

Quality Assurance Project Plan River TALC: Toxics Assessment of the Lower Columbia

Prepared by:

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Prepared for:

Environmental Protection Agency, Region 10

Quality Assurance Project Plan

River TALC: Toxics Assessment of the Lower Columbia

Approved by:

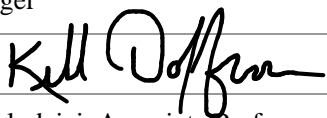
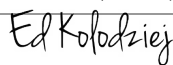
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Table of Contents

A1	<i>Distribution List.....</i>	<i>4</i>
A2	<i>Project Organization.....</i>	<i>4</i>
A3	<i>Project Definition/Background</i>	<i>7</i>
	A3.1 Problem Statement.....	<i>7</i>
	A3.2 Background Information	<i>7</i>
A4	<i>Project Description</i>	<i>8</i>
A5	<i>Quality Objectives and Criteria</i>	<i>10</i>
	A5.1 Data Quality Objectives	<i>10</i>
	A5.2 Measurement quality objectives	<i>10</i>
	A5.3 Acceptance criteria for quality of existing data	<i>11</i>
A6	<i>Special Training/Certifications</i>	<i>12</i>
A7	<i>Documents and Records.....</i>	<i>12</i>
	A7.1 Field operation records	<i>13</i>
	A7.2 Laboratory records	<i>13</i>
	A7.3 QAPP revision documents.....	<i>13</i>
B1	<i>Sampling Process Design</i>	<i>14</i>
B2	<i>Sampling Methods</i>	<i>15</i>
B3	<i>Sample Handling and Custody</i>	<i>16</i>
B4	<i>Analytical Methods</i>	<i>16</i>
B5	<i>Quality Control.....</i>	<i>17</i>
	B5.1 Field QA/QC	<i>17</i>
	B5.2 Laboratory QA/QC.....	<i>17</i>
B6	<i>Instrument/Equipment Testing, Inspection, and Maintenance</i>	<i>20</i>
B7	<i>Instrument/Equipment Calibration and Frequency</i>	<i>20</i>
B8	<i>Inspection/Acceptance of Supplies and Consumables</i>	<i>20</i>
B9	<i>Non-direct Measurements</i>	<i>20</i>

<i>B10</i>	<i>Data Management</i>	<i>20</i>
<i>C1</i>	<i>Assessments and Response Actions</i>	<i>21</i>
<i>C2</i>	<i>Reports to Management</i>	<i>21</i>
<i>D1</i>	<i>Data Review, Verification, and Validation</i>	<i>21</i>
<i>D2</i>	<i>Verification and Validation Methods</i>	<i>22</i>
<i>D3</i>	<i>Reconciliation with User Requirements</i>	<i>22</i>
	<i>References.....</i>	<i>23</i>
	<i>Appendices</i>	<i>24</i>

A1 Distribution List

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Edward Kolodziej, Associate Professor, University of Washington	Center for Urban Waters 326 East D St Tacoma, WA 98421 253-692-5659 koloj@uw.edu

A2 Project Organization

North Coast Watershed Association (NCWA): project manager, Kelli Daffron, will oversee successful implementation of field collections, volunteer recruitment/training, educational outreach, reporting, and communications with project partners. She serves as the primary contact for the project for the EPA. A Standard Operating Procedure (SOP) for field operations, including sample collection, storage, and packaging/mailing, was adapted from prior projects conducted by collaborator Ed Kolodziej, PhD, at the University of Washington, Tacoma. Maps will be generated using this project's data by Graham Klag, Executive Director of NCWA, in conjunction with Clatsop County using NetMaps software which houses detailed information about the geography of the project area. Educational materials will be gleaned from partner organizations, like the Lower Columbia Estuary Partnership (LCEP), and created by Kelli—likely handouts and power-point presentations. Educational and community events, including guest lectures at Clatsop Community College biology classes, will be organized by Kelli and Graham, where volunteers will be recruited. All volunteers will be supplied with a copy of the SOP and will have completed at least one successful sample collection under the supervision of Kelli before conducting any independent sample collection.

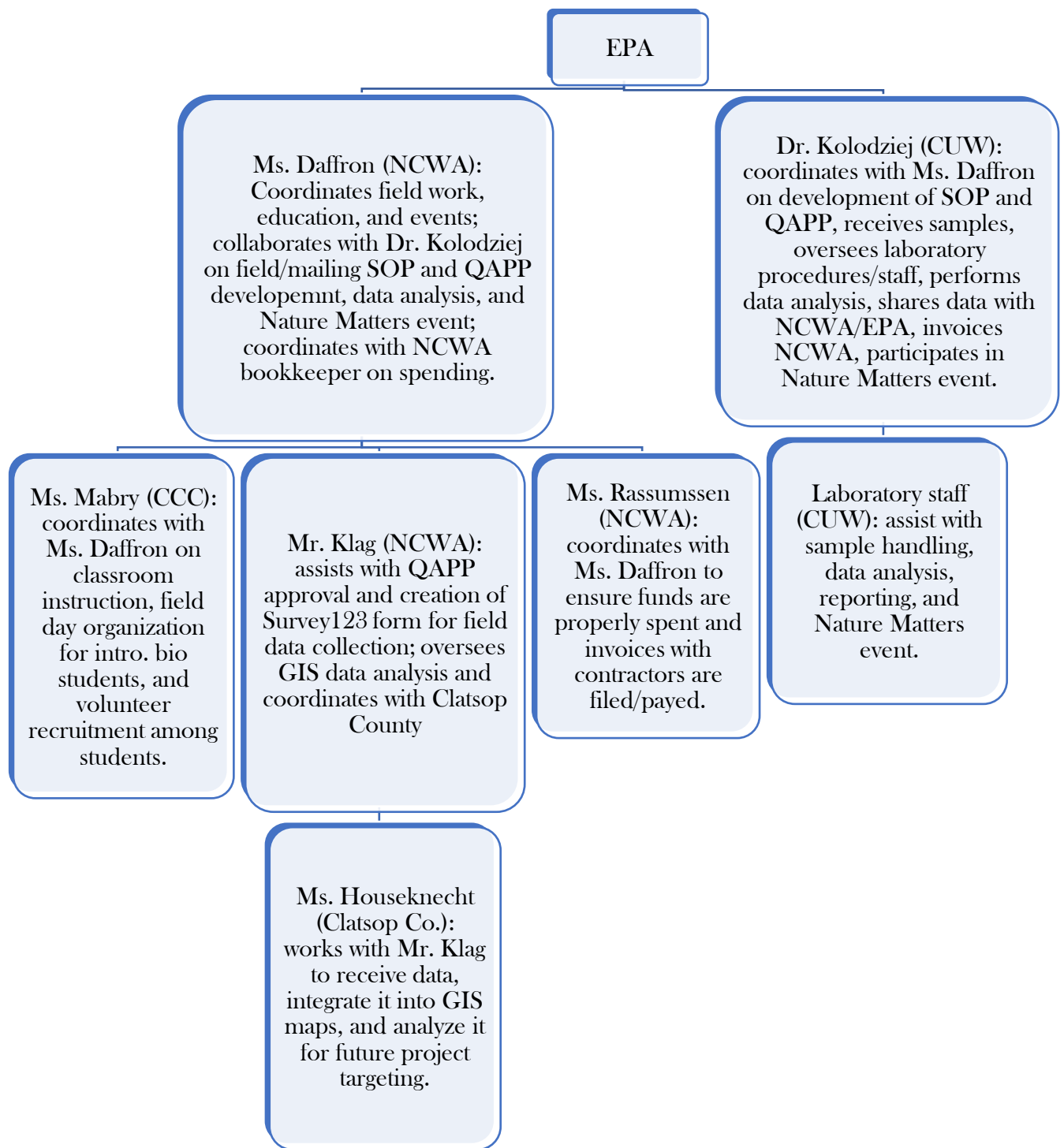
University of Washington, Tacoma: the laboratory of Edward Kolodziej at the Center for Urban Waters (CUW) will help create a Quality Assurance Project Plan (QAPP) for NCWA staff and volunteers to follow for field collection of water samples, analyze these samples, and provide preliminary and detailed analysis of the resulting data. Dr. Kolodziej and/or his staff will also communicate the results of the study at a Nature Matters event following analysis to describe our findings and their implications. Dr. Kolodziej has provided much support to the NCWA in the development of the study design thus far, and has furnished a letter of commitment to uphold the aforementioned responsibilities. He and/or his staff will help to ensure samples are handled, tested, and analyzed in accordance with an existing laboratory QAPP and best practice procedures. The role of Dr. Kolodziej and his team at the CUW is invaluable to the monitoring efforts of the NCWA, providing comprehensible results about both well-known chemical contaminants as well as contaminants of emerging concern, including 6PPDQs.

Clatsop Community College (CCC): during the fall of 2022 CCC will host Kelli Daffron for two lecture periods and one lab/field session of Biology 101/Biology 211. This provides students with real-world

experience conducting ecological research and offers the NCWA a great platform for volunteer recruitment from this and related courses. This will help to build a relationship between our organizations which serve a student body that is steeped in a culture of salmon and outdoor recreation that is dependent on healthy ecosystems. Another hopeful outcome of this growing relationship is that the Living Machine indoor wetland experimentation facility owned by CCC could be used to help conduct follow-up research on any contaminants of interest found in this study. Kelli Daffron has a working relationship with staff as a recent student in the biology department of the college and will work to maintain these ties.

Clatsop County: the county's officials in the ArcGIS, water quality, and outreach realms will be available to the NCWA for assistance with mapping, interpretation, and sharing of data gleaned from this study. The County will also offer expertise and insight into how the two organizations can work together going forward in order to address issues highlighted by the work of this grant.

Staff	Title	Responsibilities
Kelli Daffron	Project Manager, NCWA	Project management QAPP preparation Leads field operations Educational programming Volunteer training/recruitment
Edward Kolodziej	Associate Professor, UW Tacoma, UW Seattle, Center for Urban Waters	QAPP preparation Leads mass spectrometry-based laboratory analysis Data handling and analysis for MS based datasheets Nature Matters presentation of results
Melissa Gonzalez	Center for Urban Waters	Sample logistics, sample processing, sample analysis, data reporting
Graham Klag	Executive Director, NCWA	GIS spatial analysis of data Review QA/QC
Jennifer Rasmussen	Bookkeeper, NCWA	Funding management Invoice payment
Julia Mabry	Associate Professor, CCC	Provides 2 class periods for NCWA staff to instruct on Columbia River toxics Assists with class field collection logistics
Krysta Houseknecht	Clatsop County GIS Program Manager	Works with NCWA to analyze data spatially and help target future projects



A3 Project Definition/Background

A3.1 Problem Statement

This project will conduct sampling for chemicals of emerging concern (CECs) related to pharmaceuticals, personal care products, pesticides, and vehicle related chemicals (listed in Appendix E) in the lowest reaches of the Columbia River and its direct tributaries in northwest Oregon. Recent research in the Puget Sound by Dr. Kolodziej and his collaborators has highlighted the severe water quality risks to salmonids arising from tire rubber chemicals, particularly 6PPDQs (Tian et. al. 2022). We propose to test for a portfolio of emerging contaminants of concern using LC-MS/MS in year 1 sampling, then complement these quantitative analyses with screening level analysis by High Resolution Mass Spectrometry (HRMS) in year 2, focusing on sites with higher concentrations of contamination.

A3.2 Background Information

Little is known about the chemical contaminations in surface water in the lowest reaches of the Columbia River. Since the mid-1990s LCEP has published a State of the Estuary (or River) report detailing various issues in the lower Columbia River every 5 years. Their 2015 report states that the water quality of the river is largely unknown due to lack of sustained monitoring. A 2007 report in which LCEP conducted analysis on known and emerging contaminants found PCBs, PAHs, Organochloride pesticides, and PBDEs present in surface water, sediments, and/or fish tissues at Point Adams in Warrenton, OR. These substances have been linked to human health issues including neurological, developmental, and reproductive problems, cancer, liver disease, and hormone disruption, as well as health effects in salmon including impaired thyroid function, metabolism, and reproduction, disease susceptibility, and death (LCEP 2015).

In regards to roadway runoff in particular, Coho salmon have been found to be particularly susceptible to the chemical contaminants in roadway runoff (McIntyre et. al. 2018). One of the most deadly contributing factors to roadway runoff was identified as 6PPD-quinone, a rubber additive derived from car tires (Tian et. al. 2022; Stokstad, 2020). This substance has been linked to the observed sudden coho death in certain systems in the Puget Sound area (Stokstad, 2020) and could be affecting salmon health on the Oregon side of the lower Columbia River where salmon fishing industries remain central to the economic and cultural lives of its inhabitants.

Current stream water testing for indicators of overall system health, including pH, conductivity, and amounts of ammonia and nitrates/nitrites of the lower Columbia River and its tributaries is conducted regularly by the Oregon Department of Environmental Quality (DEQ) (Appendix A), and the NCWA has conducted temperature monitoring in the region since 2016. While effective as a first pass indicator of water quality, the fact that many potential sources of chemical contaminants, particularly those related to roadways, have not been studied—or even identified—implies that more research and water quality characterization is needed in these systems.

Overall, the integrated data from both the targeted LC-MS/MS and non-target HRMS methods would improve our understanding of novel, high priority contaminant identities in these systems. Targeted MS/MS methods would yield important information on the concentrations and risk of these contaminants that disproportionately impact water quality and biological health, including the “tire toxicant” 6PPD-quinone. HRMS allows for detection of contaminant sources and may sometimes be able to identify novel or unexpected chemical contaminants. These two methodologies together can further be employed to evaluate and optimize runoff

buffer systems to best improve salmon health and biological outcomes across regional Lower Columbia River basin watersheds.

In addition to conducting analysis and widely sharing this research data specifically, this project will engage in community outreach to broadly examine and communicate the history of contamination of the Columbia River with impacts at its lowest reaches in Northwest Oregon. Upriver activities such as metal smelting, nuclear plants, and urbanization as well as more localized conditions such as the WWII ship decommissioning site at Tongue Point outside of Astoria will be discussed with Clatsop Community College students in introductory biology courses as well as with local high school students. Community events will aim to keep neighbors of the study informed as well. Project partners, including the City of Astoria, Clatsop County, LCEP, Lewis and Clark National Historical Park, the Oregon Department of Environmental Quality (DEQ), and of course the Environmental Protection Agency will have data directly sent to them, integrated into relevant databases, and, in the case of local agencies, will help to use the data to target areas where projects to mitigate roadway runoff or storm water contamination can be undertaken.

This project will address Columbia River Basin Restoration Program (CRBRP) Section I.B. part 4: Monitoring to evaluate trends; by conducting sampling over the course of two seasons in an area of the lower Columbia River basin that has little current data on toxic substances, and none on some of the roadway runoff specific chemicals specific to this grant. This project will also address Section I.B. part 7: Promoting citizen engagement or knowledge; through education of both children and adults who live in the surrounding area via presentations at high schools, the Nature Matters speaker series co-sponsored by LEWI and Fort George Brewing Co., Astoria Sunday Market, and other events at breweries/public locales to be determined. Educational material will also be used to give two lectures to an introductory biology class at Clatsop Community College and also offer students one lab session spent in the field conducting field operations for the project.

A4 Project Description

This project aims to monitor the lower Columbia River and its tributaries for CECs, particularly roadway runoff toxins, and to educate inhabitants of northwestern Clatsop County on practices that can affect water quality. NCWA staff and volunteers will conduct field sampling at 10 established sites over two rainy seasons. Samples will be sent to University of Washington, Tacoma Center for Urban Waters (CUW) for testing/analysis. Results of these analyses will be shared on NCWA's website, with project partners, with the public through educational programming, and put into map-form to begin targeting mitigation projects. The NCWA will organize a series of school and community events to educate people about historical and current activities that have the ability to affect the toxic load of the Columbia River—and their effects on humans and wildlife. Through monitoring and education the NCWA will work to address data gaps, increase access to data, and generate support to implement future projects to mitigate chemical loads, especially those related to roadway runoff, in the lower Columbia River basin.

The goals of this project are to:

1. Sample water coming off of logging roads, low-use roads, and high-use highways at 10 sites in the Lower Columbia River basin over the course of two rainy seasons;
2. Utilize established targeted (LC/MS/MS) methods to detect CECs both sample years and non-target high resolution mass spectrometry (HRMS) analytical methods to detect and identify unexpected or novel chemical contaminants in up to 3 sites found to have the most variety of CECs and/or highest concentration of them in year 2;

3. Educate Lower Columbia residents, including students at Clatsop Community College and area high schools, about how legacy and current “emerging” pollutants have historically become present in the Columbia River, how they can harm people and wildlife, and potential ways to mitigate known impacts;
4. Widely share data gleaned from the study with partner organizations, tribes, municipalities, and the public;
5. Generate data and analysis that can help begin to target future projects to minimize impacts of roadway runoff chemicals and storm water on sensitive receiving waters in the Lower Columbia.

Goal 1: Sampling

The 10 sample sites (Table 1) were selected for their proximity to roadways, accessibility, and the presence of salmon; 7 of which overlap with NCWA temperature monitoring sites. Sites also represent roadways of varying usage: high (Skipanon River at Hwy 101 and Big Creek County Park at Hwy 30), low-mid (all Klaskanine River sites off Hwy 202 and Lewis & Clark River off Lewis & Clark Road), gravel/logging (Big Creek above the hatchery), and one off a walking path (Columbia River at the river walk) which is downstream of Astoria’s wastewater treatment facility and therefore could yield information relevant to CECs.

Timing of sampling is scheduled to encompass two rainy seasons, beginning in the fall/winter of 2022/2023 and again for fall/winter 2023/2024. Up to six samples per site will be taken over each season, for a total of up to 12 samples per site over the course of the study. Field staff, Kelli Daffron, will decide to sample based on multiple factors outlined in section B2, including dryness before rain events (preferred), quantity of rain, system level rise, and safety of approaching sites.

Sampling methods are outlined in the River TALC SOP (Appendix B), and include taking samples in pre-cleaned glass jars which hold 946mL of water—enough to run up to 3 250mL analysis (triplicate sampling), taking multiple photos of the site/labeled sample jar, holding procedures for samples (no more than 48 hours from sampling to processing kept at 4 degrees C), and mailing procedures.

Goal 2: Analysis

Targeted analysis using liquid chromatography-tandem mass spectrometry (LC-MS/MS) will be conducted on year 1 samples to determine which sites contain which contaminants (listed in Appendix E) and where their levels are highest. Year 2 analysis will again test for these CECs using LC/MS/MS and up to 3 sites will be selected to conduct additional HRMS analysis to explore for novel organic contaminants. Sites chosen for HRMS will demonstrate the highest levels of and/or most CECs present during year 1 testing. Sites with very few CECs in low concentrations may not be sampled in year 2, allowing time and resources to focus on sites with higher concentrations of many kinds of contaminants.

Methodologies and quality control procedures for this analytical work are detailed in section A5 as well as in SOPs (Appendices B-D).

Goal 3: Education

This project will educate Clatsop Community College (CCC) Introductory Biology students during the fall of 2022 on contaminants of emerging concern, why they are of concern, and historical sources of contamination in the Lower Columbia River Basin. These students will also spend a day in the field conducting sampling with Ms. Daffron. Over the course of the project a total of 15 community events, including Astoria Sunday Markets, local high school presentations, and a Nature Matters speaker series presentation will take place to spread the word about this work to the community at large.

Educational materials will be produced by NCWA educational staff using official sources such as USGS studies/scholarly journal articles and borrowed from project partners at LCEP. All sources will be tracked.

Goal 4: Data Sharing

Project partners, including the City of Astoria, Clatsop County, LCEP, Lewis and Clark National Historical Park, the Oregon Department of Environmental Quality (DEQ), and of course the Environmental Protection Agency will have data directly sent to them, integrated into relevant databases, and, in the case of local agencies, will help to use the data to target areas where projects to mitigate roadway runoff or storm water contamination can be undertaken.

Goal 5: Data Mapping/Future Project Targeting

Using data gleaned from this study, NCWA and Clatsop County have agreed to work together using water quality expertise and GIS mapping technology to generate maps that will help to target areas where high rates of contamination can be mitigated; the organizations will collaborate on future projects to improve water quality.

A5 Quality Objectives and Criteria

A5.1 Data Quality Objectives

The main DQOs for this project are to collect roadway runoff and their receiving surface waters and analyze them for chemicals of emerging concern. To obtain high quality datasets of chemical contaminants that meet Measurement Quality Objectives (MQOs; described below), samples will be analyzed using developed, and often previously approved, liquid chromatography-tandem mass spectrometry (LC-MS/MS) methodologies and approaches. These analyses will provide tables of concentration of detected contaminants at study locations. Complementary HRMS analysis (in year 2) will provide qualitative detections and preliminary identification of additional organic contaminants in up to 3 selected sites which demonstrated high contamination in year 1 analysis. In essence, year 1 sampling will help identify specific (targeted) contaminants that have been previously identified and clarify which sites have the most contamination; year 2 sampling will again look for specific CECs at all sites and also use non-targeted HRMS analysis at up to 3 sites whose year 1 data indicate high variety and/or concentration of CECs to potentially identify new contaminants.

A5.2 Measurement quality objectives

The MQOs for the data to be collected describe the performance metrics and criteria for acceptance that provide the basis for evaluating data quality and usability. They indicate the minimum threshold levels for measures of bias, repeatability, precision, accuracy, and sensitivity that must be associated with the data.

The primary types of quality control samples used to evaluate the control the quality of the MS-based laboratory analyses are check standards, replicates, blanks, and spikes. The level of QA/QC expected to be attained in these studies are those amenable to peer-reviewed publication in high impact journals and use of data by external agencies. In general, the frequency of QA/QC samples (blanks containing deionized water) will be held at 5%, or 1 out of every 20, of total sample numbers. Grab samples will contain 946mL of surface water; because only 250mL are needed to run MS-based analysis each grab sample contains enough water for minimum triplicate testing. Consensus protocols for data assessment from liquid chromatography-mass spectrometry (LC-MS/MS) methods used here, including both high resolution mass spectrometry (LC-HRMS) data collected using a quadrupole time-of-flight (QTOF) mass spectrometer and tandem mass spectrometry (LC-MS/MS) data collected using a triple-quadrupole mass spectrometer will reflect those internal QA/QC protocols and workflows established by CUW laboratories for both non-target and suspect contaminant screening (LC-HRMS) and targeted analysis (LC-MS/MS) of contaminants in environmental samples. These protocols and workflows are described in CUW Laboratory SOPs for sample collection, sample processing,

sample analysis, and data handling, data analysis, and data management. These SOPs are available upon request from the CUW. Data collected will be analyzed relative to the following indicators, many of which are defined per the US EPA Quality Assurance Glossary (1997).

Although these methods have not yet been standardized, data collected from LC-HRMS analyses are subject to additional quality objectives according to the confidence levels outlined in Figure 3 (reproduced from Schymanski *et al.* 2014 [4]) and described in numerous publications from Dr. Kolodziej research group. For example, Figure 1 outlines the minimum data requirements to communicate analyst confidence in the chemical identification of compounds identified from HRMS data, where “Level 1” and “Level 5” indicate the highest and lowest, respectively, levels of confidence. Within raw HRMS data, you first rely on the detection of a non-target chemical feature, or an ion that has both paired m/z and chromatographic retention time (Level 5). Through several steps of data processing, this m/z or exact mass can be used to assign a molecular formula (Level 4) and further utilizing database searching, these exact masses/molecular formulae can often be matched to a tentative chemical identity (Level 3). Further confirmation above Level 3 chemical identity involves the use of public repositories or chemical spectral libraries to confirm both precursor mass spectra as well as tandem MS/MS (MS^2) or product ion fragmentation spectra. The final level of confidence in a chemical identification is Level 1, where retention time and mass spectra are matched to an authentic reference standard that is independently analyzed and confirms exact mass and retention times as well as MS and MS/MS spectra.

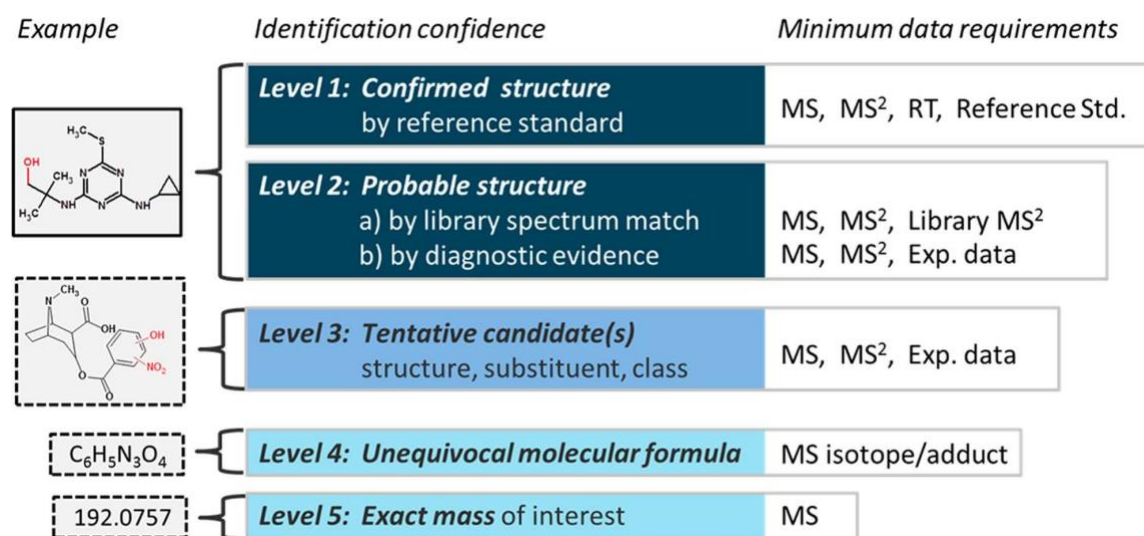


Figure 1. Identification confidence levels in high resolution mass spectrometric analysis from Schymanski *et al.* 2014 [4].

A5.3 Acceptance criteria for quality of existing data

Existing data used for educational outreach purposes will be gleaned from reputable sources, including databases of peer-reviewed journals and government agencies like the United States Geological Survey (USGS). All sources will be documented and will accompany printed and electronic forms of educational materials as a Reference section.

The project manager and any trained volunteers will determine sampling days by closely watching the weather for storms (National Oceanic and Atmospheric Association radar), and monitoring the closest stream (USGS) and rain (NOAA) gauges in the area. Due to a lack of stream gauges within any of the systems being sampled, USGS gauges on the Nehalem and Necanicum Rivers will serve as the litmus test for sampling in association with the NOAA rain gauge stationed at the Astoria Regional Airport.

A6 Special Training/Certifications

All laboratory personnel at the Center for Urban Waters are required to complete and maintain laboratory training and safety courses as administered by the UW Environmental Health and Safety program:

<https://www.ehs.washington.edu/system/files/resources/ehslabsafetytrainmatrix.pdf>

There are no additional trainings or certifications required for project personnel above and beyond what is required per the project staff job classifications. All project staff are trained to demonstrate competency in the water quality monitoring and data analysis program components. Data outputs from the Center for Urban Waters are expected to meet the highest standards of scientific peer review.

Ed Kolodziej: began his academic studies with a B.S. in Chemical Engineering from Johns Hopkins University (1998), after which he focused on environmental issues and went to the University of California at Berkeley where he received his M.S. (1999) and a Ph.D (2004) in Environmental Engineering. He came to the PNW in 2014 as part of the UW Freshwater Science Initiative after seven years as faculty at the University of Nevada, Reno, also in Civil and Environmental Engineering. He also holds a joint appointment with Interdisciplinary Arts and Sciences at UW Tacoma, and is affiliated with local and regional water quality efforts through The Center for Urban Waters.

Kelli Daffron: holds a Bachelor's degree in Psychology and Anthropology and more recently completed collegiate coursework in biology, chemistry, and botany. She has worked as a seasonal employee with the Natural Resource Management department of Lewis and Clark National Historical Park (LEWI) in Astoria since 2018 and has managed the NCWA's water quality monitoring project since 2020. She has successfully designed, implemented, and reported on studies in many fields and has much experience training field crews on scientific protocols.

Graham Klag: completed a Masters in Environmental Studies at Evergreen State College with a focus on GIS. His expertise with mapping software will allow for the synthesis of data from this monitoring into map form which can be used for project targeting, collaboration, and public education.

A7 Documents and Records

This QAPP was created, and can be updated, by Kelli Daffron and Edward Kolodziej and other project personnel. Ms. Daffron is charged with distributing the final version as well as updated versions to local collaborators and Dr. Kolodziej will distribute it to relevant laboratory staff.

Three types of documentation will be managed: 1) field operation records, 2) laboratory records, and 3) QAPP revision documentation.

A7.1 Field operation records

Field operation records will include:

- Photographs
- Field forms (to be completed for each sampling event on tablet using Survey123 form developed by NCWA). These should include:
 - Site name
 - Date/time
 - Name(s) of field personnel present
 - Weather and flow conditions
 - Sample IDs, including replicates and blanks, as appropriate
 - Estimated sample volume
 - Sampling errors or deviations from approved sampling procedures
 - General notes

A7.2 Laboratory records

The CUW laboratory will provide a data package to the Project Manager and will be available upon request to partner organizations and sponsors. The data package will report the test results clearly and accurately, largely by reporting analyte names and detected concentrations. The test report will include the information necessary for interpretation and validation of data and will include the following:

- Report title
- Name and address of laboratory
- Cover narrative
- Study name
- Sample identifiers
- Data and time of sample collection and sample analysis
- Analytical methods and results
- Results of all QA/QC samples
- An explanation of any failed QA/QC or non-standard conditions that may have affected quality, including corrective actions and plan to prevent loss of quality

Laboratory records also include suspect screening databases used to screen samples for contaminants of interest. Databases used include both commercially available compound lists (e.g., provided by or purchased from Agilent), as well as in-house compound lists developed based on literature reviews and/or in-house sample analysis. These databases are stored on CUW project computers, and the in-house database will be sent as an Excel spreadsheet to the NCWA upon request.

A7.3 QAPP revision documents

If the scope of the study changes in a substantial way, then a revised version or QAPP addendum will be prepared and submitted for review and approval as needed. The approved version of the QAPP will remain in effect until the revised version or addendum has been approved. Justifications, summaries and details of all QAPP changes will be documented and distributed by the Program Manager to all persons in the QAPP distribution list. Minor changes or deviations to the QAPP shall be discussed in the final report.

B1 Sampling Process Design

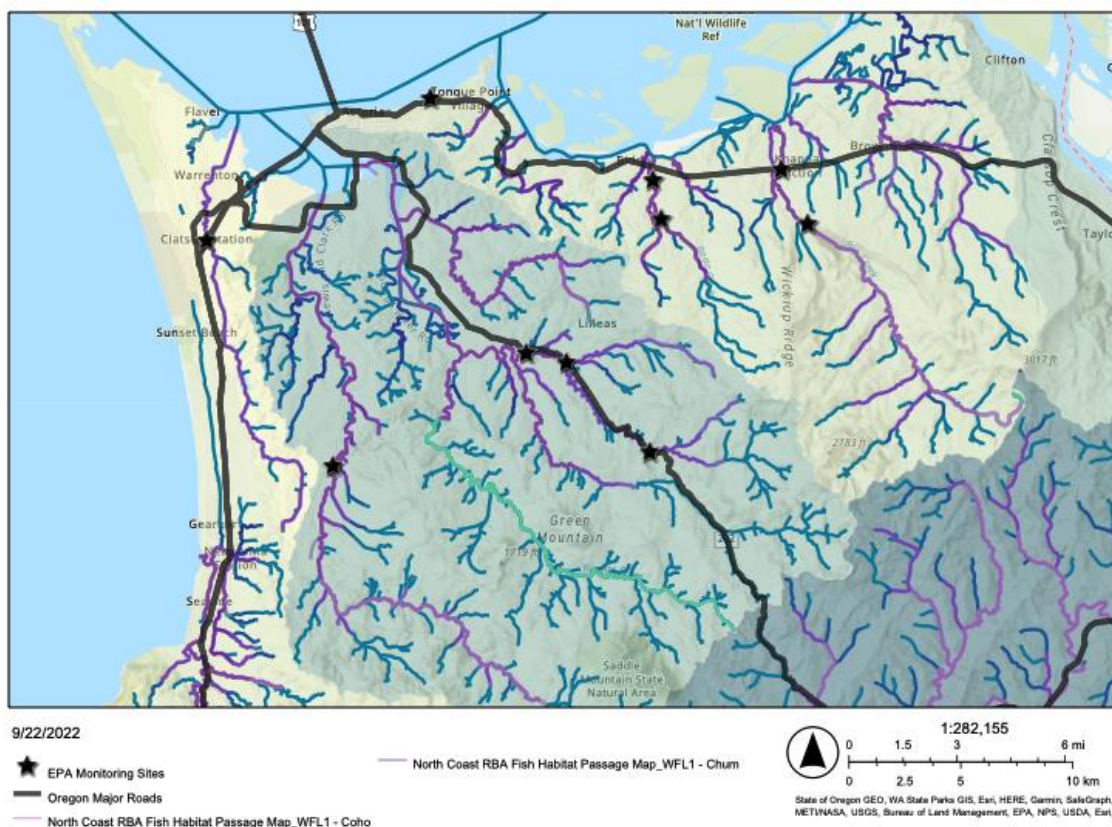
Samples for this project will consist of 946mL grab water samples from the project sites, collected in amber glass bottles pre-cleaned in the manner outlined in Section 1.2 of the River TALC Standard Operating Procedure (SOP). Locations for sampling at each site will be targeted based on proximity to roadways and possibly to visible roadway runoff. Other data collected at each site will include:

- Sample number
- Site name
- Photo with labeled jar
- Date and time
- Weather conditions
- Nearest spatial/temporal reading of stream and rain gauges
- Water temperature
- Site photo

Table 1: Site locations

Site Number	Description	Latitude	Longitude
1	Lewis & Clark River .8 miles S of Melville	46.04864	-123.85156
2	Skipanon River at Hwy 101	46.138699	-123.924552
3	SF of NF Klaskanine at 202 Bridge	46.05397	-123.66817
4	NNF Klaskanine above Hatchery	46.08978	-123.71627
5	NF Klaskanine at Green Mtn Road Olney Bridge	46.09359	-123.73949
6	Bear Creek at Old Hwy 30	46.16326	-123.66604
7	Bear Creek at Svensen Market Rd	46.14737	-123.66142
8	Big Creek above Hatchery	46.145585	-123.577047
9	Big Creek at Hwy 30 Bridge (County Park)	46.167408	-123.592325
10	Columbia River near Pier 39 Riverwalk	46.195844	-123.795059

Figure 2: Map of Site Locations



Water samples will be packaged on ice and shipped within 24 hours with their corresponding Chain of Custody (Appendix F) form to the CUW laboratories for LC/MS/MS and HRMS analysis using FedEx. The metadata from each collection event will be linked with its resulting chemical analysis.

The sampling network was designed based on proximity to various types of roads (gravel, high-use, and low-use), prior temperature monitoring, accessibility, and the presence of salmon species of concern. One site on the main stem of the Columbia River is located off of a walking path not far downstream of a water treatment facility, another potential source of contamination.

All sites will be sampled up to 6 times (approximately monthly) for the span of two rainy seasons—October 2022-March 2023 and October 2023-March 2024.

B2 Sampling Methods

The project manager and any trained volunteers will determine sampling days by closely watching the weather for storms (National Oceanic and Atmospheric Association radar), and monitoring the closest stream (USGS) and rain (NOAA) gauges in the area. Due to a lack of stream gauges within any of the systems being sampled, USGS gauges on the Nehalem and Necanicum Rivers will serve as the litmus test for sampling in association with the NOAA rain gauge stationed at the Astoria Regional Airport. When a gauged system rises substantially and/or >6 mm precipitation is measured sampling will occur, assuming at least 3-5 days of antecedent dry period.

Prior to site visits, all amber glass bottles used to take samples will be cleaned (or purchased pre-cleaned, to “trace organics analysis” standards) using methods outlined in Section 1.2 of the River TALC SOP. Used sample bottles will be returned to NCWA after contents have been analyzed pre-cleaned in the CUW lab per SOP methods for recurring use. A cooler with sufficient packaging to prevent bottle breakage will be prepared with ice to keep samples consistently below 4°C during shipping. Upon arrival at a site, a precise location from which to take a sample will be determined based on safe accessibility to surface water of the system and proximity to visible rain flow off of adjacent roadways. A photo of the sampling site will be taken on the Samsung Tablet, and other relevant field information about the sample will be entered into the form, including all information listed in Section B1. The unique sample number (or ‘blank’) will be written onto the bottle used, and a second photo taken of the bottle with the label and the site in the background as an added quality control for that sampling event.

A sample 946mL will be collected in the amber glass bottle using gloved hands. The bottle will be sealed, placed in the prepared cooler, and shipped to the CUW along with other samples associated with the same storm event within 24 hours after collection. Total sample hold times prior to processing will not exceed 48 hours in accordance with prior CUW projects. A printed form designating the chain-of-custody, outlined in Section B3, will accompany the samples in each cooler mailed. The project manager will email Dr. Kolodziej and Melissa Gonzalez (CUW technician and analyst) to notify them when a package is on the way.

B3 Sample Handling and Custody

Water samples collected will be held on ice in coolers and mailed to the CUW. A laboratory chain-of-custody form will be completed by project field staff. The information on the chain-of-custody form will include:

- Project area name
- Staff name
- Contact information
- Sample identification
- Time collected
- Method of analysis
- Any comments pertinent to the sample.

The form will be signed and dated by the project field staff, and also by laboratory staff who verify receipt of samples. An example Chain of Custody form is shown in Appendix F.

B4 Analytical Methods

Extractions of samples will be performed according to the River TALC SOP Appendix B: “Sample Preparation: Solid Phase Extraction of Trace Organic Contaminants from Water Samples for LC-MS/MS (Targeted) or LC-HRMS (Non-Target) Analysis”. In these studies, the 40 chemical contaminants of interest (Appendix E) are broadly defined as legacy, novel, and emerging chemical toxicants that are expected to both impair water quality and adversely affect salmonid health. Chemical contaminant analyses for year 1 sampling will be performed at the UWT CUW laboratory facility utilizing developed targeted LC-MS/MS that specifically targets and quantifies 40 organic contaminants of various chemical classes derived from various sources.

Samples collected during the second year of sampling will first be analyzed by a targeted LC-MS/MS method, and up to 3 sites which had high concentration and/or numbers of contaminants in year 1 will also be analyzed using LC-HRMS to identify novel contaminants. Targeted LC-MS/MS methodology is included in the CUW

SOP entitled “LC-MS/MS (Targeted) Setup, Operation, and Data Analysis” (Appendix D) and a table of the 40 targeted contaminants is included in Appendix E. Secondly, non-target LC-HRMS methods will be used to survey and screen additional chemical contaminants within samples of interest. Extensive LC-HRMS methodology is included in CUW SOP entitled “LC-HRMS (Non-Target) Setup, Operation, and Data Analysis”.

B5 Quality Control

B5.1 Field QA/QC

Quality control measures in the field include blank samples for 1 in 20 taken, day-of-sampling reviews of protocols, photographing sample bottles at their respective sites with labels visible, keeping a field notebook with notes from sites, and comparing these notes with uploaded data forms from the tablet to ensure all data was entered correctly within 48 hours of sampling. The latter quality control measure will also serve as an opportunity to generate the chain-of-custody form to be mailed with the samples to the CUW, which demonstrate site conditions and links sites to accompanying sample bottle(s).

B5.2 Laboratory QA/QC

Precision is a measure of the repeatability of a set of replicated results, and is considered to represent random error in the measurement process. Poor precision is due to difficulties in obtaining samples under identical conditions (e.g., contamination, variability of field conditions during the time replicate samples are collected) or poor sensitivity of laboratory and/or field procedures.

Four key aspects are considered to evaluate precision of LC-MS data: instrument tuning, background signals, repeated injections of reference standards, and field replicates (Tables 2,3).

- Instrument tuning: Instrument tuning procedures are described extensively in the SOPs for non-target and targeted analysis “Appendix C: LC-HRMS Setup, Operation, and Data Analysis” and “Appendix D: LC-MS/MS Setup, Operation, and Data Analysis”, respectively.
- Background signals: For instance, background signals in non-target analysis, including triethyl citrate (RT 6.13 min), oleamide (RT 15.76 min), stearamide (RT 16.36 min), and an unidentified background ion (300.2019 Da @ 3.68 min) are used to monitor chromatographic stability. In targeted LC-MS/MS analyses, multiple reaction monitoring (MRM) mode is used to monitor two individual ion transitions; both MRM transitions and their retention times are used to identify analytes in samples. Background signals will be compared to detector signal to noise ratio to assess impacts on performance.
- CEC Mix and Internal Standard injections (*Non-target analyses*): A mixture of CEC standards, each at 25-100 ng/mL (CEC-CAL-8; preparation described in CEC Calibration Set Preparation SOP) and a mixture of internal standards, each at 25-100 ng/mL (Internal Standard; preparation described in Stocks and Standards Preparation) are analyzed every 12 samples to check chromatography and sensitivity during data acquisition. Mass accuracy was limited to <5 ppm and retention time variability was limited to <0.1 minutes.
- CEC Mix and Internal Standard injections (*Targeted Analyses*): Precision will be determined by relative standard deviation (RSD, %) of replicate injections of standard samples at two concentration

levels for each compound (1 and 10 µg/L for more sensitive analytes, 10 and 100 µg/L for less sensitive analytes). For intra-day precision (repeatability), standards will be injected three times each (n=3) within a day and for inter-day precision (reproducibility), standards will be evaluated by injecting the solutions on three non-consecutive days (n=3).

- Field/Lab replicates/blanks: Field replicates/blanks are samples taken from, and are representative of, the same sampling event, and carried through all steps of the sampling and analytical procedures in an identical manner. Because field samples for this study are expected to be collected as a ~1L volume composite sample that is subsequently split into ~250 mL volumes for extraction and analysis in the laboratory, field replicates also serve as lab replicates. These field/lab replicates are used to assess variance of sampling and analysis, and prevent false positives. As such (sample volume and instrument capability) 3 replicates will be available from each 1L sampling event. For LC/MS/MS, duplicate samples will be extracted and analyzed at a frequency of 10% of sample numbers. For HRMS, both experimental and analytical replicates will be analyzed (depending on available sample volumes) and chemical features must occur in at least 3 of the instrumental replicates to validate a feature, otherwise it is excluded from consideration.

Non-target LC-HRMS data will be rejected and will not be used in further analyses if MQOs are not met, including if:

- Reference masses (defined in Appendix F), a commercially available mixture of calibration compounds concurrently analyzed within the QTOF whose ions enable the calibration of m/z , are not observed during the analytical run;
- For a sample, <100 non-target features are present at a peak area with a fold-change of 5 relative to field, method, or instrument blanks, where each blank is analyzed against the sample individually (e.g., field and method blanks typically contain more features than instrument blanks);
- CEC reference mix of analytes are not observed with mass accuracy <5 ppm, retention time variability <0.1 minutes, and area counts within 20% of initial sensitivity.
- Internal standards are not observed with mass accuracy <5 ppm, retention time variability <0.1 minutes, and area counts within 20% of sensitivity in internal standard controls.
- Background ions (oleamide, stearamide, triethyl citrate, and 300.2019 Da @ 3.68 min) are not observed at expected retention times (within <0.1 minutes)

Bias is the systematic or persistent distortion of a measurement process which makes the result non-representative (i.e., the measured parameter is different than its true value in a given sample). Potential sources of bias include sampling and analytical procedures that introduce contamination, instability of samples during transportation and storage, interference from other constituents in the sample matrix, inability of the analytical method to measure all forms of the constituent of interest, and faulty calibration of the measurement process. Field blanks are prepared coincident with sample collection and may provide an indication of contamination due to bottle cleanliness, transport conditions, exposure to surroundings during sampling, and transfer from equipment. Method (or laboratory) blanks are prepared in the laboratory and processed in the same manner as the field samples and can also provide information on any bias associated with the sample preparation process. Instrument blanks are solvent-only (e.g., methanol) samples that are injected throughout the analytical run and within analytical batches to check for potential analytical interferences, contamination, carryover or bias associated with the instrumentation. Errors of bias are minimized through use of standardized procedures by properly trained staff.

Sensitivity is a measure of the capability of a method to detect a substance, and discriminate between measurement responses representing variable levels of interest. Sensitivity is measured through reporting limit performance, and in a regulatory setting, the method detection limit (MDL) is often used to describe sensitivity. In the case of non-target LC-HRMS analyses, the sensitivity of the method can be assessed based on the detector resolving power, the results of repeated injections of reference standards, and by setting standards for minimum response of non-target features. In the case of targeted LC-MS/MS analyses, instrumental detection limits and quantification limits will be determined by direct injection of a standard mixture in pure methanol and reported as the lowest concentrations yielding signal-to-noise ratios of 3 and 10, respectively. MDLs and quantification limits (MQLs) will be defined as the mean concentration in a blank plus 3 and 10 times the standard deviation of the method blanks, respectively. See SOPs for LC-HRMS and LC-MS/MS Setup, Operation and Data Analysis.

Table 2. Measurement methods for non-target LC-HRMS (laboratory).

Analyte	Non-target organic compounds
Sample Matrix	Surface Water
Number of Field QC samples	One 946mL sample per site (allows for triplicate testing at 250 mL)
Sample Preparation Method	Solid phase extraction (Appendix B)
Analytical Method	Non-target LC-HRMS (Appendix C)
Instrument Method	Agilent Quadropole Time of Flight (QTOF) MS-only mode; ESI+ and ESI- (Appendix C)
Expected Range of Results	200-3000+ unique features; peak area 5000 to >10 million
Detection or Reporting Limit	Peak area >5000

Table 3. Measurement methods for targeted LC-MS/MS (laboratory).

Analyte	Storm water and ecotoxicologically-relevant organic contaminants
Sample Matrix	Water
Number of Field QC samples	3 field replicates (946mL) per site
Sample Preparation Method	Solid phase extraction (Appendix B)

Analytical Method	Targeted LC-MS/MS (Appendix D)
Instrument Method	Agilent Triple Quadrupole MRM mode; ESI+ and ESI- (Appendix D)
Expected Range of Results	40 targeted analytes (Appendix E)
Detection or Reporting Limit	MDL and concentrations of analytes determined from calibration curves and spikes

B6 Instrument/Equipment Testing, Inspection, and Maintenance

Instrument sensitivity on the LC/MS/MS is monitored by checking the signal to noise ratios of the lowest points of the calibration curve and calibration curve linearity. If either the lowest concentration calibration standard (generally 0.5 ppb or lower for most analytes) demonstrates a S/N ratio <10, or the linearity R² value of the calibration curve is <0.98, the instrument will be cleaned and maintained until method performance is restored.

B7 Instrument/Equipment Calibration and Frequency

This information can be found in section 2 of the SOP titled “LC-HRMS (Non-Target) Setup, Operation, and Data Analysis SOP” and “LC-MS/MS (Targeted) Setup, Operation, and Data Analysis SOP” (Appendices C and D) .

B8 Inspection/Acceptance of Supplies and Consumables

All laboratory supplies and consumables are received and inspected by the UWT at CUW lab manager, Melissa Gonzalez. Supplies are not used if they are visibly broken or damaged. All solvents and reagents will be HPLC grade (or equivalent) or higher. When necessary, supplies and consumables are solvent washed or baked in an industrial oven before use to avoid contaminating samples.

B9 Non-direct Measurements

Not applicable.

B10 Data Management

All field data relevant to sample collection mentioned in section B1 (Site location, date, time, etc.) will be collected on a Samsung Tablet using ArcGIS Survey123 software. This information will be sent to the NCWA system at the end of each work day and backed up to Dropbox. Data from each site will be visually checked by

field technician(s) the day of uploading, and field notes will be taken in a Rite in the Rain notebook at each site and compared to data uploaded from Survey123 weekly to ensure that errors did not occur.

All electronic data generated in the laboratory, including documents, analytical output, statistical analysis, reports, etc. will be stored on project computers at the CUW that are backed up by a commercial cloud-based system that maintains continuously updated copies of all materials. All electronic data generated during field collections, including Survey123 forms, Excel spreadsheets tracking samples and volunteer hours, maps, reports, etc. will be stored on computers and a tablet (in the case of Survey123 and mapping data) at the NCWA backed up to Dropbox. A Microsoft Excel-based electronic record of all sampling events, stored samples, and associated data will be maintained for the project, and will be stored on CUW project computers. Data entry errors will be detected by comparison of field records and electronic data records.

All final results from non-target analyses and chemical identification efforts will be entered into Microsoft Excel spreadsheets. The data may subsequently be reformatted for transfer into EPA's STORET or Ecology's EIM databases.

If required, the project manager will work with EPA and/or CUW staff to ensure that final results are formatted correctly for upload. The final data set for concentration data of 39 targeted LC-MS/MS analytes (Appendices D and E) from all field sampling campaigns would then be uploaded to necessary project databases.

Community participation data, including numbers of volunteer hours/activities and attendance numbers at events, will be kept in an Excel spreadsheet backed up to the NCWA's dropbox and shared in relevant reports to the EPA.

C1 Assessments and Response Actions

The quality control procedures that will help identify problems or issues associated with data collection and data analysis while the project is underway will include reviewing field notes prior to leaving each site, following the field and laboratory procedures outlined in Sections B2 and B3, following the QC procedures outlined in Sections A5 and B5, and day-of-sampling field crew meetings to review data outputs.

Because sampling events will be infrequent (approximately monthly for two six-month stints), day-of-sampling review of procedures prior to field work and debrief/download of Survey123 forms collected in the field will provide consistent internal oversight by the project manager. At the end of each sampling season (April 2023 and April 2024) NCWA staff will compare filed notes with Survey123 forms converted into spreadsheets.

C2 Reports to Management

Kelli Daffron will prepare annual reports in collaboration with Dr. Kolodziej and Melissa Gonzalez for the EPA and relevant project partners.

D1 Data Review, Verification, and Validation

Aforementioned quality assurance protocols, including redundant site photos, samples, field notes and reviews will be performed as first-lines of quality control for data collection in the field.

D2 Verification and Validation Methods

Data will be verified and validated by Center for Urban Waters staff. Chain-of-custody of data as outlined in Section B3 will include sample identification information and accompany samples from the field to the laboratory. Should issues arise in the way of sample collection or mailing, Ms. Daffron will work with associated field volunteers, review field notes, and collaborate with Mr. Klag on potential issues with ArcGIS software; mailing issues will be taken up with FedEx, with whom NCWA has an account. Sample receipt, processing, or analysis issues will be handled by Melissa Gonzalez or Dr. Kolodziej or other Center for Urban Waters staff. Data will be conveyed to partners and the public in raw Excel spreadsheets as well as in map form, both interactive and static.

D3 Reconciliation with User Requirements

The data collected in this project is being used to 1) provide a first-glimpse into chemicals of emerging concern (CECs), particularly those related to roadway runoff, in the lowest reaches of the Columbia River and its tributaries, 2) be shared with project partners and to be incorporated into outreach materials generated for public outreach, and 3) be incorporated into maps and help target projects relevant to preventing roadway runoff from entering streams unchecked.

Success in these arenas will be determined by 1) completion of the sampling and analysis, which will result in a report furnished by the CUW to the NCWA, and a final report to the EPA entailing the findings; 2) conducting all scheduled 15 community outreach activities with attendance numbers kept and contact information voluntarily given by interested parties to receive periodic NCWA reports/updates; 3) volunteer recruitment and tracking of hours; 4) receipt of finalized data from project partners at EPA, Oregon DEQ, LCEP, LEWI, Clatsop County, and the City of Astoria, as well as publication of data/reports on the NCWA website for public access; 5) a map created jointly by NCWA and Clatsop County GIS specialists to demonstrate data from this study in map form in conjunction with hydrology, roads, salmon presence, etc. used by the organizations to work towards mitigation projects; and 6) presentation of findings by CUW lab member(s) at a Nature Matters event in the spring of 2024.

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Appendices

- A. List of Parameters tested by Oregon DEQ
- B. River TALC SOP
- C. LC-HRMS (Non-Targeted) Setup, Operation, and Data Analysis SOP
- D. LC-MS/MS (Targeted) Setup, Operation, and Data Analysis SOP
- E. Table of organic contaminants
- F. Chain of Custody form

Appendix A: List of parameters tested by DEQ

Alkalinity, total

Ammonia

Biochemical oxygen demand, non-standard conditions

Organic carbon

Escherichia coli

Nitrate + Nitrite

Orthophosphate

Total solids

Total suspended solids

Conductivity

Dissolved oxygen (DO)

Dissolved oxygen saturation

pH

Temperature, water

Turbidity

Organic carbon

Appendix B: River TALC SOP

Available upon request.

Appendix C: LC-HRMS (Non-Targeted) Setup, Operation, and Data Analysis SOP

Available upon request.

Appendix D: LC-MS/MS (Targeted) Setup, Operation, and Data Analysis SOP

Available upon request.

Appendix E: List of Organic Contaminants

#	Target analyte	Linearity		Precision (%)				IQL	IDL	MQL	MDL
		Working range	R ²	Intra-day (n=3)		Inter-day (n=3)		(µg/L)	(µg/L)	(ng/L)	(ng/L)
				Con c. level 1 ^(a)	Con c. level 2 ^(b)	Con c. level 1 ^(a)	Con c. level 2 ^(b)				
Vehicle-related chemicals											
1	⁽⁺⁾ 1,3-Diphenylguanidine	0.1-100	0.9997	2	2	1	2	0.13	0.03	4.1	1.5
2	⁽⁺⁾ Hexa-(methoxymethyl)m elamine	0.1-100	0.9998	1	1	3	1	0.11	0.02	0.21	0.06
3	⁽⁺⁾ N-cyclohexyl-1.3-Benzothiazole-2-amine (NCBA)	0.05-100	0.9988	1	1	22	4	0.01	2.0×10 ⁻³	3.1	1.8
4	6PPD-quinone	0.025-50	.998					0.1	0.025	2.5	1.5-2.0
Benzothiazoles & Benzotriazole											
5	⁽⁺⁾ Benzotriazole	2-200	0.9995	9	7	1	19	2.9	0.59	2.0	0.61
6	⁽⁺⁾ 5-methyl-1-H-Benzotriazole	1-200	0.9996	10	7	7	15	0.21	0.04	0.14	0.04
7	⁽⁺⁾ 2-amino-Benzothiazole	1-100	0.9995	5	5	8	7	0.18	0.04	0.74	0.22
8	^(*) 2-hydroxy-Benzothiazole	1-100	0.9996	10	4	7	9	3.8	0.77	17	5.2
9	⁽⁺⁾ 2-(4-morpholinyl)Benzo thiazole	0.2-100	0.9986	5	2	3	4	0.30	0.06	0.90	0.27
Pesticides											
10	⁽⁺⁾ Clothianidin	1-100	0.9994	7	4	9	16	0.21	0.04	0.29	0.09

11	(*)Imidacloprid	0.5-100	0.999 0	3	2	8	17	0.10	0.02	0.16	0.05
12	(*)Thiamethoxam	5-500	0.999 8	3	8	11	7	0.71	0.14	3.5	1.06
13	(*)Fipronil	0.2-20	0.999 1	1	1	1	7	0.02	3.8× 10 ⁻³	0.01	3.8× 10 ⁻³
14	(*)Carbendazim	0.05-100	0.999 5	0.3	1	2	0.7	0.01	1.8× 10 ⁻³	2.6	1.3
15	(*)Iprodione	5-500	0.999 6	19	6	16	11	12	2.3	240	71
16	(*)Pentachlorophenol	2-500	0.998 3	5	1	4	15	1.8	0.36	2.2	0.65
17	(*)Diazinon	0.2-100	0.999 8	2	1	13	1	0.07	0.01	0.49	0.15
18	(*)Diuron	0.5-100	0.999 8	4	1	5	4	0.17	0.03	0.17	0.05
19	(*)Mecoprop	1-100	0.999 4	27	6	15	17	0.20	0.04	0.24	0.07
20	(*)Prometon	0.02-100	0.999 9	2	1	5	4	0.01	1.6× 10 ⁻³	4.3	1.5
21	(*)4-Nitrophenol	5-500	0.999 5	5	2	17	18	12	3.7	16	15
22	(*)Caffeine	0.5-100	0.999 5	12	3	6	3	0.56	0.11	1.1	0.34
23	(*)Cetirizine	0.05-100	0.999 7	2	1	4	3	0.01	1.5× 10 ⁻³	0.04	0.01
24	(*)Cotinine	0.1-100	0.999 9	4	3	4	10	0.03	0.01	2.6	1.2
25	(*)DEET	0.1-100	0.999 8	2	1	4	3	0.11	0.02	3.3	2.6
26	(*)Diclofenac	5-100	0.996 9	3	2	25	17	0.30	0.06	2.9	0.87
27	(*)Ibuprofen	20-2000	0.999 9	13	8	9	4	3.8	0.77	11	3.2

28	(+)Metformin	2-100	0.999 5	6	1	5	5	0.08	0.02	0.39	0.12
29	(*)Triclosan	2-200	0.999 8	3	1	2	9	1.1	0.22	1.2	0.37
Industrial/Commercial chemicals											
30	(+)1,3-Dicyclohexylurea	0.05-100	0.999 1	2	2	1	2	0.14	0.03	4.2	1.5
31	(*)Bisphenol A	20-2000	0.999 5	18	1	10	7	1.3	0.26	2.5	0.75
32	(*)Caprolactam	2-200	0.999 7	1	2	7	8	1.2	0.23	10	8.3
33	(*)4-Nonylphenol	20-2000	0.998 0	9	5	14	8	0.80	0.16	40	12
34	(*)4-tert-Octylphenol	10-1000	0.998 8	9	3	11	4	1.0	0.21	53	16
35	(+)SDPA-diAMS	1-100	0.999 7	1	0.5	3	7	0.02	4.0× 10 ⁻³	0.12	0.04
36	(+)SDPA-C4C8	1-100	0.999 6	3	1	7	3	0.04	0.01	0.15	0.04
37	(+)SDPA-C8C8	1-100	0.999 4	3	1	35	2	0.23	0.05	0.38	0.11
38	(+)SDPA-C9C9	1-100	0.998 5	13	2	8	6	0.66	0.13	0.75	0.22
39	(+)BTZ & UV-234	1-100	0.999 6	2	1	1	6	0.05	0.01	0.09	0.03
40	(+)BTZ & UV-326	1-100	0.999 1	25	5	12	10	0.02	4.0× 10 ⁻³	0.12	0.04

(a)Concentration level 1 = 1 µg/L and 10 µg/L for more and less sensitive analytes, respectively

(b)Concentration level 2 = 10 µg/L and 100 µg/L for more and less sensitive analytes, respectively

(+)More sensitive method analytes

(*)Less sensitive method analytes

Method performance, including linear working range, correlation coefficient (R^2), intra-day and inter-day precision (% RSD), instrumental and method limits of quantification (IQLs, MQLs) and detection (IDLs, MDLs) of the method analytes. Note that MDL and MQL values are based on SPE extraction of 1L samples. See also Appendix D SOP and Hou *et al.* 2019 [14].

Pg of

29