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PROJECT TITLE: Island County Marine Resource Committee

TASK NUMBER: 2.2 – Phytoremediation

DELIVERABLE: 2.2 – QAPP for each monitoring project

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QUALITY ASSURANCE PROJECT PLAN: Island County Marine Resources Committee Phytoremediation Program

Prepared by: Joe Hillers, program lead for Island County Marine Resource Committee

Prepared for:

Northwest Straits Commission & Washington Department of Ecology

March 2015

Based on EPA guidance CIO 2106-G-05 (2012)

Publication Information

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Each study conducted for the EPA or Ecology must have an approved Quality Assurance Project Plan (QAPP) describing the objectives of the study and the procedures to be followed to achieve those objectives. This generic QAPP serves as an umbrella under which multiple data collection, production and use activities will be conducted over an extended period of time at several different project sites. The plan and final reports for this program will be available on Island County Marine Resources Committee's website at www.islandcountymrc.org. Neither document necessarily reflects the views and policies of the EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Data for this project will be available on the Island County Marine Resources Committee's website at www.islandcountymrc.org

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Quality Assurance Project Plan
Island County Marine Resources Committee
Phytoremediation Program

March 2015

Approved by

Signature: _____ Date: _____

Sasha Horst, Project Officer, Washington State Department of Ecology

Signature: _____ Date: _____

Frances Wood, Chair, Island County Marine Resources Committee

Signature: _____ Date: _____

Lenny Corin, Island County MRC Representative, Northwest Straits Commission

Signature: _____ Date: _____

Keith Higman, Health Services Director, Island County Public Health

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Acronyms

IC DNR – Island County Department of Natural Resources

MRC – Island Marine Resources Committee

MRC PM – Marine Resources Committee Project Manager

NOAA – National Oceanic and Atmospheric Administration

PM – Project Manager

QAPP – Quality Assurance Project Plan

WADNR – Washington State Department of Natural Resources

WDFW – Washington Department of Fish and Wildlife

Project Management

Project Organization

Position/Role	Who is Responsible	As of 10/1/2014
Program Manager	MRC PM	Anna Toledo
Project Manager	MRC Liaison	Joe Hillers
Lead Scientist	MRC PM or designee	Joe Hillers
Researchers	PM and designees	Joe Hillers, PhD Mahmoud Abdul-Monem, PhD Jim Somers, DDS Lou Licht, PhD
Data Manager	PM or designee	Joe Hillers
Report Producer	PM or designee	Joe Hillers

Project Schedule

Date	Event
Year Round	Trees watered via automatic irrigation system
Year Round	Sampling occurs at least once per season when trees have leaves and once per season when trees are without leaves, dependent upon researcher availability

Project Background

Phytoremediation is an emerging technology that uses various plants to degrade, extract, contain, or immobilize contaminants from soil and water. This technology has been receiving attention lately as an innovative, cost-effective alternative to the more established treatment methods used at hazardous waste sites. The MRC is interested in the utilization of this technology for use in the treatment of other sources of water contamination, including stormwater and treatment plant effluent discharge. The MRC is interested in investigating ways to prevent or mitigate contamination that ends up in our nearshore environments.

The Island MRC began a phytoremediation project in Ebey's Prairie in 2010. The Ebey's bioswale project was in partnership with Ecolotree who provided the trees and expertise on tree management, the National Park Service who provided the location, the City of Coupeville provided the construction, and Island County Public Health whom was contracted to conduct the water sampling and arrange the sampling at this site. This project concluded in the fall of 2013.

In June 2011, a phytoremediation research site was developed at the Coupeville Treatment Plant to test the effects of this technology on treatment plant effluent. The study design was developed by the Project Manager to assess the best soil medium and tree combination.

Project/Task Descriptions

The objectives of the phytoremediation project are:

- To assess the effect of filtering treatment plant effluent through soil and roots on measures of water quality, including metal content.
- To determine if there is a seasonal effect on water quality measures (i.e. when the trees are in leaf or not).

These objectives will be achieved by measuring water quality of treatment plant effluent as it enters and leaves the different combinations of phytoboxes. Phytoboxes are boxes containing a particular combination of tree species and growing medium.

Willow (*Salix sp.)* and poplar (*Populus sp.)* tree shoots were used due to their rooting characteristics. They root along their entire shoot length that is underground. This enabled the trees to develop a more extensive root system along the entire buried shoot length as opposed to only rooting at the end of the shoot.

Data Quality Objectives

This QAPP describes where, when, and how various observations and measurements will be made. The quality objectives for the field methods herein will be evaluated using indicators of precision, accuracy/bias, representativeness, comparability, completeness, and sensitivity (as applicable).

CHEMetrics test kits use a color-matching measurement technique. The Accuracy is +/- 1 color standard increment. The increments vary depending on the kit and the concentration of the sample. Generally the higher the concentration of the parameter, the less precise the measurement.

Test Equipment	**Parameter**	**Measurement Range**	**Accuracy**	**Precision**
CHEMetrics No. 6905	Nitrate	0-3 ppm	+/- 0.25-0.5 ppm	0.25-0.5 ppm
CHEMetrics No. 8500	Phosphate	0-1 & 1-10 ppm	+/- 0.1-2.0 ppm	0.1- 1 ppm
CHEMetrics No. 1705	Hardness	50-500 ppm	+/- 5-150 ppm	5-150 ppm
Thermo Orion 420A+	pH	-2.000-19.999	+/- 0.005	0.001/0.01/0.1
YSI Model 85	Conductivity	0-4999µS/cm	+/- .5% FS	1.0 µS/cm

Metals will be sent to an accredited, State-certified laboratory for analyses. The laboratory has its own quality assurance standards for the analysis of samples. The laboratory is accredited for all routine parameters and utilizes standard methodology for sample analysis.

Representativeness: The results have a high degree of representativeness as 100% of the population – all 15 phytoboxes – will be sampled concurrently.

Comparability: Data comparability will be ensured through the application of consistent sampling procedures, analytical methods and detection limits.

Completeness: 100% of the phytoboxes will be sampled at each sampling event. Samples will be taken during the trees' senescent (dormant) and leafy growth periods to assess seasonal variation in outputs.

Special Training

The project manager holds a PhD in Agricultural Sciences with minor in statistics (35 years of experimental research at WSU with participation on 50 graduate committees). Fellow researchers also hold Post Graduate degrees and have experiences in research design, chemistry, ecology and civil and environmental engineering.

Documentation and Records Requirements

All documentation for the testkits and recorded data will be maintained by the Data Manager. The manuals for the equipment and calibration records will be maintained by the Coupeville Treatment Plant, who owns the equipment.

The written data and electronic files will be stored with the Data Manager. All electronic records will be backed up and stored in a separate location from the originals.

Data Acquisition

Sample collection

Fifteen boxes will be built out of 3" Styrofoam (bottom and sides) and have internal dimensions of 12" by 12" and will be 34" tall. A 0.75" hole will be bored into the side of each box at the bottom of the internal opening in the boxes. A 30" piece of 0.75 OD plastic tubing will be installed in the hole across the bottom of the box opening. Holes will be drilled in this tubing to allow the water to drain from the boxes. The tubing inside the box will be covered with cloth fabric to prevent the roots from entering the drain tubes.

Twelve of the boxes will be planted with 4 shoots of hybrid poplar trees and 2 shoots of willow trees, each approximately 40" in length. Each shoot will be planted the entire depth of the boxes resulting in about 32" below the surface of the growing medium. Boxes will be planted with 6 shoots to accelerate the growth of a dense mass of tree roots which assist with filtration. Trees that do not survive will be replaced if any of the following conditions apply:

1. Fewer than 4 trees survived per box
2. Both species are no longer represented in each box
3. There is an obvious bias to survival due to growing medium

Three boxes will be filled with sandy soil common to the agricultural land in central Whidbey Island.

Three boxes will be filled with sandy soil with 2 quarts of compost added.

Three boxes will be filled with perlite, an inorganic volcanic rock.

Three boxes will be filled with soil with higher clay content from central Whidbey Island, mixed with perlite (50/50) to insure perk of the effluent water. The higher clay soils will be acquired from an agricultural area in central Whidbey where standing water is present after rain.

Three boxes will be filled with only perlite and without trees to give a measurement of filtration only on contaminant removal.

Boxes will be watered with an automatic irrigation system 1 to 4 times per day depending on season and ambient temperature. Boxes will be watered with approximately 600 ml of water over 1-3 minutes per watering event.

Samples will be collected in clean, empty sample bottles. A sample will be taken from the inlet pipe and from each box, resulting in 16 samples at each event. Sample bottles will be labeled immediately after each sample is collected.

Samples will be hand carried immediately to the Treatment Plant laboratory for testing.

Analysis

Nitrate is tested with CHEMetrics kit No. 6905 which uses the Zinc Reduction Method:

> **The Zinc Reduction Method**
> **References: ASTM D 3867-09, Nitrate-Nitrite in Water, Test Method B. APHA Standard Methods, 21st ed., Method 4500-NO_3^- E (2005). USEPA Methods for Chemical Analysis of Water and Wastes, Method 353.3 (1983). Nelson, J.L., Kurtz, L.T., and R.H. Bray, Rapid Determination of Nitrates and Nitrites. Anal. Chem., V26, p. 1081-1082, (1954).** Nitrate is reduced to nitrite using zinc as the reducing agent. The resulting nitrite concentration is then determined colorimetrically. This method is applicable to industrial wastewaters, drinking, and surface waters. These test kits can also be used for the analysis of seawater. This method will measure nitrate in the presence of low levels of nitrite (by difference). Results are expressed as ppm (mg/L) NO_3-N. (http://www.chemetrics.com/Nitrate)

Phosphate is tested with CHEMetrics kit No. 8510 which uses the Stannous Chloride Method:

> **The Stannous Chloride Method**
> **References: APHA Standard Methods, 21st ed., Method 4500-P D (2005).**
> Test kits employing this chemistry utilize a stannous chloride reduction. Phosphate reacts with ammonium molybdate and is then reduced by stannous chloride to form a blue complex. Results are expressed as ppm (mg/L) PO_4. (http://www.chemetrics.com/Phosphate%2C+ortho)

Hardness is tested with CHEMetrics kit No. 1705 which uses the EGTA Method:

> **Hardness (calcium)**
> **The EGTA Method**
>
> **Reference: West, T. S., DSC, Ph.D., Complexometry with EDTA and Related Reagents, 3rd. ed., pp. 46, 164 (1969).**
> The EGTA method is specific for calcium hardness. The EGTA titrant in alkaline solution is employed with a zincon indicator. Results are expressed as ppm (mg/L) $CaCO_3$. (http://www.chemetrics.com/Hardness)

Copper, lead and zinc will be tested by an accredited outside lab using methods 200.7, 6010B, 200.8 and 6020.

Quality Control Requirements

All samples will be collected with, at a minimum, two people present, both of whom will check the labeling of the sample bottles to ensure accuracy.

All samples will be measured for one parameter before measuring the second parameter in order to develop an efficient workflow and not allow kit contents to be comingled. The instructions for each kit will be reviewed at the beginning of each sampling day. The color matching determination will be agreed upon by the researchers present to avoid one person's bias from affecting the results.

Conductivity and pH will be measured with equipment that is calibrated according to the Treatment Plants schedule.

Metals will be sent to an accredited, State-certified laboratory for analyses. The laboratory has its own quality assurance standards for the analysis of samples. The laboratory is accredited for all routine parameters and utilizes standard methodology for sample analysis.

Instrument/Equipment Testing, Inspection and Maintenance Requirements

Conductivity and pH will be measured with equipment that is calibrated according to the Treatment Plants schedule. The Coupeville Treatment plant is a Washington State certified laboratory, therefore the calibration of equipment follows the WA Dept. of Ecology's approved methodology.

Metals will be measured with equipment that is calibrated according to the laboratory's schedule. The laboratory is a Washington State certified laboratory; therefore the calibration of equipment follows the WA Dept. of Ecology's approved methodology.

Data Acquisition Requirements

Nitrate, Phosphorus and Hardness data will be recorded by the Data Manager on the record sheet as the Researchers declare the component measurement based on a color match on the CHEMetric-supplied, component-specific comparator.

Conductivity and pH will be recorded by the Data Manager on the record sheet.

Metals data will be received by the Data Manager in print-out form from the laboratory.

Data Management

All hand-recorded data will be entered into an electronic spreadsheet by the Data Manager. Print out data from the laboratory will be entered into an electronic spreadsheet by the Data Manager.

The data will be electronically backed up and stored in a separate location after each sampling event by the Data Manager.

Assessments

Assessments and Response Actions

The Project Manager will be present at each sampling event to ensure protocols are being followed. Any discrepancies between actions and protocols will be corrected when discovered. If the discrepancy is deemed to have had the potential to affect the results, the procedural step that experienced the discrepancy shall be repeated according to protocol.

Any discrepancies from the protocol that are not able to be corrected will be recorded by the Project Manager and included in the final report, along with an explanation of potential effects of the discrepancy on the results or conclusions.

Reports to Management

Bimonthly progress reports are verbally given to the MRC and the Program Manager during MRC meetings. The Report Producer will write the final report. The Program Manager will distribute it to the Island County Marine Resources Committee, the Northwest Straits Commission, and other interested parties.

Review, Evaluation of Usability, and Reporting Requirements

Data Review, Validation, Verification and Methods

Data is verified as it is recorded by the Data Manager who will repeat the number recorded back to the researcher measuring.

The hand written data forms are reviewed for completeness prior to the disposal of samples at each sampling event.

Data received from the laboratory will have been verified under their protocols. The laboratory uses standard methodology for sample analysis. The laboratory QC methods include sample spiking, duplicating, etc. and also has its own quality assurance standards for analysis of samples which include verifying the data prior to reporting results.

One hundred percent of the data entry will be reviewed for data entry errors. Any errors will be corrected upon discovery. All data will be reviewed again. This procedure will be repeated until no errors are found.

Reconciliation with Data Quality Objectives

Data quality objectives will be assumed to have been met if protocols have been followed. Any discrepancies from protocols will be recorded and potential effects declared in the final report. If discrepancies are repeated, corrective action will be taken. This may include, but is not limited to the methodology and protocols being reviewed and potentially revised, retraining of researchers, using different equipment or laboratory.