Dry	2.900	2.710	0.640	0.934
AMB19	PS10.1	09/16/15	Dry	5.810	5.540	0.530	0.954
AMB19	PS11	09/16/15	Dry	4.730	4.570	1.390	0.966
AMB21	PS01	08/30/16	Dry	3.750	2.150	4.990	0.573
AMB21	PS02	08/30/16	Dry	5.260	3.880	2.910	0.738
AMB21	PS03	08/30/16	Dry	3.870	2.780	2.120	0.718
AMB21	PS04	08/30/16	Dry	3.920	2.980	2.020	0.760
AMB21	PS05	08/30/16	Dry	2.380	1.730	2.600	0.727
AMB21	PS06	08/30/16	Dry	4.090	3.480	1.920	0.851
AMB21	PS07	08/30/16	Dry	5.150	4.250	1.830	0.825
AMB21	PS07	08/30/16	Dry	15.300	13.900	1.760	0.908
AMB21	PS08	08/30/16	Dry	3.930	3.340	2.620	0.850
AMB21	PS09	08/30/16	Dry	6.620	5.110	2.390	0.772
AMB21	PS10	08/30/16	Dry	2.590	1.810	3.130	0.699
AMB21	PS10.1	08/30/16	Dry	3.240	2.150	3.770	0.664
AMB21	PS11	08/30/16	Dry	3.970	2.820	3.000	0.710
AMB21	PS12	08/30/16	Dry	5.930	4.620	1.570	0.779
AMB21	PS07	08/31/16	Dry	12.900	10.900	2.090	0.845
AMB24	PS01	08/22/17	Dry	3.520	3.140	1.980	0.892
AMB24	PS02	08/22/17	Dry	1.870	1.660	1.400	0.888
AMB24	PS03	08/22/17	Dry	1.940	1.670	1.570	0.861
AMB24	PS03	08/22/17	Dry	2.810	2.340	2.440	0.833
AMB24	PS04	08/22/17	Dry	2.720	2.750	1.450	1.011
AMB24	PS05	08/22/17	Dry	1.800	1.690	1.150	0.939
AMB24	PS06	08/22/17	Dry	4.990	4.550	1.840	0.912
AMB24	PS07	08/22/17	Dry	5.040	4.550	1.720	0.903
AMB24	PS08	08/22/17	Dry	5.010	3.220	2.800	0.643
AMB24	PS09	08/22/17	Dry	4.200	3.780	1.660	0.900
AMB24	PS10	08/22/17	Dry	2.750	2.350	1.530	0.855
AMB24	PS10.1	08/22/17	Dry	5.130	4.480	3.140	0.873
AMB24	PS11	08/22/17	Dry	13.200	3.930	3.130	0.298

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB24	PS12	08/22/17	Dry	4.640	4.090	1.460	0.881
AMB24	PS03	08/23/17	Dry	2.830	2.400	2.890	0.848
AMB26	PS01	06/26/18	Dry	2.262	0.961	3.677	0.425
AMB26	PS02	06/26/18	Dry	3.488	1.980	2.770	0.568
AMB26	PS03	06/26/18	Dry	2.779	2.038	2.075	0.733
AMB26	PS03	06/26/18	Dry	2.795	1.980	2.899	0.708
AMB26	PS04	06/26/18	Dry	2.871	2.570	3.348	0.895
AMB26	PS05	06/26/18	Dry	4.402	2.080	2.477	0.473
AMB26	PS06	06/26/18	Dry	2.063	1.230	2.980	0.596
AMB26	PS07	06/26/18	Dry	3.393	2.870	2.665	0.846
AMB26	PS08	06/26/18	Dry	1.762	0.802	3.513	0.455
AMB26	PS09	06/26/18	Dry	4.808	3.468	3.137	0.721
AMB26	PS10	06/26/18	Dry	2.918	1.402	2.658	0.480
AMB26	PS10.1	06/26/18	Dry	2.752	0.925	2.619	0.336
AMB26	PS11	06/26/18	Dry	1.933	1.384	2.575	0.716
AMB26	PS12	06/26/18	Dry	3.157	2.345	2.559	0.743
AMB26	PS03	06/27/18	Dry	3.234	2.180	2.170	0.674
AMB27	PS01	08/22/18	Dry	5.386	4.623	13.421	0.858
AMB27	PS02	08/22/18	Dry	5.325	3.416	8.158	0.642
AMB27	PS04	08/22/18	Dry	5.235	3.387	16.487	0.647
AMB27	PS03	08/22/18	Dry	4.353	2.801	7.404	0.643
AMB27	PS04	08/22/18	Dry	3.194	2.440	1.901	0.764
AMB27	PS05	08/22/18	Dry	3.184	2.469	1.930	0.775
AMB27	PS06	08/22/18	Dry	8.026	7.361	3.298	0.917
AMB27	PS07	08/22/18	Dry	5.606	4.731	4.251	0.844
AMB27	PS08	08/22/18	Dry	1.702	1.240	2.391	0.729
AMB27	PS09	08/22/18	Dry	20.143	18.785	11.172	0.933
AMB27	PS10	08/22/18	Dry	8.657	8.052	2.685	0.930
AMB27	PS10.1	08/22/18	Dry	7.094	6.474	3.094	0.913
AMB27	PS11	08/22/18	Dry	5.774	3.822	5.291	0.662
AMB27	PS12	08/22/18	Dry	2.588	2.382	2.412	0.920
AMB27	PS03	08/23/18	Dry	3.227	3.444	5.051	1.067
AMB29	PS01	07/30/19	Dry	2.537	1.614	4.617	0.636
AMB29	PS02	07/30/19	Dry	3.860	3.563	1.946	0.923
AMB29	PS03	07/30/19	Dry	2.514	2.624	1.809	1.044
AMB29	PS03	07/30/19	Dry	3.727	3.157	2.492	0.847
AMB29	PS04	07/30/19	Dry	3.125	3.757	1.226	1.202
AMB29	PS05	07/30/19	Dry	2.519	1.844	2.162	0.732
AMB29	PS06	07/30/19	Dry	3.101	2.519	2.750	0.812
AMB29	PS07	07/30/19	Dry	5.156	4.079	2.393	0.791
AMB29	PS08	07/30/19	Dry	5.682	5.811	3.224	1.023
AMB29	PS09	07/30/19	Dry	14.463	12.770	3.260	0.883
AMB29	PS10	07/30/19	Dry	2.220	1.651	2.058	0.744
AMB29	PS10.1	07/30/19	Dry	2.441	1.719	2.288	0.704
AMB29	PS11	07/30/19	Dry	3.044	2.229	3.134	0.732
AMB29	PS12	07/30/19	Dry	1.658	1.057	3.086	0.638
AMB29	PS03	07/31/19	Dry	48.492	49.470	0.990	1.020
AMB02	PS01	02/02/10	Wet	2.508	3.882	6.000	1.548

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB02	PS02	02/02/10	Wet	7.427	7.910	6.500	1.065
AMB02	PS03	02/02/10	Wet	5.384	5.662	8.500	1.052
AMB02	PS04	02/02/10	Wet	8.054	8.134	8.500	1.010
AMB02	PS05	02/02/10	Wet	6.247	6.410	9.000	1.026
AMB02	PS06	02/02/10	Wet	7.518	7.299	9.500	0.971
AMB02	PS07	02/02/10	Wet	6.616	7.382	7.500	1.116
AMB02	PS08	02/02/10	Wet	8.165	8.457	7.000	1.036
AMB02	PS09	02/02/10	Wet	11.705	11.625	8.000	0.993
AMB02	PS10	02/02/10	Wet	9.855	11.725	7.000	1.190
AMB02	PS11	02/02/10	Wet	7.314	7.438	6.500	1.017
AMB02	PS12	02/03/10	Wet	6.659	6.271	10.500	0.942
AMB03	PS01	03/23/10	Wet	2.282	2.250	6.500	0.986
AMB03	PS02	03/23/10	Wet	3.482	3.257	5.000	0.935
AMB03	PS03	03/23/10	Wet	3.878	2.877	11.500	0.742
AMB03	PS04	03/23/10	Wet	4.882	5.265	7.000	1.078
AMB03	PS05	03/23/10	Wet	9.677	9.383	6.000	0.970
AMB03	PS06	03/23/10	Wet	4.028	3.857	6.500	0.958
AMB03	PS07	03/23/10	Wet	4.308	4.480	6.000	1.040
AMB03	PS08	03/23/10	Wet	4.180	4.626	8.000	1.107
AMB03	PS09	03/23/10	Wet	6.094	5.972	8.000	0.980
AMB03	PS10	03/23/10	Wet	6.721	5.730	5.500	0.853
AMB03	PS11	03/23/10	Wet	2.977	3.177	7.500	1.067
AMB03	PS12	03/23/10	Wet	4.739	4.419	7.500	0.932
AMB05	PS01	11/16/10	Wet	4.240	3.790	5.000	0.894
AMB05	PS02	11/16/10	Wet	5.940	5.600	5.500	0.943
AMB05	PS03	11/16/10	Wet	4.860	4.740	5.500	0.975
AMB05	PS04	11/16/10	Wet	6.500	5.780	5.000	0.889
AMB05	PS05	11/16/10	Wet	4.410	4.500	5.000	1.020
AMB05	PS06	11/16/10	Wet	7.550	7.380	5.000	0.977
AMB05	PS07	11/16/10	Wet	6.110	5.650	0.490	0.925
AMB05	PS08	11/16/10	Wet	10.800	10.700	5.000	0.991
AMB05	PS09	11/16/10	Wet	9.590	9.340	5.000	0.974
AMB05	PS10	11/16/10	Wet	10.100	10.600	5.000	1.050
AMB05	PS10.1	11/16/10	Wet	11.500	10.600	5.000	0.922
AMB05	PS11	11/16/10	Wet	9.050	8.700	5.000	0.961
AMB05	PS12	11/16/10	Wet	5.230	4.940	5.000	0.945
AMB05	PS01	11/18/10	Wet	5.850	4.430	9.500	0.757
AMB05	PS07	11/18/10	Wet	6.010	5.270	7.000	0.877
AMB05	PS08	11/18/10	Wet	7.840	8.470	5.000	1.080
AMB05	PS09	11/18/10	Wet	10.200	9.580	5.000	0.939
AMB05	PS12	11/18/10	Wet	7.180	6.470	5.000	0.901
AMB06	PS01	03/22/11	Wet	5.830	4.350	1.820	0.746
AMB06	PS02	03/22/11	Wet	3.550	3.150	1.840	0.887
AMB06	PS03	03/22/11	Wet	4.130	3.850	2.150	0.932
AMB06	PS04	03/22/11	Wet	7.960	7.650	0.847	0.961
AMB06	PS05	03/22/11	Wet	7.130	6.880	0.927	0.965
AMB06	PS06	03/22/11	Wet	4.220	4.070	1.230	0.964
AMB06	PS07	03/22/11	Wet	5.220	4.890	2.390	0.937

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB06	PS07	03/22/11	Wet	7.000	6.260	2.490	0.894
AMB06	PS08	03/22/11	Wet	5.080	4.570	1.200	0.900
AMB06	PS09	03/22/11	Wet	8.870	8.380	1.110	0.945
AMB06	PS10	03/22/11	Wet	8.630	8.360	0.924	0.969
AMB06	PS10.1	03/22/11	Wet	7.660	7.520	1.850	0.982
AMB06	PS11	03/22/11	Wet	8.050	6.520	1.480	0.810
AMB06	PS12	03/22/11	Wet	10.100	7.260	12.900	0.719
AMB09	PS01	12/06/11	Wet	2.680	2.720	0.500	1.015
AMB09	PS02	12/06/11	Wet	3.070	3.120	0.700	1.016
AMB09	PS03	12/06/11	Wet	2.700	2.670	0.500	0.989
AMB09	PS03	12/06/11	Wet	4.020	3.870	0.500	0.963
AMB09	PS04	12/06/11	Wet	3.250	4.870	0.540	1.498
AMB09	PS05	12/06/11	Wet	2.760	2.660	0.500	0.964
AMB09	PS06	12/06/11	Wet	3.520	3.290	0.500	0.935
AMB09	PS07	12/06/11	Wet	6.920	6.830	0.500	0.987
AMB09	PS08	12/06/11	Wet	8.240	7.870	0.500	0.955
AMB09	PS09	12/06/11	Wet	9.470	8.890	0.500	0.939
AMB09	PS10	12/06/11	Wet	14.500	7.620	2.580	0.526
AMB09	PS10.1	12/06/11	Wet	7.620	6.190	1.690	0.812
AMB09	PS11	12/06/11	Wet	5.840	4.910	0.500	0.841
AMB09	PS12	12/06/11	Wet	5.640	4.530	0.500	0.803
AMB10	PS01	03/13/12	Wet	1.990	1.690	2.200	0.849
AMB10	PS02	03/13/12	Wet	2.960	2.530	1.140	0.855
AMB10	PS03	03/13/12	Wet	6.090	5.450	1.480	0.895
AMB10	PS04	03/13/12	Wet	23.100	22.300	1.270	0.965
AMB10	PS05	03/13/12	Wet	6.370	6.710	0.620	1.053
AMB10	PS06	03/13/12	Wet	6.250	6.560	0.620	1.050
AMB10	PS07	03/13/12	Wet	4.290	4.100	1.560	0.956
AMB10	PS08	03/13/12	Wet	6.780	6.290	0.880	0.928
AMB10	PS09	03/13/12	Wet	5.960	5.650	0.620	0.948
AMB10	PS10	03/13/12	Wet	9.350	8.450	0.620	0.904
AMB10	PS10.1	03/13/12	Wet	12.900	12.800	0.790	0.992
AMB10	PS11	03/13/12	Wet	8.020	7.950	0.720	0.991
AMB10	PS03	03/14/12	Wet	6.140	4.590	2.140	0.748
AMB10	PS12	03/14/12	Wet	5.770	5.480	0.620	0.950
AMB10	PS03	03/16/12	Wet	6.160	5.930	0.620	0.963
AMB12	PS01	02/12/13	Wet	4.070	4.140	0.730	1.017
AMB12	PS02	02/12/13	Wet	4.620	4.690	0.710	1.015
AMB12	PS03	02/12/13	Wet	6.720	6.470	0.600	0.963
AMB12	PS04	02/12/13	Wet	7.290	7.190	0.400	0.986
AMB12	PS05	02/12/13	Wet	7.400	7.440	0.800	1.005
AMB12	PS06	02/12/13	Wet	11.500	9.800	1.480	0.852
AMB12	PS07	02/12/13	Wet	3.730	3.620	0.640	0.971
AMB12	PS08	02/12/13	Wet	4.780	5.250	0.610	1.098
AMB12	PS09	02/12/13	Wet	25.900	24.700	0.410	0.954
AMB12	PS10	02/12/13	Wet	5.210	5.180	0.600	0.994
AMB12	PS10.1	02/12/13	Wet	5.860	5.860	0.490	1.000
AMB12	PS11	02/12/13	Wet	4.160	4.030	1.120	0.969

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB12	PS12	02/12/13	Wet	5.670	5.180	0.910	0.914
AMB12	PS03	02/13/13	Wet	5.450	5.340	0.970	0.980
AMB14	PS01	02/19/14	Wet	4.750	4.700	0.490	0.989
AMB14	PS02	02/19/14	Wet	4.110	3.960	1.770	0.964
AMB14	PS03	02/19/14	Wet	8.420	8.250	0.720	0.980
AMB14	PS03	02/19/14	Wet	4.620	4.300	0.620	0.931
AMB14	PS04	02/19/14	Wet	6.470	6.030	0.690	0.932
AMB14	PS05	02/19/14	Wet	4.100	4.620	0.810	1.127
AMB14	PS06	02/19/14	Wet	4.660	4.950	1.250	1.062
AMB14	PS07	02/19/14	Wet	5.450	5.200	0.860	0.954
AMB14	PS08	02/19/14	Wet	5.170	5.500	1.080	1.064
AMB14	PS09	02/19/14	Wet	8.910	8.500	0.800	0.954
AMB14	PS10	02/19/14	Wet	5.460	5.240	0.970	0.960
AMB14	PS10.1	02/19/14	Wet	6.170	5.590	1.340	0.906
AMB14	PS11	02/19/14	Wet	3.780	3.530	0.620	0.934
AMB14	PS03	02/20/14	Wet	5.630	5.220	0.670	0.927
AMB17	PS01	04/07/15	Wet	2.030	1.600	1.190	0.788
AMB17	PS02	04/07/15	Wet	3.310	2.820	1.680	0.852
AMB17	PS03	04/07/15	Wet	4.620	4.290	1.350	0.929
AMB17	PS04	04/07/15	Wet	3.240	2.890	1.070	0.892
AMB17	PS05	04/07/15	Wet	4.890	4.470	1.560	0.914
AMB17	PS06	04/07/15	Wet	4.320	3.930	1.090	0.910
AMB17	PS07	04/07/15	Wet	2.150	1.800	1.350	0.837
AMB17	PS07	04/07/15	Wet	2.540	2.140	2.180	0.843
AMB17	PS08	04/07/15	Wet	3.320	2.940	1.100	0.886
AMB17	PS09	04/07/15	Wet	8.060	7.670	1.350	0.952
AMB17	PS10	04/07/15	Wet	3.670	3.410	1.530	0.929
AMB17	PS10.1	04/07/15	Wet	7.310	6.610	2.400	0.904
AMB17	PS11	04/07/15	Wet	5.590	4.570	4.680	0.818
AMB17	PS12	04/07/15	Wet	4.450	3.160	1.960	0.710
AMB17	PS03	04/08/15	Wet	2.630	2.450	0.453	0.932
AMB17	PS07	04/08/15	Wet	3.380	3.190	2.890	0.944
AMB20	PS01	03/15/16	Wet	5.650	5.700	0.574	1.009
AMB20	PS02	03/15/16	Wet	5.830	5.890	0.762	1.010
AMB20	PS03	03/15/16	Wet	7.550	7.080	0.557	0.938
AMB20	PS04	03/15/16	Wet	4.760	5.130	1.070	1.078
AMB20	PS05	03/15/16	Wet	4.010	3.890	0.925	0.970
AMB20	PS06	03/15/16	Wet	5.160	5.060	0.928	0.981
AMB20	PS07	03/15/16	Wet	5.310	5.440	0.857	1.024
AMB20	PS07	03/15/16	Wet	7.950	7.500	0.911	0.943
AMB20	PS08	03/15/16	Wet	9.670	9.580	0.747	0.991
AMB20	PS09	03/15/16	Wet	11.700	10.300	1.870	0.880
AMB20	PS10	03/15/16	Wet	7.540	7.050	1.410	0.935
AMB20	PS10.1	03/15/16	Wet	8.670	8.560	0.665	0.987
AMB20	PS11	03/15/16	Wet	5.500	5.220	0.506	0.949
AMB20	PS12	03/15/16	Wet	4.770	4.780	0.724	1.002
AMB20	PS07	03/16/16	Wet	5.700	5.740	0.652	1.007
AMB20	PS07	03/16/16	Wet	9.490	8.920	0.678	0.940

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB22	PS01	12/06/16	Wet	3.665	3.367	0.759	0.919
AMB22	PS02	12/06/16	Wet	2.294	2.027	1.110	0.884
AMB22	PS03	12/06/16	Wet	2.966	2.358	0.650	0.795
AMB22	PS04	12/06/16	Wet	4.128	3.810	0.645	0.923
AMB22	PS05	12/06/16	Wet	3.713	3.377	0.515	0.909
AMB22	PS06	12/06/16	Wet	4.726	4.206	0.794	0.890
AMB22	PS07	12/06/16	Wet	2.786	2.424	1.290	0.870
AMB22	PS07	12/06/16	Wet	4.123	3.989	1.020	0.967
AMB22	PS08	12/06/16	Wet	3.200	2.887	1.160	0.902
AMB22	PS09	12/06/16	Wet	6.284	6.005	1.270	0.956
AMB22	PS10	12/06/16	Wet	5.901	5.461	1.040	0.925
AMB22	PS10.1	12/06/16	Wet	5.011	3.885	0.969	0.775
AMB22	PS11	12/06/16	Wet	4.315	3.911	1.110	0.906
AMB22	PS12	12/06/16	Wet	3.611	3.110	1.330	0.861
AMB22	PS07	12/07/16	Wet	4.484	3.871	1.130	0.863
AMB22	PS07	12/07/16	Wet	4.702	4.312	1.080	0.917
AMB23	PS01	03/28/17	Wet	3.339	2.968	1.990	0.889
AMB23	PS02	03/28/17	Wet	4.257	3.664	1.590	0.861
AMB23	PS03	03/28/17	Wet	12.992	11.111	1.030	0.855
AMB23	PS04	03/28/17	Wet	11.264	8.988	1.210	0.798
AMB23	PS05	03/28/17	Wet	6.742	6.166	1.250	0.915
AMB23	PS06	03/28/17	Wet	14.622	13.157	1.150	0.900
AMB23	PS07	03/28/17	Wet	6.500	6.412	0.939	0.987
AMB23	PS07	03/28/17	Wet	10.857	10.109	1.300	0.931
AMB23	PS08	03/28/17	Wet	6.980	6.351	1.710	0.910
AMB23	PS09	03/28/17	Wet	11.100	10.131	1.270	0.913
AMB23	PS10	03/28/17	Wet	12.385	11.518	1.130	0.930
AMB23	PS10.1	03/28/17	Wet	12.780	12.188	1.240	0.954
AMB23	PS11	03/28/17	Wet	11.815	12.841	1.550	1.087
AMB23	PS12	03/28/17	Wet	6.278	5.875	1.470	0.936
AMB23	PS07	03/29/17	Wet	7.832	7.067	0.988	0.902
AMB23	PS09	04/05/17	Wet	12.148	9.442	2.640	0.777
AMB25	PS01	02/27/18	Wet	2.240	1.960	2.570	0.875
AMB25	PS02	02/27/18	Wet	2.657	2.304	1.310	0.867
AMB25	PS03	02/27/18	Wet	4.434	3.755	1.190	0.847
AMB25	PS03	02/27/18	Wet	4.170	3.740	0.636	0.897
AMB25	PS04	02/27/18	Wet	3.390	2.865	0.660	0.845
AMB25	PS05	02/27/18	Wet	4.638	4.174	0.660	0.900
AMB25	PS06	02/27/18	Wet	4.520	4.018	0.640	0.889
AMB25	PS07	02/27/18	Wet	2.910	2.523	1.420	0.867
AMB25	PS08	02/27/18	Wet	5.439	5.227	0.860	0.961
AMB25	PS09	02/27/18	Wet	8.316	6.918	1.010	0.832
AMB25	PS10	02/27/18	Wet	6.256	5.815	0.760	0.930
AMB25	PS10.1	02/27/18	Wet	6.108	5.602	0.670	0.917
AMB25	PS11	02/27/18	Wet	8.995	7.669	1.260	0.853
AMB25	PS12	02/27/18	Wet	5.924	6.038	0.540	1.019
AMB25	PS03	02/28/18	Wet	4.221	4.082	0.638	0.967
AMB28	PS01	03/19/19	Wet	2.723	2.600	1.489	0.955

Project	Site Code	Collection Date	Season	Total Zn (µg L^{-1})	Dissolved Zn (µg L^{-1})	TSS	Dissolved/ Total
AMB28	PS02	03/19/19	Wet	4.504	4.474	3.206	0.993
AMB28	PS03	03/19/19	Wet	4.790	5.274	2.148	1.101
AMB28	PS03	03/19/19	Wet	4.471	6.560	3.234	1.467
AMB28	PS04	03/19/19	Wet	4.357	4.966	2.592	1.140
AMB28	PS05	03/19/19	Wet	5.120	4.636	0.699	0.906
AMB28	PS06	03/19/19	Wet	7.217	6.871	1.650	0.952
AMB28	PS07	03/19/19	Wet	17.742	6.841	0.975	0.386
AMB28	PS08	03/19/19	Wet	11.706	10.691	0.992	0.913
AMB28	PS09	03/19/19	Wet	11.823	12.088	1.156	1.022
AMB28	PS10	03/19/19	Wet	6.573	6.079	1.545	0.925
AMB28	PS10.1	03/19/19	Wet	5.919	6.440	1.175	1.088
AMB28	PS11	03/19/19	Wet	7.218	6.640	0.893	0.920
AMB28	PS12	03/19/19	Wet	6.331	5.942	1.739	0.939
AMB28	PS03	03/20/19	Wet	5.044	7.546	1.436	1.496
				Total:		*n*	428
						average	0.895
						σ	0.167
						TSS Correlation	-0.030
						p	0.542
				Dry Season:		*n*	221
						average	0.846
						σ	0.188
						TSS Correlation	0.023
						p	0.739
				Wet Season:		*n*	207
						average	0.947
						σ	0.121
						TSS Correlation	0.0742
						p	0.263
				season t-test:		*p*	1.02E-10

Appendix D– Critical Publications

The following publications are appended to this report for (1,2) understanding of C_{DGT} Cu CMC derivation, (3) demonstration of C_{DGT} Cu sensitivity/reproducibly and visualization of C_{DGT} Cu pulse capture in an area impacted primarily by stormwater, and (4) understanding the impact to long-term data trends when advancements in analytical methods occur.

1. Strivens J.E., N. Hayman, G. Rosen, and A.N. Myers-Pigg. 2020. Toward Validation of Toxicological Interpretation of Diffusive Gradients in Thin Films in Marine Waters Impacted by Copper. Environmental Toxicology and Chemistry 39, no. 4:873-881. PNNL-SA-150328. doi:10.1002/etc.4673

2. Strivens J.E., N. Hayman, R.K. Johnston, and G.H. Rosen. 2019. Effects of Dissolved Organic Carbon on Copper Toxicity to Embryos of Mytilus galloprovincialis as Measured by Diffusive Gradient in Thin Films. Environmental Toxicology and Chemistry 38, no. 5:1029-1034. PNNL-SA-139169. doi:10.1002/etc.4404

3. Strivens J.E., R.K. Johnston, G.H. Rosen, N. Hayman, N.J. Schlafer, and J.M. Brandenberger. 2019. Diffusive Gradient Thin-Films: Time Integrated Passive Sampling for Trace Metals in Receiving Waters of Puget Sound. 2018 Salish Sea Toxics Monitoring Review, Puget Sound Ecosystem Monitoring Program 2018. PNNL-SA-135681

4. Strivens J.E., J.M. Brandenberger, and R.K. Johnston. 2019. Data Trend Shifts Induced by Method of Concentration for Trace Metals in Seawater: Automated Online Preconcentration vs Borohydride Reductive Coprecipitation of Nearshore Seawater Samples for Analysis of Ni, Cu, Zn, Cd, and Pb via ICP-MS. Limnology and Oceanography Methods 17, no. 4:266-276. PNNL-SA-140847. doi:10.1002/lom3.10311

Environmental Toxicology and Chemistry—Volume 39, Number 4—pp. 873–881, 2020
Received: 9 December 2019 | Revised: 7 January 2020 | Accepted: 20 January 2020

Environmental Toxicology

Toward Validation of Toxicological Interpretation of Diffusive Gradients in Thin Films in Marine Waters Impacted by Copper

Jonathan Strivens,[a,*] Nicholas Hayman,[b] Gunther Rosen,[b] and Allison Myers-Pigg[a]

[a]Pacific Northwest National Laboratory, Sequim, Washington, USA
[b]Naval Information Warfare Center Pacific, San Diego, California, USA

Abstract: Determination of the median effective concentration (EC50) of Cu on *Mytilus galloprovincialis* larvae by diffusive gradient in thin films (DGT) has been shown to effectively reduce the need to consider dissolved organic carbon (DOC) concentration and quality. A standard toxicity test protocol was used to validate previously modeled protective effects, afforded to highly sensitive marine larvae by ligand competition, in 5 diverse site waters. The results demonstrate significant narrowing of *M. galloprovincialis* toxicological endpoints, where EC50s ranged from 3.74 to 6.67 μg/L as C_{DGT} Cu versus 8.76 to 26.8 μg/L as dissolved Cu (Cu_{DISS}) over a DOC range of 0.74 to 3.11 mg/L; *Strongylocentrotus purpuratus* EC50s were 10.5 to 19.3 μg/L as C_{DGT} Cu versus 22.7 to 67.1 μg/L as Cu_{DISS} over the same DOC range. The quality of DOC was characterized by fluorescence excitation and emission matrices. The results indicate that the heterogeneity of competing Cu binding ligands, in common marine waters, minimizes the need for class determinations toward explaining the degree of protection. Using conservative assumptions, an *M. galloprovincialis* C_{DGT} Cu EC50 of 3.7 μg/L and corresponding criterion maximum concentration C_{DGT} Cu of 1.8 μg/L, for universal application by regulatory compliance-monitoring programs, are proposed as a superior approach toward both integration of dynamic water quality over effective exposure periods and quantification of biologically relevant trace Cu speciation. *Environ Toxicol Chem* 2020;39:873–881. © 2020 SETAC

Keywords: Diffusive gradients in thin films; Bioavailability; Copper; Dissolved organic carbon

INTRODUCTION

The operationally defined dissolved fraction of grab or composite samples, which includes biologically inert forms of analytes of concern, has been heavily used in legislative directives to monitor pollutants in coastal seawater. Ongoing efforts toward validation of scientifically defendable passive samplers are driven by recognition that combining integration of dynamic water quality over effective exposure periods with biologically relevant measurement of speciation is a preeminent method of ecosystem health assessment (Angel et al. 2015; US Environmental Protection Agency 2016). Among the priority pollutants listed by the US Environmental Protection Agency and equivalent environmental councils is Cu. This ubiquitous metal, a micronutrient in the coastal marine environment, is often elevated above toxic thresholds because of industry reliance on the antifouling, preservative, and thermal conductivity properties it provides. The need for a reliable passive sampling approach to Cu-impacted waters, capable of mimicking bioavailability to the most sensitive saltwater organisms, is highlighted by recent efforts toward a biotic ligand model (Chadwick et al. 2008; US Environmental Protection Agency 2016) and results from the understanding that ligand competition in marine waters modulates biotic uptake by encompassing >99% of dissolved Cu (Cu_{DISS}; Arnold et al. 2005, 2006, 2010). The primary diffusive gradients in thin films (DGTs) passive sampling approach, which operationally measures trace concentrations integrated over time by chelation of free and weakly complexed transition metals (essentially measuring the free ion activity [Davison 2016]), has been demonstrated to more accurately represent the potential for biological effects resulting from Cu exposure (Strivens et al. 2019b) and is therefore an enhanced option for assessment of protection goals.

The agarose crosslinked polyacrylamide (APA)/Chelex DGT configuration (Zhang and Davison 1995) functions in a manner that generally mimics larval-stage uptake of bioavailable metals (Strivens et al. 2019b), which are the basis for aquatic life criteria development (Stephan et al. 1985; US Environmental Protection Agency 2016). Based on size discrimination, diffusion rates, and complexing ability (equilibrium constants and free energy–based

This article includes online-only Supplemental Data.
* Address correspondence to Jonathan.Strivens@pnnl.gov
Published online 31 January 2020 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/etc.4673

dissociation rates), DGT retention of Cu will largely follow the order cupric ion > chlorides ~ fluorides > sulfates > carbonates > polysaccharides > amino acids > humic substances. Also, DGT provides a standardized geometry (i.e., diffusion window) through which effects on analyte flux can be interpreted with conservative assumptions. In addition, field trials have previously reported high precision, reproducibility, and reliability of DGT measurements in natural waters, over windows of 24 h to 14 d (Strivens et al. 2019c). With this understanding, Strivens et al. (2019b) modeled *Mytilus galloprovincialis* median effective concentrations (EC50s) as the concentration of Cu in solution (Sequim Bay seawater), as measured by DGT (C_{DGT} Cu), versus dissolved organic carbon (DOC) concentrations.

The dose responses in Strivens et al. (2019b) were reflective of the protective effects of allochthonous DOC derived from Suwannee River natural organic matter (SRNOM; International Humic Substances Society). The summary proposed a conservatively protective criterion maximum concentration (CMC), against which to interpret C_{DGT} Cu, of 2.4 µg/L. Although this initial effort showed a significant decrease in the Cu EC50 range (i.e., 10.8–48.8 µg/L as Cu_{DISS} vs 4.81–11.5 µg/L as C_{DGT} Cu over a DOC range of 0.896–8.36 mg/L), the effects of DOC quality (i.e., varying complexation stability and capacity) were not addressed in the initial model.

The present study is a follow-up to the initial C_{DGT} Cu EC50 determinations for *M. galloprovincialis* of Strivens et al. (2019b). The intent was to validate the previously derived model through EC50 additions determined by exposing *M. galloprovincialis* embryos and DGTs to seawaters containing a range of DOC quality, as characterized by fluorescence excitation emission spectra. *Strongylocentrotus purpuratus* C_{DGT} Cu EC50s were also collected for initial consideration of a second genus in C_{DGT} Cu CMC formation. The resulting C_{DGT} threshold is then compared to a water-effects ratio (WER) approach to regulatory monitoring of Cu bioavailability. Finally, spatial/temporal health in a marine monitoring area are demonstrated with consideration of the proposed C_{DGT} Cu CMC.

MATERIALS AND METHODS

Laboratory validation of C_{DGT} Cu CMC

To validate use of the allochthonous DOC-derived C_{DGT} Cu CMC proposed in Strivens et al. (2019b), seawater samples were collected with the intent of covering the prevailing natural range of coastal DOC concentrations (Barrón and Duarte 2015) and to be representative of varying autochthonous sources and allochthonous inputs. Seawaters were collected by regional field teams, following "clean hands–dirty hands" protocol (US Environmental Protection Agency 1996a), on 3 June 2019, with the exception of Pearl Harbor (which was collected on 30 May 2019). All samples were collected by peristaltic pump from the top meter of the water column, with the exception of Granite Canyon (which was collected from the laboratory supply system at the University of California Davis' Marine Pollution Studies Laboratory at Granite Canyon). Samples were filtered in-line by 0.45 µm polyethersulfone and shipped overnight to the Naval Information Warfare Center in acid-cleaned 15-L low-density polyethylene carboys. During transit the samples were maintained at 4 ± 2 °C. On arrival, sites were screened to abate concern of select common costressor effects toward the bioassays (Table 1).

Preparation of laboratory test solutions. On 4 June 2019, site water salinities were adjusted by addition of high-purity deionized water (>18 MΩ cm) or Crystal Sea Marinemix (Marine Enterprises International) to the 15-L carboys; this was performed in accordance with the west coast marine and estuarine organisms' chronic toxicity test protocol specifications for *Mytilus* (US Environmental Protection Agency 1995a). Prior to use, a sample of the Crystal Sea Marinemix lot was prepared to 30 practical salinity units (PSU), screened for DOC and trace metal content, and qualitatively assessed by fluorescence. The DOC was <0.3 mg/L, and trace metals were also negligible with respect to the ambient waters' levels. Excitation and emission of the Marinemix showed minor peaks in A, B, and T areas (<4 quinine sulfate equivalence [QSE] ppt/L/mg DOC). Next, seven 2-L splits of seawater from each carboy were nominally spiked with Cu (as Cu[II]SO_4, trace metal basis; Aldrich) to span ranges centered on expected *M. galloprovincialis* EC50 values, at site respective DOC levels, based on observations previously reported (e.g., Arnold et al. 2006, 2010; Rosen et al. 2008; Strivens et al. 2019b). The splits were allowed 24 h for binding kinetics to reach equilibrium in a dark, 4 ± 2 °C environment before being brought to 15 °C on a shaker table. Post-equilibration, aliquots from each 2-L split were taken for confirmatory trace metal and DOC quantification, fluorescence characterization, and embryo exposures.

TABLE 1: Ambient water quality of sites used for validation of Strivens et al. (2019b) C_{DGT} Cu CMC approach

			Ambient water quality								
Station	Latitude (N)	Longitude (W)	Salinity (PSU)	pH	Temp. (°C)	DOC (mg/L)	Cu_{DISS} (µg/L)	Ni_{DISS} (µg/L)	Zn_{DISS} (µg/L)	Cd_{DISS} (µg/L)	Pb_{DISS} (µg/L)
Granite Canyon	36°26′23.5″	121°55′31.3″	33.8	7.4	15.0	0.74	0.164	0.716	5.16	0.0623	0.00810
Sinclair Inlet	47°32′58.5″	122°38′34.8″	29.5	8.4	15.4	1.50	0.941	0.508	1.85	0.0615	0.0340
South San Diego	32°37′54.0″	117°06′57.0″	34.5	7.9	19.9	1.62	2.46	0.628	3.60	0.0556	0.0110
Pearl Harbor	21°21′51.9″	158°00′34.6″	32.8	8.2	28.0	2.39	0.933	0.980	1.70	0.0113	0.0275
Dumbarton Bridge	37°30′48.5″	122°08′04.7″	22.2	7.9	20.1	3.11	4.22	5.31	4.65	0.0801	0.676

C_{DGT} = concentration measured by diffusive gradients in thin films; CMC = criterion maximum concentration; DISS = dissolved; PSU = practical salinity units.

Cu_{DISS} and C_{DGT} Cu EC50 determinations. DGTs were purchased from DGT Research, where they are commercially available in the LSNM-NP (loaded, solution deployment type, Chelex100, APA [agarose crosslinked polyacrylamide], polyethersulphone) model for measurement of cations in solution. Duplicate DGTs were exposed in each of the 2-L splits, in the environmental chamber that housed subsampled embryo test vials, for 48 h at 75 rpm. The C_{DGT} data are reported as an average of the replicate measurements, which varied, as average relative percentage of difference, 4 ± 4%. Additional confirmatory water samples were analyzed at commencement and nullified any concern of significant mass balance depletion or DOC degradation. All sample handling was performed in a class 100 clean room.

Toxicological endpoints were determined by exposing embryos to seawater aliquots, following US Environmental Protection Agency (1995a) protocol. To begin, adult gravid *M. galloprovincialis* and *S. purpuratus* were collected from the mouth (north jetty) of Mission Bay (San Diego, CA, USA) and induced to spawn by thermal shock or an injection of potassium chloride, respectively. Larvae were transferred to glass scintillation vials within 4 h of fertilization. Each test exposure was replicated 5 times. Vials were incubated for 48 h (*M. galloprovincialis*) and 96 h (*S. purpuratus*) under a 16:8-h light:dark photoperiod. All water quality data met the constraints for *M. galloprovincialis* acceptability; the salinities were within 3.5 PSU of *S. purpuratus* criteria (Supplemental Data, Table S1). At endpoints, the tests were terminated by adding 0.5 mL 10% (v/v) buffered formalin acetate to each vial. Evaluation of the number of surviving larvae of *M. galloprovincialis* that developed normally ("D"-shaped, prodissoconch I stage) relative to the number of total embryos initially added to each vial was assessed (percentage of normal alive endpoint), and the proportion of normally developed larvae relative to the number of larvae counted (percentage of normal development) was also calculated. For *S. purpuratus*, a total of 100 embryos were evaluated from each vial for percentage of normal development (pyramid shape, pluteus stage) and survival. Because the survival and development endpoint results (within each species assessment) were essentially identical, the data are reported herein as percentage of normal development for simplicity.

Characterization of DOC quality. To characterize the variation of ligand sources, seawater aliquots (collected at the time of DGT initiation) were held at 4 ± 2 °C and then analyzed for fluorescence and absorbance using an Yvon Horiba Aqualog® 800. Analyses were conducted within 24 h of collection. To begin, the spectrophotometer was blanked with deionized water at >18 MΩ cm and continuously thereafter, every 20 acquisitions. Next, absorbance and fluorescence data were acquired at 15 °C in a 1-cm quartz cuvette, using a temperature-controlled flow-through cell. Excitation–emission matrices were collected within an excitation range of 230 to 800 nm at 3-nm intervals, and emissions were recorded between 246 and 828 nm over a 1-s integration time. Then, blank signals were subtracted from all absorbance and fluorescence data, and removal of interfilter effects was completed using Aqualog software (Ver 4.0). Rayleigh and Raman scattering were further corrected in MATLAB® using a smoothing algorithm (Powers et al. 2018). In addition, sample fluorescence data were normalized to the emission at 450 nm of a quinine sulfate–blanked 1-mg/L quinine sulfate standard solution (Starna) in the Aqualog software. All reported fluorescence parameters and index calculations are detailed in Supplemental Data, Table S2. Data are reported as an average of replicate measurements, which varied generally <2%.

Field demonstration of utility

Field trials were conducted at marine monitoring stations in and adjacent to Sinclair Inlet, Puget Sound (PS), WA, USA (Supplemental Data, Table S3), and have allowed for improved capture of Cu input/cycling and the resulting lability (health) trends. For in situ use of DGT, basic considerations tied to sampling physics, water column stratification, biota behavior, and station selection are essential for proper representation of ecosystem health. A preliminary assessment on impact of resupply at the diffusive boundary layer (DBL) of the LSNM-NP DGTs in the Sinclair Inlet study area reviewed the results of a bottom-mounted Acoustic Doppler Current Profiler. The profiler was moored near station PS09 (Supplemental Data, Table S3) from 11 November to 6 December 2005 (generating a continuous data set to evaluate tidal currents throughout the water column, over a 14-d neap tidal cycle). The data confirmed that the maintained current speed in the upper 5 m of the water column is expected to be above the 2-cm/s threshold for DBL negation (Gimpel et al. 2001); thus, the abbreviated C_{DGT} equation in Zhang and Davison (1995) was employed for quantification. Temperature inputs were obtained from codeployed HOBO™ loggers. Positioning of DGTs in the water column was also considered by 1) minimizing the degree of biofouling-induced DBL impediment, inherent to samplers placed above the disphotic boundary, by inverting samplers and limiting deployment periods; 2) protecting samplers from large debris by placement inside polypropylene cages (2.0-cm mesh); and 3) using 1-m depth as the primary observation point in the water column to ensure cross-sectional homogeneity and representativeness of grab sample collection protocols.

The general approach of the program, into which DGTs have been incorporated for the present demonstration, consists of seasonal grab sampling of approximately 40 marine stations (Strivens et al. 2018) within the Kitsap basin (WA, USA). The subset of 9 stations selected for DGT deployments are nearshore and nonstochastic, where station port orchard passage port of Illahee Dock is representative of receiving marine waters adjacent to rural/residential land use, dyes inlet old town Silverdale is adjacent to urban/commercial land use, and PS stations are positioned within an industrial shipyard. The industrial shipyard stations are deliberately located near potential sources, making the comparison to reference locations qualitative (Strivens et al. 2018). With the totality of these

factors considered, the resulting data provide an assessment of DGT labile Cu toward *M. galloprovincialis* larvae in a deterministic manner.

To demonstrate the utility of DGTs versus a WER approach, passive samplers were deployed for 3 d pre– and 3 d post–grab sample collections and the results assessed against their respective CMCs. Three-day deployments were selected to represent the midpoint of *M. galloprovincialis* and *S. purpuratus* embryo-larval development toxicity test specifications and were conducted over a period with >6 cm of rainfall. Results are assessed against a C_{DGT} CMC of 2.4 μg/L, in agreement with the EC50 equation (determined by the present study) and the average DOC concentration for these sites (1.40 mg/L [Strivens et al. 2018]). The Cu_{DISS} CMC, 6.8 μg/L, was taken from Rosen et al. (2009), which calculated a WER for the Sinclair Inlet study area and reported an *M. galloprovincialis* EC50 result in agreement with the present study. The long-term health of the Sinclair Inlet study area is also presented as a demonstration of C_{DGT} Cu interpretation against the proposed site CMC.

Trace metals and DOC quantification

For analysis of dissolved metals in seawater, samples were first prepared using a total recoverable metal digestion and then preconcentrated via a seaFast® chelation step (Strivens et al. 2019a). For labile metals, Chelex resins were eluted in 1 mL concentrated Optima™ grade nitric acid (Fisher Scientific) for 24 h, at room temperature, then diluted to 15 times. Seawater samples and DGT elutions were then analyzed by inductively coupled plasma–mass spectrometry in accordance with US Environmental Protection Agency methods 1638 (1996b) and 1640 (1997). Limits of detection (LOD) for coanalyzed metals (Ni, Zn, Cd, Pb, and Fe [monitored as a fluorescence interferant]) were 0.0015, 0.0093, 0.0008, 0.001, and 0.012 μg/L, respectively; and the LOD for Cu was 0.002 μg/L. The C_{DGT} method's limit of quantification was <0.02 μg/L for all data sets.

Levels of DOC were quantified, in accordance with SM5310B (American Public Health Association et al. 2005), using a Shimadzu TOC-L instrument equipped with a high-salt sample combustion tube kit and halogen scrubber. The data are reported as nonpurgeable organic carbon, with an LOD of 0.049 mg/L.

Statistical analysis

Toxicity tests were evaluated for quality control based on test acceptability criteria of survival and percentage of normal development of surviving larvae in the site controls (US Environmental Protection Agency 1995a). Next, the percentage of normally developed larvae from the multiconcentration tests were used to calculate the EC50s of measured Cu_{DISS} and C_{DGT} Cu with the toxicity statistics program CETIS™ (Tidepool Scientific). The C_{DGT} Cu EC50s were then assessed for agreement with the Strivens et al. (2019b) model and integrated into the previous data set after acceptability, the null hypothesis being no significant difference between slopes or intercepts ($\alpha = 0.05$). Regression analysis was used to model Cu EC50s, on the basis of DOC concentration, for site-specific applications. An update to the previously proposed C_{DGT} Cu CMC is then given, with conservative assumptions, following the US Environmental Protection Agency's (1995b) current consensus for deriving criteria values.

Qualitative analyses of the range in DOC, using normalized peak and index values of samples applied to the CMC derivation, consisted of one-way analysis of variance (ANOVA) by site; re-creations of the SRNOM series in Sequim Bay Seawater (detailed in Strivens et al. 2019b) were also included in the ANOVAs. Post hoc analyses by Tukey's honestly significance difference were performed on peak and index values when applicable.

Spatial data, displayed as box and whisker plots, provide lower and upper hinges corresponding to the first and third quartiles. Whiskers extend from the upper and lower hinges to the largest value no further than 1.5 times the inner quartile range.

RESULTS AND DISCUSSION

Toxic effects as Cu_{DISS} and C_{DGT} Cu

Assessment of the bioassays confirmed acceptance of the data. All but one negative control met acceptability for *M. galloprovincialis*, with >90% development and >50% survival (US Environmental Protection Agency 1995a). The Pearl Harbor site's negative control demonstrated 83.2% normal development; however, Pearl Harbor treatments with low Cu_{DISS} (below levels that would cause adverse effects) showed >90% normal development. This suggests that the low normal development result in the negative control was not indicative of inherent toxicity in the Pearl Harbor water. For *S. purpuratus*, >96% normal development was observed in all negative controls versus a >80% acceptability threshold. The EC50 confidence intervals were 95% for all tests (with the exception that the *S. purpuratus* series for Sinclair Inlet was not adequately spiked to produce a dose response), and all treatments were significantly different ($\alpha = 0.05$).

M. galloprovincialis. As illustrated in Figure 1, a shift from allochthonous to mixed allochthonous/autochthonous DOC sources did not conflict with the assumption of Strivens et al. (2019b): that the integrated pools of ligands found in natural seawater do not require classification for determination of their protective capacity; rather, DOC concentration alone may be adequate for universal monitoring efforts when using DGT. The Cu_{DISS} EC50s in the present study agreed with the model (Cu_{DISS} EC50 = 5.10[DOC] + 7.65 [Strivens et al. 2019b]), and the percentage of differences from predicted values ranged from 87 to 107%; merging the data sets resulted in an R^2 shift of <2%. The same is true of the shift in the C_{DGT} Cu EC50 trend, where percentage of differences from the model (C_{DGT} Cu EC50 = 0.861[DOC] + 4.89 [Strivens et al. 2019b]) ranged from 78 to 94%. Slopes and intercepts between the present

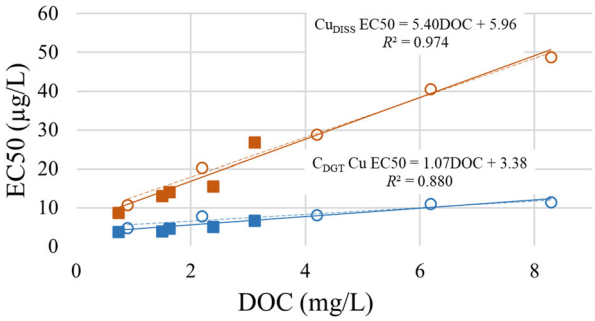

FIGURE 1: Median effective concentrations of *Mytilus galloprovincialis* over a range of dissolved organic carbon concentrations. Combined data sets are displayed as Cu_{DISS} (orange, $F_{(1,8)} = 301$, $p < 0.001$) and C_{DGT} Cu (blue, $F_{(1,8)} = 58$, $p < 0.001$) with solid trend lines. Open circles and dashed lines indicate the points and trends of Strivens et al. (2019b), respectively; filled squares signify the data found in Table 2. Cu_{DISS} = dissolved Cu; DOC = dissolved organic carbon; EC50 = median effective concentration.

data set and the model were determined as not significantly different ($p < 0.05$) prior to combining datasets. The C_{DGT} Cu values obtained from the spiked Cu_{DISS} solutions (0.164–92.4 µg/L) in the present study ranged from 0.0194 to 27.0 µg/L, and DOC ranged from 0.74 to 3.11 mg/L (Table 2). The results of a multiple regression indicated that Cu_{DISS} and DOC explained 96.8% of the C_{DGT} variance ($F_{(2,32)} = 484$, $p < 0.001$); the combined data set indicated that the 2 analytes explained 90.6% of the variance ($F_{(2,67)} = 325$, $p < 0.001$). The combined relationship is C_{DGT} Cu = –0.908[DOC] + 0.362[Cu_{DISS}] + 2.21. Solely, DOC concentration explains 88% of the variance in the combined C_{DGT} Cu EC50 over a range of 0.74 to 8.36 mg/L DOC (Figure 1).

With the understanding that the majority of coastal marine waters possess DOC concentrations within the range given in Table 2 (Chadwick et al. 2008; Barrón and Duarte 2015), to normalize the EC50 to 3.7 µg/L C_{DGT} Cu, for regulatory monitoring, may conservatively negate the need for DOC analysis. For deriving site-specific criteria, the model is given in Figure 1. However, it should be understood that Granite Canyon, Sinclair Inlet, South San Diego, Pearl Harbor, and Sequim Bay do not exhibit largely different toxicological endpoints as C_{DGT} Cu. The differences between the C_{DGT} Cu EC50s for these stations are well within the range of biological variability, and the variance attributable to diffusion window expansion in this DOC range (0.74–3.11 mg/L) appears minimal (i.e., the EC50 slope is 0.975 vs the Cu_{DISS} slope of 6.60). With the present *Mytilus* data set, a proposed CMC C_{DGT} Cu of 1.8 µg/L may allow universal field studies to readily place DGT results in the context of water quality criteria. This criteria concentration is representative of the most conservative toxicological dose and was calculated by setting the C_{DGT} Cu EC50 at 0.74 mg/L DOC equal to a final acute value (which by this method is equal to the final chronic value; Stephan et al. 1985). Although the proposed CMC is sufficiently conservative with respect to the known lability constituents, future exploration should assess the capacity of DGT to mimic the impact to larvae physiology by synergistic cofactors (e.g., salinity, temperature, Zn). In the interim, the proposed CMC offers an uncomplicated and protective approach to C_{DGT} Cu interpretation.

S. purpuratus. To generate the initial data exploring C_{DGT} Cu toxicological dose formation for a second sensitive saltwater bioassay endpoint, *S. purpuratus* larvae were included in the present study. The *S. purpuratus* Cu_{DISS} EC50s (Table 2) were higher than, but within an order of magnitude of, previously reported data series (Rosen et al. 2008; Arnold et al. 2010). Comparison of the C_{DGT} Cu EC50s to the Cu_{DISS} EC50s shows a meaningful decrease in the spread of EC50 values over the range of 0.74 to 3.11 mg/L DOC. It is apparent, as is seen in the *M. galloprovincialis* results, that diffusion window expansion toward DGT lability affects the slope. However, conservative assumptions still greatly improve the predictive ability toward toxicological effects in comparison to measurements of Cu_{DISS} alone. To preserve a conservative C_{DGT} Cu CMC, as is currently done by the US Environmental Protection Agency, *S. purpuratus* were not incorporated with *M. galloprovincialis* results to form an adjusted final acute value.

Effects of DOC quality

Differences in fluorescence indices across sites suggest that a range of DOC types were captured with these samples (Table 3; Supplemental Data, Figure S1). The fluorescence index (FI), often used to assess the relative contribution of terrestrial and microbial sources of DOC (McKnight et al. 2001; Cory et al. 2010), showed no apparent relationship against either DOC concentration or EC50 as Cu_{DISS}, meaning that the

TABLE 2: Cu_{DISS} and C_{DGT} Cu CETIS statistics, as proportion normal EC50, ordered by DOC concentration

		Mytilus galloprovincialis		*Strongylocentrotus purpuratus*	
Station	DOC (mg/L)[a]	Cu_{DISS} (µg/L)[b]	C_{DGT} Cu (µg/L)[b]	Cu_{DISS} (µg/L)[b]	C_{DGT} Cu (µg/L)[b]
Granite Canyon	0.74 ± 0.01	8.76 ± 0.03	3.74 ± 0.01	22.7 ± 0.40	10.5 ± 0.22
Sinclair Inlet	1.50 ± 0.02	13.0 ± 0.08	3.93 ± 0.03	> 31.5	> 11.1
South San Diego	1.62 ± 0.02	14.1 ± 0.12	4.71 ± 0.07	32.7 ± 0.28	12.2 ± 0.11
Pearl Harbor	2.39 ± 0.01	15.5 ± 0.05	5.01 ± 0.01	38.7 ± 0.73	13.8 ± 0.30
Dumbarton Bridge	3.11 ± 0.02	26.8 ± 0.07	6.67 ± 0.02	67.1 ± 0.96	19.3 ± 0.20

[a]Values are expressed as mean ± standard deviation.
[b]Values are expressed as slope ± 95% margin of error.
C_{DGT} = concentration measured by diffusive gradients in thin films; DOC = dissolved organic carbon; DISS = dissolved; EC50 = median effective concentration.

TABLE 3: Fluorescence properties of ambient water samples from each site[a]

					Specific peak (ppb QSE/L/mg DOC)								
Site	DOC mg/L	FI*	BIX*	HIX*	A	B*	C	M	N	T*	Peak C/A	Peak C/T	Peak C/M
Granite Canyon	0.74	1.43[b]	0.74[b]	0.75[b,c]	5.44	1.37[b]	2.80	2.75	2.26	2.14[b]	0.52	1.31	1.02
Sinclair Inlet	1.50	1.54[c,d]	0.87[b]	0.66[b,c,d]	4.39	1.92[b]	2.14	2.50	3.02	3.19[b]	0.49	0.68	0.86
South San Diego	1.62	1.41[b]	0.83[b]	0.76[b,d]	7.79	1.86[b]	3.78	3.85	3.46	3.11[b]	0.49	1.21	0.98
Pearl Harbor	2.39	1.39[b]	0.90[b]	0.58[d]	3.56	2.06[b,c]	1.73	2.50	3.34	3.72[b]	0.49	0.47	0.69
Dumbarton Bridge	3.11	1.58[d]	0.89[b]	0.76[b]	14.78	3.31[c]	6.99	7.10	6.45	5.67[c]	0.47	1.23	0.98
SBSW	0.87	1.65[e]	0.94[b]	0.76[b,d]	6.68	1.87[b]	2.92	2.90	2.57	2.47[b]	0.44	1.20	1.01
SBSW + SRNOM	2.01	1.52[c]	0.57[c]	0.93[e]	16.83	1.14[b]	7.68	6.51	2.95	2.01[b]	0.46	3.83	1.18
SBSW + SRNOM	3.72	1.51[c]	0.53[c]	0.95[e]	20.94	0.90[b]	9.72	7.98	3.18	1.94[b]	0.46	5.01	1.22
SBSW + SRNOM	5.52	1.51[c]	0.51[c]	0.95[e]	21.97	0.84[b]	10.34	8.40	3.22	1.92[b]	0.47	5.38	1.23
SBSW + SRNOM	7.47	1.51[c]	0.51[c]	0.96[e]	22.54	0.79[b]	10.70	8.65	3.25	1.89[b]	0.47	5.65	1.24

[a]Letters represent post hoc Tukey honestly significant difference similarities or differences; columns with no letters indicate no significant difference between site-wise comparisons.
*$p < 0.05$, indicated by letter.
BIX = biological index; DOC = dissolved organic carbon; FI = fluorescence index; HIX = humification index; QSE = quinine sulfate equivalence; SBSW = Sequim Bay seawater; SRNOM = Suwannee River natural organic matter (2R101N; International Humic Substances Society).

protective effects of DOC do not appear to be related to the differences in DOC composition expressed by this index. The FI was significantly different by site, with site-wise comparisons revealing 4 groupings (Table 3). The biological index (BIX), an index associated with autotrophic DOC (where values >1 are suggestive of recent autochthonous DOC input; Huguet et al. 2009), was lowest in SRNOM and Granite Canyon and highest in Sequim Bay seawater. The BIX was also significantly different by site, with a post hoc Tukey honestly significance difference indicating that SRNOM was significantly different from the sampled sites' DOCs. As with the FI, the BIX did not correlate to DOC or Cu_{DISS} EC50 concentrations. The FI and BIX are sensitive to the location of these ranges in relation to the overall emission maxima and do not always follow property balance principles (Korak et al. 2014), such that the intercomparison of indices across concentrations with varying inputs can be difficult and should be interpreted with caution. Increasing protectiveness (as Cu_{DISS} EC50) also did not coincide with increases in the humification index (HIX; Ohno 2002). The HIX was also different by site, with site-wise comparisons revealing 4 groupings (Table 3). For all indices, SRNOM was significantly different from mixed DOC-source sites.

Specific fluorescence peaks (Table 3; Supplemental Data, Figure S1) of ambient waters also provide insight toward the lability effects and the range of DOC quality captured in the present study. It is generally accepted that peak regions A and C are indicators of terrestrial humic-like materials, region M is representative of a combination of terrestrial and marine humic material (Hansen et al. 2016), region N indicates plankton-derived DOC, and the T and B regions are the fluorescing ligands of aromatic amino acids (Cory and McKnight 2005; Hansen et al. 2016). Increasing protectiveness (as Cu_{DISS} EC50) with increasing DOC coincided with increases in fluorescence of specific A, C, and M peaks, whereas specific N, T, and B peaks displayed the opposite trend, such that the specific fluorescence in these regions decreased with increasing protectiveness and DOC concentration. Post hoc analyses revealed that, of the site-wise comparisons, Dumbarton Bridge–specific fluorescence peaks B and T were significantly different from those of the other sites (with the exception of specific peak B [$p = 0.057$] for Dumbarton Bridge:Pearl Harbor); no other site comparisons were significantly different. Multiple regression analysis showed that no specific peak area response significantly ($\alpha = 0.05$) drove either Cu_{DISS} or C_{DGT} Cu EC50s. Qualitatively, Sinclair Inlet and Pearl Harbor have a "more marine" signature, whereas the other sites have a "more terrestrial" influence (classically seen in the SRNOM excitation–emission matrix; Supplemental Data, Figure S1).

Specific peak ratios can provide additional qualitative assessment of DOC. The ratio of specific peaks C to A has been related to the relative proportion of humic-like fluorescence photo- or biodegradation (Kothawala et al. 2012) or ascribed to terrestrial soil DOC at ratios <0.6 (Hansen et al. 2016). As reported in Table 3, all peak ratios were <0.6, indicating degradation and/or the preservation of terrestrial soil-like DOC. The range of the ratio of specific peaks C to T may be indicative of "degraded" to "fresh" organic matter (Baker et al. 2008; Hansen et al. 2016). The range displayed at the study sites is indicative of relatively fresh algal materials. In addition, a high ratio of C:M has been proposed as suggestive of more terrestrial humic-like DOC presence, versus marine (Para et al. 2010), which is seen (with a ratio >1) in SRNOM and Granite Canyon.

Importantly, there were no major shifts in fluorescence spectral indices between waters with ambient DOC concentrations and those with elevated Cu content (spike levels equivalent to site EC50s), meaning that minimal quenching of Cu occurred and suggesting that quantification of ligand density at toxicologically relevant Cu concentrations is likely to offer low resolution determinations. This is a function of the heterogeneity of marine waters and the low EC50s for many aquatic species.

Although the data cannot conclusively rule out that coastal marine DOC quality significantly impacts Cu complexation, the results suggest that the range in DOC sources, in the present study, does not have a dominant effect on the

protectiveness (as determined by Cu_{DISS} EC50s). The lack of clear systematic trends in Cu_{DISS} EC50s versus the HIX, and the BIX, indicates that DOC protectiveness follows DOC concentration irrespective of those fluorescence signatures of DOC quality. This is likely attributable to heterogenous, yet all strongly Cu-complexing, organic ligands in the study systems (because both terrestrial and aquatic DOC sourced complexes have been found to have strong Cu binding affinity [Moffett 1995; Shank et al. 2004; Hoffmann et al. 2007]). However, for broad application of DGT, it should be considered that some autochthonous organic matter contains relatively low amounts of phenolic-like fluorophores (illustrated by the relationship of N, T, and B peaks to Cu_{DISS} *Mytilus* EC50s). For this reason, toxicological endpoints such as C_{DGT} have an advantage over models that use dissolved Cu and DOC concentrations as inputs (i.e., DGT corrects for binding strength, whereas modeling uses a predetermined binding strength [e.g., the marine biotic ligand model heavily favors the L-2 ligand]). This advantage will be subtle in many cases because of Cu-complexing ligands in coastal seawater largely occurring as an integrated pool of both allochthonous and autochthonous sourced organics; however, it has the potential to be more or highly deterministic in some cases. The labile results, presented in Table 2, suggest that the toxicological endpoint, as free Cu activity integrated by DGT, is essentially unchanged in the prevailing range of coastal marine DOC concentrations by DOC quality.

Field demonstrations

The intent of a Cu CMC development for the LSNM-NP DGT is efficient health assessment of marine waters, which are stewarded by the National Pollutant Discharge Elimination System permit program or equivalent protections. In the data set selected to contrast C_{DGT} and WER approaches (Figure 2), the impact to health assessments is illustrated as time- versus non-time-integrated. The data show that, although there is general agreement, pairing of these measures allowed the monitoring program to assess the probability of elevated Cu seen in grab samples being bioavailable over relevant exposure windows in the dynamic system. Using the example of station PS03, a short-term disruption or inhomogeneous grab sample gives the appearance that the station is elevated by nearly double against the Cu_{DISS} CMC. With the understanding

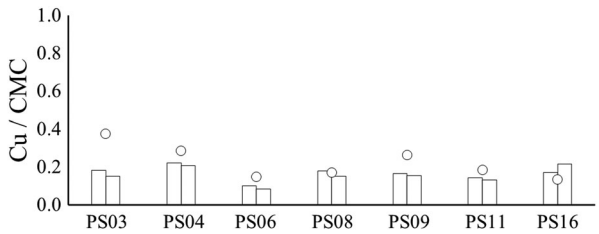

FIGURE 2: Demonstration of grab sampling (open circles; 28 March 2017) versus 3-d DGT deployments (bars; 25–28 March 2017 and 28–31 March 2017) as a ratio of their respective criterion maximum concentrations. CMC = criterion maximum concentration; PS = Puget Sound.

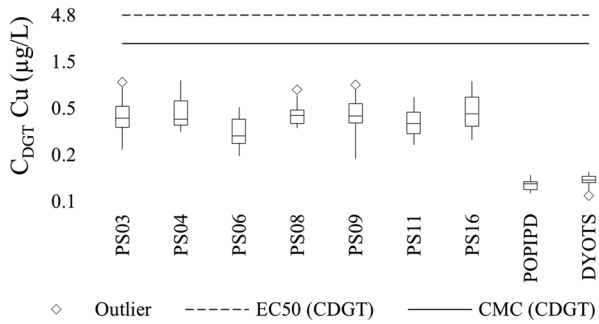

FIGURE 3: Long-term health of Sinclair Inlet and reference stations within the Kitsap basin. The compiled data consist of 3-d DGT deployments (Puget Sound stations; $n = 28$/station) and 14-d deployments (reference locations; $n = 7$/station) between December 2016 and July 2019. C_{DGT} = concentration measured by diffusive gradients in thin films; CMC = criterion maximum concentration; PS = Puget Sound.

that pulsed trace metal inputs can be tolerated when offset over biologically relevant windows (e.g., Angel et al. 2015), DGTs have the potential to replace grab sampling in the future as an improved predictor of water body health.

The long-term health of the Sinclair Inlet study area, shown in Figure 3, demonstrates successful adoption of the DGT technique into a regulatory compliance program. Inclusion of reference points, reflective of differing land use adjacent to the receiving waters (i.e., industrial vs commercial or rural), provides a qualitative comparison. Although clear baseline shifts are evident, the data indicate that successful protection of beneficial uses is occurring with respect to the proposed CMC calculation. Continued work toward C_{DGT} toxicological endpoint determinations for additional heavy metals of interest will naturally increase the cost-effectiveness of this passive sampling approach and should be pursued considering the available evidence of DGT utility.

CONCLUSION

A conservative C_{DGT} Cu EC50 of 3.7 µg/L, and a corresponding CMC C_{DGT} Cu of 1.8 µg/L, for universal application by regulatory compliance-monitoring programs has been proposed. This threshold can lessen the need for DOC quantification and will allow shifts in the measured protective effect, afforded to biota, to be driven primarily by deviations in binding capacity and strength. This approach was previously modeled by Strivens et al. (2019b) and is now reproduced as an effective approximation toward conservation of beneficial uses of coastal marine waters. In addition, the appraisal of 6 marine water bodies with mixed-source allochthonous and autochthonous DOC inputs agrees with the sentiment that ligands found in coastal seawater may not require classification for determination of their protective capacity. Future incorporation of this methodology into standardized monitoring frameworks has the potential to accomplish the end goals of current efforts toward both integration of dynamic water quality over effective exposure periods and quantification of biologically relevant trace metal speciation.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at https://doi.org/10.1002/etc.4673.

Acknowledgment—Funding was provided by the Puget Sound Naval Shipyard (Bremerton, WA, USA) and the Navy Environmental Sustainability Development to Integration Project 523. We also thank M. Colvin, I. Rivera-Duarte, and K. Kowal for help with the technical work.

Data Availability Statement—Data, associated metadata, and calculation tools are available from the corresponding author (Jonathan.Strivens@pnnl.gov).

REFERENCES

American Public Health Association, American Water Works Association, Water Environment Federation. 2005. Method SM 5310B: High temperature combustion method. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC.

Angel BM, Simpson SL, Chariton AA, Stauber JL, Jolley DF. 2015. Time-averaged copper concentrations from continuous exposures predicts pulsed exposure toxicity to the marine diatom, *Phaeodactylum tricornutum*: Importance of uptake and elimination. *Aquat Toxicol* 164:1–9.

Arnold W, Cotsifas JS, Ogle RS, DePalma SG, Smith DS. 2010. A comparison of the copper sensitivity of six invertebrate species in ambient salt water of varying dissolved organic matter concentrations. *Environ Toxicol Chem* 29:311–319.

Arnold WR, Cotsifas JS, Corneillie KM. 2006. Validation and update of a model used to predict copper toxicity to the marine bivalve *Mytilus* sp. *Environ Toxicol* 21:65–70.

Arnold WR, Santore RC, Cotsifas JS. 2005. Predicting copper toxicity in estuarine and marine waters using the biotic ligand model. *Mar Pollut Bull* 50:1634–1640.

Baker A, Bolton L, Newson M, Spencer RG. 2008. Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment. *Hydrol Process* 22:2325–2336.

Barrón C, Duarte CM. 2015. Dissolved organic carbon pools and export from the coastal ocean. *Global Biogeochem Cycles* 29:1725–1738.

Chadwick DB, Rivera-Duarte I, Rosen G, Wang P, Santore RC, Ryan AC, Choi W. 2008. Demonstration of an integrated compliance model for predicting copper fate and effects in DoD harbors (No. SPAWAR/CP-TR-1973). Space and Naval Warfare Systems Center Pacific, San Diego, CA, USA.

Cory RM, McKnight DM. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environ Sci Technol* 39:8142–8149.

Cory RM, Miller MP, McKnight DM, Guerard JJ, Miller PL. 2010. Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra. *Limnol Oceanogr* 8:67–78.

Davison W, ed. 2016. *Diffusive Gradients in Thin-films for Environmental Measurements*. Cambridge University Press, Cambridge, UK.

Gimpel J, Zhang H, Hutchinson W, Davison W. 2001. Effect of solution composition, flow and deployment time on the measurement of trace metals by the diffusive gradient in thin-films technique. *Anal Chim Acta* 448:93–103.

Hansen AM, Kraus TE, Pellerin BA, Fleck JA, Downing BD, Bergamaschi BA. 2016. Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. *Limnol Oceanogr* 61:1015–1032.

Hoffmann SR, Shafer MM, Armstrong DE. 2007. Strong colloidal and dissolved organic ligands binding copper and zinc in rivers. *Environ Sci Technol* 41:6996–7002.

Huguet A, Vacher L, Relexans S, Saubusse S, Froidefond JM, Parlanti E. 2009. Properties of fluorescent dissolved organic matter in the Gironde estuary. *Org Geochem* 40:706–719.

Korak JA, Dotson AD, Summers RS, Rosario-Ortiz FL. 2014. Critical analysis of commonly used fluorescence metrics to characterize dissolved organic matter. *Water Res* 49:327–338.

Kothawala DN, von Wachenfeldt E, Koehler B, Tranvik LJ. 2012. Selective loss and preservation of lake water dissolved organic matter fluorescence during long-term dark incubations. *Sci Total Environ* 433: 238–246.

McKnight DM, Boyer EW, Westerhoff PK, Doran PT, Kulbe T, Andersen DT. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol Oceanogr* 46:38–48.

Moffett JW. 1995. Temporal and spatial variability of copper complexation by strong chelators in the Sargasso Sea. *Deep Sea Res Part 1 Oceanogr Res Pap* 42:1273–1295.

Ohno T. 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environ Sci Technol* 36:742–746.

Para J, Coble P, Charrière B, Tedetti M, Fontana C, Sempere R. 2010. Fluorescence and absorption properties of chromophoric dissolved organic matter (CDOM) in coastal surface waters of the northwestern Mediterranean Sea, influence of the Rhône River. *Biogeosciences* 7:4083–4103.

Powers LC, Luek JL, Schmitt-Kopplin P, Campbell BJ, Magen C, Cooper LW, Gonsior M. 2018. Seasonal changes in dissolved organic matter composition in Delaware Bay, USA in March and August 2014. *Org Geochem* 122:87–97.

Rosen G, Rivera-Durate I, Chadwick B, Ryan A, Santore RC, Paquin PR. 2008. Critical tissue copper residues for marine bivalve (*Mytilus galloprovincialis*) and echinoderm (*Strongylocentrotus purpuratus*) embryonic development: Conceptual, regulatory and environmental implications. *Mar Environ Res* 66:327–336.

Rosen G, Rivera-Duarte I, Johnston RK, Podegracz J. 2009. Sinclair and Dyes Inlets toxicity study: An assessment of copper bioavailability and toxicity in surface waters adjacent to the Puget Sound Naval Shipyard and Intermediate Maintenance Facility. SPAWAR/SCP-TR-1985. Space and Naval Warfare Systems Center Pacific, San Diego, CA, USA.

Shank GC, Skrabal SA, Whitehead RF, Kieber RJ. 2004. Fluxes of strong Cu-complexing ligands from sediments of an organic-rich estuary. *Estuar Coast Shelf Sci* 60:349–358.

Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. US Environmental Protection Agency, Washington, DC.

Strivens JE, Brandenberger JM, Johnston RK. 2019a. Data trend shifts induced by method of concentration for trace metals in seawater: Automated online preconcentration vs. borohydride reductive coprecipitation of nearshore seawater samples for analysis of Ni, Cu, Zn, Cd, and Pb via ICP-MS. *Limnol Oceanogr* 17:266–276.

Strivens JE, Hayman N, Johnston R, Rosen G. 2019b. Effects of dissolved organic carbon on copper toxicity to embryos of *Mytilus galloprovincialis* as measured by diffusive gradient in thin-films. *Environ Toxicol Chem* 38:1029–1034.

Strivens JE, Johnston RK, Rosen GH, Hayman NT, Schlafer NJ, Brandenberger JM. 2019c. Diffusive gradient in thin-films: Time integrative passive sampling for trace metals in receiving waters of Puget Sound. In James CA, Jordan R, Langness M, Lanksbury J, Lester D, O'Niell S, Song K, Sullivan C, eds, *2018 Salish Sea Toxics Monitoring Synthesis: A Selection of Research*. Puget Sound Monitoring Program, Tacoma, WA, USA.

Strivens JE, Johnston RK, Schlafer N, Brandenberger JM. 2018. ENVVEST ambient monitoring program: In-progress summary 2009–2017. Prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST. PNNL Marine Sciences Laboratory, Sequim, WA, USA.

US Environmental Protection Agency. 1995a. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. EPA/600/R-95/136. Cincinnati, OH.

US Environmental Protection Agency. 1995b. Ambient water quality criteria—Saltwater copper addendum (draft). Office of Water, Washington, DC.

US Environmental Protection Agency. 1996a. Method 1669: Sampling ambient water for determination of metals at EPA water quality criteria levels. Washington, DC.

US Environmental Protection Agency. 1996b. Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma-mass spectrometry. Washington, DC.

US Environmental Protection Agency. 1997. Method 1640: Determination of trace elements in water by preconcentration and inductively coupled plasma-mass spectrometry. Washington, DC.

US Environmental Protection Agency. 2016. Draft aquatic life ambient estuarine/marine water quality criteria for copper. EPA Publication 822-P-16-001. Rockville, MD.

Zhang H, Davison W. 1995. Performance characteristics of diffusion gradients in thin-films for the in situ measurement of trace metals in aqueous solution. *Anal Chem* 67:3391–3400.

Environmental Toxicology and Chemistry—Volume 38, Number 5—pp. 1029–1034, 2019
Received: 8 December 2018 | Revised: 23 February 2019 | Accepted: 28 February 2019

Environmental Toxicology

Effects of Dissolved Organic Carbon on Copper Toxicity to Embryos of *Mytilus galloprovincialis* as Measured by Diffusive Gradient in Thin Films

Jonathan Strivens,[a,*] Nicholas Hayman,[b] Robert Johnston,[c] and Gunther Rosen[b]

[a]Pacific Northwest National Laboratory, Sequim, Washington, USA
[b]Space and Naval Warfare Systems Center Pacific, San Diego, California, USA
[c]Puget Sound Naval Shipyard & Intermediate Maintenance Facility, Bremerton, Washington, USA

Abstract: Diffusive gradient in thin films (DGT) potentially better quantifies bioavailable copper (Cu) in seawater. Laboratory exposure of DGTs and *Mytilus galloprovincialis* embryos at varying concentrations of dissolved organic carbon and Cu were performed to resolve the degree to which mimicry of toxicity buffering occurs in passive sampler quantification. The results provide preliminary median effect concentrations (EC50s) ranging from 4.8 to 11.5 µg/L as C_{DGT} Cu over the span of 0.896 to 8.36 mg/L DOC. Environ Toxicol Chem 2019;38:1029-1034. Published 2019 Wiley Periodicals, Inc. on behalf of SETAC. This article is a US government work and, as such, is in the public domain in the United States of America.

Keywords: Bioavailability; Copper; Diffusive gradient in thin films; Dissolved organic carbon

INTRODUCTION

Researchers are currently working toward the development of passive samplers (which would reflect toxicologically relevant biological exposures) to assess trace toxicants in seawater. The central requisites of these innovative techniques are reflection of toxicant speciation and relevant exposure windows to variable effluent toxicity. Copper (Cu), a pervasive contaminant in the coastal marine environment (e.g., Nriagu 1979; Langston 1990; Chadwick et al. 2008; US Environmental Protection Agency 2016), is regarded as highly toxic to developing marine life, when micronutrient levels are exceeded, based on low median effect concentrations (EC50s) for many aquatic species (i.e., the EC50 values for *Hydnum rufescens, Mytilus edulis, Mytilus galloprovincialis, Tigriopus californicus, and Strongylocentrotus purpuratus* are 3.944 to 7.971 µg/L dissolved Cu [Cu_{DISS}]; Flemming and Trevors 1989; United Nations Environment Programme 2005; US Environmental Protection Agency 2016). Currently, states have set the marine water acute and chronic aquatic life criteria for dissolved Cu at levels that fail to account for organic ligand complexation (as discussed in US Environmental Protection Agency 2016), which can significantly reduce bioavailability (e.g., Arnold et al. 2005; Nadella et al. 2009; Bosse et al. 2014). In addition, recent studies have suggested that a time-integrated measure of metal exposure more accurately describes resulting toxicity effects in environmentally realistic pulsed exposure regimes (Angel et al. 2015). Diffusive gradient in thin films (DGT), which operationally measures trace metal concentrations integrated over time via chelation of labile metals (i.e., free and weakly complexed ions; Davison 2016) may therefore more accurately represent the potential for biological effects resulting from Cu exposure, which is the goal of regulatory programs.

Although the efficacy of DGT for in situ passive sampling of metals in natural systems has been demonstrated (e.g., Dunn et al. 2003; Warnken et al. 2004; Amato et al. 2018), an increased understanding of the relationship between the concentration in solution as measured by DGT (C_{DGT}) and toxicity/bioaccumulation measurements is necessary for implementation of DGTs in surface water monitoring programs. The appropriate choice for application to seawater monitoring is the relation of C_{DGT} to embryo–larval development tests using the Mediterranean mussel, *M. galloprovincialis*, which is among the most sensitive saltwater bioassay endpoints used for aquatic life criteria development (US Environmental Protection Agency 1995b, 2016; Arnold et al. 2005; Rosen et al. 2005). The present study aimed to generate the initial data to explore C_{DGT} Cu toxicological dose formation for *M. galloprovincialis* in coastal seawater under a range of dissolved organic carbon (DOC) concentrations.

* Address correspondence to Jonathan.Strivens@pnnl.gov
Published online 6 March 2019 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/etc.4404

MATERIALS AND METHODS

Preparation of test solutions

Seawater was collected, following the "clean hands–dirty hands" protocol (US Environmental Protection Agency 1996a), into acid-cleaned 2-L low-density polyethylene bottles, using water pumped from Sequim Bay (WA, USA) at a depth of 10 m, and is referred to herein as Sequim Bay seawater (SBSW). Filtration was achieved by first passing seawater through an Arkal Spin Klin™ filter system (nominal pore size 40 µm) to remove large particles. The partially filtered seawater was then stored in a 15-kL reservoir tank, gravity fed through sequential 5- and 1-µm cellulose filters, and collected in an aerated 180-L fiberglass reservoir. Finally, seawater was pumped through a 0.45-µm polyethersulfone filter (Memtrex MP; GE Power and Water). At collection, samples were at 15.5 °C, 31.2 PSU, and pH 7.85. The individual 2-L samples of seawater were nominally spiked with Cu (as Cu(II)SO_4, trace metals basis; Aldrich) and DOC at ranges centered on expected *M. galloprovincialis* EC50 values and natural range (Table 1) based on a screening study and observations previously reported (e.g., Arnold et al. 2006, 2010; Rosen et al. 2008; Nadella et al. 2009), and allowed 24 h for binding kinetics to reach equilibrium in a dark, 4 °C environment.

Preparation of DOC

Suwannee River natural organic matter (SRNOM; 2R101N; International Humic Substances Society), which is largely allochthonous based on the carbon–nitrogen ratio (Green et al. 2015), was selected, to minimize variance that would arise from evaluation of seawater samples collected from multiple water bodies during proof of concept (i.e., variation in cotoxicities, ligand affinities, and lipophilic compounds), and to reflect in situ protection (De Schamphelaere et al. 2005). The SRNOM was used in quantities to encompass the natural DOC range of approximately 0.5 to 8.5 mg/L (Barrón and Duarte 2015). It is presumed in the present study that there are no specific DOC sources for defined L1–L3 ligand classes in coastal seawater, that the dissociation constant of Cu–DOC complexes to DGT depends on the in situ ratio (supported by the binding characteristics discussed in Pesavento et al. (1999) and Chadwick et al. (2008)), and that the Cu complexing ligands in seawater are an integrated pool of both allochthonously and autochthonously formed organics (Town and Filella 2000; DePalma et al. 2011; Mostofa et al. 2012; Tait et al. 2016).

A 1-g/L stock solution was prepared in 0.1 µm Supor® filtered SBSW by first allowing 48-h equilibration at 4 °C in a dark environment, and then filtering at 0.45 µm (polyvinylidene fluoride) to remove insoluble ash.

DGT 48-h C_{DGT} determination

The DGTs were purchased from DGT® Research (Lancaster, England); for measurement of cations in solution, the commercially available model is the loaded, solution deployment-type (Chelex 100, agarose crosslinked polyacrylamide [APA], polyethersulphone). Two DGTs were suspended in each 2-L test solution by monofilament and placed on an orbital table at 75 rpm in the same environmental chamber that housed subsampled *M. galloprovincialis* embryo test vials. Prior to suspension of DGTs, subsamples for trace metals and DOC analysis were collected from each test solution. After 48 h, DGTs were collected, and resins were immediately removed to eliminate continued diffusion from the APA. Confirmatory water samples were analyzed at commencement to nullify any concern of mass balance depletion. All work was performed in a class 100 clean room.

DGT and seawater analysis

The basis for converting the mass of metal accumulated by the resin to the concentration in solution as measured by DGT (C_{DGT}) is provided by the classical equation in Zhang and Davison (1995), and can be summarized as

$$C_{DGT} = \left[\frac{C_e(V_g + V_e)}{f_e}\right]\Delta g/D_G A t \quad (1)$$

where C_e is the concentration metal eluted from the resin, V_g is the volume of the resin, V_e is the volume of HNO_3, f_e is the elution efficiency, Δg is the thickness of the diffusional path, D_G is the temperature-dependent diffusion coefficient, A is the area of the polyethersulphone face exposed to seawater, and t is the deployment time.

TABLE 1: Verified spiking levels for study solutions

Type	DOC[a] (mg/L)	Dissolved Cu (µg/L)							
Nominal	0	0	3	6	8	12	17	25	36
Measured	0.896 ± 0.02	0.331	3.41	6.63	9.09	13.8	19.8	28.9	42.9
Nominal	2	0	8	12	17	24	35	49	
Measured	2.18 ± 0.01	0.401	9.05	13.6	19.3	28.0	40.6	57.7	
Nominal	4	0	13	19	27	38	54	77	
Measured	4.21 ± 0.02	0.625	15.1	22.4	31.8	45.1	63.5	89.9	
Nominal	6	0	13	19	27	38	54	77	
Measured	6.09 ± 0.06	0.850	15.8	22.6	32.7	45.7	64.4	90.8	
Nominal	8	0	17	24	35	50	71	101	
Measured	8.36 ± 0.07	1.09	20.2	29.4	42.7	61.3	85.8	119	

[a] *n* is equal to the number of dissolved copper (Cu) samples listed in the row. Data are expressed as mean ± standard deviation.

In the use of a single-diffusion coefficient, there is an assumption of nonternary binding (DOC–Chelex) and no impact on flux from natural ligand mixtures (Davison 2016); although ligands clearly cause multiple diffusion rates in a natural environment (Zhang and Davison 2000; Balch and Guéguen 2015a), for regulatory monitoring, conservative critical C_{DGT} theoretically can be set based on modeling of accumulated datasets with the knowledge that Cu-dissolved organic matter (DOM) is the major form of labile Cu, and the D_G of DOM is likely to remain within 1 order of magnitude of the free ion (Uribe et al. 2011; Balch and Guéguen 2015b). There also exists a likelihood that use of the standardized equation (i.e., neglecting size-dependent lability degree) can reflect biotic absorption by generating a value that allows a degree of mobility and binding layer penetration-induced diffusion window expansion to be included in the sum C_{DGT} (Shafaei Arvajeh et al. 2012; Galceran and Puy 2015). Although these functions may be reflective, equating procedural lability with bioavailability must be considered an estimation in natural environments, as is true for other techniques (e.g., electrochemical speciation).

For analysis, dissolved Cu in seawater was first prepared using a total recoverable metals digestion, and then preconcentration via a sea*FAST*® (Elemental Scientific) chelation step. Seawater samples and DGT elutions were analyzed by inductively coupled plasma–mass spectrometry in accordance with US Environmental Protection Agency methods 1638 (1996b) and US Environmental Protection Agency methods 1640 (US Environmental Protection Agency 1997). In the present study, Ni, Zn, Cd, and Pb levels in test solutions were monitored, as costressors, and remained low, at 0.509 ± 0.0730, 1.46 ± 0.527, 0.0742 ± 0.00137, and 0.0578 ± 0.0416 µg/L dissolved, respectively. Limits of detection (LODs) for coanalyzed analytes were 0.0015, 0.0093, 0.0008, and 0.001 µg/L, respectively, and the LOD for Cu was 0.002 µg/L.

The DOC samples were analyzed using a high-temperature catalytic oxidation method in accordance with standard method 5310B (American Public Health Association 2005). A Shimadzu© TOC-L instrument was equipped with a high-salt sample combustion tube kit and halogen scrubber for seawater analysis. The data are reported as nonpurgeable organic carbon values, with an LOD at 0.0490 mg/L.

M. galloprovincialis 48-h embryo test and EC50 evaluation

The EC50 values were determined by exposing *M. galloprovincialis* embryos to seawater aliquots from the individual 2-L DGT test preparations, and one laboratory control sample from San Diego Bay seawater (SDBSW; CA, USA; US Environmental Protection Agency 1995a). Exposures were conducted in 20-mL glass scintillation vials, replicated 5 times, with each vial containing a 10-mL aliquot. All samples, including those for toxicity and DGT, were equilibrated to 15 °C prior to initiation.

Adult gravid *M. galloprovincialis* were collected from the mouth (north jetty) of Mission Bay (San Diego) and induced to spawn by thermal shock. Within 4 h of fertilization, 180 ± 23 larvae were transferred to each scintillation vial.

Vials were incubated at 15.6 ± 0.2 °C for 48 h under a 16:8-h light: dark photoperiod. All water quality data met acceptability criteria following US Environmental Protection Agency guidelines (1995a); the pH was 8.00 ± 0.10, the salinity 29.5 ± 0.1 PSU, and percentage of dissolved oxygen saturation 100 ± 10. At 48 h, the tests were terminated by adding 0.5 mL 10% (v/v) buffered formalin acetate to each vial. Evaluation of the number of surviving larvae that developed normally (D-shaped, prodissoconch I stage) relative to the number of total embryos initially added to each vial was assessed (% normal alive endpoint), and the proportion of normally developed larvae relative to the number of larvae counted (% normal development) was also calculated. Because these endpoints were essentially identical, the data we report are for % normal development.

Statistical analysis

The percentage of normally developed larvae from the multiconcentration tests were used to calculate EC50s using measured Cu_{DISS} or C_{DGT} Cu with the toxicity statistics program CETIS™ (Tidepool Scientific). Toxicity tests were also evaluated for quality control by verifying that test conditions were adhered to, based on test acceptability criteria including at least 50% survival and 90% normal development of surviving larvae in the SBSW controls (US Environmental Protection Agency 1995a).

To assess the predictive power that DOC and/or Cu_{DISS} had on uptake by DGT, a 2-factor multiple regression was run with DOC concentration and Cu_{DISS} as independent variables and C_{DGT} Cu as the dependent variable. In addition, regression analysis was used to model Cu EC50s on the basis of DOC concentration. The Cu_{DISS} model was then assessed against previous literature in relation to relative percentage difference (RPD) at minimum and maximum intercepts.

RESULTS AND DISCUSSION

Median effective concentration test quality

All *M. galloprovincialis* tests met acceptability criteria, with > 82% survival and > 97% normal development in both the SBSW and SDBSW negative controls (US Environmental Protection Agency 1995a), and in SBSW DOC confined controls. The EC50 confidence intervals were 95% for all tests, and all treatments were significantly different ($\alpha = 0.05$). No DOC-related mortalities or developmental anomalies were observed, and the source did not impact replication of previous studies that had used unmodified NOM (e.g., Arnold et al. 2010).

Toxic effects as Cu_{DISS} and DOC

The dissolved Cu EC50 values (Figure 1 and Table 2) calculated in the present study are in best agreement with the data of Arnold et al. (2010), with the RPD across the DOC range in the present study being < 12.5. When we compared our results with those of Chadwick et al. (2008), the RPD between EC50 values was found to be positively skewed in low-DOC

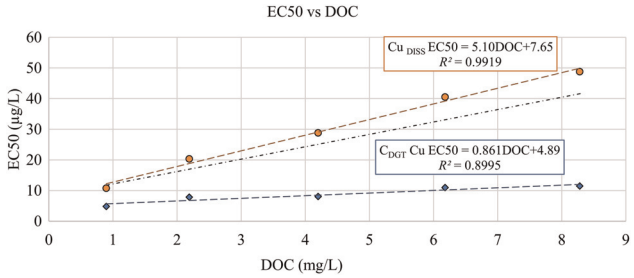

FIGURE 1: Median effect concentration (EC50) of *Mytilus galloprovincialis* over a range of dissolved organic carbon concentrations as Cu_{DISS} (circles, $F_{(1,3)} = 279$, $p < 0.001$) and C_{DGT} Cu (concentration of Cu in diffusive gradient in thin films; diamonds, $F_{(1,3)} = 29$, $p = 0.015$) proportion normal endpoints. The dashed-dotted line represents the Arnold et al. (2010) Cu_{DISS} EC50 model.

environments; the RPD between studies was 56% at the 0.896-mg/L DOC intercept. However, the models were in agreement at the 8.36-mg/L intercept (RPD = 4). Comparison with the results of Nadella et al. (2009), who also used SRNOM modified seawater, showed a significant shift in Cu_{DISS} EC50 (RPD = 36 ± 2, uniformly, across the range of DOC values), highlighting the need for further understanding of biological variation and consideration of sample co-toxicities. Both Arnold et al. (2010) and Chadwick et al. (2008) attained DOC ranges via natural seawater collections, which strengthens the argument that seawater ligand classes are an integration of allochthonous and autochthonous sources based on agreement between the present study and Arnold et al. (2010). However, these studies also highlight the range in EC50 literature values likely due to shifts in binding site class density not captured by measures of bulk DOC. Determination of site-specific ligand class fractions is a factor that DGT may, in future studies, show the ability to negate as a necessary component of bioavailability assessment by directly mimicking the resulting binding potentials and capturing spatial and temporal shifts induced by perturbations such as discharge, tidal flux, and biological processes. Although natural variation will exist in biological endpoints, the Cu_{DISS} EC50s in the present study replicated expected quantities and emphasized the importance of considering costressors and ligand class balance when deriving net survival values for calculation of water quality objectives as Cu_{DISS}. In terms of the agreement of the present study results with previous literature data, the C_{DGT} EC50 values from these solutions, which reflect bioavailability, are relevant to natural seawater measures.

To assess the correlation of the present study against marine water quality criteria, the current consensus for deriving criteria values from *Mytilus* spp. was used (US Environmental Protection Agency 1995b). To protect commercial interests, this guideline ultimately sets the final acute value (FAV) for seawater to be equal to the lowest genus mean acute value (GMAV), which is equal to the species mean acute value (SMAV) of *M. edulis*, 9.625 µg/L, making the criterion maximum concentration (CMC) 4.8 µg/L. Using the conservative data-point in the present study (0.896 mg/L DOC) in this manner shifts the CMC to 4.9 µg/L Cu_{DISS}, which is in agreement with the current water quality standards. More recent draft recommendations by the US Environmental Protection Agency (2016) use a marine biotic ligand model normalized (DOC = 1 mg/L, temperature = 22 °C) SMAV value of 7.338 µg/L for *M. galloprovincialis* based on an expanded dataset, and a GMAV of 5.577 µg/L due to a significant reduction of the *M. edulis* SMAV from the previous US Environmental Protection Agency (1995b) level. This updated recommendation is based on, and thus in agreement with, the model of Chadwick et al. (2008). Temporal shifting of SMAV values, while reflecting an expanded pool of data, are also possibly influenced by undefined, and uncontrolled, costressors and ligand class densities between studies.

TABLE 2: Dissolved copper (Cu_{DISS}) and Cu concentration by diffusive gradient in thin films (C_{DGT}) Cu CETIS™ statistics, as proportion of normal median effective concentration, ordered by dissolved organic carbon concentration (DOC)

Treatment: Nominal DOC	DOC (mg/L)[a]	Cu_{DISS} (µg/L)[b]	C_{DGT} Cu (µg/L)[b]
SBSW: 0	0.896 ± 0.02	10.8 ± 0.09	4.81 ± 0.03
SBSW: 2	2.18 ± 0.01	20.3 ± 0.27	7.84 ± 0.16
SBSW: 4	4.21 ± 0.02	28.8 ± 0.32	8.06 ± 0.10
SBSW: 6	6.09 ± 0.06	40.5 ± 0.63	11.0 ± 0.21
SBSW: 8	8.36 ± 0.07	48.8 ± 0.57	11.5 ± 0.15
SDBSW: LCS	1.20	10.9 ± 0.17	

[a]Values are expressed as mean ± standard deviation.
[b]Values are expressed as slope ± 95% margin of error.
SBSW = Sequim Bay seawater; SDBSW = San Diego Bay seawater; LCS = laboratory control sample.

Toxic effects as C_{DGT} Cu

The C_{DGT} values obtained from the Cu_{DISS} solutions ranged from 0.0347 to 36.5 µg/L. Multiple regression analysis was used to test whether the spike levels significantly predicted lability degree to the DGTs; C_{DGT} Cu was normally distributed, and error was homoscedastic. The results of the multiple regression indicated that the 2 analytes explained 90.6% of the variance ($F_{(2,32)} = 153$, $p < 0.001$). Individually, both Cu_{DISS} ($t_{33} = 17.4$, $p < 0.001$) and DOC concentration ($t_{33} = -5.43$, $p < 0.001$), were found to significantly predict DGT uptake. These relationships support the null hypothesis; as Cu_{DISS} concentration increased, an increase in Cu accumulation by DGT was observed, and as DOC increased, a decrease in Cu uptake by DGT was observed. The model equation is C_{DGT} Cu = $-1.24[DOC] + 0.369[Cu_{DISS}] + 4.58$.

The C_{DGT} Cu method has demonstrated an ability to reduce the toxicity measurement range in 0.896 to 8.28 mg/L DOC seawater by 83% with data input consisting solely of temperature and deployment time (Figure 1). The proportion normal endpoints, over that DOC range, span from 4.8 to 11.5 µg/L C_{DGT} Cu, indicating that the difference in diffusional residence time between *M. galloprovincialis* and DGT likely allowed for unequal dissociation of weakly bound Cu–DOM complexes. Although this variance exists, it is possible to normalize the EC50 to 4.8 µg/L C_{DGT} Cu for regulatory monitoring when DOC is not analyzed; the natural range of DOC in coastal

environments is not expected to fall significantly (EC50 factor of 2 increase) outside this endpoint with the exception of lagoons/marshes and dense algal blooms (Chadwick et al. 2008; Hobbs et al. 2018). For deriving site-specific criteria, the model is given in Figure 1. The results indicate that, to a degree, biomimicry is obtainable with this passive sampling method; however, temperature correction may prove necessary for physiology-based divergences in growth rates based on future findings.

A preliminary determination of a CMC C_{DGT} Cu of 2.4 μg/L may allow for inprogress field studies to place DGT results in the context of water quality criteria. This pilot criteria concentration allows for conservative toxicological dose (based on most sensitive life stage of a single EC50 test) to be quantified by setting the C_{DGT} EC50 at 0.896 mg/L DOC, equal to the FAV (Stephan et al. 1985). It should be clear, however, that the C_{DGT}-derived EC50 is not necessarily equivalent to the traditional operationally defined dissolved Cu concentration currently used for development of water quality standards.

Additional C_{DGT} Cu EC50s, determined using seawater samples covering the tested DOC range, as well as determination of an *M. edulis* SMAV are recommended for model validation and verification that an adequate protection level is provided by the C_{DGT} CMC, respectively. The highest priority next step, in a pragmatic regulatory aspect, is validation of the model through laboratory screening of seawater samples sourced to be representative of the DOC range in the current model, with the addition of fluorescence quenching or analogous comeasurements to characterize binding strength and ligand density advised for DGT performance confirmation (Tait et al. 2018).

CONCLUSIONS

The bioavailability of Cu_{DISS} reported in the present study is in agreement with previous studies that focused on the protective effects of Cu-DOC on *Mytilus* spp., lending credibility to the comeasured C_{DGT} values. The DGT passive samplers successfully mimicked the highly protective effects afforded to *M. galloprovincialis* by Cu-DOC kinetics within a margin of error that is acceptable for conservative water quality objective monitoring that does not include DOC analysis; C_{DGT} Cu EC50 is currently recommended to be conservatively viewed as 4.8 μg/L when DOC concentrations are unknown. The data we summarize also provide preliminary EC50s over the span of expected marine coastal DOC concentrations. Future research should incorporate naturally sourced seawater, naturally ranging in DOC concentration, to gauge the fitness of these preliminary toxicological thresholds. Eventual implementation of this monitoring method by regulatory compliance programs will potentially allow for datasets that better represent biological effects at relevant scales.

Acknowledgment——Funding was provided by the Puget Sound Naval Shipyard (Bremerton, WA, USA) and Navy Environmental Sustainability Development to Integration (NESDI) Project 523. We would also like to thank M. Colvin, I. Rivera-Duarte, and K. Kowal for help with the technical work.

Data Accessibility—Data, associated metadata, and calculation tools are available from the corresponding author (Jonathan.Strivens@pnnl.gov).

REFERENCES

American Public Health Association, American Water Works Association, Water Environment Federation. 2005. Method SM 5310B: High temperature combustion method. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC, USA.

Angel BM, Simpson SL, Chariton AA, Stauber JL, Jolley DF. 2015. Time-averaged copper concentrations from continuous exposures predict pulsed exposure toxicity to the marine diatom, *Phaeodactylum tricornutum*: Importance of uptake and elimination. *Aquat Toxicol* 164:1–9.

Arnold WR, Santore RC, Cotsifas JS. 2005. Predicting copper toxicity in estuarine and marine waters using the biotic ligand model. *Mar Pollut Bull* 50:1634–1640.

Arnold WR, Cotsifas JS, Corneillie KM. 2006. Validation and update of a model used to predict copper toxicity to the marine bivalve *Mytilus* sp. *Environ Toxicol* 21:65–70.

Arnold W, Cotsifas JS, Ogle RS, DePalma SG, Smith DS. 2010. A comparison of the copper sensitivity of six invertebrate species in ambient salt water of varying dissolved organic matter concentrations. *Environ Toxicol Chem* 29:311–319.

Amato ED, Wadige CPM, Taylor AM, Maher WA, Simpson SL, Jolley DF. 2018. Field and laboratory evaluation of DGT for predicting metal bioaccumulation and toxicity in the freshwater bivalve *Hyridella australis* exposed to contaminated sediments. *Environ Pollut* 243:862–871.

Balch J, Guéguen C. 2015a. Determination of diffusion coefficients of dissolved organic matter in the Churchill River estuary system, Hudson Bay (Canada). *Environ Chem* 12:253–260.

Balch J, Guéguen C. 2015b. Effects of molecular weight on the diffusion coefficient of aquatic dissolved organic matter and humic substances. *Chemosphere* 119:498–503.

Barrón C, Duarte CM. 2015. Dissolved organic carbon pools and export from the coastal ocean. *Global Biogeochem Cycle* 29:1725–1738.

Bosse C, Rosen G, Colvin M, Earley P, Santore R, Rivera-Duarte I. 2014. Copper bioavailability and toxicity to *Mytilus galloprovincialis* in Shelter Island Yacht Basin, San Diego, CA. *Mar Pollut Bull* 85:225–234.

Chadwick DB, Rivera-Duarte I, Rosen G, Wang P, Santore RC, Ryan AC, Choi W. 2008. *Demonstration of an integrated compliance model for predicting copper fate and effects in DoD Harbors (No. SPAWAR/CP-TR-1973)*. Space and Naval Warfare Systems Center Pacific San Diego, CA, USA.

Davison W, ed., 2016. *Diffusive gradients in thin-films for environmental measurements*. Cambridge University, Cambridge, UK.

De Schamphelaere KAC, Unamuno VIR, Tack FMG, Vanderdeelen J, Janssen CR. 2005. Reverse osmosis sampling does not affect the protective effect of dissolved organic matter on copper and zinc toxicity to freshwater organisms. *Chemosphere* 58:653–658.

DePalma SG, Arnold WR, McGeer JC, Dixon DG, Smith DS. 2011. Effects of dissolved organic matter and reduced sulphur on copper bioavailability in coastal marine environments. *Ecotoxicol Environ Saf* 74:230–237.

Dunn RJK, Teasdale PR, Warnken J, Schleich RR. 2003. Evaluation of the diffusive gradient in thin films technique for monitoring trace metal concentrations in estuarine waters. *Environ Sci Technol* 37:2794–2800.

Flemming CA, Trevors JT. 1989. Copper toxicity and chemistry in the environment: A review. *Water Air Soil Pollut* 44:143–158.

Galceran J, Puy J. 2015. Interpretation of diffusion gradients in thin films (DGT) measurements: A systematic approach. *Environ Chem* 12:112–122.

Green NW, McInnis D, Hertkorn N, Maurice PA, Perdue EM. 2015. Suwannee River natural organic matter: Isolation of the 2R101N reference sample by reverse osmosis. *Environ Eng Sci* 32:38–44.

Hobbs W, McCall M, Lanksbury J. 2018. Copper, zinc, and lead concentrations at five Puget Sound marinas. Report, July 2009. Washington State Department of Ecology, Olympia, WA, USA. [cited 2018 July 22]. Available from: https://fortress.wa.gov/ecy/publications/SummaryPages/1803001.html

Langston WJ. 1990. Toxic effects of metals and the incidence of metal pollution in marine ecosystems. In Furness RW, Rainbow PS, eds, *Heavy Metals in the Marine Environment*. CRC, New York, New York, USA.

Mostofa KM, Yoshioka T, Mottaleb A, Vione D. 2012. *Photobiogeochemistry of organic matter: Principles and practices in water environments*. Springer Science & Business Media, New York, NY, USA.

Nadella SR, Fitzpatrick JL, Franklin N, Buckling C, Smith S, Wood CM. 2009. Toxicity of dissolved Cu, Zn, Ni, and Cd to developing embryos of the blue mussel (*Mytilus trossolus*) and the protective effect of dissolved organic carbon. *Comp Biochem Physiol C Pharmacol, Toxicol Endocrinol* 149:340–348.

Nriagu JO. 1979. *Copper in the environment: Part I: Ecological cycling*. Wiley-Interscience, Hoboken, NJ, USA.

Pesavento M, Biesuz R, Baffi F, Gnecco C. 1999. Determination of metal ions concentration and speciation in seawater by titration with an iminodiacetic resin. *Anal Chim Acta* 401:265–276.

Rosen G, Rivera-Duarte I, Kear-Padilla L, Chadwick DB. 2005. Use of laboratory toxicity tests with bivalve and echinoderm embryos to evaluate the bioavailability of copper in San Diego Bay, California, USA. *Environ Toxicol Chem* 24:415–422.

Rosen G, Rivera-Durate I, Chadwick B, Ryan A, Santore RC, Paquin PR. 2008. Critical tissue copper residues for marine bivalve (*Mytilus galloprovincialis*) and echinoderm (*Strongylocentrotus purpuratus*) embryonic development: Conceptual, regulatory and environmental implications. *Mar Environ Res* 66:327–336.

Shafaei Arvajeh MR, Lehto N, Garmo ØA, Zhang H. 2012. Kinetic studies of Ni organic complexes using diffusive gradients in thin films (DGT) with double binding layers and a dynamic numerical model. *Environ Sci Technol* 47:463–470.

Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA. 1985. *Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses* US. Environmental Protection Agency, Washington, DC. p.98.

Tait TN, Cooper CA, McGeer JC, Wood CM, Smith DS. 2016. Influence of dissolved organic matter (DOM) source on copper speciation and toxicity in *Brachionus plicatilis*. *Environ Chem* 13:496–506.

Tait TN, McGeer JC, Smith DS. 2018. Testing the underlying chemical principles of the biotic ligand model (BLM) to marine copper systems: Measuring copper speciation using fluorescence quenching. *Bull Environ Contam Toxicol* 100:76–81.

Town RM, Filella M. 2000. Dispelling the myths: Is the existence of L1 and L2 ligands necessary to explain metal ion speciation in natural waters? *Limnol Oceanogr* 45:1341–1357.

United Nations Environment Programme. 2005. Fact sheets on marine pollution indicators. UNEP (DEC)/MED/WG.264/Inf.14. Nairobi, Kenya.

Uribe R, Mongin S, Puy J, Cecília J, Galceran J, Zhang H, Davison W. 2011. Contribution of partially labile complexes to the DGT metal flux. *Environ Sci Technol* 45:5317–5322.

US Environmental Protection Agency. 1995a. *Short-term methods for estimating the chronic toxicity of effluents and receiving waters to West Coast Marine and Estuarine organisms. EPA/600/R- 95/136*. National Exposure Research Laboratory, Cincinnati, OH, USA.

US Environmental Protection Agency. 1995b. *Ambient water quality criteria —Saltwater copper addendum (draft), April 14*. Office of Water, Washington, DC.

US Environmental Protection Agency. 1996a. *Method 1669: Sampling ambient water for determination of metals at EPA water quality criteria levels*. Office of Water, Washington, DC.

US Environmental Protection Agency. 1996b. *Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma-mass spectrometry*. Office of Water, Washington, DC.

US Environmental Protection Agency. 1997. *Method 1640: Determination of trace elements in water by preconcentration and inductively coupled plasma-mass spectrometry*. Office of Water, Washington, DC.

US Environmental Protection Agency. 2016. *Draft aquatic life ambient estuarine/marine water quality criteria for copper. EPA 822-P-16-001*. Office of Water, Washington, DC.

Warnken J, Dunn RJ, Teasdale PR. 2004. Investigation of recreational boats as a source of copper at anchorage sites using time-integrated diffusive gradients in thin film and sediment measurements. *Mar Pollut Bull* 49:833–843.

Zhang H, Davison W. 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Anal Chem* 67:3391–3400.

Zhang H, Davison W. 2000. Direct in situ measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films. *Anal Chem* 72:4447–4457.

Diffusive gradient in thin-films: time integrated passive sampling for trace metals in receiving waters of Puget Sound

Jonathan Strivens[1], Robert Johnston[2], Gunther Rosen[2], Nicholas Hayman[2], Nicholas Schlafer[1], Jill Brandenberger[1]

1. PNNL; 2. SPAWAR Systems Center Pacific

Contact: Jonathan Strivens, Jonathan.Strivens@pnnl.gov, 360-681-3652 https://marine.pnnl.gov/

- **Cd, Cu and Ni C_{DGT} capture linearity from 1 to 14 days displayed $R^2 > 0.987$, indicating high resolution.**
- **The ability to conduct constant surveillance of labile metals greatly improves the assessment of potential ecological effects from exposure.**

The Puget Sound Naval Shipyard (PSNS) & Intermediate Maintenance Facility at Naval Base Kitsap conducts an ambient monitoring program that measures trace metals and toxicity in the receiving waters of Sinclair and Dyes Inlets, Puget Sound. The ambient monitoring program provides an approach to assessing water quality in receiving waters and tracks progress in achieving water quality goals. The program recently added a new type of sampling called diffusive gradient in thin-film (DGT) to provide a time-integrated measurement of the bioavailable fraction of selected trace metals. This passive sampling allows for integrated capture as opposed to 1) grab sampling, which captures a single point in time, or 2) an auto-sampler setup, which is cost prohibitive when monitoring across large areas. The utilization of DGTs allows for the measurement of trace metal concentrations via chelation of labile metals (free and weakly complexed species), which more effectively represents the concentration of bioavailable metals and, therefore, more accurately represents the potential for biological effects compared to traditional dissolved metal analysis.

Field campaigns to record labile (C_{DGT}) Cd, Cu, Ni, Pb, and Zn concentrations have layered deployments in a manner that allows for response linearity to be defined for deployment times ranging from 24 hours to 14 days in areas with low to moderate ambient concentrations, and also in a manner that allows for capture of stormwater related pulses.

Uptake linearity and reproducibility by DGT for the program's three priority analytes Cu, Pb, and Zn displayed a range of results. In situ monitoring of Cu showed acceptable field reproducibility at 24 hours integrated C_{DGT} (14±17% as RPD; *n*=16), and uptake linearity of R^2=0.988 (Figure 1) over 1-14 day test periods. C_{DGT} Cu includes only weakly complexed Cu-DOC; providing an in situ correction for bioavailability due to DOC toxicity buffering. Ambient levels in the monitoring area averaged 6ng L^{-1} C_{DGT} Pb. While trend capture has been demonstrated at these levels using 72 hour deployments, 24 hour quantification was variable due to proximity of background concentrations on the DGT material; due to the time-integrated nature of this device an inverse relationship exists between DGT background levels and deployment time. Zn quantification via C_{DGT} displayed moderate variability at ≤7 days deployment at the low levels investigated. This is likely due to DGT resin binding selectivity, Zn-DOC kinetics, and proximity to sources. Cd and Ni performance were comparable to that of Cu. Condensing these results, balance between metals of concern and level of quantification must be considered when selecting DGT exposure periods.

The storm event C_{DGT} pulse capture studies in receiving waters at PSNS demonstrated successful quantification of Cu, which is shown in Figure 2. This figure also demonstrates non-saturation of resin after 50 days of deployment.

Research is demonstrating the value of integrating DGT sampling into ambient and stormwater monitoring programs. However, additional research is needed to understand the quantification limits, reproducibility, and representativeness of these measurements prior to incorporating into regulatory programs. Overall, DGT is expected to be an unparalleled tool for quantification of labile trace metals.

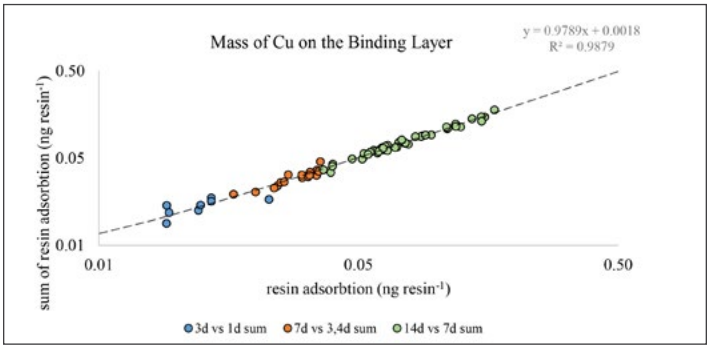

Figure 1. Analyte sensitivity when moving from 14 day to 1 day deployment time (*n* 1-day = 24; *n* 3 & 4-day = 32, *n* 14-day = 46, and *n* 7-day = 92). This comparison was made via overlaid deployments, where 3 and 4 day deployments were overlaid by a corresponding 7 day deployment; and consecutive 1 day deployments were overlaid by a 3 day deployment.

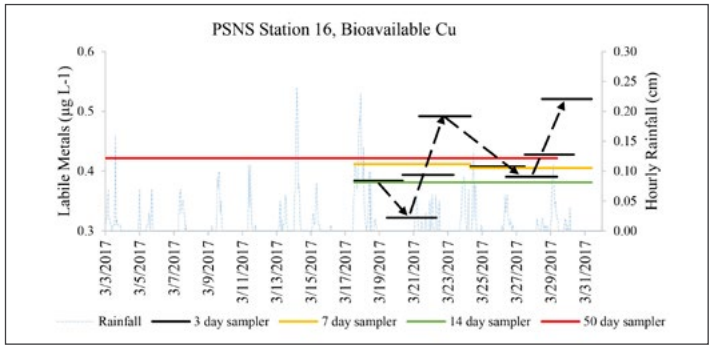

Figure 2. C_{DGT} Cu trend capture at PSNS field station PS16 during the spring of 2017; 72 hour deployments were staggered to capture stormwater related pulses (dashed black lines indicate pulse-induced shifts), in comparison to longer integrations.

LIMNOLOGY
and
OCEANOGRAPHY: METHODS

ASLO

Limnol. Oceanogr.: Methods 17, 2019, 266–276

doi: 10.1002/lom3.10311

Data trend shifts induced by method of concentration for trace metals in seawater: Automated online preconcentration vs. borohydride reductive coprecipitation of nearshore seawater samples for analysis of Ni, Cu, Zn, Cd, and Pb via ICP-MS

Jonathan E. Strivens,[1]* **Jill M. Brandenberger**,[2] **Robert K. Johnston**[3]

[1]Marine Sciences Laboratory, Pacific Northwest National Laboratory, Sequim, Washington
[2]Battelle Seattle Research Center, Pacific Northwest National Laboratory, Seattle, Washington
[3]Marine Environmental Support Office – NW Space and Naval Warfare Systems Center Pacific, Bremerton, Washington

Abstract

This research compares performance, reproducibility, and detection limits of ambient seawater analysis for trace metals using both borohydride reductive coprecipitation and an automated chelation column (seaFAST™ 2) preconcentration for matrix interferent elimination on total and dissolved grab samples in nearshore to marine waters, over a broad concentration range, prior to inductively coupled plasma mass spectrometry (ICP-MS) injection. A move to an online preconcentration method both minimizes sample preparation, and eliminates correction errors when accounting for trace impurities in precipitated samples, induced via reagents. The reproducability of the online preconcentration method described, coupled with low blanks and method detection limits (MDLs), demonstrates the effectiveness of the automated procedure using ethylenediaminetriacetic and iminodiacetate acid chelation exchange resin and multianalyte determination by ICP-MS for total and dissolved Ni, Cu, Zn, Cd, and Pb in marine water samples. Average CASS-5 recoveries using the online preconcentration method (n = 9) were 109% ± 7%, 104% ± 5%, 103% ± 7%, 101% ± 3%, and 86% ± 8%, respectively. The MDLs obtained from the automated method for Ni, Cu, Zn, Cd, and Pb were 3.3, 1.8, 13.5, 4, and 10 times lower, respectively, than for the Borohydride method. There were statistically significant differences between the methods for CASS-5 recoveries of Ni, Cu, Zn ($p < 0.0001$), and Pb ($p = 0.0024$). Comparison of methods gave high concordance ($r_C \geq 0.90$) between methods for total and dissolved Ni, Cu, Zn, and Pb, and total Cd.

The accuracy of marine trace metals determination-methodology chosen by research and compliance laboratories is both imperative and evolving. In marine biogeochemistry, trace metals in both dissolved and particulate form can serve as critical micronutrients, but also as potential toxicants to primary producers and marine organisms. The capacity to serve as a bio-limiting or toxic element often manifests over a fairly narrow free ion concentration range (Hudson and Morel 1993; Sunda and Huntsman 1998). While trace metal inputs to the coastal zone are driven largely by physical weathering of continents, anthropogenic inputs markedly disrupt free ion concentrations. To combat this, the U.S. Environmental Protection Agency (EPA) sets regulatory benchmarks for metals designated as priority pollutants (U.S. Environmental Protection Agency 2017); all metals discussed here have been designated priority under the Clean Water Act 40 CFR Part 423, Appendix A in seawater. EPA established environmental quality standards for metals, as well as those of the European Economic Commission, are based on dissolved concentrations (0.45 μm filtered) (European Economic Council 2008), while the Australian and New Zealand Environment and Conservation Council has established tiered environmental quality guidelines based on total and dissolved metal concentrations (Australian and New Zealand Environment and Conservation Council 2000). The narrow ranges of beneficial concentration make critical the ability to quantify trace metals of potential concern at very low concentrations in both transition areas and mixing zones, moving out from terrestrial run-off (e.g., harbor activities, storm water run-off, and sewage treatment plant outfalls).

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used for trace metal detection in aqueous samples. Precise quantification of trace metal levels in seawater by ICP-MS must overcome spectral interferences caused by Ar support gas impurities and salts in the seawater matrix (Na, Cl, Mg, and Ca) which can lead to isobaric polyatomic ion introduction (Hirata et al. 2001). Naturally occurring high dissolved solids (~ 3%) in

*Correspondence: jonathan.strivens@pnnl.gov

the seawater matrix are also problematic due to salt deposition on skimmer cones, resulting in flow restrictions that will impede both sensitivity and stability, leading to drift over an analytical run. Additionally, ionization suppression must be addressed due to high Na levels which pronounce the space-charge effect (Chapple and Byrne 1996; Rosland and Lund 1998). Some reduction of these interferences can be achieved by manipulation of instrument parameters, while others can be minimized by matrix-matched blank corrections or removal of the matrix via reductive precipitation. Dilution also attenuates these effects, but these methods all significantly decrease precision and sensitivity at ultra-trace levels. Consequently, analysts often seek the optimal method to separate the high salt background from the analytes of interest prior to analysis by ICP-MS.

A common analytical approach employed by the community for detection of Ni, Cu, Zn, Cd, and Pb in seawater samples is matrix separation coupled with analyte coprecipitation via borohydride reductive coprecipitation using a Fe and Pd mixture (Skogerboe et al. 1985; Nakashima et al. 1988; U.S. Environmental Protection Agency 1997*a*). This technique is an involved and lengthy process, which includes 15 h reaction time for precipitation as well as numerous manual steps, increasing the possibility of sample contamination. Additionally, the method requires reagent blank corrections to account for impurities introduced by precipitation reagents.

To decrease the contamination window and increase sample throughput, chelation exchange resins containing ethylenediaminetriacetic (EDTA) and iminodiacetate acids (IDA) have been developed to separate transition metals from matrices containing Na^+, Cl^-, Mg^{2+}, and Ca^{2+} (Hirata et al. 1989; Warnken et al. 1999, 2000; Beck et al. 2002; Milne et al. 2010). These chelating ion exchange resins have been incorporated into a commercially available online preconcentration introduction system, seaFAST™ (Elemental Scientific, Omaha, Nebraska). The utility of this system for analysis of several elements by ICP-MS of open ocean seawater has recently been reported (Lagerström et al. 2013). The current study evaluates the utility of using this method in coastal waters where the concentrations range quite significantly from sub $\mu g\ L^{-1}$ to 10 $\mu g\ L^{-1}$ levels.

This study compares borohydride reductive precipitation and seaFAST™ online preconcentration recoveries of certified seawater reference material (CASS-5) and filtered and unfiltered seawater samples from Sinclair (47.5486N, 122.6386W) and Dyes Inlets (47.6183N, 122.6896W) in Puget Sound, WA. The field samples were collected from naval dry-dock effluents, nearshore receiving waters, and marine reference areas as part of an ambient monitoring program conducted by the US Navy under an environmental quality improvement project (ENVVEST, Strivens et al. 2018). Field samples obtained from two collection campaigns conducted 07–08 April 2015 (spring) and 15–16 September 2015 (autumn) were analyzed using both methods. The major objective of the current study was to validate the seaFAST™ preconcentration method for use on nearshore marine water samples, and to characterize any effect on long-term data sets.

The method-bridging implications provided in the current study define and quantify risk level to inform the approach for method transfer. In long-term data sets, shifts in baseline due to method improvement have probability to alter stability predictions in modeling. The implications of this, when assessing narrow acceptable ranges of trace metals in the marine environment, must be understood in studies of ecosystem health and accounted for in regulatory efforts, such as application of discharge mixing zones. The objective of method validation (demonstration of suitability) gauges quality, while the measure equivalency provided by the current study allows quantification of baseline shift and therefore a means of data-bridging.

Materials and procedures

Instrumentation

A Thermo Scientific™ iCAP™ Q ICP-MS (Waltham, Massachusetts, U.S.A.) was used for all measurements. The sample introduction system consisted of a Peltier-cooled spray chamber (Elemental Scientific, Omaha, Nebraska, U.S.A.), a low-flow PFA Nebulizer, semi-demountable concentric quartz torch with a 2.0 mm interior diameter (ID) quartz injector (Elemental Scientific, Omaha, Nebraska, U.S.A.), and Pt sample and skimmer cones (Thermo Scientific, Waltham, Massachusetts, U.S.A.) equipped with replaceable tip inserts to eliminate memory effect. A high-precision syringe driven system (seaFAST™) was used for sample introduction. The ICP-MS was operated in standard mode (STD) for borohydride reductive samples as Cl^- had already been eliminated from the matrix. A single collision cell mode with kinetic energy discrimination (KED), using pure He as collision gas, was used for seaFAST™ preconcentration samples to dually allow for direct injection for analysis of nonchelating trace metals.

The seaFAST™ system, referenced hereafter as the "Online" method, uses EDTA and IDA immobilized on a hydrophilic methacrylate polymer (part number CFN-0200) to preconcentrate transition elements. Under pH 6 conditions, maintained by an ammonium acetate solution, Na^+, Cl^-, Mg^{2+}, and Ca^{2+} matrix ions pass through the columns, while the analytes of interest are chelated. After the preconcentration step, analytes are eluted using 1.5 M HNO_3 directly to the nebulizer. A (CF-M-0600) cleanup column was used to eliminate any trace analytes from both deionized water (DI) and buffer solutions.

Reagents

Concentrated Optima™ grade reagents (nitric, hydrochloric and acetic acids, and ammonium hydroxide) were purchased from Fisher (Pittsburgh, Pennsylvania, U.S.A.). High-purity DI water (> 18 MΩ cm) was produced by a system composed of reverse osmosis and deionizing resins. Primary standards used for working standard mixtures, and an internal standard

premixed solution, were purchased from High-Purity Standards (Charleston, South Carolina, U.S.A.). Sodium borohydride and ammonium pyrrolidinedithiocarbamate (APDC) were purchased from Sigma-Aldrich (St. Louis, Missouri, U.S.A.).

Certified reference materials

In each analytical batch, the certified seawater reference material (CRM) CASS-5 was used to verify accuracy in a similar matrix. CASS-5 was obtained from the National Research Council of Canada (NRC, Ottawa, Ontario, Canada) and is marketed for use during analysis of nearshore seawater for trace metals. This water was collected from Halifax Harbor at a depth of 12 m, with a salinity of 33.5 psu. The field samples in the current study had a salinity range of 22.6–29.2 psu. The CASS-5 CRM was certified for all trace metals of interest in this study (Table 1).

Vessel cleaning

For sampling, Teflon™ bottles were cleaned with 50% (v/v) HNO_3 (Baker Instra-Analyzed®) at 85°C for 48 h. The Teflon™ was then triple rinsed with high-purity water and filled with 0.1% Optima™ grade HCl for 7 d to remove all residual traces of HNO_3. Prior to use, bottles were thoroughly rinsed with high-purity water and dried in a class-100 laminar flow clean-air hood.

For borohydride reductive coprecipitation, 50 mL polypropylene graduated centrifuge tubes with screw caps were cleaned using 80°C 10% (v/v) HNO_3 (Baker® Instra-Analyzed®) for 12 h followed by 80°C 1%/1% HCl/HNO_3 for an additional 12 h. This method was also applied to analytical tubes for the Online approach.

Sampling

Sampling followed ultra-clean collection procedures recommended for trace metals at EPA water quality criteria levels in EPA Method 1669 (U.S. Environmental Protection Agency 1996*a*). Surface grab (≤ 1 m depth) samples were collected directly into the sample bottle with a nonmetallic sampling pole from a small boat. Subsurface collections at depths of 3-5 m were obtained with a Teflon-coated Go-Flo water sampler (General Oceanics, Miami, Florida, U.S.A.) suspended by nylon rope. Samples for dissolved metals were held at < 4°C and filtered through a 0.45 μm polyvinylidene fluoride membrane within 8 h of collection in a class 100 clean room. All samples were preserved to 0.2% Optima™ grade HNO_3 and stored for a minimum of 48 h prior to aliquoting.

Table 1. Certified values of CASS-5 seawater CRM.

Element	Certified value ($\mu g\ L^{-1}$)	Method of determination
Ni	0.33 ± 0.023	*,†,‡
Cu	0.38 ± 0.028	*,†,‡
Zn	0.719 ± 0.068	*,†,§,‖
Cd	0.0215 ± 0.0018	*,†,‡,‖
Pb	0.011 ± 0.002	†,‖

*Immobilized ligand separation, determination by graphite furnace atomic adsorption.
†Immobilized ligand separation, determination by isotope dilution ICP-MS.
‡Reductive precipitation separation, determination by graphite furnace atomic absorption spectroscopy.
§Immobilized ligand separation, determination by ICP-MS.
‖Immobilized ligand separation, determination by inductively coupled plasma time-of-flight mass spectrometer.

Borohydride coprecipitation method

A modified version of EPA method 1640 (U.S. Environmental Protection Agency 1997*a*; Strivens et al. 2018) was performed within laminar air-flow benches, providing a class 100 working environment. Forty milliliters of sample were added to acid-cleaned centrifuge tubes. Addition of 0.3–0.5 mL of a Fe-Pd mixture (1:1 volume from 1000 $\mu g\ mL^{-1}$ stock) was followed by pH adjustment using ammonium hydroxide to 8.5, then, 0.5 mL of 5% (w/v) sodium borohydride solution was added. Prior to reductive precipitation, 0.25 mL of a 2% (w/v) APDC solution was added to the samples. Samples were allowed to settle overnight, then centrifuged at 3500 rpm for 30 min and decanted. Next samples were centrifuged for an additional 15 min and all remaining supernatant pipetted off. The addition of 0.1 mL of concentrated Optima™ grade HNO_3 to each Fe-Pd pellet was performed prior to placement in an oven at 80 ± 2°C for 20 min. Samples were then diluted to 5 mL volume with DI water for analysis. This procedure produced a sample preconcentration of eightfold. The calibration curve for this method included the Fe and Pd in the matrix to correct associated trace metal impurities. A set of method blanks was prepared and analyzed with each batch of samples to provide a characterization of the impurities in APDC, ammonium hydroxide, and sodium borohydride. Method blanks also provided a measure of any additional Al and Ni leaching from the polypropylene during the high temperature Fe-Pd reactions. The average blank value was subtracted from each sample value before reporting the data. Blank subtraction was also applied to laboratory control standards (LCS), CRMs, replicates, and spikes. In data analyzed prior to July 2015, this method was performed without addition of Fe-Pd to the curve and correction subtracted post analysis.

ESI seaFAST™ 2 online preconcentration method

The seaFAST™ 2, sample preconcentration system which fed into the ICP-MS, consisted of a 2 mL sample loop, a prepacked EDTA/IDA preconcentration column on an SC-DX Fast and a Fast DX 3 valve system (Elemental Scientific, Omaha, Nebraska). Ten milliliters of undiluted seawater samples were loaded onto the SC-DX Fast auto-sampler. Prior to this step, metals samples were acidified to 1% HNO_3 and digested for 2 h at 85°C. The polytetrafluoroethylene loop of the seaFast™ 2 system was filled with 2 mL of sample and buffered via 2 M ammonium acetate, which then passed through the EDTA/IDA

Table 2. Fast operating parameters.

Step	Fast valves (action: method timer)	Syringe action (flow rate: volume)	Summary
(1a) Precheck	V1: Load V2: Load V3: Load		Fast valves are activated
(1b) Start preconcentration		S1: 2500 μL min^{-1}: 8000 μL S2: 730 μL min^{-1}: 2333 μL S4: 200 μL min^{-1}: continuous	(S1) DI water and (S2) buffer rinse preconcentration column; (S4) eluent is directed to the nebulizer
(1c) Load 2 mL sample loop for 2 s	V2: Inject: 10 s		After loop loading, the sample is directed through preconcentration column at same time as (S2) buffer
(2) DI wash	V2: Load: 170 s	S3: 200 μL min^{-1}: continuous	Salt matrix is rinsed from preconcentration column using (S1) DI water
(3) Elution	V1: Inject: 190 s	S3: 200 μL min^{-1}: continuous S4: 750 μL min^{-1}: continuous	Preconcentrated metals are back-eluted to the nebulizer by the (S3/S4) diluent/carrier eluent
(4a) Loop rinse	V2: Load		Probe moves to rinse Sta. 1 and 2 for 3 s each.
(4b) Column cleanup	V1: Inject: 320 s	S3: 3000 μL min^{-1}: continuous S4: 1500 μL min^{-1}: continuous	(S3) eluent is back-eluted through the preconcentration column; (S4) eluent is back eluted through the trace metals cleanup column
(4c) Condition columns	V1: Load	S1: 2500 μL min^{-1}: 2000 μL S2: 833 μL min^{-1}: 667 μL	DI water (S1) and buffer (S2) pass through the preconcentration column to condition for next sample
(4d) Fill syringes		S1: 20,000 μL min^{-1}: continuous S2: 10,000 μL min^{-1}: continuous S3: 10,000 μL min^{-1}: continuous S4: 10,000 μL min^{-1}: continuous	Syringes are refilled
(4e) Predispense		S1: 3000 μL min^{-1}: 600 μL S2: 1000 μL min^{-1}: 150 μL S3: 1000 μL min^{-1}: 150 μL S4: 1000 μL min^{-1}: 150 μL	Lines are primed
	Total method timer time: 480 s		

column. The pH was held constant by continuous rinsing with 2 M ammonium acetate solution. The interstitial volume of the line was rinsed with DI water to remove the residual components of the sample matrix. Meanwhile, the sample on the column was flushed to remove Na^+, Cl^-, Mg^{2+}, and Ca^{2+} matrix ions. The elution was achieved with 1.5 M HNO_3 which backflushed the analytes of interest to the PFA-ST nebulizer. The base method for this process is provided in U.S. Environmental Protection Agency (1997*b*); operating parameters for the current study are given in Table 2. The calibration curve for this method, using High-Purity Standards diluted with 1% HNO_3, was generated using the preconcentration method, thereby incorporating any signal from the reagents.

ICP-MS method

The ICP-MS procedure (Strivens et al. 2018) was based on EPA Method 1638 (U.S. Environmental Protection Agency 1996*b*). Internal standards (^{45}Sc, ^{73}Ge, ^{89}Y, ^{115}In, and ^{185}Re) were used to account for variations in sensitivity over the sample run for analysis of borohydride coprecipitated samples; for the Online method, peak acquisition drift was monitored by quality control (QC) samples as internal standards do not preconcentrate. QC samples for both methods included: a 1% HNO_3 acidified DI blank, a LCS, two matrix spikes (1 μg L^{-1} or 2 μg L^{-1} and 5 μg L^{-1}), two matrix spike duplicates, a sample duplicate (DUP), and a CASS-5 CRM. The LCS was a sample of 0.45 μm filtered Sequim Bay (48.077759 N, 123.045005 W) seawater spiked with 2 μg L^{-1} of each analyte, carried through the entire preparation scheme of each preconcentration method, with the purpose of determining whether the method was within accepted control limits. One suite of the aforementioned QC samples was run for every 20 environmental samples. Operating conditions of the iCAP Q are detailed in Table 3. Isotopes monitored were ^{27}Al, ^{60}Ni, ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{68}Zn, ^{112}Cd, ^{114}Cd, ^{206}Pb, and ^{208}Pb. The calibration curves for initial analyses by the Borohydride method

extended to 50 μg L^{-1}; the extent of the consequent Online analyses were adjusted to cover the determined ranges with a minimum extent up to 5 μg L^{-1}.

Table 3. ICP-MS instrument operating conditions.

Parameter	Value
RF power	1550 W
Coolant airflow	14 L min^{-1}
Auxiliary airflow	0.8 L min^{-1}
Carrier airflow	1.05 L min^{-1}
Nebulizer	0.3 mL min^{-1}
Spray chamber	Buffered cyclonic
Detector mode	Pulse and analog
Dwell times	0.01–0.04 s
Sweeps	25
Sample depth	5 mm

Table 4. Method detection limits determined for this study using the iCapQ ICP-MS and Sequim Bay seawater. Units are expressed as μg L^{-1}.

Method	Ni	Cu	Zn	Cd	Pb
Borohydride STD mode	0.050	0.014	0.175	0.004	0.0040
Online preconcentration, KED mode	0.015	0.008	0.013	0.001	0.0004

Statistical data evaluation

Data were imported into R-Studio (v98.1091, r-studio.com, Boston, Massachusetts) running R (v3.01.1, R Foundation for Statistical Computing, www.r-project.org) for statistical analysis. A two-way ANOVA was conducted to evaluate the null hypothesis that there were no differences between methods and events for the analysis of CRMs for the metals of interest:

$$F = \mathrm{aov}(Y \sim \mathrm{Method}^{*}\mathrm{Event}, \mathrm{data} = \mathrm{CRMdata}) \quad (1)$$

where Y = variable of interest; Method = Borohydride or Online; Event = Spring or Autumn campaign; and CRMdata = data set of CRM results with n = 5 or 4 CRM measurements for each method and event. The null hypothesis was rejected if $p \le 0.05$. Box and whisker plots for each metal were constructed to visualize statistical comparisons, compare to certified values, and evaluate the magnitude of the differences between the methods.

Results from the field sampling campaigns were compared by plotting the difference between methods ($D = Y_B - Y_O$) vs. the mean ($\mu = [Y_B + Y_O]/2$) of the methods (Altman and Bland 1983; Bland and Altman 1986) to evaluate any constant or proportional bias. The agreement between methods was then determined by calculating the correlation coefficient (r), concordance coefficient (r_C) (Magari 2002; Watson and Petrie 2010), and Gold-standard correlation (r_G) (St. Laurent 1998; Magari 2002) as:

$$r = \mathrm{CORREL}(Y_{Bi} : Y_{Bn}, Y_{Oi} : Y_{On}) \quad (2)$$

Table 5. Quality control comparison from sampling events spring and autumn, using both borohydride reductive coprecipitation and Online preconcentration methods.

			Spike		Average recoveries*				
	QC parameter	Method	(μg L^{-1})	n	Ni	Cu	Zn	Cd	Pb
Spring campaign	Low spike	Borohydride	1	10	82.7 ± 6.3	83.5 ± 6.3	86.2 ± 11.0	94.1 ± 3.0	89.5 ± 1.8
		Online	2	4	101.9 ± 12.3	102.5 ± 9.1	105.6 ± 8.6	100.4 ± 4.6	100.1 ± 2.4
	High spike	Borohydride	5	6	79.9 ± 3.2	80.4 ± 3.9	71.8 ± 4.4	91.9 ± 4.0	88.6 ± 2.7
		Online	5	—	—	—	—	—	—
	SB LCS†	Borohydride	2	5	81.7 ± 4.7	82.5 ± 4.3	83.3 ± 6.7	92.3 ± 1.9	87.6 ± 1.4
		Online	2	4	106.3 ± 7.2	106.4 ± 6.2	105.5 ± 7.3	102.9 ± 2.7	101.8 ± 3.0
	Replicate RPD	Borohydride	—	5	1.7 ± 1.8	1.8 ± 1.6	5.1 ± 2.7	3.0 ± 1.6	2.6 ± 1.5
		Online	—	5	1.4 ± 0.5	1.6 ± 0.7	1.5 ± 1.1	1.0 ± 0.9	1.4 ± 1.9
Autumn campaign	Low spike	Borohydride	1	10	80.9 ± 9.2	81.3 ± 8.4	74.7 ± 24.9	93.2 ± 2.1	92.2 ± 2.2
		Online	2	4	106.3 ± 1.9	105.5 ± 0.5	105.0 ± 0.7	102.3 ± 0.8	98.4 ± 1.8
	High spike	Borohydride	5	10	83.1 ± 8.6	82.4 ± 8.5	64.2 ± 27.8	91.8 ± 4.3	91.2 ± 4.2
		Online	5	4	101.9 ± 4.5	99.7 ± 2.0	102.5 ± 2.4	102.7 ± 1.6	100.0 ± 1.4
	SB LCS†	Borohydride	2	5	87.9 ± 3.2	85.9 ± 4.5	87.5 ± 4.1	94.2 ± 0.9	93.3 ± 2.0
		Online	2	5	110.5 ± 6.0	107.4 ± 4.1	108.5 ± 2.3	104.4 ± 2.0	100.5 ± 2.5
	Replicate RPD	Borohydride	—	5	2.5 ± 2.2	2.1 ± 2.1	2.7 ± 1.7	1.8 ± 1.7	3.3 ± 4.1
		Online	—	3	0.8 ± 1.0	1.2 ± 0.8	1.0 ± 0.4	0.8 ± 0.4	1.8 ± 0.2

*All values are reported as percent recovery with the exception of the replicates as RPD.
†SB LCS is a Sequim Bay laboratory control sample spiked at 2 μg L^{-1} with an SB Blank correction applied.

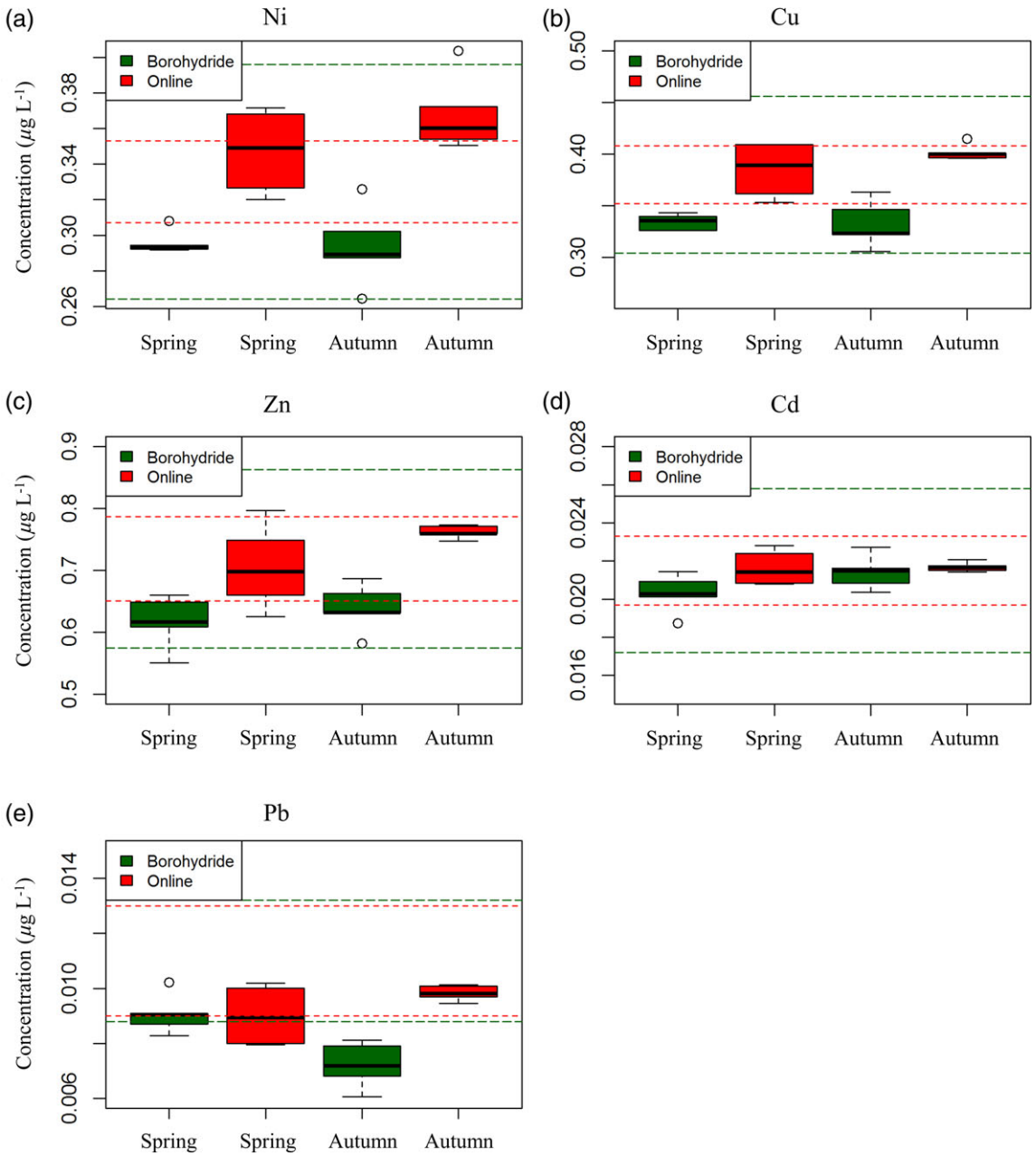

Fig. 1. (**a**–**e**) Box and whisker plots of CASS-5 recoveries (μg L^{-1}) for Ni, Cu, Zn, Cd, and Pb during analysis of sampling events, spring and autumn, using the Borohydride and Online methods. Certified concentrations are signified by red dashed lines, and 20% difference QC limits by green dashed lines.

Table 6. Results of two-way ANOVA for method and event for each metal analyzed in CASS-5 CRM samples.

p	Ni	Cu	Zn	Cd	Pb
Method	<0.0001	<0.0001	<0.0001	0.0541	0.0024
Event	0.3620	0.4430	0.0738	0.1283	0.1260
Method*Event	0.2320	0.2900	0.3876	0.1955	0.0022

$$r_C = \frac{2S_{OB}}{S_B^2 + S_O^2 + (O-B)^2} \quad (3)$$

$$r_G = \frac{1}{1 + \frac{S_D}{S_B^2(n-1)}} \quad (4)$$

where Y_{Bi} and Y_{Oi} were the measurement results using the Borohydride and Online methods, respectively; n was the

Table 7. Trace metal impurities in Fe and Pd reagent solutions.

			Trace metal impurity (μg L^{-1})*				
Study	**Analyte**	**Lot#**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Spring	Fe	1,109,003	10	0.01	0.02	0.02	0.02
	Pd	1,112,902	1	3	1	0.01	0.05
	Total		11	3.01	1.02	0.03	0.07
Autumn	Fe	1,503,405	2	1	2	0.02	2
	Pd	1,504,103	7	7	2	0.1	0.03
	Total		9	8	4	0.12	2.03
	Difference		−2	4.99	2.98	0.09	1.96

*Values taken from High Purity Standards Certificate of Analysis for 99.99% Fe and Pd.

Table 8. Percent recovery of CASS-5 certified analytes using the Borohydride and Online methods for the current study. Results from the long-term data set are also presented.

Method	***n***	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Study recovery						
Borohydride	10	89.3 ± 4.8	87.7 ± 4.2	87.4 ± 5.6	97.0 ± 5.0	74.1 ± 11.1
Online	9	108.8 ± 7.3	103.8 ± 5.3	102.5 ± 7.4	100.7 ± 2.9	86.1 ± 7.9
Long-term data set (2009–2015)						
Borohydride	*	100.3 ± 9.3	108.2 ± 12.9	101.6 ± 38.1	114.4 ± 15.2	97.5 ± 35.2
Borohydride†	*	96.2 ± 7.9	97.3 ± 17.2	92.5 ± 38.2	113.9 ± 14.9	89.3 ± 33.3
Long-term data set (2015–2018)						
Online	39	108.4 ± 5.4	101.5 ± 4.6	103.0 ± 4.7	104.8 ± 5.0	95.4 ± 12.8

*Ni = 80; Cu, Zn, Cd, Pb = 102.
†Reagent blank corrected.

number of paired measurements; S_{OB} was the covariance between the Online and Borohydride method; S_B^2 was the variance of the Borohydride method; S_O^2 was the variance of the Online method; O and B were the means of the Online and Borohydride methods, respectively; and $S_D = \Sigma D^2$. These indices of reliability (Watson and Petrie 2010) were calculated for each metal grouped by dissolved and total results.

Assessment

Blanks and accuracy

For DI water blanks bracketing sample groups, recoveries for online preconcentration were below the method detection limits (MDLs) for all analytes given; matrix corrected borohydride reductive coprecipitation method blanks were less than two times the MDLs given in Table 4. MDLs were determined using seven replicates, of 0.45 μm filtered Sequim Bay seawater spiked to attain a concentration 2–10 times the estimated detection limit, and calculated in accordance with 40 CFR Part 136, Appendix B. The MDLs obtained from the Online method for Ni, Cu, Zn, Cd, and Pb were 3.3, 1.8, 13.5, 4, and 10 times lower, respectively, than the Borohydride method. LCS values, as with other QC samples, recovered with consistently greater accuracy using Online preconcentration. This trend, as well as an overall higher yield, is seen throughout the comparison of recoveries, and is also highlighted in the spike recoveries in Table 5. One line of reasoning is that the Borohydride method produces lower recoveries due to trace metal analytes coprecipitation sensitivities to pH, while Online preconcentration allows for a much wider range (Biller and Bruland 2012). Another factor to consider for Online accuracy is loading rate and volume of the preconcentration column; Rapp et al. (2017), for example, obtained significantly low recoveries for Ni using a resin volume of 15 μL in contrast to the 200 μL column in the current study. Sample replicates for each study recovered all analytes within 9% as relative percent difference (RPD).

Precision

The results of CRM analysis are shown in Fig. 1, the results of the ANOVA are presented in Table 6 for both methods and sampling events. There were statistically significant differences ($p < 0.0001$) between the methods for Ni, Cu, and Zn, statistical differences between methods for Pb ($p = 0.0024$), and minor differences for Cd ($p = 0.054$). For Ni, the Online method had higher accuracy while the Borohydride method was more precise, and both methods fell within the QC limits with the exception of one outlier from the autumn Online analysis (Fig. 1a). The Online method was remarkably accurate

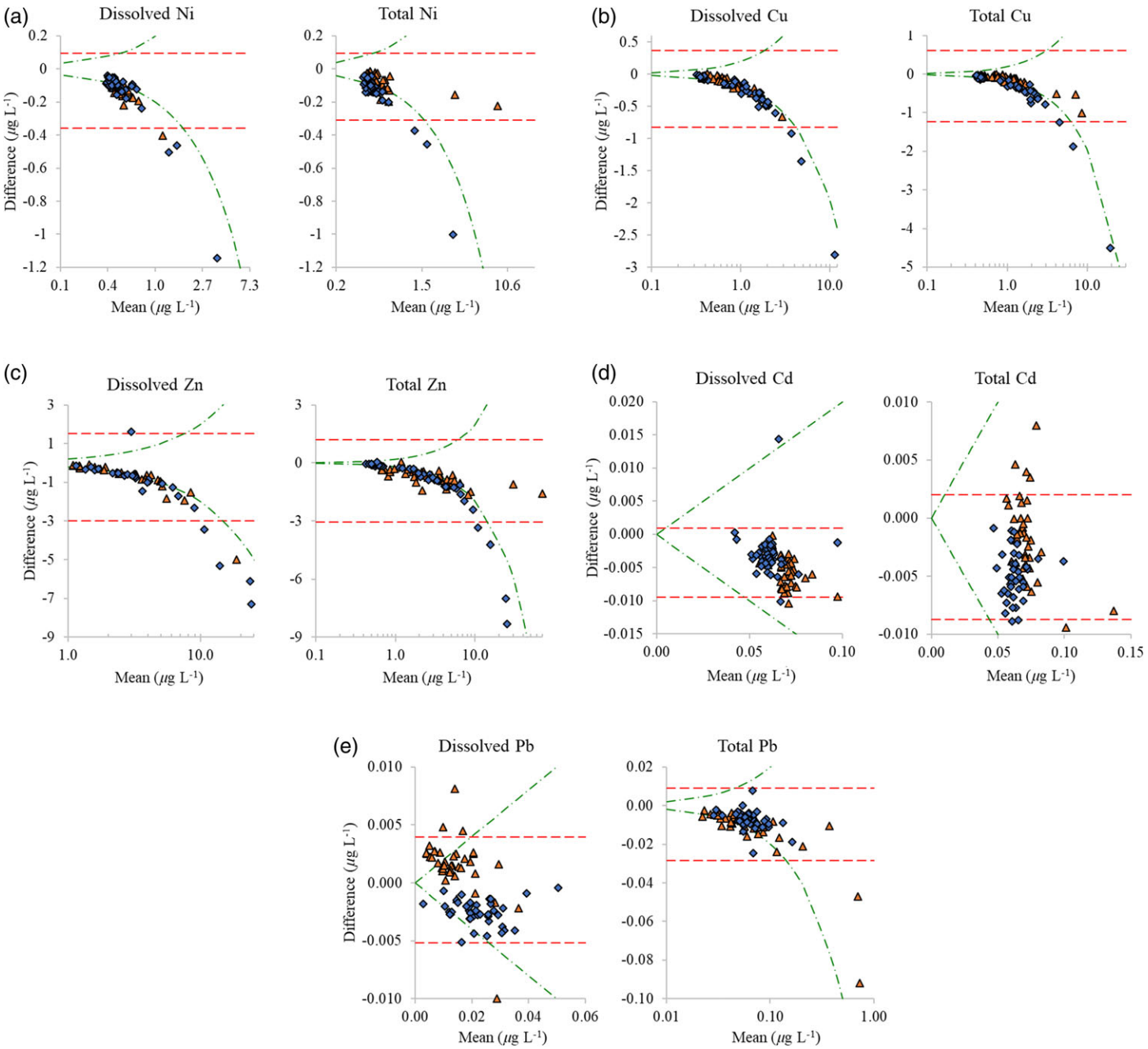

Fig. 2. (**a**–**e**) Difference plots of dissolved and total trace metal concentrations determined using borohydride reductive preconcentration vs. the chelating ion exchange method (*n* provided in Table 9). Triangles represent spring samples, diamonds represent autumn, red dashed lines indicate the 95th percentile, and green dash-dot lines signify 20% variance from unity.

for Cu and Zn, and both methods were exceptionally accurate for Cd (Fig. 1b–d). There were no statistical differences ($p > 0.05$) for any of the metals between events, but there was a statistically significant interaction between method and event for Pb ($p = 0.0022$; Table 6; Fig. 1e).

The box and whisker plots show that the Borohydride method had lower recoveries and was less accurate for Ni, Cu, and Zn than the Online method (Fig. 1). The CRM recoveries observed for the Borohydride method for the two events displays the significance of purity levels of reagents available on the market. Different batches of Fe-Pd solution for the Borohydride method were used on the two events. The two batches had significantly different impurities for the metals of interest (Table 7). Note that the Pb concentration in the Fe solution used for autumn sampling was 100-fold higher than the Fe solution used for spring event. This radical concentration

Table 9. The number of samples, mean percent differences (PD ± standard deviation), correlation coefficient (r), concordance (r_C), and Gold-Standard (r_G) statistics calculated between methods for metals grouped by dissolved and total results.

				Correlation	Concordance	Gold-standard
		n	Mean PD	*r*	r_C	r_G
Ni	Dissolved	80	23% ± 6%	0.997	0.897	0.756
	Total	81	18% ± 9%	0.994	0.987	0.972
Cu	Dissolved	81	17% ± 7%	0.999	0.956	0.893
	Total	81	17% ± 9%	0.997	0.966	0.920
Zn	Dissolved	81	13% ± 18%	0.997	0.942	0.858
	Total	81	27% ± 14%	0.993	0.985	0.968
Cd	Dissolved	81	6% ± 5%	0.947	0.847	0.720
	Total	81	5% ± 5%	0.962	0.924	0.861
Pb	Dissolved	81	−2% ± 23%	0.965	0.951	0.896
	Total	81	13% ± 7%	0.999	0.991	0.981

difference offers an explanation for the drop in Pb recovery for the Borohydride method between sampling events (Fig. 1e). The CASS-5 Pb recovery with the Borohydride method was problematic due to reagent impurities holding the MDL near the CRM value, and matrix correcting at levels nearly twice the certified value; 0.0210 μg L^{-1} during the Autumn event.

The historical accuracy of the borohydride reduction method for the project associated to these samples is given in Table 8, showing determinations of the CASS-5 CRM during, preanalytical, and postanalytical method shift, and highlighting the disadvantage associated with the weight of correction levels. Historically, good average accuracy has been obtained with the blank corrected average Borohydride recoveries, ranging from a low of 89.3% for Pb to a high of 113.9% for Cd. All Borohydride determined analytes (2009–2015) had a 95% confidence level within 20% variation for accuracy to the CRM both preblank and postblank correction. Precision and repeatability are given by the percent standard deviation showing that the magnitude of dispersion is generally unaffected by blank correcting, leaving the average recovery ranges outside of a 20% limit to the certified reference values for Zn, Cd, and Pb.

Environmental sample analysis

The comparison of the results obtained by the Online and Borohydride methods from the analysis of field samples collected from Sinclair and Dyes Inlets is shown in Fig. 2 as the difference between the methods as a function of the mean of paired measurements using the Borohydride and Online methods for total and dissolved fraction measurements of samples collected from two sampling events. The difference plots provide a better comparison of the methods than correlation and regression analysis because methods designed to measure the same thing will be invariably highly correlated (Altman and Bland 1983; Bland and Altman 1986) and regression analysis will not necessarily reveal any constant or proportional bias between the methods (Magari 2002; Watson and Petrie 2010). A summary of the indices of reliability calculated for each metal grouped by dissolved, and total results are provided in Table 9.

For dissolved and total Ni, Cu, and Zn, there were constant proportional biases toward the Online method with the average PD of dissolved Ni and total Zn exceeding 20% (Table 9). The dissolved and total Cd results remained well within 20% of unity with a constant bias of ~ 0.003 μg L^{-1} toward the Online method. Dissolved Pb was near unity, with spring results biased toward the Borohydride method and the autumn samples biased toward the Online method. Total Pb showed a proportional bias toward the Online method.

As expected, there were substantial correlations ($r \geq 0.95$) between the methods for all metals. There was almost perfect concordance ($r_C \geq 0.99$) between methods for Total Pb, and substantial concordance ($r_C \geq 0.95$) for total Ni, Cu, Zn, and dissolved Ni, Cu, and Pb. Dissolved Cd had the minimum concordance; indicating 85% agreement (Table 9). The r_C values indicate variation from best fit and shift from unity. Dissolved Cd variation in r_C was 9% linearity and 6% unity fitment; the outlier observed in Fig. 2d had minimal impact on this ratio. In relation to r, dissolved Ni and Cd displayed the most significant shift (10%). When assessing total Ni, it becomes apparent that the two maximal spring samples in Fig. 2a result in the shift in r_C between total and dissolved fractions; sans these points both concordance values would display 4% variance from linearity (r) and 6% from unity fitment; this is true also of the delta r_C in Zn species and is likely a result of inhomogeneity of particulates in total sample aliquots.

The Gold-standard statistic, using Borohydride as the gold standard, was substantial ($r_G \geq 0.95$) for total Ni, Zn, and Pb and moderate ($r_G \geq 0.90$) for total Cu; for other measures, the variation between methods was significant in relation to the range of ambient levels. The r_G is provided as a measure of the strength of r_C over the ambient ranges of analytes tested.

In general, the shifts in method recoveries of field samples reflect the trend of increased recovery by the Online method equivalent to that of the QC samples. This is likely due to a combination of overcorrecting the Borohydride method for impurities seen in Table 8, and loss of nanoparticles in the Borohydride method supernatant. Based on CRM percent differences, these shifts are correcting, not skewing the data, with Ni being a questionable exception. The shifts given as mean PD ± standard deviation in Table 9 allow decisions of confidence in method replacement based on individual project's historical ranges and thresholds. While these biases are minimal they must be accounted for when combining data-sets using the differing methods.

Discussion

The borohydride reductive coprecipitation method from EPA Method 1640 is commonly used to quantify Ni, Cu, Zn, Cd, and Pb in seawaters via analysis by ICP-MS. However, the chelating reagents required to induce precipitation contain trace impurities that require a reagent blank correction to accurately represent the trace metal concentrations in ambient seawaters. The current study demonstrates that moving to an automated online procedure using EDTA/IDA resulted in good reproducibility compared to the borohydride reductive precipitation method, and eliminated the systematic negative bias generated during the Fe-Pd reagent blank correction. The comparability of the methods was demonstrated over a range of trace metal concentrations representative of a nearshore industrial harbor for both total recoverable metals and the dissolved fraction. The greatest benefit of a transition to EDTA/IDA is that detection limits for analytes are no longer tied to the level of impurities in the chelating reagents; thus, matrix interferences are eliminated without additional data corrections being necessary. This allows for more quantitative measurements, at lower detection limits, that are more relevant to ambient trace metal concentrations in seawaters. The systematic data bias ranged from −2% to +27% when comparing the Borohydride to the Online method. The robust results of the side by side method comparison demonstrate that EDTA/IDA is the preferred method. As research programs utilize empirical modeling to determine trace metal fate and transport, this online method should be considered capable of providing highly precise data that are needed to conduct low-level trace metal modeling and toxicity assessment in nearshore and marine coastal systems.

References

Altman, G., and J. M. Bland. 1983. Measurement in medicine: The analysis of method comparison studies. Statistician **32**: 307–317. doi:10.2307/2987937

Australian and New Zealand Environment and Conservation Council. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Australian Water Association.

Beck, N. G., R. P. Franks, and K. W. Bruland. 2002. Analysis for Cd, Cu, Ni, Zn, and Mn in estuarine water by inductively coupled plasma mass spectrometry coupled with an automated flow injection system. Anal. Chim. Acta **455**: 11–22. doi:10.1016/S0003-2670(01)01561-6

Biller, D. V., and K. W. Bruland. 2012. Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS). Mar. Chem. **130**: 12–20. doi: 10.1016/j.marchem.2011.12.001

Bland, J. M., and D. G. Altman. 1986. Statistical methods for assessing agreement between two pairs of clinical measurement. Lancet **327**: 307–310. doi:10.1016/S0140-6736(86)90837-8

Chapple, G., and J. P. Byrne. 1996. Direct determination of trace metals in sea-water using electrothermal vaporization inductively coupled plasma mass spectrometry. J Anal Atom Spectrom **11**: 549–553. doi:10.1039/JA9961100549

European Economic Council. 2008. Directive 2008/105/EC of the European Parliament and of the council of 16 December 2008. Annex I: Environmental quality standards for priority substances and certain other pollutants. Official Journal of the European Union. 24.12.2008: L 348/84–348/97.

Hirata, S., K. Honda, and T. Kumamaru. 1989. Trace metal enrichment by automated on-line column preconcentration for flow-injection atomic absorption spectrometry. Anal. Chim. Acta **221**: 65–76. doi:10.1016/S0003-2670(00)81939-X

Hirata, S., Y. Ishida, M. Aihara, K. Honda, and O. Shikino. 2001. Determination of trace metals in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry. Anal. Chim. Acta **438**: 205–214. doi: 10.1016/S0003-2670(01)00859-5

Hudson, R. J., and F. M. Morel. 1993. Trace metal transport by marine microorganisms: Implications of metal coordination kinetics. Deep-Sea Res. Part I Oceanogr. Res. Pap. **40**: 129–150. doi:10.1016/0967-0637(93)90057-A

Lagerström, M. E., M. P. Field, M. Séguret, L. Fischer, S. Hann, and R. M. Sherrell. 2013. Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: Application to the GEOTRACES program. Mar. Chem. **155**: 71–80. doi:10.1016/j.marchem.2013.06.001

Magari, R. T. 2002. Statistics for laboratory method comparison studies. BioPharm **2002**: 28–32. doi:10.1016/j.marchem.2013.06.001

Milne, A., W. Landing, M. Bizimis, and P. Morton. 2010. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). Anal. Chim. Acta **665**: 200–207. doi:10.1016/j.aca.2010.03.027

Nakashima, S., R. E. Sturgeon, S. N. Willie, and S. S. Berman. 1988. Determination of trace elements in sea water by graphite-furnace atomic absorption spectrometry after preconcentration by tetrahydroborate reductive precipitation. Anal. Chim. Acta **207**: 291–299. doi:10.1016/S0003-2670(00)80804-1

Rapp, I., C. Schlosser, D. Rusiecka, M. Gledhill, and E. P. Achterberg. 2017. Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry. Anal. Chim. Acta **976**: 1–13. doi:10.1016/j.aca.2017.05.008

Rosland, E., and W. Lund. 1998. Direct determination of trace metals in sea-water by inductively coupled plasma mass spectrometry. J Anal Atom Spectrom **13**: 1239–1244. doi:10.1039/A804350G

Skogerboe, R. K., W. A. Hanagan, and H. E. Taylor. 1985. Concentration of trace elements in water samples by reductive precipitation. Anal. Chem. **57**: 2815–2818. doi:10.1021/ac00291a016

St. Laurent, R. T. 1998. Evaluating agreement with a gold standard in method comparison studies. Biometrics **54**: 537–545. doi:10.2307/3109761

Strivens, J. E., R. K. Johnston, N. Schlafer, and J. M. Brandenberger. 2018. ENVVEST Ambient Monitoring Program: In-Progress Summary 2009–2017. PNNL-28116, prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility under Project ENVVEST by the Pacific Northwest National Laboratory, Marine Sciences Laboratory, Sequim, Washington. Final Report, Sept. 2018, 53pp + appendices.

Sunda, W. G., and S. A. Huntsman. 1998. Processes regulating cellular metal accumulation and physiological effects: Phytoplankton as model systems. Sci. Total Environ. **219**: 165–181. doi:10.1016/S0048-9697(98)00226-5

U.S. Environmental Protection Agency. 1996a. Method 1669: Sampling ambient water for determination of metals at EPA water quality criteria levels. U.S. Environmental Protection Agency, Office of Water.

U.S. Environmental Protection Agency. 1996b. Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma – mass spectrometry. US EPA Office of Water.

U.S. Environmental Protection Agency. 1997a. Method 1640: Determination of trace elements in water by preconcentration and inductively coupled plasma-mass spectrometry. Office of Water and Office of Science and Technology.

U.S. Environmental Protection Agency. 1997b. Method 200.10: Determination of trace elements in marine waters by on-line chelation preconcentration and inductively coupled plasma – mass spectroscopy, p. 15. Revision 1.6. Office of Research and Development.

U.S. Environmental Protection Agency. 2017. National recommended water quality criteria - aquatic life criteria table. Office of Water. Available from https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table

Warnken, K., G. Gill, L. Griffin, and P. Santschi. 1999. Trace metal analysis of natural waters by ICP-MS with on-line preconcentration and ultrasonic nebulization. J Anal Atom Spectrom **14**: 247–252. doi:10.1039/A806822D

Warnken, K. W., D. Tang, G. A. Gill, and P. H. Santschi. 2000. Performance optimization of a commercially available iminodiacetate resin for the determination of Mn, Ni, Cu, Cd and Pb by on-line preconcentration inductively coupled plasma-mass spectrometry. Anal. Chim. Acta **423**: 265–276. doi:10.1016/S0003-2670(00)01137-5

Watson, P. F., and A. Petrie. 2010. Method agreement analysis: A review of correct methodology. Theriogenology **73**: 1167–1179. doi:10.1016/j.theriogenology.2010.01.003

Acknowledgments

Funding for this research was provided by the United States Department of Defense MIPR#N4523A15MP00151, and performed in partnership between Pacific Northwest National Laboratory (PNNL), Marine Sciences Laboratory (MSL) Sequim, Washington, and the Space and Naval Warfare Systems Center Pacific (SSC-Pac), San Diego, California. Managerial and sampling support was provided by L. Doyle, A. Thurman, L. Hsu, M. Aylward, and R. Lee (Puget Sound Naval Shipyard & IMF); S. Curtis, G. Rosen, and M. Colvin (SSC-Pac); G. Gill, N. Schlafer, L. Kuo, and C. Suslick (PNNL MSL); and M. Hardiman, D. Bunch, and T. Beryele (Naval Base Kitsap). ICP-MS operation was performed by J. Wood (PNNL MSL). The citation of trade names and names of manufacturers is for information purposes only and is not to be construed as official government endorsement or approval for use.

Conflict of Interest

None declared.

Submitted 09 November 2018
Revised 28 January 2019
Accepted 02 February 2019

Associate editor: Steven Wilhelm

Appendix E– Analytical Chemistry Data Packages

E.1 Grab Sample Data Packages AMBs 01-29

E.2 Passive Sampler Data Packages

E.3 Toxicological Data Packages

Distribution

No. of Copies

4 Naval Information Warfare Center Pacific
- J Frew
- G Rosen
- M Colvin
- N Hayman

2 Puget Sound Naval Shipyard
- T Richardson
- J Hubbs

No. of Copies

0 Foreign Distribution

2 Local Distribution
Pacific Northwest National Laboratory
- J Brandenberger
- L Kuo

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

U.S. DEPARTMENT OF
ENERGY

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov