DEPARTMENT OF ECOLOGY
State of Washington

Quality Assurance Project Plan

Monitoring Persistent, Bioaccumulative, and Toxic Chemicals (PBTs) Using Age-Dated Lake Sediment Cores: 2023-2027

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The final QAPP is available on Ecology's website at
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Quality Assurance Project Plan

Monitoring Persistent, Bioaccumulative, and Toxic Chemicals (PBTs) Using Age-Dated Lake Sediment Cores, 2023-2027

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June 2023

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EAP: Environmental Assessment Program
SCS: Statewide Coordination Section

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2.0 Abstract

The Washington State Department of Ecology (Ecology) has been monitoring persistent, bioaccumulative, and toxic chemicals (PBTs) using age-dated lake sediment cores since 2006. Mercury was the target analyte for the first several years of the program, then polycyclic aromatic hydrocarbons (PAHs), and finally a rotating suite of analytes selected from the state's PBT List. Since 2012, the rotating suite of analytes, or target PBT list, has included PAHs, per- and polyfluoroalkyl substances (PFAS), hexabromocyclododecane (HBCD), chlorinated paraffins (CPs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs).

This Quality Assurance Project Plan (QAPP) outlines the continued monitoring of PBTs using sediment cores for sampling during 2023 through 2027. The PBT Monitoring Program collects a single sediment core from three lakes per year for analysis of a rotating PBT analyte. Selected sediment core horizons are analyzed for the target PBT analyte as well as a suite of parameters to age-date the sediment layers. Contaminant profiles are then reconstructed to characterize trends in concentrations and fluxes of the PBT.

The target analytes for the next five years of sampling are: PBDEs (2023), PCBs (2024), PAHs and mercury (2025), PFAS (2026), and HBCD (2027). Chlorinated paraffins will no longer be analyzed due to difficulties with the method. Based on criteria discussed in this QAPP, three different waterbodies have been selected for each sampling year. Study locations represent a wide range in PBT contamination potential, pathways of interest, and physical characteristics.

The goal of this 2023-2027 study is to characterize temporal trends of PBT deposition in sediments from lakes throughout Washington State through age-dated sediment cores. Ecology will use the information to fill data gaps on whether PBTs from the state PBT List are increasing or decreasing in freshwater lakes of Washington.

3.0 Background

3.1 Introduction and problem statement

In 2000, the Washington State Department of Ecology (Ecology) published a strategy to address persistent, bioaccumulative, and toxic chemicals (PBTs) through proposed actions such as chemical action plans (CAPs), environmental monitoring, and tracking reductions (Gallagher, 2000). The strategy was in response to growing concern about environmental exposures to PBTs as well as serious risks to wildlife and human health. PBTs remain in the environment for a very long time, build up in the food chain, and are toxic to organisms. In addition, many PBTs are capable of long-range transport (moving long distances from their sources), making them challenging to control once released.

In 2006, the PBT Rule (WAC 173-333) listed 24 chemicals or chemical groups, and two metals of concern, that met criteria for PBTs and laid out a plan to address them through CAPs. The goal of the rule was to reduce and phase out PBT uses, releases, and exposures in Washington state through recommendations of multi-media and cross-program measures. To date, Ecology and the Washington State Department of Health (DOH) have developed CAPs for mercury (Peele, 2003), polybrominated diphenyl ethers (PBDEs) (Ecology et al., 2006), lead (Davies et al., 2009), polycyclic aromatic hydrocarbons (PAHs) (Davies et al., 2012), polychlorinated biphenyls (PCBs) (Davies et al., 2015), and per- and polyfluoroalkyl substances (PFAS) (Ecology and DOH, 2022).

To carry out environmental monitoring of PBTs, as recommended in the PBT Strategy, Ecology received funding from the legislature for a PBT Monitoring Program. One of the first studies that the PBT Monitoring Program developed was a long-term study to characterize temporal trends of mercury in Washington state through age-dated lake sediment cores (Coots, 2006). This long-term monitoring study drew on the literature review by Yake (2001) of using sediment cores to reconstruct PBT trends in the environment in support of the PBT chemical initiative. The original intent of the monitoring study, as it began in 2006, was to support the mercury CAP. In 2008, PAHs were added to the target analyte list (Meredith and Furl, 2008), and in 2012, the project plan evolved to include a rotating list of PBTs from the PBT List (Mathieu, 2012). Figure 1 shows the target PBT analytes by year from 2006 through 2021.

Ecology's PBT Monitoring Program collects a single sediment core from three lakes per year as part of the long-term monitoring study. Selected sediment core horizons are analyzed for the target PBT as well as a suite of parameters to date the sediment layers. PBT contaminant profiles are then reconstructed to characterize trends in concentrations and fluxes of the PBT analyte. The original Quality Assurance Project Plan (QAPP) was written for this study in 2006 (Coots, 2006), and an updated QAPP was written in 2016 (Mathieu, 2016). This document will serve as an updated and current QAPP for the long-term monitoring study. The current QAPP will provide an outline for the sampling years 2023 through 2027.

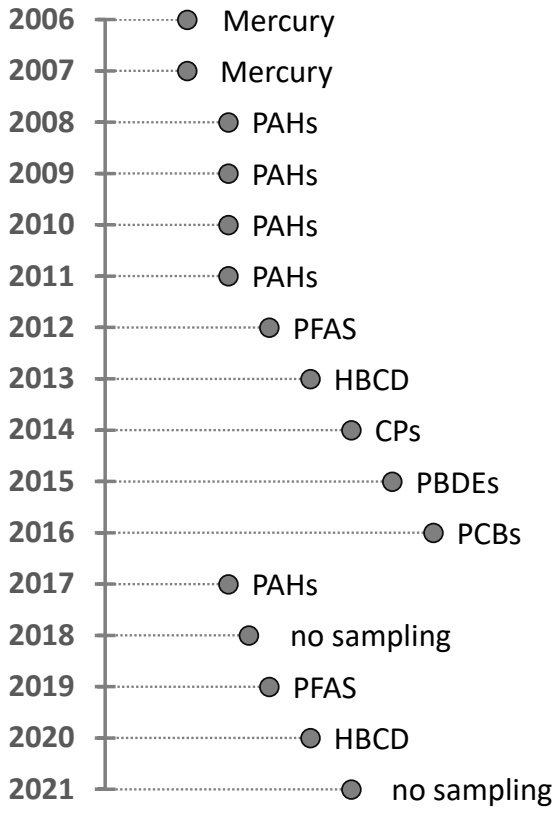

Figure 1. Target PBT analytes for the long-term monitoring study, 2006-2021.

Target PBTs are displayed at varying horizontal distances to help illustrate when the parameter rotation starts over.

3.2 Study area and surroundings

This long-term monitoring project is a statewide study. Three waterbodies are selected each year for collection of sediment cores based on many criteria. The site selection process starts with all accessible natural lakes of the state. Man-made lakes and reservoirs are generally not included. The project manager then takes the following criteria into account to select locations to be sampled. This is a targeted design study, with the intention of leveraging the high cost of sediment core analysis with lakes of interest based on the site selection criteria.

The primary consideration for annual site selection is proximity to known or potential PBT sources. Depending on the target PBT analyte for the sampling year, sites are selected in an attempt to reflect a variety of sources. Generally, two sites are selected that are likely to contain pathways or sources of the target PBT (e.g., stormwater, regional deposition, or traffic) to the waterbody. At least one of the sites chosen each year is located far from PBT sources and represents a waterbody where atmospheric deposition is the predominant source. Other criteria for lake selection are:

- Achieving statewide coverage of lakes as they are distributed across the state.
- Suitable site access, including boat ramps and permissions.

- Considering lake depositional patterns and potential for undisturbed sediments. Lakes with dredging, physical disturbance, or dumping are not considered for site selection.
- Capturing a range of physical features of watersheds and lakes.
- Selecting waterbodies where results from other studies are available, and where data gaps could be filled.
- Collaborating with other programs and agencies.

Figure 2 presents target sites for the 2023 – 2027 sampling. Sites were selected in an attempt to provide broad coverage of the state, keeping in mind the lack of lakes along the southern portion of the state.

Figure 2. Map of larger study area.

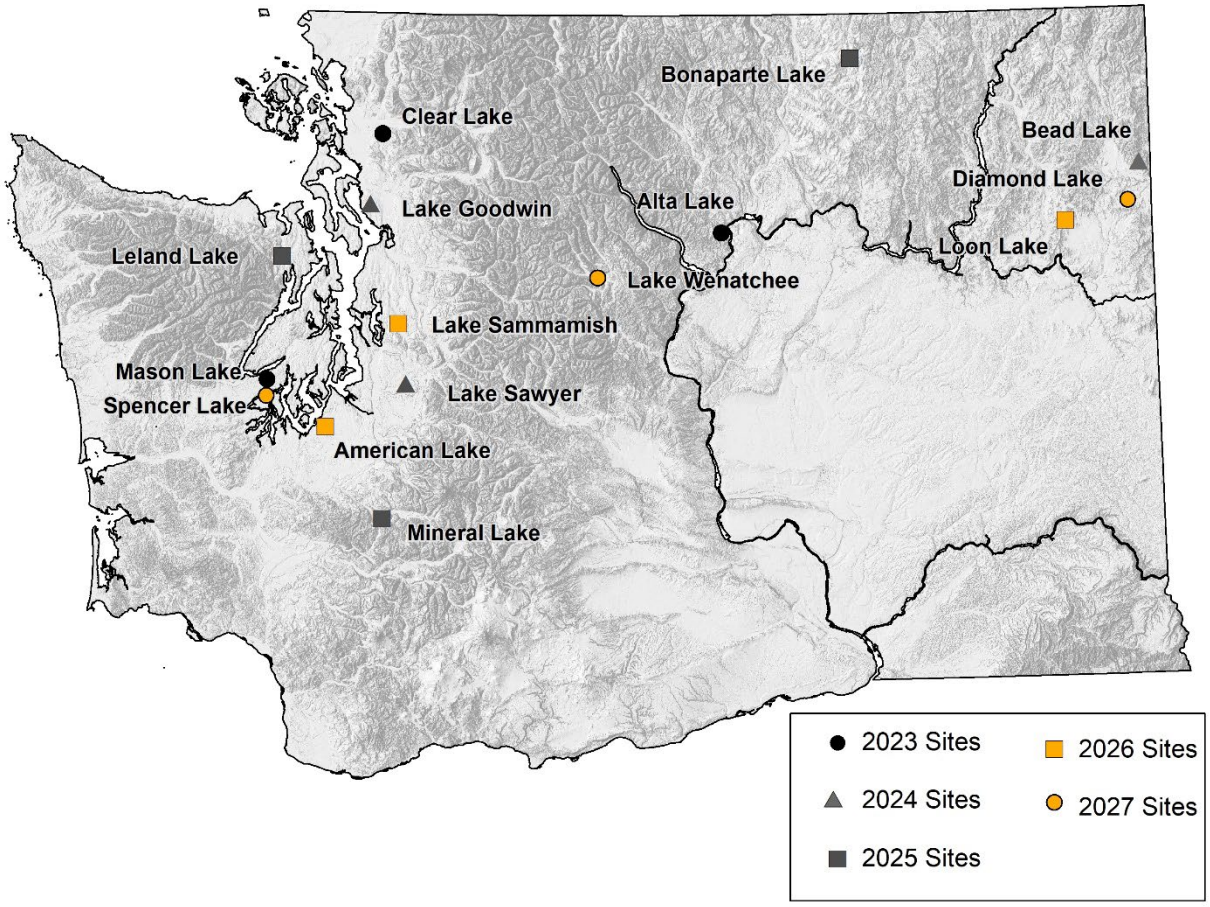

Table 1 describes relevant physical characteristics of the sites. A table with physical descriptions of alternate sites to be used when coring attempts are unsuccessful at a waterbody can be found in Appendix A. The sites selected are all natural lakes and represent a range of physical factors. Sites include lakes at low elevation and high elevation, lakes with large and small watershed areas, and lakes with a broad range of watershed area to lake surface area ratios (WA:LA). The WA:LA ratio provides an indicator of potential sedimentation rates, with larger ratios correlating with higher sedimentation rates (USGS, 2004). The site selection process attempted to capture

lakes across a range of dominant contaminant delivery types. Small lakes with smaller WA:LA ratios may indicate direct atmospheric fallout of contaminants as the primary contaminant driver, whereas larger WA:LA ratios mean that the lake typically receives more of the contaminant load from fluvial transport (i.e., carried by rivers and tributaries) (USGS, 2004).

Table 1. Study locations for the 2023 – 2027 sampling years

Sampling Year	Target Analyte	Waterbody	Elevation (ft)	Max Depth (ft)	Mean Depth (ft)	Lake Area (ac)	Watershed Area (ac)	WA:LA
2023	PBDEs	Alta Lake	1163	79	39	180	3206	18
2023	PBDEs	Clear Lake	30	44	23	200	1536	8
2023	PBDEs	Mason Lake	194	90	48	100	13440	134
2024	PCBs	Bead Lake	2800	170	n/a	721	6000	8
2024	PCBs	Lake Goodwin	324	50	23	560	3315	6
2024	PCBs	Lake Sawyer	512	58	25	310	8320	27
2025	PAHs, Hg	Bonaparte Lake	3556	110	33	151	4467	30
2025	PAHs, Hg	Leland Lake	190	20	13	110	3648	33
2025	PAHs, Hg	Mineral Lake	1450	38	26	280	1402	5
2026	PFAS	American Lake	235	90	53	1100	16256	15
2026	PFAS	Loon Lake	2381	100	46	1100	9024	8
2026	PFAS	Lake Sammamish	30	105	58	4900	62720	13
2027	HBCD	Diamond Lake	2340	58	27	800	11136	14
2027	HBCD	Spencer Lake	170	36	22	230	1075	5
2027	HBCD	Lake Wenatchee	1868	240	150	2500	174720	70

WA:LA = watershed area to lake area ratio.
See Glossary and Abbreviations in Appendix C for the full spelling of target analytes.

3.2.1 History of study area

Table 2 describes primary watershed land uses of all sites selected for this study, as well as a qualitative ranking of contamination potential for the target PBT analyte of that sampling year. The target PBTs for this study can enter lakes through several environmental pathways. Atmospheric deposition is likely the most important pathway for the target PBTs, as they can be deposited directly onto the lake surface, as well as onto watershed surfaces and ultimately enter the lake via surface water runoff. Other potential sources and pathways include stormwater inputs to the lakes, groundwater, agricultural runoff, septic systems, and combined sewer overflows. Potential sources specific to the PBT and waterbody of each sampling year will be discussed in annual ArcGIS StoryMaps (StoryMaps) and the final report.

Table 2. Land use and qualitative contamination potential of study locations

Waterbody	Land use/type	Target analyte	Contamination potential*	Primary pathways of interest
Alta Lake	forested, undeveloped barren	PBDEs	low	atmospheric deposition
Clear Lake	forested, residential, agriculture	PBDEs	medium	atmospheric deposition, runoff
Mason Lake	forested, residential	PBDEs	medium	atmospheric deposition, runoff
Bead Lake	forested, undeveloped barren	PCBs	low	atmospheric deposition
Lake Goodwin	residential, forested	PCBs	medium	runoff, atmospheric deposition
Lake Sawyer	residential, suburban, forested	PCBs	medium	runoff, atmospheric deposition
Bonaparte Lake	forested, undeveloped barren	PAHs, Hg	low	atmospheric deposition
Leland Lake	forested, residential	PAHs, Hg	medium	atmospheric deposition
Mineral Lake	forested	PAHs, Hg	low	atmospheric deposition
American Lake	urban/residential, military	PFAS	high	runoff, stormwater, atmospheric deposition
Loon Lake	forested, residential, highway	PFAS	low	atmospheric deposition, runoff
Lake Sammamish	urban/residential, forested	PFAS	medium	runoff, stormwater, atmospheric deposition
Diamond Lake	forested, agriculture, residential	HBCD	low	atmospheric deposition, runoff
Spencer Lake	forested, residential	HBCD	medium	atmospheric deposition, runoff
Lake Wenatchee	forested	HBCD	low	atmospheric deposition

* Contamination potential is a qualitative estimate made by the author based on surrounding land use.
Analyte abbreviations are spelled out in Appendix C.

3.2.2 Summary of previous studies and existing data

Ecology's PBT Monitoring Program has been collecting sediment cores for analysis of PBTs since 2006. Previous sampling results are stored in Ecology's EIM database[1] and summarized in Tables 3, 4, and 5.

Mercury

The program analyzed mercury in sediment cores from 2006 through 2015 (Table 3). In general, mercury concentrations in sediments have been declining since the 1990s. This has been particularly true for lakes in urban areas, near point sources that ceased in the 1980s-1990s, and lakes impacted by mining (e.g., Wannacut Lake) and wastewater treatment plant effluent (e.g., West Medical Lake). Lakes with increases of, or no change in, mercury concentrations over the past two decades were generally those in rural forested watersheds where the leading source of

[1] For EIM data retrieval visit:
https://apps.ecology.wa.gov/eim/search/MonitoringProgramDefault.aspx?StudyMonitoringProgramUserId=PBT&StudyMonitoringProgramUserIdSearchType=Equals

mercury is likely from wet deposition of the global pool and sediment-bound mercury has been mobilized by landscape disturbances in recent years (e.g., logging, development).

Table 3. Previous results of mercury in sediment cores

Sampling Year	Waterbody	Date of surface layer (year)	Hg surface conc. (ug/kg)	Peak Hg conc. (year)	Peak Hg conc. (ug/kg)	Peak Hg flux. (year)	Peak Hg flux ($ug/m^2/yr$)	Ref.*
2006	Ozette	2005	170	1997	271	1997	261	(1)
2006	Sammamish	2006	150	1934	409	1934	116	(1)
2006	St. Clair	2006	370	2006	370	1975	151	(1)
2007	Loon	2005	82	1975	93	1995	8.6	(2)
2007	Wannacut	2004	56	1950	1580	1950	274	(2)
2008	Lacamas	2007	100	1958	139	1975	103	(3)
2008	Offutt	2006	182	1998	208	1998	122	(3)
2008	Washington	2007	160	1957	411	1957	213	(3)
2009	American	2008	60.7	1902	588	1969	121	(4)
2009	Black	2006	216	1996	389	1969	22	(4)
2009	Upper Twin	2008	39.6	< 1900	46	1969	27	(4)
2010	Wenatchee	2007	85.5	1999	103	1999	58	(5)
2011	Angle	2008	1160	1970	1440	1999	373	(6)
2011	Samish	2010	176	1944	213	2005	131	(6)
2012	Deer	2009	143	2005	150	1950	57	(7)
2012	Stevens	2010	261	1965	685	1965	146	(7)
2012	West Medical	2010	112	< 1900	967	1963	1263	(7)
2013	Cavanaugh	2008	519	1977	882	2008	119	(8)
2013	Kitsap	2012	182	2002	207	2006	105	(8)
2013	Sawyer	2011	231	1985	352	1985	102	(8)
2014	Bead	2008	69	1994	87.9	1949	9.4	(9)
2014	Goodwin	2007	199	2007	199	2007	95	(9)
2014	Mason	2013	135	1991 & 2010	142	2013	48	(9)
2015	Meridian	2013	118	1956	663	1956	95	(10)
2015	Whatcom	2013	147	1970	240	1970	66	(10)
2015	Williams	2010	108	1990	126	1990	13	(10)

* 1 = Furl (2007); 2 = Furl (2008); 3 = Furl et al. (2009); 4 = Furl and Roberts (2010); 5 = Furl and Roberts (2011); 6 = Mathieu and Friese (2012); 7 = Mathieu (2013); 8 = Mathieu and McCall (2014); 9 = Mathieu and McCall (2015); 10 = Mathieu and McCall (2016)

Polycyclic aromatic hydrocarbons (PAHs)

PAHs were analyzed in sediment cores between 2008 and 2011, and then again in 2017. Table 4 summarizes total (T-) PAH results in the cores. PAHs have mostly decreased or displayed no change in sediments deposited after major pollution controls began in the 1970s and 1980s. T-PAH concentrations peaked between the 1950s and 1990s in most of the lakes. Sites with the highest peak T-PAH concentrations saw decreases between the 1970s and the top of the core (most recent sample). The exception to this was Angle Lake in King County where

concentrations increased in recent decades. The other lakes exhibited no consistent temporal pattern in T-PAH concentrations or fluxes over the last few decades.

PAH ratio indicators (e.g., low molecular weight to high molecular weight ratios) examined in previous reports suggest that recent PAH sources can be allocated to combustion sources, from the burning of wood for heat and/or vehicle exhaust (Mathieu, 2020). Wood burning appears to be important to areas outside of major traffic sources, and petroleum combustion has been attributed to high PAH loads in lakes near major highways (e.g., Angle Lake near Interstate-5) (Mathieu and Friese, 2012).

Table 4. Previous results of T-PAHs in sediment cores

Sampling Year	Waterbody	Date of surface layer (year)	surface conc. (ug/kg)	Peak conc. (year)	Peak conc. (ug/kg)	Peak flux. (year)	Peak flux ($ug/m^2/yr$)	Ref.
2008	Washington	2007	638	1990	1117	1990	887	(1)
2008	Lacamas	2006	33	< 1930	577	1931	129	(1)
2008	Offutt	2006	82	2004	219	2004	79.3	(1)
2009	Upper Twin	2008	< 150	n/a	all ND	n/a	all ND	(2)
2009	Black	2009	< 210	1974	236	1974	97	(2)
2009	American	2008	< 290	1931	1825	1931	247	(2)
2010	Wenatchee	2007	140	1963	347	1963	109	(3)
2011	Angle	2008	7110	1999	7606	1999	2069	(4)
2011	Samish	2010	1203	1923	2536	2005	930	(4)
2017	Bosworth	2010	812	1948	5538	1971	649	(5)
2017	Martha	2014	3279	1959	4841	1973	823	(5)
2017	Wilderness	2014	1182	1957	2567	1957	350	(5)

References: 1 = Furl (2007); 2 = Furl (2008); 3 = Furl et al. (2009); 4 = Furl and Roberts (2010); 5 = Mathieu (2020)
T-PAHs are the sum of 16 PAH analytes, calculated as described in the references given.

Other PBTs

PBT analytes besides mercury and PAHs (e.g., PFAS, HBCD, PBDEs, PCBs) have been analyzed on a rotating basis since 2012 (Table 5). In general, the three analyte suites with chemicals that have been used in consumer and industrial products until recently have showed increases in sediment-bound concentrations and fluxes from the 1970s-1990s through the 2010s. These include PFAS, HBCD, and PBDEs. Only one site did not show an increase in the last several decades; a remote lake in northeastern Washington (Deer Lake) had few PFAS detections and no apparent pattern. Almost all sites had a peak concentration and flux year that corresponded to the most recent sediments (the top layer of the core).

PCB concentrations and fluxes have declined since peak levels occurring in the 1990s and early 2000s at two of the sites sampled (Deep and Spanaway Lakes). A third sediment core collected from Lake Spokane displayed fairly stable levels of T-PCBs from the late 2000s through the early 2016, with the highest concentration in the top-most layer of the core. However, because of high sedimentation rates of the reservoir at this site, the core only captured sediments deposited after 2001. When compared to a longer period of time obtained in a core collected by Serdar et

al. (2011), concentrations were similar to sediments deposited since about 1985, following peak concentrations in the 1960s.

Table 5. Previous results of T-PFAS, HBCD, T-PBDEs, and T-PCBs in sediment cores

Sampling Year	Waterbody	PBT Analyte	Date of surface layer (year)	surface conc. (ug/kg)	Peak conc. (year)	Peak conc. (ug/kg)	Peak flux. (year)	Peak flux (ug/m^2/yr)	Ref.
2012	Deer	T-PFAS	2009	0.4	1956	0.8	1956	0.7	(1)
2012	Stevens	T-PFAS	2010	2.4	2010	2.4	2010	0.6	(1)
2012	West Medical	T-PFAS	2010	7.0	2010	7.0	1999	4.0	(1)
2013	Cavanaugh	HBCD	2008	8.6	2008	8.6	2008	2.0	(2)
2013	Kitsap	HBCD	2012	18	2012	18	2012	9.4	(2)
2013	Sawyer	HBCD	2011	28	2009	30	2009	9.7	(2)
2015	Meridian	T-PBDEs	2013	32	2009	32	2013	4.9	(3)
2015	Whatcom	T-PBDEs	2013	8.2	2013	8.2	2013	3.5	(3)
2015	Williams	T-PBDEs	2010	3.0	2010	3.0	2010	0.1	(3)
2016	Deep	T-PCBs	2016	0.8	2001	2.2	2001	0.5	(4)
2016	Spanaway	T-PCBs	2016	35	1992	69	1992	4.6	(4)
2016	Spokane	T-PCBs	2016	144	2016	144	2016	50.20	(4)

References: 1 = Mathieu (2013); 2 = Mathieu and McCall (2014); 3 = Mathieu and McCall (2016); 4 = Mathieu (2018).
Analyte abbreviations are spelled out in Appendix C.
T-PFAS = sum of 13 individual PFAS analytes; HBCD = sum of 3 HBCD diastereomers.
T-PBDEs = sum of 40 congeners; T-PCBs = sum of 209 congeners.

3.2.3 Parameters of interest and potential sources

The target analytes for this study are PBTs: chemicals that are persistent in the environment, are bioaccumulative, and are toxic to aquatic or human life. Ecology and DOH have created CAPs for all target PBTs, except for HBCD. Chlorinated paraffins have been a target analyte for this study in the past but will not be continued due to difficulties with the method. See Section 7.2.2 for a full list of analytes for this study.

More detailed information on the target analytes can be found in the CAPs, and the Ecology website has information on how the state is addressing these priority toxic chemicals[2]. PBTs analyzed for this study, in the order of sampling year, are briefly addressed below.

PBDEs

PBDEs are a large class of chemicals used in consumer products, such as furniture, textiles, and electronics, to prevent or slow the spread of fire. Additive flame retardants are not chemically bound to the material in the product and leach out of products over time, accumulating in indoor dust. Chemical manufacturers voluntarily stopped production of two of the most widespread and persistent commercial formulations of PBDEs (penta- and octa-) in the mid-2000s and phased out most uses of deca-BDE in 2012.

[2] https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Addressing-priority-toxic-chemicals

PCBs

PCBs are a group of man-made chemicals that were manufactured and used in the U.S. from the 1930s through the 1970s. Production stopped after regulations in the 1970s, but some legacy uses were allowed to continue (Davies, 2015). The largest remaining legacy sources to the Puget Sound are likely from leaking electrical equipment (large and small capacitors and transformers), residential trash burning, and building materials (primarily sealants) (Roberts et al., 2011).

PAHs

PAHs are formed primarily from the incomplete combustion of carbon-containing materials and occur in natural deposits of oil, coal, and tar. The main releases of PAHs to the environment in the Puget Sound area are thought to be from woodstove and fireplace use, combustion of gasoline by vehicles, leaching of creosote-treated wood such as pilings and railroad ties, and petroleum spills (Ecology and King County, 2011). The state's PAH CAP recommended reducing residential wood-smoke emissions, developing outreach programs to reduce exposure from vehicles (e.g., eliminating drips and leaks and implementing anti-idling campaigns), and investigating the removal of PAH-contaminated pilings and roofing materials (Ecology and Health, 2012).

Mercury

Mercury (Hg) is naturally present in the environment, but human activity has greatly increased the release and cycling of it throughout the world. The largest global release of mercury to the atmosphere comes from combustion of fossil fuels, with coal power emitting the largest portion (Pacyna et al., 2006). Washington state has acted on several of the recommendations made in the mercury CAP to reduce sources in the state (Peele, 2003). Some mercury containing products such as thermometers were banned in 2003 (MERA Chapter 10A.230 RCW) and several mercury replacement and disposal programs have helped remove mercury from the state by keeping dental amalgams, mercury switches in automobiles, and fluorescent lights out of waste streams. The state's only coal-fired power plant installed new equipment to reduce mercury emissions by 50% in the 2010s and the plant will be phased out completely by 2025.

PFAS

Per- and polyfluoroalkyl substances are a large class of chemicals containing carbon-fluorine bonds used extensively in personal, consumer, and industrial products. PFAS are found in water-, stain-, and oil-repellant coatings, metal plating suppressants, and aqueous film-forming foams (AFFFs) used to fight hydrocarbon fires. PFAS have been used since the 1950s, but U.S. manufacturers largely phased out the most highly bioaccumulative substances in the 2000s and 2010s. In the 2020s, Washington state has moved to restrict PFAS in food packaging, AFFFs, cosmetics, carpets, and after-market stain and water-proofing treatments. Ecology is currently considering action on other priority products such as textiles, ski wax, non-stick cookware, cleaning products, and fire-fighter protective gear by 2025.

HBCD

Hexabromocyclododecane is a flame retardant used primarily in extruded (XPS) and expanded (EPS) polystyrene for building insulation, as well as in furniture textiles, automotive upholstery, and other consumer products such as electronics. HBCD was a high production volume chemical, but use of it declined in the 2010s as replacements became available. Major

manufacturers reported that they have stopped using or importing HBCD in the United States as of 2018 and the EPA issued a final risk determination for HBCD in 2022, designating it as an unreasonable risk to the environment and human health (EPA, 2022).

3.2.4 Regulatory criteria or standards

This study does not collect data to determine compliance with regulatory standards or criteria. However, freshwater sediment standards exist for some target analytes and may be used to provide context and comparison for concentrations reported.

The freshwater sediment cleanup objective (SCO) and cleanup screening level (CSL) (WAC 173-204-563), based on protection of the benthic community in freshwater sediment, are:

- Total PCBs: 110 ug/kg dw (SCO) and 2,500 ug/kg dw (CSL), derived from the cleanup screening level for the sum of Aroclors.
- Total PAHs[3]: 17,000 ug/kg dw (SCO) and 30,000 ug/kg dw (CSL)
- Mercury: 0.6 6 mg/kg dw (SCO) and 0.8 mg/kg dw (CSL)

[3] Sum of the following PAHs: 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(ghi)perylene, chrysene, dibenz(ah)anthracene, fluoranthene, fluorene, indeno(123-cd)pyrene, naphthalene, phenanthrene, pyrene, and total benzofluoranthenes (b+k+j).

4.0 Project Description

4.1 Project goals

The goal of this study is to characterize temporal trends of PBT deposition in sediments from lakes throughout Washington state through age-dated sediment cores. Ecology will use the information to help fill data gaps on whether PBTs from the state PBT List are increasing or decreasing in freshwater waterbodies of Washington.

4.2 Project objectives

Specific objectives for this project are to:

- Collect a single sediment core from three lakes per year for analysis of a rotating target analyte from the PBT List: PBDEs, PCBs, PAHs, mercury (Hg), PFAS, and HBCD.
- Analyze sections of the core for age-dating radioisotopes (^{210}Po and ^{226}Ra) and other analytes to support interpretation: total lead, total organic carbon (TOC), and grain size.
- Reconstruct contaminant deposition profiles of the target PBT and report results.

4.3 Information needed and sources

This project is being conducted to generate new environmental data and will not require additional background data to carry out objectives.

4.4 Tasks required

The following annual tasks will be necessary to carry out this project:

- Conduct desktop reconnaissance of waterbodies (e.g., bathymetry, access).
- Secure necessary permits for conducting the field collections.
- Compile existing information on target parameters for the study locations.
- Work with Ecology's Manchester Environmental Laboratory (MEL) staff to notify them of upcoming analyses required and establish laboratory contracts for analyses not offered by MEL.
- Collect sediment cores from the study locations and section into 1 cm sediment layers at field sites. Collect a sediment grab at coring location for grain size analysis.
- Select sediment core layers for analysis based on length of core and field observations of the core.
- Subsection the selected 1 cm horizons for analysis into respective sampling jars.
- Send samples to MEL and contract laboratories for analysis.
- Review and assess data quality of laboratory results.
- Age-date sediment core intervals using ^{210}Po data and supporting ^{226}Ra data. Construct contaminant profiles.

- Develop draft StoryMaps summarizing annual results, route StoryMap drafts following Ecology's Environmental Assessment Program (EAP) review procedures, and publish StoryMaps to Ecology's website.
- Load data into EIM database, follow internal database QA review procedures, and finalize the data entry.
- Write a final five-year synthesis report draft, route the draft final report following EAP review procedures, and publish final report to Ecology's website.

4.5 Systematic planning process

This Quality Assurance Project Plan addresses the elements of the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 1 shows the responsibilities of those who will be involved in this project.

Table 6. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Jessica Archer EAP – SCS Phone: 360-407-6698	Client and Section Manager	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP. Provides internal review of final report.
James Medlen Toxic Studies Unit EAP – SCS Phone: 360-407-6194	Client and Supervisor for Project Manager	Clarifies scope of the project. Provides internal review of the QAPP, annual StoryMaps, and final report. Approves the final QAPP. Manages budget and staffing needs.
Callie Mathieu Toxic Studies Unit EAP – SCS Phone: 360-407-6965	Project Manager and Principal Investigator	Writes the QAPP and final report. Coordinates with labs and oversees field collections. Conducts QA review of data, analyzes data, and interprets data.
Katelyn Foster Toxic Studies Unit EAP – SCS Phone: 360-706-4888	Field Lead	Leads field collections, records field information, and sends samples to the laboratory. Enters data into EIM. Develops StoryMaps for annual sampling results.
Dean Momohara MEL Phone: 360-871-8801	Acting Director	Reviews and approves the final QAPP.
Contract Laboratory	Project Manager	Reads QAPP, coordinates with MEL QA Coordinator.
Arati Kaza Phone: 360-407-6964	Ecology QA Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
SCS: Statewide Coordination Section
EIM: Environmental Information Management database
MEL: Manchester Environmental Laboratory
QAPP: Quality Assurance Project Plan

5.2 Special training and certifications

All field crew carrying out sampling will have specialized training and experience in collection of sediment cores using a box corer. Staff conducting the fieldwork for this study will obtain necessary training through education and field experience. All staff working in the field are led by a senior staff member.

Field staff will follow the requirements in the EAP's Safety Program for all aspects of field work, including operating the pontoon coring boat. EAP staff certify that they review the EAP Safety Manual procedures every two years and signed certification is retained by staff supervisors. To obtain and maintain boat operator status, staff will follow the process detailed in the EAP Safety Manual. Lab personnel are expected to have the required experience and skills to carry out lab activities.

5.3 Organization chart

Not Applicable. See Table 1 for roles and responsibilities. All staff involved with this project are Ecology staff.

5.4 Proposed project schedule

Tables 7, 8, and 9 list key activities, due dates, and lead staff for this project.

Table 7. Schedule for completing annual field and laboratory work.

Task	Due date	Lead staff
Field work	July-August annually	Katelyn Foster
Laboratory analyses	December annually	Callie Mathieu
Contract lab data validation	February of the year following sample collection	Callie Mathieu
StoryMap preparation for annual results	June of the year following sample collection	Katelyn Foster / Callie Mathieu
StoryMap of annual results on web, after reviews	September of the year following sample collection	Katelyn Foster / Callie Mathieu

Table 8. Schedule for data entry

Task	Due date	Lead staff
EIM data loaded*	July of the year following sample collection	Katelyn Foster
EIM QA	August of the year following sample collection	Callie Mathieu
EIM complete	September of the year following sample collection	Katelyn Foster

*EIM Project ID: SEDCORE## (## = the last two digits of the sampling year; e.g. 2023 sampling results will have the EIM Project ID of SEDCORE23).
EIM: Environmental Information Management database.

Table 9. Schedule for final five-year report

Task	Due date	Lead staff / Support staff
Draft to supervisor	July 2028	Callie Mathieu / Katelyn Foster
Draft to client/ peer reviewer	August 2028	Callie Mathieu / Katelyn Foster
Final draft to publications team	September 2028	Callie Mathieu / Katelyn Foster
Final report due on web	November 2028	Callie Mathieu / Katelyn Foster

5.5 Budget and funding

Table 10 shows the lab analysis budget for this study. The number of samples per core for the target PBT analyte varies from year to year depending on lab costs for that analyte. Funding for the lab analyses, staff time, and equipment and supplies comes from the PBT Monitoring Program, which is provided by the state toxics control account.

Table 10. Laboratory analysis budget

Parameter	Field Samples (# of samples)	QA Samples* (# of samples)	Total Number of Samples	Cost per Sample	2023 Lab subtotal	2024 Lab subtotal	2025 Lab subtotal	2026 Lab subtotal	2027 Lab subtotal
T-Pb	30	4	34	$50	$1,700	$1,700	$1,700	$1,700	$1,700
TOC	30	2	32	$46	$1,472	$1,472	$1,472	$1,472	$1,472
^{210}Po**	45	3	48	$120	$7,488	$7,488	$7,488	$7,488	$7,488
^{226}Ra**	9	1	10	$100	$1,300	$1,300	$1,300	$1,300	$1,300
Grain Size**	3	1	4	$100	$520	$520	$520	$520	$520
PBDE congeners**	21	2	23	$940	$28,106				
PCB congeners**	21	2	23	$895		$26,761			
PAHs	30	6	36	$560			$20,160		
Hg	30	6	36	$50			$1,800		
PFAS	30	6	36	$500				$18,000	
HBCD**	24	2	26	$650					$21,970
					2023 lab total:	2024 lab total:	2025 lab total:	2026 lab total:	2027 lab total:
				Lab Grand Total:	$40,586	$39,241	$34,440	$30,480	$34,450

*Includes only QA samples that are not free of charge with the analysis (lab duplicates, matrix spikes, and matrix spike duplicates.

** Lab subtotal for this parameter includes MEL contract fee of 30% for managing the contract and providing data validation.

Parameter/Analyte abbreviations are spelled out in Appendix C.

6.0 Quality Objectives

6.1 Data quality objectives[4]

The main data quality objective (DQO) for this project is to collect three sediment cores per year, analyze 7-10 sections of individual cores for the target PBT analyte, and age-date the cores to reconstruct PBT contaminant profiles. The analyses will use standard methods, when available, and data will meet measurement quality objectives (MQOs) as described below.

6.2 Measurement quality objectives

Table 11 outlines the MQOs for all lab analyses to be conducted for this study. The project MQOs are expressed in terms of acceptable precision, bias, and sensitivity, as described in this section.

6.2.1 Targets for precision, bias, and sensitivity

Table 11. Measurement quality objectives

Parameter	LCS (recovery)	Method Blanks	Matrix Spike (recovery)	Matrix Spike Duplicates (RPD.)	Lab Duplicates (RPD)	Surrogate Standards (% recov.)
T-Pb	85-115%	< RL	75-125%	< 20%	n/a	n/a
TOC	80–120%	< RL	n/a	n/a	< 20%	n/a
^{210}Po	80-120%	< RL	n/a	n/a	< 30%	n/a
^{226}Ra	80-120%	< RL	n/a	n/a	< 30%	n/a
grain size	n/a	n/a	n/a	n/a	< 20% (RSD)	n/a
PBDE congeners	50-150%	< 1/2 RL	n/a	n/a	< 50%	25-150%[1]
PCB congeners	50-145%	< 1/2 RL	n/a	n/a	< 50%	5-145%
PAHs	50-150%	< 1/2 RL	50-150%	< 40%	< 40%	20-200%
Hg	80-120%	< RL	75-125%	< 20%	< 25%	n/a
PFAS	50-150%	< 1/2 RL	50-150%	< 30%	< 40%	50-150%
HBCD	70-130%	< 1/2 RL	n/a	n/a	< 40%	40-150%

[1]decaBDE = 20 - 200%
[2]MDLs vary among congeners. Deca and nona-BDEs have substantially higher MDLs.
MDL = method detection limit.
Analyte abbreviations are spelled out in Appendix C.

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

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Laboratory analysis precision will be assessed through lab duplicate samples for all analyses, except for grain size. Precision for grain size analysis will be evaluated through triplicate analysis of a sample, split at the lab. Table 11 provides the MQOs for lab duplicate (triplicate for grain size) samples. No field replicates will be collected for this project.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Laboratory analysis bias will be assessed through laboratory control samples, matrix spikes (except for the isotopic dilution methods used for PCB, PBDE, and HBCD analysis), and surrogate standards. MQOs for these tests are included in Table 11.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above background noise. Laboratory analysis sensitivity is defined for the study as the quantitation limit. See Table 14 for quantitation (reporting) limits.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Sediment core samples will be collected according to Ecology's standard operating procedures (SOPs) to help ensure comparability between results from previous and future sampling events. Section 8.2 discusses SOPs followed for this study. Ecology SOPs are reviewed and recertified every three years. Laboratory analyses will follow standard methods listed in Table 14 to maintain comparable laboratory results.

6.2.2.2 Representativeness

Sediment cores provide a representative, time-integrated, historical deposition profile of sediment-bound contaminants. Issues of representativeness for long-term monitoring studies, such as inconsistent reporting limits and missing data, are alleviated by using sediment cores, as samples from multiple dates are being analyzed at once instead of over time. Study locations are selected to represent lakes with a range of contamination potential, watershed land uses, and physical characteristics (e.g., watershed area to lake area ratios).

6.2.2.3 Completeness

The completeness goal for field collections and lab analyses is 100% of the samples collected and analyzed within MQOs. However, because analytical issues may arise due to the matrix of the samples or with the difficulty of low-level organics analyses, the project manager will consider the study to have achieved completeness if 95% of the samples are analyzed acceptably.

6.3 Acceptance criteria for quality of existing data

This study collects new data and will primarily include only the results of this study in the final report. Historical state and federal data, as well as results from the literature, may be presented along with the results of this study to provide context. In this respect, only data that have been

published as part of peer-reviewed state reports or journal articles will be used, and only after a review of the methods and data quality.

6.4 Model quality objectives

Not applicable.

7.0 Study Design

Ecology's PBT Monitoring Program will collect a single sediment core from three lakes per year to characterize the occurrence and temporal trends of sediment-bound PBTs in select waterbodies of Washington state. Sediment core samples will be age-dated and analyzed for a rotating PBT, following the schedule in Figure 3. The rotating PBT analytes were selected from the state's PBT List to gain information on whether PBTs of interest are increasing or decreasing in the state's freshwater.

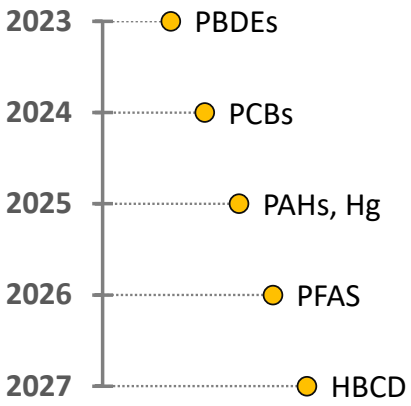

Figure 3. Rotating target PBT analyte schedule for 2023 – 2027 sampling years

At each study location, a single sediment core will be collected from the deepest flat section of the waterbody, where fine-grained sediments concentrate. The deepest area of a natural lake serves as a sink for sediments to deposit and remain undisturbed, making the deepest area a representative target location from which to reconstruct contaminant profiles. Because characterizing the spatial variability of the waterbody is not a goal of this project, only one core is collected from each lake, from the most representative location in the lake. This design allows us to balance the cost of analyzing each core, while gaining information on three different waterbodies, each year.

The entire sediment core will be sampled in 1 cm sediment layers (0-2 cm at the top), and then select layers of the core will be analyzed for target PBTs and radiochemistry to age-date the core. Sediment layers selected for analysis will be based on the total length of the core and field observations (e.g., sediment color and consistency changes). Interval selection for analysis will be spaced farther apart between the selected layers moving down the core. In general, 7-10 sediment layers will be selected for target PBT analysis, per core. Fifteen sediment layers will be selected for radiochemistry analysis.

Sediment cores will be age-dated using ^{210}Po measurements as a proxy for ^{210}Pb. Calculation of dates and sedimentation rates will be performed using the constant rate of supply (CRS) model, when applicable (Appleby and Oldfield, 1978). The CRS model allows for varying sedimentation rates and is typically the method of choice for this program's study locations. Other dating methods, such as the CF:CS (constant flux: constant sedimentation) model, may be considered in situations where the core does not reach supported ^{210}Pb activities, and the relationship between unsupported ^{210}Pb activities on a logarithmic scale against cumulative dry mass appear linear (Appleby and Oldfield, 1992). Cores will be analyzed for ^{226}Ra at three points in the core (upper, middle, and lower) to help determine supported ^{210}Pb.

7.1 Study boundaries

This study will examine PBT contaminant profiles from waterbodies located across Washington. Table 12 presents site location such as county, water resource inventory area (WRIA), and hydrologic unit codes (HUCs).

Table 12. Study locations, WRIA and HUC numbers, and sample collection coordinates

Sampling Year	Waterbody	County	WRIA	HUC	Sample Collection lat. / long.
2023	Alta Lake	Okanogan	48 - Methow	17020008	48.019 / -119.93
2023	Clear Lake	Skagit	3 - Lower Skagit	17110007	48.459 / -122.225
2023	Mason Lake	Mason	14 - Kennedy - Goldsborough	17110019	47.335 / -122.960
2024	Bead Lake	Pend Oreille	62 - Pend Oreille	17010216	48.298 / -117.112
2024	Lake Goodwin	Snohomish	7 - Snohomish	17110019	48.136 / -122.294
2024	Lake Sawyer	King	9 - Duwamish - Green	17110013	47.333 / -122.037
2025	Bonaparte Lake	Okanogan	49 - Okanogan	17020006	48.000 / -119.055
2025	Leland Lake	Jefferson	17 - Quilcene - Snow	17110018	47.896 / -122.892
2025	Mineral Lake	Lewis	11 - Nisqually	17110015	46.727 / -122.174
2026	American Lake	Pierce	12 - Chambers - Clover	17110019	47.135 / -122.559
2026	Loon Lake	Stevens	59 - Colville	17020003	48.037 / -117.616
2026	Lake Sammamish	King	8 - Cedar - Sammamish	17110012	47.595 / -122.097
2027	Diamond Lake	Pend Oreille	55 - Little Spokane	17010308	48.133 / -117.187
2027	Spencer Lake	Mason	14 - Kennedy - Goldsborough	17110019	47.266 / -122.957
2027	Lake Wenatchee	Chelan	45 - Wenatchee	17020011	47.821 / -120.769

WRIA = water resources inventory area
HUC = hydrologic unit code

7.2 Field data collection

7.2.1 Sampling locations and frequency

Study locations are targeted and selected based on criteria outlined in Section 3.2. Sediment core samples will be collected once during the summer (typically August) at each of the three waterbodies. All three sediment cores will be collected within the same week or within a two-week timeframe.

Sampling locations for each waterbody are given in Table 12 as coordinates and in Appendix B with their location on bathymetric maps. Alternate locations are listed in Appendix A.

7.2.2 Field parameters and laboratory analytes to be measured

The lab analytes to be measured annually include ^{210}Po, ^{226}Ra, TOC, total lead, and grain size. The rotating schedule of target PBT analytes to be measured is shown in Table 14. Individual analytes to be included in parameter suites (e.g., PFAS) are those named in the method, as described in Table 14. For HBCD, the analyte list will include the alpha, beta, and gamma diastereomers of HBCD.

7.3 Modeling and analysis design

Not applicable.

7.4 Assumptions underlying design

This study assumes that the target analytes are persistent in sediments and that concentrations measured at depth in the core are a preserved representation of what was deposited at the time of sedimentation. Smearing, bioturbation, and migration of analytes through porewater can impact the preservation of chemicals within the sediment profile and may affect this assumption. At least one deep layer sample will be analyzed for the rotating PBT analyte to attempt to reach sediment dated before production of the chemical began. This will help inform the project manager whether smearing has occurred.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Suitable access has been a limiting factor for waterbody selection in the past. During 2006-2022, sediment cores were collected by staff aboard a 28' research vessel that required well-developed boat launch access. Ecology is currently procuring a custom-made 16’ pontoon boat with electronic winch and motors that will allow access to a broader range of waterbodies, particularly undeveloped lakes and lakes that do not allow combustion motors.

In past sampling efforts, physical characteristics of the sediments at some waterbodies have hampered efforts to collect a suitable sediment core. The sediment grain size and percent water content of the core can make for unsuccessful sediment core collection. Unfortunately, desk reconnaissance is not adequate in identifying these potential issues. For some areas, preliminary grab samples from the waterbody are possible during the planning phase. However, particularly

for eastern Washington lakes, this is not feasible. Instead, several alternate lakes have been selected for sampling if a sediment core cannot be collected from the primary target lake.

High water content in sediments of a core can also affect lab analyses. Low percent solids can result in too little sample material for analytical methods or could result in raised reporting limits. Obtaining sufficient material for organic contaminant analyses has been difficult in past sampling years. To mitigate this problem, samples to be analyzed for the organic PBT analyte will be centrifuged and overlying water decanted before shipment to the lab. The organic PBT analyses typically require the largest amount of material. Priority of analyses when limited sample material occurs will be in the order of target PBT > ^{210}Po > lead > TOC.

7.5.2 Practical constraints

Practical constraints for this project include availability of specially trained staff. This will be minimized by careful scheduling of staff resources. The timing of sediment core sampling is dependent on calm weather, which typically can be relied upon during July through September in Washington. Within that time frame, the sampling dates are not dependent on other criteria (e.g., tides, storms) and therefore staffing schedules are flexible.

7.5.3 Schedule limitations

The timeframes necessary for securing sampling permits has impacted the project schedule in the past. For 2023-2027, the project team will seek a five-year general statewide permit to more efficiently use the hydraulic approval permit application process. Other schedule limitations in the past have included the time required for lab analysis and for writing a final report. To minimize these impacts, the lab analyses completion dates were extended and a final report will be written after all five sampling years to maximize efficiency with the writing process. Retaining support staff to assist with data management and report writing will help to keep the project schedule on time.

8.0 Field Procedures

8.1 Invasive species evaluation

Staff will inspect and decontaminate boat and sampling gear following Ecology's SOP EAP070 for Procedures to Minimize the Spread of Invasive Species, Version 2.3 (Parsons, 2023). All staff are required to be familiar with the SOP and refresh their training annually. Prior to each sampling year, reconnaissance will include determining what invasive species are present at the study locations, and the appropriate steps in the SOP will be followed.

8.2 Measurement and sampling procedures

The following Ecology SOPs will be used when collecting field samples:

- SOP EAP038, Version 1.4. Collection of Freshwater Sediment Core Samples Using a Box or KB Corer (Mathieu, in publication).
- SOP EAP040, Version 1.4. Obtaining Freshwater Sediment Samples (Wong, 2020).

Sediment core collection

Sediment cores will be collected from a custom-built 16' pontoon coring research vessel. Field crews will use a Wildco stainless-steel box corer fitted with an acrylic liner with inner dimensions of 13 cm x 13 cm x 50 cm. The box corer will be deployed through a moon pool in the center of the pontoon boat using an electric winch with variable speed. The corer will be lowered down through the sediments, triggered to close the corer jaws, and raised back up to the working deck and table. An acceptable core will be 35 to 45 cm depth, not overfilled, and with a clear sediment-water interface. Acceptable sediment cores will be retained and processed on-board.

Sediment core processing

Field crews will extrude and slice the sediment core into 1 cm layers over the length of the entire core. The top 0-2 cm will be combined into one layer to ensure sufficient sample material for analyses, due to the high-water content of the uppermost sediments. The sediment-filled acrylic liner will be placed on an extruder table outfitted with a manual gear-driven piston to push sediments up and out of the top of the liner. Sediment layers will be sliced using a small subsection liner and thin aluminum plates at the top and placed in pre-labeled 8 oz glass jars and immediately stored in plastic bags on ice. Sediment material in contact with the liner will be excluded from the sample. In-between layers, the subsection liner and plates will be washed in clean ambient water from the site and visually inspected to ensure no particles remain.

For all sampling years except 2026, the individual sediment layers will be stored in 8 oz glass jars and transported to Ecology Headquarters for homogenization and subsectioning into jars for analysis. For 2026, the PFAS analyses cannot be stored in glass jars; therefore, the homogenization and subsectioning will occur on-board at the time of extruding.

All intervals will be measured for bulk wet weight prior to homogenization and subsampling. Select intervals will be processed by thoroughly homogenizing the sediment layer and then splitting into subsamples for analyses. The sediment layers selected for analysis will be based on total length of core and field observations (e.g., sediment color and consistency). Field crews will homogenize the sediment layer using clean stainless-steel bowls and spoons and mixing until the material appears uniform in color and consistency. The homogenized sediment will be subsectioned into separate jars for analyses, as listed in Table 13. After subsectioning, the samples will be preserved as outlined in Table 13. All samples will be shipped to the laboratory at the same time.

Surface sediment collection

At each coring location, a surface sediment sample will be collected for analysis of grain size. Field crews will deploy a standard ponar at the same coordinates targeted for the sediment core collection. A sediment grab will be considered acceptable if it is not overfilled, overlying water is present but not turbid, and at least 5 cm sediment depth was obtained. Field staff will collect the top 0-2 cm via a stainless-steel spoon and fill directly into the labeled sampling jar. The surface sediment sample will then be stored on ice and transported to Ecology Headquarters, then shipped to MEL or a contract laboratory on ice.

8.3 Containers, preservation methods, holding times

Table 13 presents the appropriate containers, preservation techniques, and holding times for all analyses.

Table 13. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Field preservation	Preservation after processing	Holding Time
T-Pb	sediment	25 g ww	4 oz. glass jar	cool to 4° C	freeze, -20° C	1 year
TOC	sediment	25 g ww	4 oz. glass jar	cool to 4° C	freeze, -20° C	1 year
^{210}Po	sediment	20 g ww	2 oz. glass jar	cool to 4° C	none required	n/a
^{226}Ra	sediment	360 g ww	8 oz. glass jar	cool to 4° C	none required	n/a
Grain Size	sediment	150 g ww	8 oz. HDPE jar	cool to 4° C	cool to 4° C	6 months
PBDE congeners	sediment	20 g ww	8 oz. glass jar	cool to 4° C	freeze, -20° C	1 year
PCB congeners	sediment	20 g ww	8 oz. glass jar	cool to 4° C	freeze, -20° C	1 year
PAHs	sediment	100 g ww	8 oz. glass jar	cool to 4° C	freeze, -20° C	1 year
Hg	sediment	50 g ww	4 oz. glass jar	cool to 4° C	freeze, -20° C	28 days
PFAS	sediment	50 g ww	500 mL HDPE	cool to 4° C	freeze, -20° C	90 days
HBCD	sediment	100 g ww	8 oz. glass jar	cool to 4° C	freeze, -20° C	1 year

Parameter/Analyte abbreviations are spelled out in Appendix C.

8.4 Equipment decontamination

Field staff will follow Ecology's SOP Number EAP090, Decontaminating Field Equipment for Sampling Toxics in the Environment, Version 1.2 (Friese, 2021) to clean the sampling equipment prior to field collection. Acrylic liners and subsectioning equipment will be scrubbed with Liquinox and hot tap water, followed by a 10% nitric acid rinse, and then a final rinse of the following depending on the target PBT analyte for that year:

- PBDEs, PCBs, PAHs, and HBCD – acetone, and hexane
- Hg – none, the 10% nitric acid rinse is sufficient
- PFAS – methanol

Equipment will be dried in a hood, and then wrapped in aluminum foil for transport to the field location. While sectioning the sediment core in the field, equipment will be rinsed (and scrubbed, if necessary) with ambient water from the lake surface in between 1 cm sediment intervals. Excess water will be shaken off prior to sectioning the next interval.

8.5 Sample ID

While sectioning the sediment core in the field, each 1 cm layer (0-2 cm for the top) will be placed into an 8 oz. glass jar and labeled with the three-letter waterbody abbreviation plus sediment interval (e.g., Alta Lake 0-2 cm = ALT0-2; Alta Lake 2-3 cm = ALT2-3) written on the

jar and lid in permanent ink. Once individual layers are homogenized and split into laboratory samples at Ecology's Headquarters, the samples will be assigned a sample ID using MEL's work order number followed by a consecutive number.

8.6 Chain of custody

Chain of custody will be maintained for all samples throughout the project. Samples will be stored in a cooler or freezer in Ecology's locked chain-of-custody room at Headquarters. MEL's chain of custody form will be used for documentation of shipment to laboratories.

8.7 Field log requirements

Field data will be recorded in a bound, waterproof notebook on Rite-in-the-Rain paper. Corrections will be made with single line strikethroughs, initials, and date. The following information will be recorded in the field log:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP
- Environmental conditions
- Date, time, and location of sediment core collection
- Length and description of full core
- Description of core intervals, such as color, odor, and appearance
- Unusual circumstances that might affect interpretation of results

8.8 Other activities

The field lead will coordinate with MEL by notifying them of upcoming sampling and laboratory analyses needed, requesting sampling bottles, and scheduling shipment to MEL. For contract laboratory services, MEL's QA coordinator will work with the project manager to identify a suitable laboratory and develop a scope of work for analyses.

9.0 Laboratory Procedures

9.1 Lab procedures table

MEL will perform all analyses listed in Table 14 except for ^{210}Po, ^{226}Ra, PBDE congeners, PCB congeners, and HBCD. Those analyses will be contracted out to a commercial laboratory. MEL will manage the contract for those analyses and provide data validation of the results.

Sensitivity is presented in Table 14 as a reporting limit. However, laboratories will report results down to the method detection limit. Results above the method detection limit, but below the reporting limit, will be qualified "J" as estimates.

Table 14. Measurement methods (laboratory).

Analyte	Matrix	Number of samples	Sample arrival to lab date	Expected range of results (dw)	Reporting limit[1] (dw)	Sample preparation method	Method	Analytical instrument
T-Pb	sediment	30	August, annually	1.0-1,000 mg/Kg	0.1 mg/Kg	EPA 3050B	EPA 6020	ICP-MS
TOC	sediment	30	August, annually	1.0-30 %	0.10%	n/a	PSEP-EPA, 1986	Acidification and CO_2 measurement
^{210}Po	sediment	45	August, annually	< 0.45-30 pCi/g	0.45 pCi/g	lab specific	HASL-300 A-01-R*	alpha spectroscopy
^{226}Ra	sediment	9	August, annually	< 0.5-2.0 pCi/g	0.5 pCi/g	lab specific	HASL-300 A-01-R*	alpha spectroscopy
Grain Size	sediment	3	August, annually	---	0.10%	n/a	PSEP-EPA, 1986	sieve-pipette
PBDE congeners	sediment	21	August 2023	< 0.1-10,000 pg/g	0.1 pg/g	EPA 1614	EPA 1614	HRGC/MS
PCB congeners	sediment	21	August 2024	< 0.01 pg/g-100 ng/g	0.01-200 pg/g	EPA 1668	EPA1668C	HRGC/MS
PAHs	sediment	30	August 2025	< 1.0-10,000 ng/g	4-20 ng/g	EPA 3541	EPA 8270D SIM	GC-MS-SIM
Hg	sediment	30	August 2026	0.005-0.50 mg/kg	< 0.005 mg/kg	EPA 245.5	EPA 245.5	CVAA
PFAS	sediment	30	August 2027	<0.2-100 ng/g	0.01 - 0.4 ng/g	EPA 1633 draft 2**	EPA 1633 draft 2**	LC-MS/MS
HBCD	sediment	24	August 2028	<0.25-20 ng/g	0.25 ng/g	Soxhlet with DCM; GPC cleanup	lab-specific, isotopic dilution	LC-MS/MS

* Or lab-specific equivalent
** Draft 2 was available as of time of writing QAPP. The finalized version of EPA Method 1633 will be required when available.
[1] The term "reporting limit" is considered synonymous with "limit of quantitation," "quantitation limit," and "minimum level."
dw = dry weight.
DCM = dichloromethane.
GPC = gel permeation chromatography.
EPA = Environmental Protection Agency.
PSEP = Puget Sound Estuary Protocol.
ICP-MS = inductively coupled plasma mass spectrometry.
HRGC/MS = high resolution gas chromatography with mass spectrometry.
GC-MS-SIM = gas chromatography mass spectrometry in selective ionization mode.
CVAA = cold vapor atomic absorption.
LC-MS/MS = liquid chromatography with tandem mass spectrometry.
Analyte abbreviations are spelled out in Appendix C.

9.2 Sample preparation methods

Preparation methods for lab analyses are listed in Table 14. All analyses will use standard preparation methods except for the radiochemistry and HBCD. For those analyses, the contract laboratory will be required to provide their preparation method to the project manager and MEL's QA Coordinator to review. Preparation steps for those analyses should be close to preparation steps used in the past for this project. Previous analyses of HBCD have used Soxhlet extraction with dichloromethane, followed by gel permeation chromatography.

9.3 Special method requirements

To obtain data within the relevant concentrations necessary for sediment cores, all PBT analyses were selected to measure very low levels. No modifications need to be made to the methods, as all are were developed with the intention of low-level analysis. There is no standard method for analysis of HBCD. The contracted lab selected for HBCD analysis will need to demonstrate the ability to successfully analyze HBCD in sediments at the levels required in Table 14. The analysis of HBCD will need to use liquid chromatography – tandem mass spectrometry (LC-MS/MS) with isotopic dilution. The three diastereomers (alpha, beta, and gamma) will be reported separately, and labeled surrogates will be used for each isomer. The extraction and analysis of HBCD will be described in the final report.

9.4 Laboratories accredited for methods

All labs used for this project will be accredited for the method employed, with the following exceptions. Because there is no standard method for HBCD, an accreditation waiver will be sought for the analysis. In addition, Ecology does not currently accredit labs for grain size so the accreditation requirement will be waived. The contract labs will be required to demonstrate that they have successfully performed the analyses in the past and provide client references for the requested analysis.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Quality control (QC) samples that will be analyzed with each parameter suite are presented in Table 15. See Appendix C, QA Glossary, for definitions of the QC sample types.

Table 15. Quality control samples, types, and frequency.

Parameter	LCS	Method blanks	Matrix spikes	Matrix spike duplicates	Lab duplicates	Surrogates
T-Pb	1/batch	1/batch	1/batch	1/batch	---	---
TOC	1/batch	1/batch	---	---	1/batch	---
^{210}Po	1/batch	1/batch	---	---	1/batch	---
^{226}Ra	1/batch	1/batch	---	---	1/batch	---
Grain Size	---	---	---	---	1/batch	---
PBDE congeners	1/batch	1/batch	---	---	1/batch	each sample
PCB congeners	1/batch	1/batch	---	---	1/batch	each sample
PAHs	1/batch	1/batch	1/batch	1/batch	1/batch	each sample
Hg	1/batch	1/batch	1/batch	1/batch	1/batch	---
PFAS	1/batch	1/batch	1/batch	1/batch	1/batch	each sample
HBCD	1/batch	1/batch	---	---	1/batch	each sample

Batch = 20 or fewer samples

10.2 Corrective action processes

MEL and contract labs will be expected to follow corrective actions outlined in the methods listed in Table 14. This includes examining results that fall outside of acceptance limits and determining whether the data should be re-analyzed, rejected, or deemed usable with appropriate qualification.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

All field data and observations will be recorded on waterproof paper kept in field notebooks. After they return from the field, staff will transfer information contained in field notebooks to Excel spreadsheets. Data entries will be independently verified for accuracy by another member of the project team.

Field measurements (sediment core interval depths) and lab data for this project will be entered into Ecology's EIM database. Lab data will be uploaded into EIM, using the EIM XML results template. The EIM Study ID for this project is "SEDCORE##" with the ## representing the last two digits of the sampling year. For instance, data from sampling year 2023 will be stored in EIM under the Study ID "SEDCORE23".

11.2 Laboratory data package requirements

Contract laboratories will be required to submit a Tier 4 Level data package to MEL with the complete raw laboratory dataset. After reviewing data packages from the contract lab, MEL will provide case narratives to the project manager with the final qualified results and a description of the quality of the contract lab data. MEL will also provide case narratives for analyses performed in-house. Case narratives should include any problems encountered with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Narratives will also address the condition of samples on receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests.

11.3 Electronic transfer requirements

Contract labs will be required to submit data packages to MEL electronically, as specified in the scope of work for the analysis. Typically, the scope of work will specify an electronic file sharing location for the data package to be stored.

MEL will deliver case narratives to the project manager in PDF format. MEL will also provide electronic data deliverables of contract lab data in an Excel spreadsheet format, via email. Data generated by MEL (analyses done in-house) will be delivered to the project manager via LIMS.

11.4 EIM/STORET data upload procedures

All lab data will be uploaded to Ecology's EIM database following EAP protocols and business rules. An independent reviewer will conduct a QC review of this data upload, following internal EAP protocols.

11.5 Model information management

Not applicable.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

MEL and contract laboratories for this project must participate in performance and system audits of their routine procedures. No field audits are planned for this project.

12.2 Responsible personnel

Not applicable.

12.3 Frequency and distribution of reports

A story map of the annual sampling results will be completed in July of each year, and a final report will be published after all five years of sampling have been completed. See Table 4 for the final report schedule. The final five-year summary report will include, at a minimum, the following:

- An introduction and background of the project.
- A map showing sampling locations.
- A description of field and laboratory methods.
- A discussion of data quality.
- Summary tables of contaminant concentrations and fluxes.
- Graphs showing contaminant profiles of sediment cores.
- A discussion of the results, including age-dating of the core, sedimentation rates, contaminant concentration profiles and contaminant flux profiles.
- Conclusions and recommendations based on the sampling results.

12.4 Responsibility for reports

The project manager/principal investigator will be the lead responsible for the final report.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Field notes will be verified by the project manager. No data will be generated in the field.

13.2 Laboratory data verification

MEL staff will verify laboratory data before entering results into their LIMS database. Verification will include examining the data for errors, omissions, and compliance with QC acceptance criteria and the method. MEL will include a case narrative that discusses whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions. The case narrative will also define qualifiers and the reason for their use. The case narrative will be released to the project manager. Laboratory staff may be asked to review QC data that are normally retained by MEL.

The project manager is responsible for the final acceptance of project data. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will be accepted, accepted with qualifications, or rejected and re-analysis considered.

13.3 Validation requirements, if necessary

MEL will be responsible for carrying out validation of the contract laboratory data. The contract lab data will undergo an EPA Stage 4 data validation as defined in EPA (2009). If MEL is unable to perform the data validation with current staff, a contract vendor with the appropriate qualification will be selected to complete it. MEL or the contract vendor will provide a case narrative summarizing the findings of the data validation, as well as an electronic data deliverable (EDD) with the final results and final result qualifiers as provided by the data validator.

13.4 Model quality assessment

Not applicable.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

Following data verification and validation, the project manager will determine if the data are of sufficient quality to meet project goals and objectives. The project manager will review case narratives and results of QC tests to determine whether lab analyses met MQOs. Lab and QA staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted. Some analytes will be reported near the detection capability of the selected methods; MQOs may be difficult to achieve for these results. MEL's SOP for data qualification, procedures in the analytical methods, EPA National Functional Guidelines, and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification.

14.2 Treatment of non-detects

Non-detect samples will be qualified "U" or "UJ" at the reporting limit specific to the method. Results below the reporting limit, but above the method detection limit, will be reported if qualitative criteria are met and the analyte is not present in the method blank. These values will be qualified "J" as an estimate.

Several of the analyte suites have multiple substances that will be presented as totals or summed values in the final report. These summed values will not be entered into EIM. Summed values in the final report will include only detected congener results that are unqualified and/or have been qualified "J" (indicating that the analyte was positively identified, and the associated numerical value is approximate). Individual analyte values that have been qualified "NJ" (indicating that the analyte has been "tentatively identified" and the associated value represents its approximate concentration) will not be included in summed values. If a sample is comprised of all non-detected congener results, the final summed value will be assigned "ND" for not detected. Summed values will be qualified "J" if more than 10% of the total result is composed of congener values containing "J" qualifiers.

All samples will be censored against method blanks following the method protocol. This can include different action levels; for instance, methods that require the "5x times rule" would censor sample results if the result is less than five times the associated method blank detection. The following action levels will be used for this project:

- PBDE congeners: 5x
- PCB congeners: 5x
- PAHs: 5x
- PFAS: 5x
- HBCD: 10x

14.3 Data analysis and presentation methods

A summary of the data will be presented in the final report. Contaminant results will be presented as both concentrations and fluxes. Fluxes will be calculated as the contaminant

concentration multiplied by the sediment accumulation rate for the sediment core interval (g/cm^2 /yr). The final report summarizing sediment core results will present the separately reported analytes (e.g., PCB congeners), as well as total analyte suite values (e.g., Total PCBs).

14.4 Sampling design evaluation

The number and type of samples collected is expected to be sufficient to meet the objectives of this project. The sampling design for this study was developed after considering guidance from Yake (2001) and Van Metre et al. (2004).

14.5 Documentation of assessment

The final report will provide documentation of assessment.

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16.0 Appendices

Appendix A. Alternate sites

Table A-1. Alternate sites for sediment core collection.

Waterbody	Elevation (ft)	Max Depth (ft)	Mean Depth (ft)	Lake Area (ac)	Watershed Area (ac)	WA:LA	Sample Collection lat. / long.	County
Lake St. Clair	72	110	40	88	9280	105	46.998 / -122.727	Thurston
Offut Lake	230	25	15	200	1728	9	46.919 / -122.826	Thurston
Marshall Lake	2724	92	67	190	3085	16	48.261 / -117.076	Pend Oreille
Cain Lake	391	62	30	72	2125	30	48.650 / -122.331	Whatcom
Silver Lake	2341	80	30	490	12160	25	47.562 / -117.657	Spokane

WA:LA = watershed area to lake area ratio.

Appendix B. Bathymetric maps and coring locations

Figure B-1. 2023 Sediment core locations.

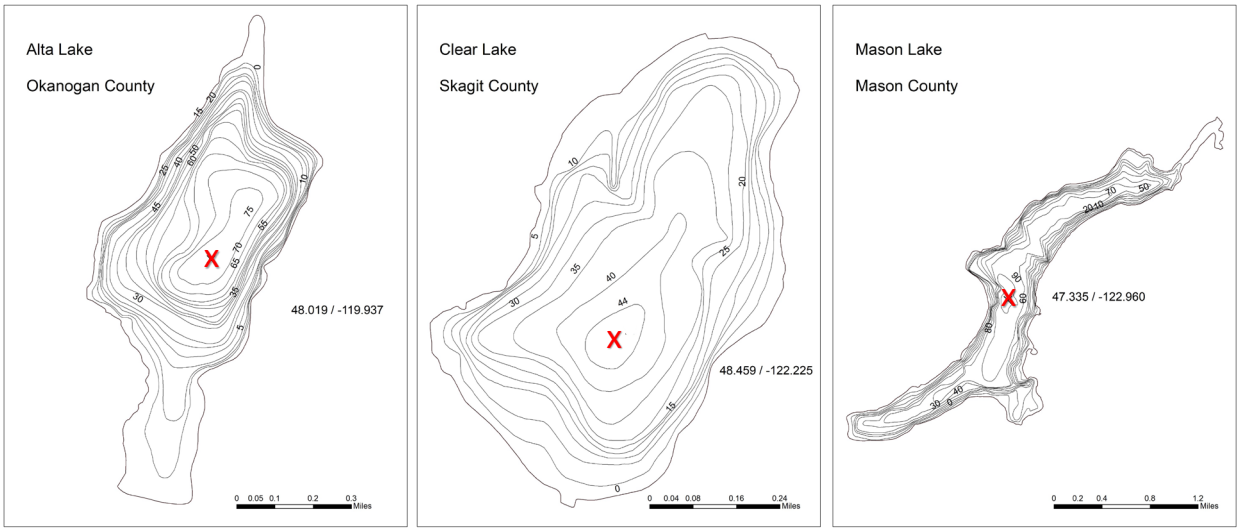


Figure B-2. 2024 Sediment core locations.

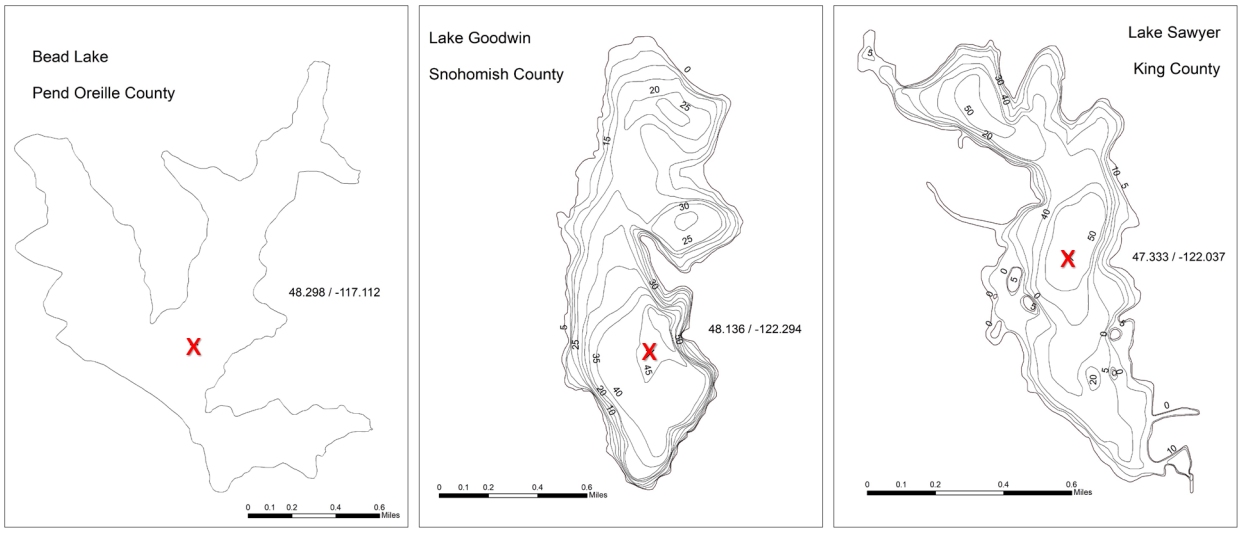


Figure B-3. 2025 Sediment core locations.

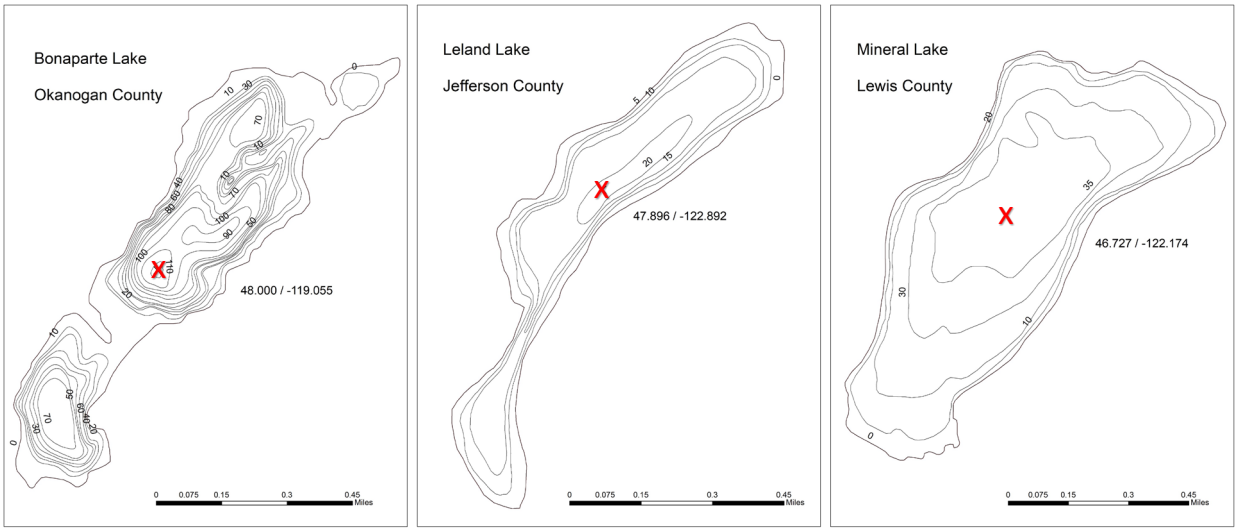


Figure B-4. 2026 Sediment core locations.

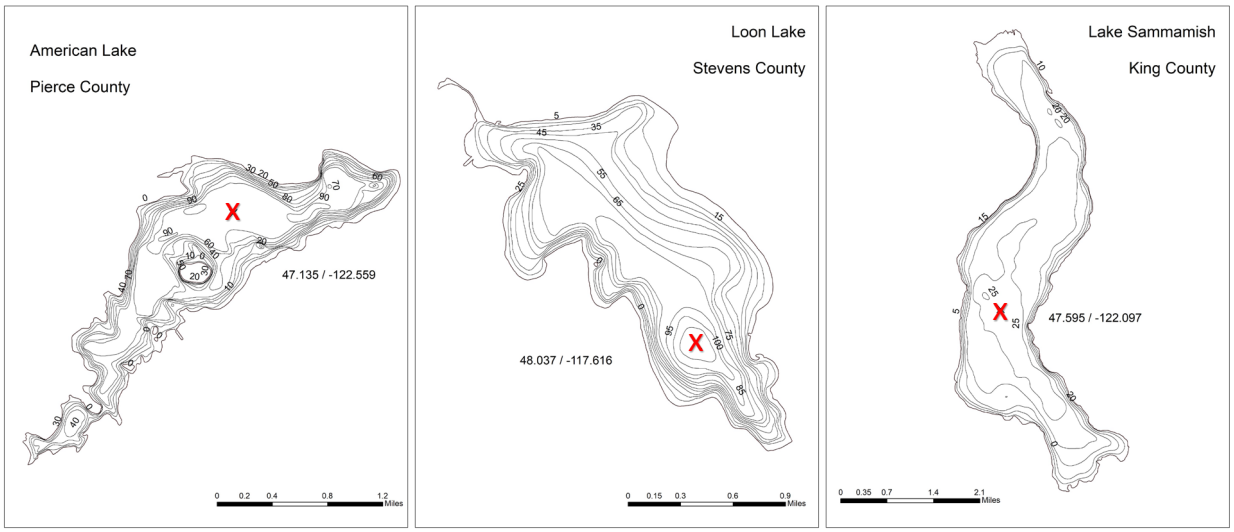


Figure B-5. 2027 Sediment core locations.

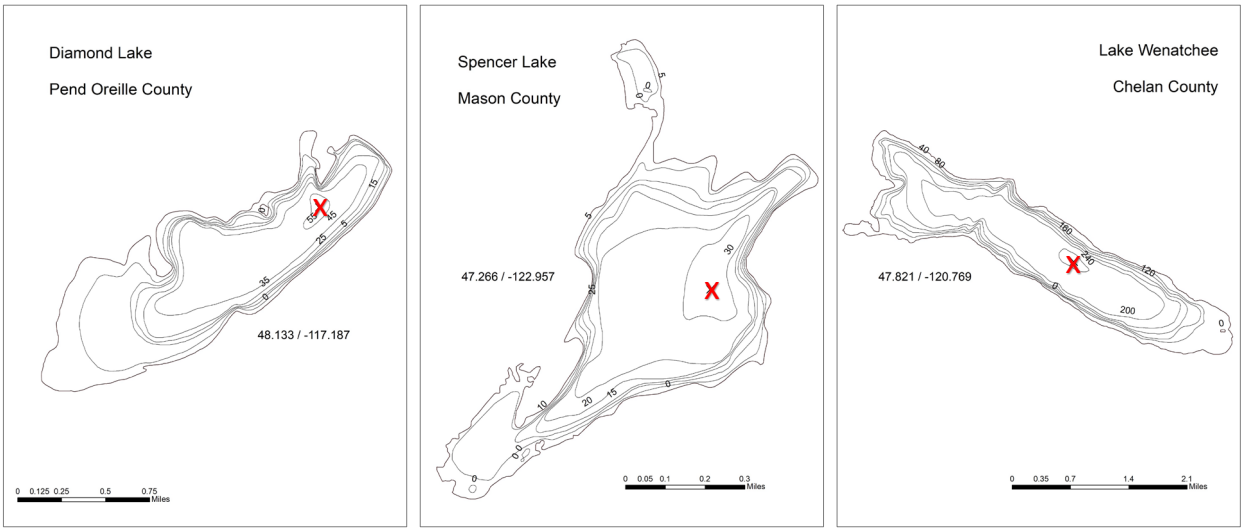
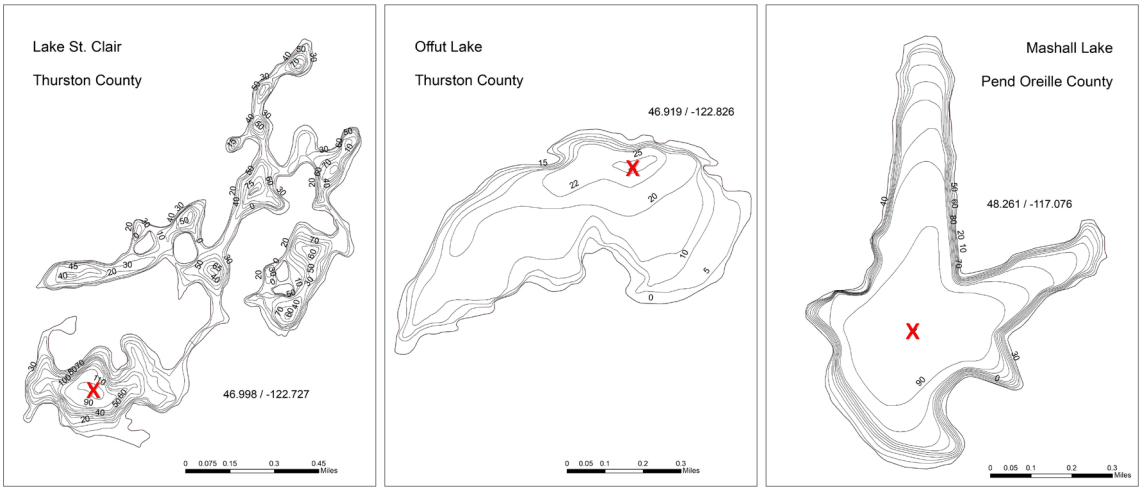
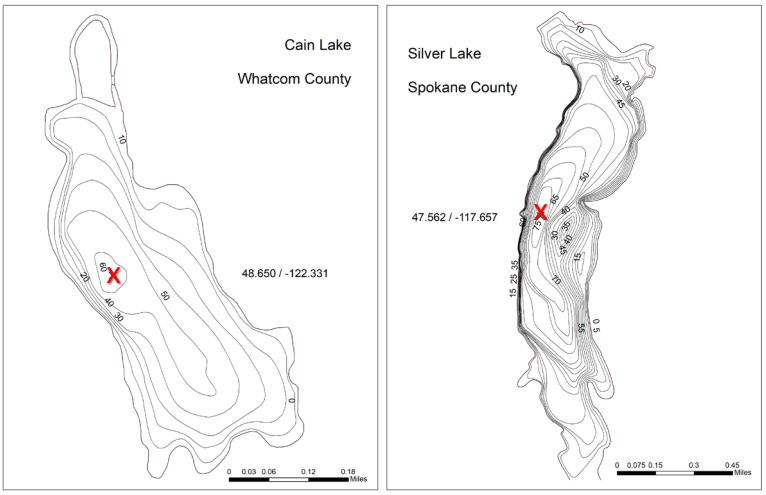


Figure B-6. Alternate Sediment core locations.




Cain Lake
Whatcom County
48.650 / -122.331
0 0.03 0.06 0.12 0.18 Miles
Silver Lake
Spokane County
47.562 / -117.657
0 0.075 0.15 0.3 0.45 Miles

Appendix C. Glossaries, acronyms, and abbreviations

Glossary of general terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Anthropogenic: Human-caused.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and abbreviations

^{210}Pb	210 lead isotope
^{210}Po	210 polonium isotope
^{226}Ra	226 radium isotope
CAP	Chemical action plan
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
e.g.	for example
et al.	And others
GIS	Geographic Information System software
HBCD	hexabromocyclododecane
Hg	mercury
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PAH	polycyclic aromatic hydrocarbon

PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative, and toxic
PCB	Polychlorinated biphenyls
PFAS	per- and polyfluoroalkyl substances
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
TOC	Total organic carbon
WAC	Washington Administrative Code
WA:LA	Watershed area to lake area ratio
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

Units of measurement

°C	degrees centigrade
dw	dry weight
g	gram, a unit of mass
mg/kg	milligrams per kilogram (parts per million)
ng/g	nanograms per gram (parts per billion)
pCi/g	picocuries per gram
pg/g	picogram per gram (parts per trillion)
µg/kg	micrograms per kilogram (parts per billion)
$\mu g/m^2/yr$	micrograms per square meter per year

Quality Assurance Glossary

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

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

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

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

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

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

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

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

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

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

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Ecology 2004).

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

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

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

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

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

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective

criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

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

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

- No qualifier – data are usable for intended purposes.
- J (or a J variant) – data are estimated, may be usable, may be biased high or low.
- REJ – data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

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

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology, 2004).

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

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

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

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

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

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

Measurement result: A value obtained by performing the procedure described in a method (Ecology, 2004).

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

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

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

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

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

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

Population: The hypothetical set of all possible observations of the type being investigated (Ecology, 2004).

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

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

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Ecology, 2004).

Quality control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology, 2004).

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

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

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

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

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

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

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

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

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

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

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

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

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

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

References for QA Glossary

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