STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
PO Box 47600, Olympia, WA 98504-7600 • 360-407-6000

March 20, 2025

TO: Heather R. Bartlett, Deputy Director

THROUGH: Vince McGowan, Water Quality Program Manager

THROUGH: Leslie Connelly, Water Quality Program Strategic Planning Section Manager

FROM: Chelsea Morris, Stormwater Action Monitoring Program Scientist

SUBJECT: **Revised agreement for regional status and trends monitoring of small streams for Stormwater Action Monitoring (SAM) program**

This memo represents a signature request for an amendment to Agreement C2500096 with the US Geological Survey (USGS) developed for the Stormwater Action Monitoring (SAM) program. The proposed amendment aims to assess occurrence of 6PPDQ and identify tire particles in urban streams known to be used by coho salmon for spawning in the Green-Duwamish Watershed. Funding for this work will be provided entirely by the USGS through the Urban Waters Federal Partnership Cooperative Matching Funds program.

This work began under Agreement C2000148, Amendment 2, which closes April 30, 2025. In this amendment to Agreement C2500096, the study will continue with the same goal. The USGS is contributing an additional $100,000 to the new contract, and they may contribute up to $100,000 annually for the duration of the study, subject to available funding.

If you have any questions, please contact Chelsea Morris at chelsea.morris@ecy.wa.gov for more information.

6000000020/25YGJFA30137- Amend1

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
AMENDMENT OF JOINT FUNDING AGREEMENT
FOR
WATER RESOURCES INVESTIGATIONS

This amendment is for the agreement dated March 1, 2025

Paragraphs 2a and 2b of the agreement are hereby modified to read as follows:

(a) $100,000 by the party of the first part during the period March 1, 2025 to June 30, 2031.

(b) $2,853,500 by the party of the second part during the period March 1, 2025 to June 30, 2031.

The Joint Funding Agreement (JFA) between the USGS and the Washington State Department of Ecology for a fixed priced agreement to provide regional status and trends monitoring of small streams for the Stormwater Action Monitoring (SAM) program is hereby amended to add funds to the USGS portion in the amount of $100,000.

The total fixed cost of the amended agreement is changed by increasing USGS funds and is now $2,953,500.

All remaining terms and conditions as included in the original JFA are unchanged.

UNITED STATES DEPARTMENT OF THE INTERIOR GEOLOGICAL SURVEY	WA State Dept of Ecology 300 Desmond Drive SE Lacey, WA 98503
SCOTT VANDERKOOI Digitally signed by SCOTT VANDERKOOI Date: 2025.03.19 11:25:14 -07'00'	
(Signature)	(Signature)
Scott VanderKooi	
(Name)	(Name)
Center Director	
(Title)	(Title)
Date	Date

Directed CMF: Co-Occurrence of Tire Wear Particles and 6PPD-q in Coho Spawning Streams

SUMMARY

By Andrew Spanjer

A proposal prepared by the U.S. Geological Survey for Washington State Department of Ecology and USGS/EPA UWFP Directed Matching Funds

1/25/2024

Problem.—Coho pre-spawn mortality events are documented throughout underserved areas of the Green-Duwamish watershed, and many non-surveyed coho spawning streams in the watershed are predicted to be at high risk for "urban runoff mortality syndrome" (Feist and others, 2011). Much remains unknown about the 6PPD-q behavior in freshwater streams, such as its persistence, ongoing sources, bioaccumulation, and uptake. Importantly, little is known about the correlation and timing of tire wear particle entry into the water way and continued leaching of 6PPD-q.

Objective(s).—This project will develop analytical methods with emerging capabilities at two USGS laboratories: the Wisconsin Research Mercury Lab (microplastics) and the Kansas Organic Geochemistry Research Laboratory (tire-derived chemicals). We will build upon field sampling methods developed from Urban Water's CMF in the northeast for microplastic sampling with improvements for sampling smaller microplastic-sized tire particles (<220 microns). The dataset will form the first co-occurrence study of tire particles and 6PPD-q concentrations in water and sediment. It will address the challenges of stormwater sampling by utilizing innovative methods.

Relevance and Benefits.—The EPA Trash Free Waters program recently identified the need for additional tire particle research in our nation's waters: https://www.epa.gov/trash-free-waters/science-case-studies#Tire. Researching and developing methods to quantify the persistent source of 6PPD-q and the occurrence of tire particles throughout the watershed streams supports WMA goals of quantifying the ecosystem threat of water quality degradation, provides local stakeholders with needed data to assess stormwater management, and fosters federal, state, and local partnerships identified in the Green-Duwamish UWFP work plan.

Approach.—We propose a descriptive study of tire particles and chemical occurrence in urban streams with known coho spawning in the Urban Waters Federal Partnership recognized Green-Duwamish Watershed. We'll investigate by using three methods: 1) a recently released ASTM method for microplastic collection using ISCO pumped water samples over a sieve stack; flow-through water will also be collected for 6PPDq measurement, 2) passive samplers in sediment and surface water to investigate dissolved fractions of 6PPD-q, and 3) sediment samples throughout the watershed to quantify tire particle deposition and occurrence.

Directed CMF: Co-Occurrence of Tire Wear Particles and 6PPD-q in Coho Spawning Streams

By Andrew Spanjer

A proposal prepared by the U.S. Geological Survey for Washington State Department of Ecology and USGS/EPA UWFP Directed CMF

1/25/2024

BACKGROUND/INTRODUCTION

Pacific salmon, specifically coho (*Oncorhynchus kisutch*), are at risk from untreated road runoff. In 2020, the contaminant N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD), a common tire additive, was found to transform into a highly toxic quinone byproduct, 6PPD-q (Lo and others, 2023; Greer and others, 2023; Tian and others 2022). 6PPD-q is responsible for the high rate of coho pre-spawn mortality observed in Puget Sound Lowland streams (Tian and others, 2022). While much has been learned about 6PPD-q since 2020, including its physical properties, toxicity to other organisms, and proper sampling techniques, many questions remain regarding its fate and transport. Many predicted high-risk streams in the Puget Sound (Feist and others, 2017) still have not been characterized. Additionally, little is known about the persistence of 6PPD and 6PPD-q in the environment and the risk of continued leaching from tire particles both in and around the waterway. The co-occurrence of 6PPD-q and tire wear particles (TWPs) - a type of microplastic - in stream bed sediments have the potential to pose ecological risks beyond the acutely toxic concentrations observed in the water column after a storm., There is a strong potential for sublethal ecological health effects from 6PPD-q and other tire rubber antioxidants (Xu and others, 2022). Negatively-buoyant tire rubber will settle in stream sediments, and could leach these toxic contaminants for years to come, potentially exposing benthic invertebrates, salmon embryos and juvenile fry, and other sensitive species.

The U.S. Geological Survey is a leader in microplastic and 6PPD-q research. Agency scientists developed microplastic methods concurrent with the publication of early descriptions of microplastic occurrence in the nation's water (e.g., Baldwin and others, 2020; Lenaker and others, 2020; Spanjer and others, 2020) and a soon to be published Bureau Microplastic Science Strategy (Iwanowicz and others, in press). As 6PPD-q is a recently recognized toxicological threat to aquatic species, our agency is just beginning to develop sediment, water, and tissue methods, determine the best field protocols to characterize this contaminant, and perform the exposure studies needed to understand its interspecies toxicity, including sublethal effects. As more cooperators approach the USGS for help characterizing these emerging contaminants, we must focus on developing the robust methods needed to accurately and consistently characterize their presence in our environment. This study will pilot these new capabilities while informing 6PPD-q and tire wear particle co-occurrence in a heavily populated and salmon-producing watershed.

PROBLEM

Coho pre-spawn mortality events are documented throughout underserved areas of the Green-Duwamish watershed, and many non-surveyed coho spawning streams in the watershed are predicted to be at high risk for "urban runoff mortality syndrome" (Feist and others, 2011). The Duwamish watershed has a long legacy of industrial land use that has disproportionately impacted residents as well as tribal fisheries dependent clean river habitats. Much remains unknown about the 6PPD-q behavior in freshwater streams, such as its persistence, ongoing sources, bioaccumulation, and uptake. Additionally, because the effects of 6PPD-q are closely related to stormwater events, more work is needed to understand the best monitoring strategies to accurately capture the magnitude of contamination, the timing of peak concentration, and the ongoing threat of TWPs and chemical sorption to sediments. Few studies have measured the dissolved fraction of 6PPD-q and source particles.

Tire particles leach toxicants into waterways both on the roadway and in waterways. Seiwert et al. (2022) showed that up to 90% of the 6PPD-q load (by mass) was in the particulate fraction of roadway snow samples and they postulate that a similar fraction would remain in particles entering waterways from storm runoff. Tire particles left on roadways vary from less than 1 micron (nanosized) up to 200 microns. Generally, these particle sizes have yet to be well characterized by sieve and net-based field and laboratory microplastic methods, and their potential to leach tire chemicals continually is poorly understood.

OBJECTIVES and SCOPE

This project will develop analytical methods with emerging capabilities at two USGS laboratories: the Wisconsin Research Mercury Lab (microplastics) and the Kansas Organic Geochemistry Research Laboratory (tire-derived chemicals). We will build upon field sampling methods developed from a separate Urban Waters Federal Partnership project in the northeast for microplastic sampling with improvements for sampling smaller microplastic-sized tire particles (<220 microns). The dataset will form the first co-occurrence study of tire particles and 6PPD-q concentrations in water and sediment. It will address the challenges of stormwater sampling by utilizing integrative passive samplers, ISCOs, and potentially a flowthrough centrifuge method (Conn and others, 2016) for fine particles in the water column. Results will be published in an open-access academic journal and provide local cooperators with a watershed baseline to assess future stormwater management actions and improved stormwater sampling.

RELEVANCE and BENEFITS

Many agency guidance and policy documents have called for increased investigations into 6PPD-q and, more broadly, into the risk and presence of tire-derived chemicals. The EPA Trash Free Waters program recently identified the need for additional tire particle research in our nation's waters: https://www.epa.gov/trash-free-waters/science-case-studies#Tire. Researching

and developing methods to quantify the persistent source of 6PPD-q and the occurrence of tire particles throughout the watershed streams supports WMA goals of quantifying the ecosystem threat of water quality degradation (USGS, 2021; Evenson et al., 2013), provides local stakeholders with needed data to assess stormwater management, and fosters federal, state, and local partnerships identified in the Green-Duwamish UWFP work plan.

APPROACH

We propose an occurrence study of tire particles and chemical occurrence in urban Coho spawning streams in Washington State. We'll investigate by using three methods: 1) using a recently released ASTM method for microplastic collection using ISCO pumped water samples over a sieve stack; flow-through water will be collected for 6PPD-q measurement, 2) passive samplers in sediment and surface water to investigate dissolved fractions of 6PPD-q, and 3) sediment samples throughout the watershed to quantify tire particle deposition and occurrence. Sampling locations will be determined based on a gradient of upland road use. Given anticipated funding, we propose an intensive study of two locations that target stormwater events with simplified sediment and passive sampler assessment at six additional locations.

Task 1: Site identification, Reconnaissance, and QAPP development.

Washington State Department of Ecology (WSDOE) requires a Quality Assurance Project Plan (QAPP) to be published for each of the projects they are involved with. During FY24, we will write a WSDOE-formatted QAPP that captures a detailed description of our field sampling methods, laboratory analytical procedures, and site descriptions. While developing the QAPP, we will visit potential sampling locations within the Green-Duwamish watershed (Figure 1). To align sampling resources with the objectives of this project, we will co-locate sampling with USGS or King County stream gages. We can summarize seasonal 6PPD-q loading without additional expense by focusing our assessment on gaged streams. The eight sites will take a land-use gradient approach to better understand how stream? size and upland urbanization influence 6PPD-q and TWP loading.

Task 2: Environmental sampling

Storm Sampling

We will target two significant storm events in the fall of 2024 at the two intensive monitoring sites to coincide with Coho presence and stormwater following an antecedent dry period. During each event, we will run ISCO autosamplers to composite samples over 72 hours (24 water samples) to sample the hydrograph's rising limb and fall limbs. Only a subset of 12 whole water samples will be analyzed for each event based on a comparison with the hydrograph and sample timing to coincide with peak stormwater flow.

A pump and sieve method (ASTM D8332-20) will also collect microplastic samples during the storm. This collection will be at the river's thalweg, using a submersible pump over a stainless steel sieve stack (5mm, 1mm, 333 microns, and 63 microns).

Following one of the storm events, bed sediment samples will be collected at the "non-intensive" and “intensive” sampling sites using a handheld stainless steel ponar sampler.

Passive Sampling

At all locations, Diffusive Layer in Thin Film (DGT) samplers with an HLB sorbent layer will be deployed in the water column and buried in the sediment (0-20 cm depth from sediment water interface) for 60 days (roughly Oct. 15-Dec. 15) to capture dissolved 6PPD-q from storm events.

Task 3: Microplastic analysis of sediment, sieve-pumped water samples, and flow-through centrifuge samples

Microplastic samples of sediment, water, and flow-through centrifuge solids will be processed by the Wisconsin Mercury lab following steps similar to ASTM method D8333-20 (the lab is currently finalizing its protocols). If methods are determined to be insufficient to identify tire particles, sub-samples may be sent to an EPA ORD lab in Narraganset, RI, to conduct pyrolysis GC-MS.

Task 4: 6PPD-q analysis of water, sediment, and passive samplers

Samples will be analyzed for 6PPD-q at the USGS Organic Geochemistry Research Laboratory in Lawrence, KS, by a direct-inject isotope dilution ultraperformance liquid chromatography/tandem mass spectrometry (UPLC/MS/MS) method (Greer and others, 2023). Method detection limits for water are 0.002 µg/L.

Task 5: Reporting

Chemical concentration, microplastic counts, and polymer spectral data will be published via a USGS ScienceBase Data Release. Data will be interpreted in a peer-reviewed manuscript for submission to Environmental Science and Technology or a similar journal. The results of this study will be of sufficient quality and academic interest to merit submission to an academic journal.

QUALITY ASSURANCE/QUALITY CONTROL/LAB EVALUATION

Data will be collected per the WAWSC Quality Assurance Plans for water-quality activities (Conn and others, 2017). As feasible, field sampling methods will follow standard USGS methods for organic contaminants in sediment and water (U.S. Geological Survey, 2018). Laboratories used for this project will be assessed under the USGS laboratory evaluation protocol (LEP). They must include appropriate internal QA/QC (e.g., blanks, matrix spikes, surrogate, and internal standards) procedures and reporting (Office of Water Quality Technical

Memorandum 2007.01). Approximately 10 percent of samples will be quality control samples, such as field replicates and blank samples. The USGS Mercury Research Laboratory will perform laboratory quality control per their developing protocols for microplastics, which will include laboratory blank samples, replicate samples, reference samples, and spike samples. Evaluation of the Mercury Laboratory's quality assurance and control procedures and results from reference samples, spike samples, and blank samples will occur at the end of the project and will be used to update the Laboratory Evaluation. Similarly, the Kansas Water Science Center runs internal QA/QC (e.g., blanks, matrix spikes, surrogate, and internal standards), and these will be evaluated at the end of the project. Both analytes, 6PPD-q and microplastics, have quickly changing and developing methods. Given that the analysis of samples is more than a year away, we plan to make appropriate updates to our LEP as the project progresses.

DATA MANAGEMENT AND MODEL ARCHIVES

Data will be managed in accordance with the WAWSC Data Management Plan (Conn and others, 2019). Chemistry and microplastic data will be reviewed and published in a USGS ScienceBase Data Release. Field forms will be used to collect data on water and sediment collection days. These include sampling location, time, method, substrate observations, and sampling notes. These forms will be digitized and archived following the WAWSC Data Management Plan (Conn and others, 2019). Chain-of-custody forms will also be archived under the same protocol.

See Data Management Plan Table 2

TIMELINE and PRODUCTS

A USGS Data Release will be created in 2026 for public dissemination of data and methods. A USGS report or academic journal article providing an overview of the project and an interpretive summary of the data presented in the Data Release will also be created in 2026. Stakeholder outreach in each sampled location will be coordinated to present findings information about tire particles, 6PPD-q, and microplastics tied to how the USGS is working together with partners to understand the links between roadway pollution and human and ecological health, particularly in underserved areas such as the UWFP locations. Groups can include the Duwamish River Community Coalition (DRCC, Fishing on the River — Duwamish River Community Coalition (drcc.org)) or a Lower Duwamish River Roundtable event (coordinated by EPA and presented in multiple languages). Results will also be shared through the Green/Duwamish stormwater group and Puget Sound Partnership's Ecosystem Monitoring Program (PSEMP). The project will

support the efforts of our USGS laboratories to develop important methods for an emerging water-quality concern of nationwide importance.

	FY24				FY25				FY26			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1: Site identification, recognizance, and QAPP development.												
Task 2: Stormwater sampling												
Task 3: Microplastic analysis of sediment, sieve-pumped water sample, and flow-through centrifuge samples												
Task 4: 6PPD-q analysis of water, sediment, and passive samplers												
Task 5: Reporting												

PERSONNEL

Andrew Spanjer, Hydrologist: Project Manager

Kathleen Conn, WAWSC QW specialist: Analysis and flowthrough centrifuge oversight

Rachel Lane, KAWSC Research Chemist: 6PPD-q Sample Analysis

Sarah Jansen, WIWSC Research Chemist: Microplastic Sample Analysis

Field Technical Support: sampling, data handling, and logistics

REFERENCES

ASTM D8332-20, Standard Practice for Collection of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers; ASTM International: West Conshohocken, PA, 2020.

ASTM D8333-20, Standard Practice for Preparation of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers Using Raman Spectroscopy, I.R. Spectroscopy, or Pyrolysis-GC/M.S.; *ASTM International: West Conshohocken, PA, 2020.*

Baldwin, A.K., Spanjer, A.R., Rosen, M.R. and Thom, T., 2020. Microplastics in Lake Mead national recreation area, USA: occurrence and biological uptake. *PloS one*, *15*(5), p.e0228896.

Conn, K.E., Dinicola, R.S., Black, R.W., Cox, S.E., Sheibley, R.W., Foreman, J.R., Senter, C.A. and Peterson, N.T., 2016. *Continuous-flow centrifugation to collect suspended sediment for chemical analysis* (No. 1-D6). U.S. Geological Survey.

Conn, K.E., Huffman, R.L., and Barton, C., 2017, Quality-assurance plan for water-quality activities in the U.S. Geological Survey Washington Water Science Center: U.S. Geological Survey 2017–1044, accessed February 14, 2023, at Open-File Report at https://pubs.er.usgs.gov/publication/ofr20171044.

Conn, K.E., Mastin, M.C., Long, A.J., Dinicola, R.S., and Barton, C., 2019, Data management plan for the U.S. Geological Survey Washington Water Science Center: U.S. Geological Survey Open-File Report 2019-1049, 23 p., https://doi.org/10.3133/ofr20191049.

Evenson, E.J., Orndorff, R.C., Blome, C.D., Böhlke, J.K., Hershberger, P.K., Langenheim, V.E., McCabe, G.J., Morlock, S.E., Reeves, H.W., Verdin, J.P., Weyers, H.S., and Wood, T.M., 2013, U.S. Geological Survey water science strategy—Observing, understanding, predicting, and delivering water science to the Nation: U.S. Geological Survey Circular 1383–G, 49 p., https://pubs.er.usgs.gov/publication/cir1383G.

Feist, B.E., Buhle, E.R., Baldwin, D.H., Spromberg, J.A., Damm, S.E., Davis, J.W. and Scholz, N.L., 2017. Roads to ruin: conservation threats to a sentinel species across an urban gradient. *Ecological Applications*, *27*(8), pp.2382-2396.

Greer, J.B., Dalsky, E.M., Lane, R.F. and Hansen, J.D., 2023. Tire-derived transformation product 6PPD-quinone induces mortality and transcriptionally disrupts vascular permeability pathways in developing coho salmon. *Environmental Science & Technology*, *57*(30), pp.10940-10950.

Iwanowicz, D.D., Baldwin, A.K., Larry, B., Blazer, V.S., Corsi, S.R., Duris, J., Fisher, S.C., Focazio M., Janssen, S.E., Jasmann J.R., Kolpin, D.W., Kraus, J.M., Lane, R.F., Lee M., McSwain, K.B., Oden T., Reilly T., and Spanjer, A.R. (in press, anticipated publication 2024). *Integrated Science for the Study of Microplastics in the Environment - A Strategic Science Vision for the U.S. Geological Survey.* U.S. Geological Survey Circular.

Lenaker, P.L., Corsi, S.R. and Mason, S.A., 2020. Spatial distribution of microplastics in surficial benthic sediment of Lake Michigan and Lake Erie. *Environmental science & technology*, *55*(1), pp.373-384.

Lo, B.P., Marlatt, V.L., Liao, X., Reger, S., Gallilee, C., Ross, A.R. and Brown, T.M., 2023. Acute Toxicity of 6PPD-Quinone to Early Life Stage Juvenile Chinook (Oncorhynchus tshawytscha) and Coho (Oncorhynchus kisutch) Salmon. *Environmental Toxicology and Chemistry*, *42*(4), pp.815-822.

Scholz, N.L., Myers, M.S., McCarthy, S.G., Labenia, J.S., McIntyre, J.K., Ylitalo, G.M., Rhodes, L.D., Laetz, C.A., Stehr, C.M., French, B.L. and McMillan, B., 2011. Recurrent die-offs of adult coho salmon returning to spawn in Puget Sound lowland urban streams. *PloS one*, *6*(12), p.e28013.

Spanjer, A.R., Liedtke, T.L., Conn, K.E., Weiland, L.K., Black, R.W. and Godfrey, N., 2020. Evidence for rapid gut clearance of microplastic polyester fibers fed to Chinook salmon: A tank study. *Environmental Pollution*, *265*, p.115083.

Seiwert, B., Nihemaiti, M., Troussier, M., Weyrauch, S. and Reemtsma, T., 2022. Abiotic oxidative transformation of 6-PPD and 6-PPD quinone from tires and occurrence of their products in snow from urban roads and in municipal wastewater. Water Research, 212, p.118122.

Tian, Z., Gonzalez, M., Rideout, C.A., Zhao, H.N., Hu, X., Wetzel, J., Mudrock, E., James, C.A., McIntyre, J.K. and Kolodziej, E.P., 2022. 6PPD-quinone: Revised toxicity assessment and quantification with a commercial standard. *Environmental Science & Technology Letters*, *9*(2), pp.140-146.

U.S. Geological Survey, 2021, U.S. Geological Survey 21st-Century Science Strategy 2020–2030: U.S. Geological Survey Circular 1476, 20 p., https://doi.org/10.3133/cir1476.

U.S. Geological Survey, 2018, National Field Manual for the Collection of Water-Quality Data U.S. Geological Survey Techniques and Methods, book 9, https://www.usgs.gov/mission-areas/water-resources/science/national-field-manual-collection-water-quality-data-nfm.

Xu, J., Hao, Y., Yang, Z., Li, W., Xie, W., Huang, Y., Wang, D., He, Y., Liang, Y., Matsiko, J. and Wang, P., 2022. Rubber antioxidants and their transformation products: environmental occurrence and potential impact. *International Journal of Environmental Research and Public Health*, *19*(21), p.14595.

MAP OF STUDY AREA

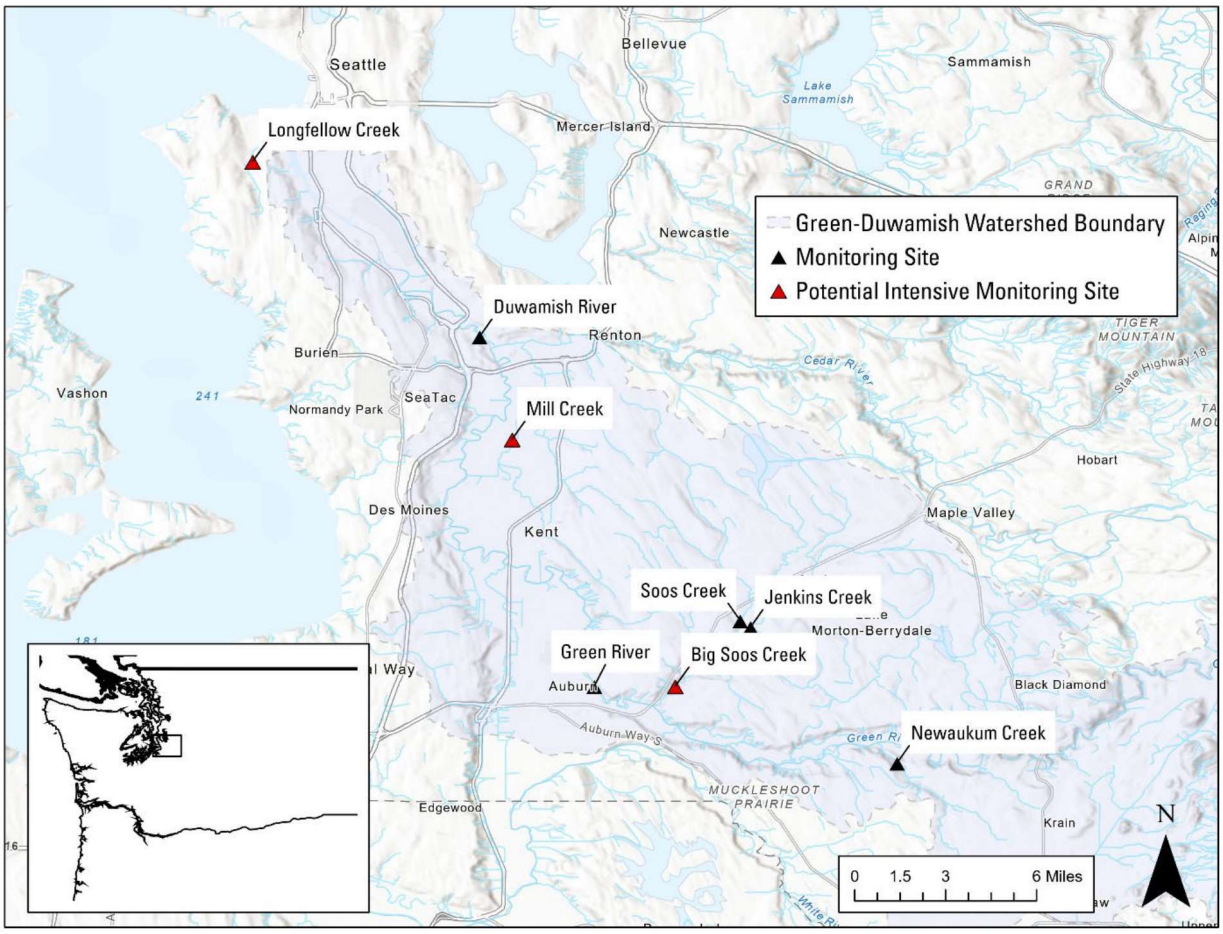

Figure 1. Coho bearing streams that are potential site locations for this study.

Table 1. Sample numbers

Collection method	*Total number of samples*	*Matrix*	*Details*	*Analysis*
DGT passive samplers	40	dissolved	4 per site (2 in water, 2 in sediment) x 8 sites x 1 60-d deployment + 8 QC	6PPD-q
ISCO	52	whole water	12 per site x 2 sites x 2 storm events + 4 QC	6PPD-q
Stacked sieves	20	particulates	4 sieves per site x 2 sites x 2 storm events + 4 QC	MP
Bed sediment	12	particulates	1 per site x 8 sites x 1 post-storm event + 4 QC	MP
Flow-through centrifuge	4	particulates	1 per site x 2 sites x 2 storm events + 0 QC	MP and 6PPD-q