Mercury Species and Other Selected Constituent Concentrations in Water, Sediment, and Biota of Sinclair Inlet, Kitsap County, Washington, 2007–10

Data Series 658

U.S. Department of the Interior
U.S. Geological Survey

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Contents

Abstract 1
Introduction 1
Description of Study Area 3
History of Remediation and Environmental Investigations Related to Mercury 8
Methods 10
- Equipment 10
- Watershed Sources Project Sampling Methods 10
  - Groundwater 10
    - Basewide Wells 10
    - Tidal Studies 11
  - Industrial and Municipal Sources 12
  - Surface Water 12
- Methylation and Bioaccumulation Project Sampling Methods 14
  - Marine Sediment 14
    - Incubation Cores (>10 cm overlying water) 16
    - Sediment Cores (<10 cm overlying water) 16
      - Cores for Redox-Sensitive Species in Porewater 16
      - Sediment in the Top 2 Centimeters 16
  - Marine Water 17
  - Zooplankton 18
- Laboratory Processing 18
  - Watershed Sources Project 18
    - Mercury 18
    - Total Suspended Solids 19
    - Carbon and Nitrogen 19
  - Methylation and Bioaccumulation Project 19
    - Marine Sediment 19
    - Porewaters 20
      - Mercury and Dissolved Organic Carbon 20
      - Reduction-Oxidation Sensitive Constituents 20
    - Incubation Core Experiments 21
    - Tumbling-Core Experiments 22
    - Marine Water Column 22
      - Mercury 22
      - Total Suspended Solids 23
      - Phytoplankton and Suspended Solids 23
      - Zooplankton 24
- Laboratory Analyses 24
  - Water Samples 24
    - Mercury 24
    - Carbon and Nitrogen 25
    - Metals and Major Ions 25
    - Chlorophyll 25

Contents—Continued

Methods—Continued
Laboratory Analyses—Continued
Marine Sediment Samples 25
Physical Properties 25
Mercury 25
Methylmercury Production Potential 26
Sulfur Species 27
Iron Species 27
Zooplankton 27
Taxonomy 27
Mercury 27
Stable Isotopes 27
Quality Assurance and Assessment of Data 28
Data 28
Watershed Sources Project 28
Methylation and Bioaccumulation Project 28
Acknowledgments 28
References Cited 48
Appendix A: Tables Describing Water and Sediment Sampling Stations and Fequency of Sampling for the Watershed Sources and Methylation and Bioaccumulation Projects, Sinclair Inlet, Washington 51
Appendix B: Quality Assurance and Assessment of Data Collected for Watershed Source Project 52
Appendix C. Quality Assurance and Assessment for Marine Sediment Collected for the Methylation and Bioaccumulation Project 55
Appendix D. Quality Assurance and Assessment for Marine Water Column Samples Collected for the Methylation and Bioaccumulation Project 60
Appendix E. Data Tables of Total and Particulate Mercury and Selected Constituents for Freshwater Inputs to Sinclair Inlet and Vicinity, Water Sources Project, Sinclair Inlet, Washington 63
Appendix F. Data Tables of Methylmercury and Selected Constituents for Freshwater Inputs to Sinclair Inlet and Vicinity, Watershed Sources Project, Sinclair Inlet, Washington 63
Appendix G. Data Tables of Total Mercury, Methylmercury, and Selected Constituents in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Summer 2008 63
Appendix H. Data Tables of Total Mercury, Methylmercury, and Selected Constituents in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Fall 2008 63
Appendix I. Data Tables of Total Mercury and Methylmercury, and Selected Constituents, in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Winter 2008–10 63
Appendix J. Data Tables of Total Mercury, Methylmercury, and Selected Constituents in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Spring 2009 64

Figures

Figure 1. Map showing location of Sinclair Inlet, and Holmes Harbor (HH) and Budd Inlet (BI) sampling stations, Puget Sound, Washington 2
Figure 2. Map showing location of Agate, Port Orchard, and Rich Passages and Liberty Bay and Sheridan Road Sampling stations, Puget Sound, Washington 4
Figure 3. Map showing location of Operable Units of the Bremerton Naval Complex, creek drainage basins sampled in 2008, and marine sediment stations sampled in the convergence zone (CZ) and Sinclair Inlet (SI) 2008–10, Sinclair Inlet, Washington 5
Figure 4. Map showing location of the marine sediment stations and groundwater wells sampled in the five general areas of the Bremerton naval complex (BNC), Sinclair Inlet, Washington, 2008–09 7
Figure 5. Map showing location of stream, stormwater, and marine water column stations sampled, Sinclair Inlet drainage basin, Washington, 2008–10 13
Figure 6. Sampling schematic for sediment methylation potential, porewater analyses, tumbling-core experiments and incubation experiments 15

Tables

Table 1. Study sites and numbers of samples for filtered and particulate mercury and selected constituents collected during the Watershed Sources Project, Sinclair Inlet, Washington 29
Table 2. Study sites and numbers of samples for filtered methylmercury and selected constituents collected during the Watershed Sources Project, Sinclair Inlet, Washington 30
Table 3. Numbers and types of samples collected during August 2008 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington 31
Table 4. Numbers and types of samples collected during summer and fall 2008 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington 33
Table 5. Numbers and types of samples collected during winter 2009–10 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington 35
Table 6. Numbers and types of samples collected during winter 2008–09 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington 37
Table 7. Numbers and types of samples collected in June 2009 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington 39
Table 8. Numbers and types of samples collected during spring 2009 (April to June) for the Methylation and Bioaccumulation Project in association with the water column sampling program, Sinclair Inlet, Washington 41
Table 9. Numbers and types of samples collected in August 2009 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington 43
Table 10. Numbers and types of samples collected in summer 2009 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington 45

Conversion Factors, Datums, and Abbreviations and Acronyms

Conversion Factors

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.6093	kilometer
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)
section (640 acres or 1 square mile)	259.0	square hectometer (hm^2)
square foot (ft^2)	929.0	square centimeter (cm^2)
square foot (ft^2)	0.09290	square meter (m^2)
square inch (in^2)	6.452	square centimeter (cm^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L), micrograms per liter (µg/L), or nanograms per liter (ng/L).

Datums

Vertical coordinate information is referenced to National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Conversion Factors, Datums, and Abbreviations and Acronyms—Continued

Abbreviatons and Acronyms

BNC	Bremerton Naval Complex
C	Carbon
CAD	Confined Aquatic Disposal
CCV	Continuous calibration verification
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFWR	Camp Far West Reservoir
CIA	Controlled Industrial Area
CRM	Certified reference material
CVAFS	Cold vapor atomic fluorescence spectrometry
DI	Deionized water
DIGCHK	Digestion checks
DO	dissolved oxygen
DOC	Dissolved organic carbon
FC	Fecal Coliform
Fe	Iron
FP	Fluorocarbon polymer
FMHg	Filtered methylmercury
FTHg	Filtered total mercury
GFF	Glass fiber filter
HCl	Hydrochloric acid
HDPE	High-density polyethylene
Hg	Mercury
$HgCl_2$	Mercuric chloride
Hg(II)	Inorganic mercury
Hg(II)R	Reactive mercury in sediment
HNO_3	Nitric acid
KOH	Potassium hydroxide
LCS	Laboratory control samples
LTMP	U.S. Navy Long-Term Monitoring Program
M	Molar
MHg	Methylmercury
Mn	Manganese
MS	Matrix spike
N	Nitrogen
N_2	Nitrogen gas
NBK	Naval Base Kitsap
NPDES	National Point Discharge Elimination System
NPL	National Priorities List
NRP	National Research Program (Menlo Park, CA)
NSC	Naval Supply Center
NWQL	USGS National Water Quality Laboratory

Conversion Factors, Datums, and Abbreviations and Acronyms—Continued

Abbreviatons and Acronyms—Continued

OUBT	Operable Unit B Terrestrial
OU	Operable Unit
PCBs	Polychlorinated biphenyls
P	Phosphorous
PE	Polyethylene
PETG	Polyethylene terephthalate G copolyester
PFA	Perfluoroalkoxy copolymer
PMHg	Particulate methylmercury
PSNS&IMF	Puget Sound Naval Shipyard and Intermediate Maintenance Facility
PTFE	Polytetrafluoroethylene
PTHg	Particulate total mercury
PVC	Polyvinylchloride
QA	Quality assurance
QFF	Quartz fiber filter
REDOX	Reduction-oxidation
RO	Reverse Osmosis
RPD	Relative percent difference
RPDev	Relative percent deviation
RSD	Relative standard deviation
SD	Standard deviation
SI	Sinclair Inlet
SiO_2	Silicon dioxide
SMHg	Sediment methylmercury
$SnCl_2$	Stannous (tin) chloride
SOAL	State-owned aquatic lands
SRM	Standard reference material
SRS	Standard reference sample
STHg	Sediment total mercury
THg	Total mercury
TOC	Total organic carbon
TN	Total nitrogen
TPC	Third party controls
TPCN	Particulate carbon and particulate nitrogen
TSS	Total suspended solids
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UW	University of Washington
WAWSC	Washington Water Science Center
WMRL	Wisconsin Mercury Research laboratory
YSI	Yellow Springs Instruments

Mercury Species and Other Selected Constituent Concentrations in Water, Sediment, and Biota of Sinclair Inlet, Kitsap County, Washington, 2007–10

By R.L. Huffman, R.J. Wagner, J. Toft, J. Cordell, J.F. DeWild, R.S. Dinicola, G.R. Aiken, M. Marvin-DiPasquale, A.R. Stewart, P.W. Moran, A.J. and Paulson

Abstract

This report presents data collected for two U.S. Geological Survey field sampling projects related to mercury (Hg) in Sinclair Inlet: (1) the Watersheds Sources Project that evaluated the sources of mercury to Sinclair Inlet during December 2007 to March 2010, and (2) the Methylation and Bioaccumulation Project, a comprehensive examination of mercury biogeochemistry in sediment, water, and zooplankton during August 2008–February 2010.

For the Watershed Sources project, nonpoint and point sources of mercury to Sinclair Inlet from the Bremerton naval complex (BNC) were evaluated by using filtered total mercury and particulate total mercury measured in water samples collected from 11 wells, 2 dry dock sump discharges, and a steam plant's effluent at the BNC. Methylmercury sources to the inlet were examined by determining filtered methylmercury concentrations in water samples collected from five wells, two dry dock sump discharges, a steam plant's effluent, five intertidal piezometers, and three stormwater drains on the BNC, as well as in samples from five creeks, two wastewater treatment facilities, and three stormwater drains in the Sinclair Inlet watershed outside of the BNC. An improved understanding of tidally modulated mercury migration to Sinclair Inlet from the BNC was gained through three intensive nearshore (tidal) sampling events of mercury species in groundwater and a nearby stormwater drain.

The Methylation and Bioaccumulation Project included a comprehensive field study of mercury biogeochemistry in marine sediment, water, and zooplankton in Sinclair Inlet. Mercury, iron, and sulfur species in sediment porewater from six sites within and three sites outside of Sinclair Inlet were measured to provide insight into the processes that produce methylmercury in the sediments. Total mercury, methylmercury, dissolved organic carbon, and redox-sensitive species were measured in porewaters in the top 2 centimeters of sediment, and these data were paired with sedimentary flux measurements from core incubation experiments to connect sedimentary processes to the water column. A broad-scale study of mercury methylation potential and mercury species at 20-plus stations in Sinclair Inlet was conducted in February 2009 and 2010, June 2009, and August 2009. Sedimentary flux measurements and analysis of mercury and biogeochemicals in sediment porewater and bottom water were made at six of the broad-scale stations. Bioaccumulation processes in the water column in the context of the sedimentary flux of methylmercury were examined using monthly survey data collected between August 2008 and August 2009. The survey data included concentrations of methylmercury and isotope ratios of carbon and nitrogen in bulk zooplankton measured at four stations in Sinclair Inlet in the context of the population of bulk zooplankton ascertained by taxonomical identification. The analysis of filtered total mercury, total particulate mercury, filtered methylmercury, particulate methylmercury, chlorophyll *a*, isotopes of carbon and nitrogen in suspended matter, and other biogeochemical data will facilitate the examination of the biogeochemistry of mercury in Sinclair Inlet.

Introduction

As early as the 1980s, the sediment of Sinclair Inlet (SI) (fig. 1) was known to have elevated concentrations of a number of elements and organic compounds (Malins and others, 1982). A remedial investigation of the marine waters off the Bremerton naval complex (BNC), Bremerton, Washington, was completed in 1996 (U.S. Navy, 2002), and a final Record of Decision (U.S. Environmental Protection Agency, 2000) was issued in 2002. The remedial actions included isolating a considerable volume of contaminated sediment from interactions with the benthic food web by capping and disposing of dredge spoils in a covered, confined aquatic disposal pit in 2001. The primary objective of the marine sediment cleanup was to reduce the risk to humans, particularly those engaged in a subsistence lifestyle, from consumption of bottom-dwelling fish with polychlorinated biphenyls (PCBs) in their tissues (U.S. Navy, 2002). Three

Figure 1. Location of Sinclair Inlet, and Holmes Harbor (HH) and Budd Inlet (BI) sampling stations, Puget Sound, Washington.

pathways were identified with the capability to transport chemicals from the terrestrial landscape of the BNC to the marine environment. The pathways have potential to recontaminate the recently remediated marine sediments; and include dry dock discharges to the inlet, groundwater discharge direct to marine water, and discharge of stormwater runoff.

In 2007, the U.S. Navy requested the U.S. Geological Survey (USGS) to evaluate: (1) the status of mercury at the BNC and in the sediment, water, and biota of Sinclair Inlet; (2) the sources of sinks of total mercury (THg); and the (3) potential to methylate mercury in Sinclair Inlet sediments. In this report, the word "total" refers to the total analytical concentration of an element in filtered water, sediment, suspended solids, or zooplankton, and not the analytical concentration in an unfiltered water sample.

For the Watersheds Sources Project, the USGS quantified the loadings of filtered total mercury (FTHg) and particulate total mercury (PTHg) from a number of municipal and industrial discharges, groundwater, stormwater, and streams by using existing and new data collected from December 2007 to March 2010. In addition, filtered methylmercury (FMHg) and ancillary constituents were measured in a subset of these sources.

For the Methylation and Bioaccumulation Project, the potential to methylate mercury in Sinclair Inlet sediments was evaluated by the USGS in a comprehensive field study examining the mercury biogeochemistry in Sinclair Inlet sediment, water, and biota, conducted between August 2008 and February 2010. The overall objectives of this study are to describe and quantify the biogeochemical processes that lead to the conversion of divalent inorganic mercury in sediment (STHg), to methylmercury in sediment (SMHg), the release of FTHg and FMHg from sediment, and the bioaccumulation of methylmercury into the base of the pelagic food web (zooplankton). Specific goals of this project are to (1) determine the spatial and temporal variability of methylmercury (MHg) concentrations in zooplankton and particulate methylmercury (PMHg) in Sinclair Inlet relative to the spatial and temporal variability of the four species of filtered and particulate total mercury and methylmercury (FTHg, FMHg, PTHg, and PMHg), dissolved organic carbon (DOC), and other constituents in the water column; (2) assess the seasonality of benthic mercury methylation throughout Sinclair Inlet; and (3) assess the seasonal flux of FTHg and FMHg from Sinclair Inlet sediment to the overlying water column at six sites by using sediment-core incubation experiments.

Description of Study Area

Sinclair Inlet is a shallow embayment (maximum depth of 20 m) on the western side of the Puget Sound lowlands and within the north-central Puget Sound Action Area of the Puget Sound Partnership. Sinclair Inlet is adjacent to another shallow embayment, Dyes Inlet (fig. 2). The Sinclair Inlet-Dyes Inlet system is hydrologically complex not only because of the geometry of the Dyes Inlet-Sinclair Inlet connection, but because Bainbridge Island blocks the connection between the Dyes Inlet-Sinclair Inlet system and central Puget Sound. The Dyes Inlet-Sinclair Inlet system is connected to central Puget Sound through the Port Madison-Agate Passage-Port Orchard Passage system on the northern side of Bainbridge Island and through Rich Passage on the southern side of Bainbridge Island. Rich Passage shallows to 20 m; the maximum depth in Agate Passage is 6 m. The shallowness of these passages results in extensive vertical mixing of the incoming tidal water. Tides in Puget Sound are mixed diurnally and have a maximum tidal range of about 5 m relative to a maximum depth of about 20 m for Sinclair Inlet. The relative proportion of tidal flows through Port Orchard Passage and Rich Passage that affects changes in tidal elevation in Sinclair and Dyes Inlet is unknown. Because the tidal prism volume of Dyes Inlet is about three times that of Sinclair Inlet, tidal currents in Port Washington Narrows, which connects Dyes Inlet to Sinclair Inlet, often lag those of Sinclair Inlet (Wang and Richter, 1999).

Sinclair Inlet is an irregularly shaped, triangular embayment about 1.9 km across and 6.4 km long (fig. 3). More than 20 small streams drain the Sinclair Inlet watershed and influence surface-water quality in the basin. The larger streams in the area include Gorst, Blackjack, Anderson, and Wright Creeks. The outer boundary of Sinclair Inlet for this study is defined as the seaward side of a cable area that extends from the Bremerton dock of the Washington State Ferry System to the pointed shoreline near Annapolis Creek on the south side of the inlet. This definition of the study area yields a surface area of 8.37 km^2 and a cross-sectional area at its entrance of 27,050 m^2. For this report, the area of Sinclair Inlet outside the BNC is defined as greater Sinclair Inlet.

Sinclair Inlet is essentially "a tidally dominated, non-stratified, saline body of water" (U.S. Navy, 1992) because of vertical mixing in the Rich and Agate Passages, the shallowness (20 m) of Sinclair Inlet relative to the tidal range, and the relatively small inflow of freshwater.

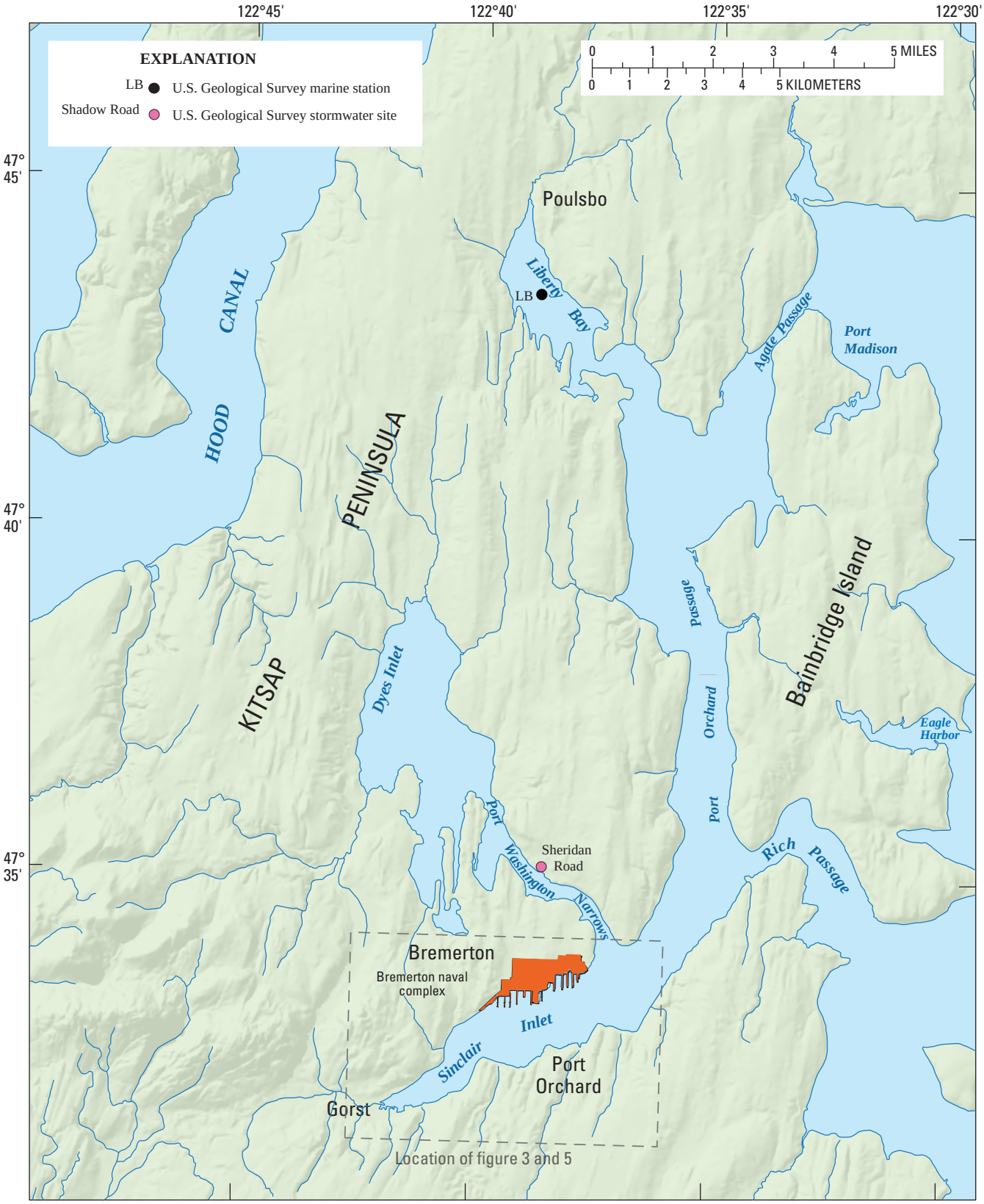

Figure 2. Location of Agate, Port Orchard, and Rich Passages and Liberty Bay and Sheridan Road Sampling stations, Puget Sound, Washington.

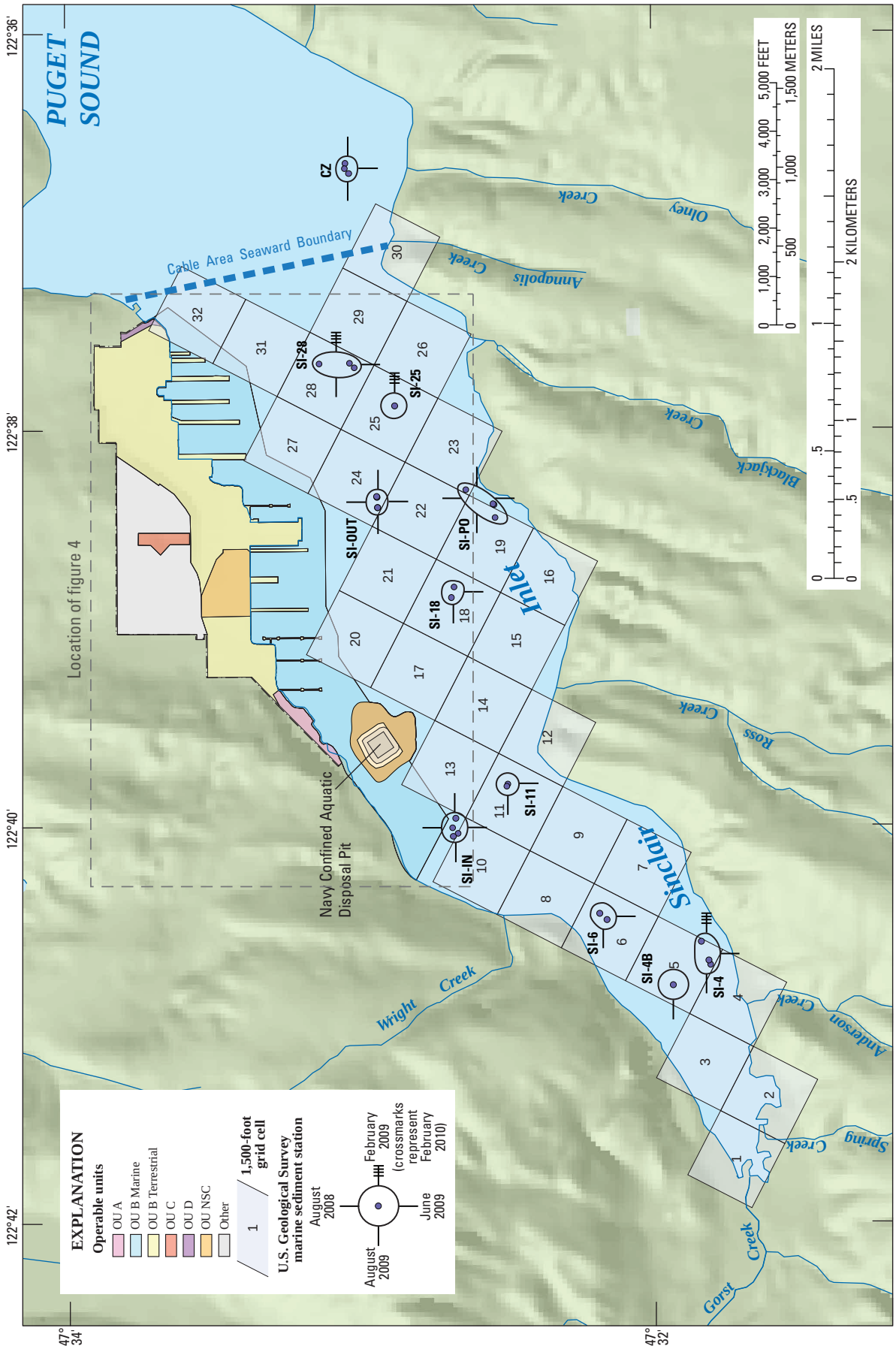

Figure 3. Location of Operable Units of the Bremerton Naval Complex, creek drainage basins sampled in 2008, and marine sediment stations sampled in the convergence zone (CZ) and Sinclair Inlet (SI) 2008–10, Sinclair Inlet, Washington.

The physical oceanographic study of Gartner and others (1998) also determined that Sinclair Inlet was nonstratified. In August 1994, the water column of Sinclair Inlet was essentially isothermal. During the wet season in March 1994, when surface runoff would be near its maximum, the surface stratification was less than 1 salinity unit in 30 units. Other studies (Katz and others, 2004; Washington State Department of Ecology, 2011a) have shown that Sinclair Inlet may be stratified under certain conditions. Gartner and others (1998) determined that typical current speeds were 5–10 cm/s. Wind forcing caused residual currents (time-averaged currents filtered with a 35-hour low-pass filter) in the bottom layer to flow in the opposite direction of the currents of the surface layer and the wind. Unlike systems dominated by estuarine circulation, residual currents in Sinclair Inlet were similar in magnitude to the tidal currents.

The BNC (approximately 2 km^2) is located on the northern shore of Sinclair Inlet in Bremerton, Washington (fig. 3). The BNC houses two separate Navy commands: Naval Base Kitsap Bremerton (NBK Bremerton) and Puget Sound Naval Shipyard and Intermediate Maintenance Facility (PSNS & IMF), Bremerton site.

The primary role of NBK Bremerton is to serve as a deep-draft home port for aircraft carriers and supply ships. Facilities on the NBK Bremerton property (0.4 km^2) include six piers and moorings, a steam plant, parking, housing, shopping, recreation, and dining facilities for military personnel and their families. NBK Bremerton also hosts several tenant commands, including the Naval Inactive Ships Movement Office, which is responsible for providing long-term care of inactive naval vessels, and the Fleet and Industrial Supply Center, which provides material acquisition and warehouse services to West Coast Navy commands. NBK occupies the western part of the naval complex and is a fenced, secure area.

The primary role of PSNS & IMF (1.5 km^2) is to provide overhaul, maintenance, conversion, refueling, defueling, and repair services to the naval fleet. The PSNS & IMF can dry dock and maintain all classes of Navy vessels and is the Nation's sole nuclear submarine and ship recycling facility. PSNS & IMF has six dry docks, eight piers and moorings, and numerous industrial shops to support its industrial operations. Like NBK Bremerton, PSNS & IMF is host to many tenant commands. PSNS & IMF occupies the eastern part of the naval complex and is a fenced high-security area.

For the purposes of environmental remediation, the BNC was divided into Operable Units (OU): OU A, OU B, OU C, OU D, and OU NSC (Naval Supply Center). OU B was further divided into OU B Marine and OU B Terrestrial (fig. 3). OU C is an upland area and OU D is a waterfront parcel on the eastern side of the BNC that has been remediated and turned over to the City of Bremerton. OUs C and D were not sampled during the project.

OU A consists of approximately 0.049 km^2 of manmade land and the adjacent marine environment of Sinclair Inlet. It is located in the southwestern portion of the BNC. The site is relatively level except for the riprap seawall, and most of its surface is paved. OU A is currently used as a parking lot for shipyard and deployed personnel and has been temporarily used as a staging area for dredge spoils. In the past, it was used as a helicopter pad and as a disposal area for industrial wastes associated with shipbuilding and decommissioning. Most of the land at OU A is composed of industrial fill to a depth of 2.1–10.7 m below the current ground surface. The fill increases in thickness toward the shore, where it is overlain with a layer of riprap stone. This industrial fill is composed of sandblast grit, scrap metal, brick, glass, wood, and other debris. Several shallow pits were established near the former helicopter pad and used for disposal of liquid wastes (U.S. Navy, 1995a).

OU NSC formerly contained the Defense Reutilization Marketing Office, which recycled materials and contained an acid drain pit that was removed in 1995. Much of the western part of OU NSC consists of various former disposal sites and shoreline fill areas used for leveling and extending PSNS boundaries. The material used as fill varies with the location, but includes oily sludge, automobile scrap, construction debris, shipyard debris, spent abrasive grit, and other materials (U.S. Navy, 1995b). Contaminants found during site investigations included PCBs, heavy metals, organics, and organotins (U.S. Navy, 2002).

OU B Terrestrial contains the NBK Bremerton and PSNS & IMF, excluding OU NSC. A number of waterfront areas in OU B Terrestrial served as former disposal sites and shoreline fill areas used for leveling and extending PSNS & INF. These areas received fill material that included oily sludge, automobile scrap, construction debris, shipyard debris, spent abrasive grit, and other materials (U.S. Navy, 1992). A suspected fill area at the eastern boundary of PSNS & IMF is now covered with gravel and some asphalt pavement and used to store bulk materials.

About 0.012 km^2 in the central PSNS & IMF in OU B Terrestrial (fig. 4) was used as a fill area from 1960 to 1974 and contains about 53,500 m^3 of fill ranging in thickness from 11.3 to 15.2 m. Fill materials included construction debris, rubble, spent abrasive grit ("blaster sand" and copper slag), and dredged sediment. In 1998, this area was paved and the Defense Reutilization Marketing Office was relocated from the OU NSC. As part of the remedial action for OU B Marine in 2000 and 2001, the shoreline perimeter was stabilized. This site also is part of the disposal site and shoreline fill area in central PSNS & IMF. The primary concern at this site is oil from two tanks at the site of a powerplant used for steam generation from 1910 to 1942, which was demolished in 1994.

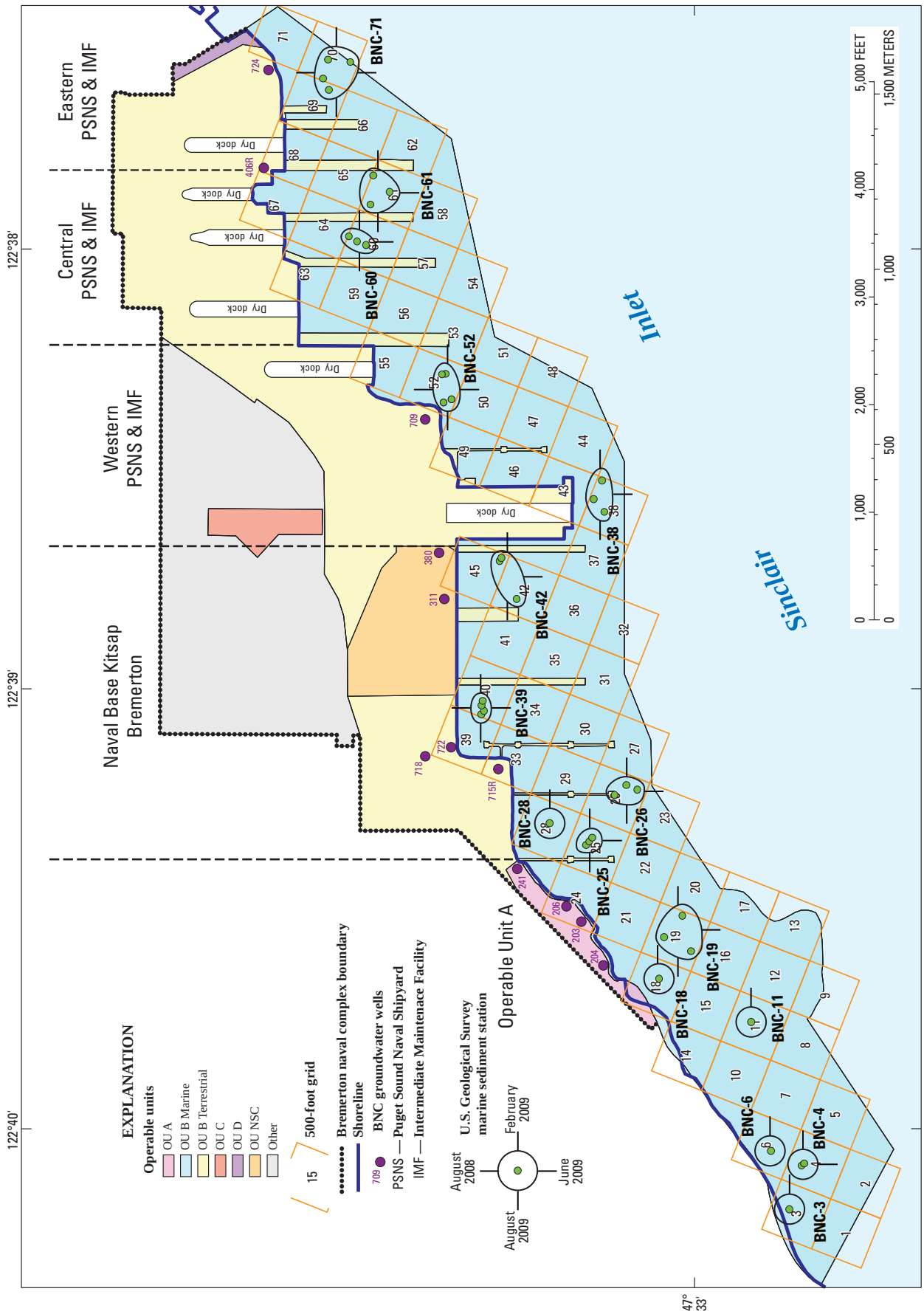

Figure 4. Location of the marine sediment stations and groundwater wells sampled in the five general areas of the Bremerton naval complex (BNC), Sinclair Inlet, Washington, 2008–09.

The western part of OU B Terrestrial contains NBK Bremerton and includes two possible sources of contamination, including the landfill for the former town of Charleston, Washington, of about 4 acres and just west of the OU NSC, that historically contained a number of wooden and concrete block structures. This location included a garbage can cleaning facility and a storage area for PCB waste and off-line transformers. In the 1980s, two dark-stained soil spots were removed during a time-critical removal action. Subsequently, the buildings were demolished and a hazardous and flammable materials warehouse and associated parking areas were constructed on the site from 1994 to 1996. Some soils contaminated with lead and other substances were removed during the construction of the hazardous and flammable materials warehouse (U.S. Navy, 1992).

Farther west in the NBK Bremerton area of OU B Terrestrial is a large former disposal site and shoreline fill area. A concrete tank used for the neutralization of acids, bases, and spent electroplating solutions was observed to be degrading to the extent that metal reinforcement bar was exposed. This observation prompted shipyard personnel to arrange alternative liquid-waste-disposal methods and to take the tank out of service in 1983 (URS Consultants, Inc., 1991).

History of Remediation and Environmental Investigations Related to Mercury

The historical data on sediment, water, and biota of Sinclair Inlet from 1989 to 2007 was compiled and presented in Paulson and others (2009). An early synthesis study of mercury concentrations throughout Puget Sound indicated that STHg concentrations within OU B Marine in central PSNS & IMF were twice as high as STHg concentrations in other urban areas of Puget Sound (Evans-Hamilton, Inc., and D.R. Systems, Inc., 1987). The level of STHg contamination was of the same magnitude as reported in sediment from Bellingham Bay associated with the Georgia-Pacific chlor-alkali plant and in sediment from Commencement Bay associated with the Asarco copper smelter. In 1989, the State of Washington Puget Sound Ambient Monitoring Program began monitoring the marine waters and sediment of Puget Sound. The sediment of Sinclair Inlet had the highest concentrations of THg and PCBs of all the long-term sediment monitoring sites in the first Puget Sound-wide sampling (Tetra Tech, Inc., 1990). The State of Washington continues long-term monitoring of sediment at one site in Sinclair Inlet and one site in Dyes Inlet. In addition, numerous marine sediment samples throughout the entire extent of various estuaries of Puget Sound were collected between 1997 and 1999, with Sinclair Inlet being sampled in 1998 (Long and others, 2000).

An Initial Assessment Study (URS Consultants, Inc., 1991) in 1990 assessed if previous PCB cleanup efforts associated with the two dark spots at the PCB storage area on NBK Bremerton were successful. The maximum PCB concentration measured in soil during the investigation was 1.94 mg/kg, a concentration less than the Model Toxics Control Act, Method A industrial soil cleanup level of 10 mg/kg for total PCBs. Soil samples analyzed for total metals showed the presence of lead and mercury. Soil samples from boring operations were analyzed for total mercury, which exceeded the Model Toxics Control Act, Method A industrial soil cleanup level (1 mg/kg) at 17 locations. The results of this initial assessment study were included in the Final Remediation Report (U.S. Navy, 1995b).

In 1990, the URS team began a site investigation of nine sites on the BNC under contract with the U.S. Navy (1992), and suggested that further evaluation was needed. The remedial investigation of OU A was initiated in 1992 and continued in two phases through 1994 (U.S. Navy, 1995a). OU A (fig. 4) is located on the southwestern edge of the BNC site and contained a helicopter landing pad at one time. Presently, the majority of OU A is occupied by a paved parking lot outside of the security fence of the BNC.

Likewise, the remedial investigation of OU NSC, which contained an acid drain slab, was initiated in 1992 and continued in two phases through 1994 (U.S. Navy, 1995b). Project management plans for OU B were developed in 1994 to guide the Remedial Investigation process for OU B, which took place between 1994 and 1996 in two phases; the final report was issued in 2002 (U.S. Navy, 2002). The remediation investigation of OU B included most of the working waterfront, including the piers and dry docks of the Controlled Industrial Area (CIA) of the PSNS, and contained most sites sampled as part of the Site Investigation. The operable units were reorganized for the Feasibility Study, and a new operable unit (OU B Marine) was established that included marine sediment within the former OU A and OU B. The investigations of OU A and OU B Terrestrial were devoted to the soils, groundwater, and surface water of their respective land areas. The Navy proposed dredging 80,360 m^3 (105,100 yd^3) of sediment on both sides of a pier off NBK Bremerton in 1991. The agencies of the Puget Sound Dredged Disposal Analyses issued a suitability determination in February 1994 for the unconfined open-water disposal of approximately 39,500 m^3 (51,700 yd^3) of material at a disposal site in Elliott Bay (fig. 1). The remaining 40,900 m^3 (53,400 yd^3) of material were designated for disposal at an upland disposal site. The dredging of the eastern side of the pier was completed in December 1994, and dredging of the western side of the pier was completed in March 1995. Annual monitoring of the dredged area occurred from 1995 through 1997 (U.S. Navy, 1998).

In June 1994, the U.S. Environmental Protection Agency (USEPA) designated the BNC for inclusion on the National Priorities List (NPL). A Feasibility Study was completed in 1998 to evaluate several alternatives for developing home port facilities for three Nimitz-class aircraft carriers (U.S. Navy, 1999) in which dredging of 303,600 m^3 (397,159 yd^3) of sediment was proposed. Dredging off western and central PSNS & IMF and off NBK Bremerton, as well as dredging of the turning basins for berths at BNC, also was proposed. Sediment sections from the surface to a depth of 122 cm were collected from 77 locations, and subsurface sections (deeper than 122 cm) from 7 locations were collected and analyzed (U.S. Navy, 1999). The composition of proposed dredged spoils was further studied (U.S. Navy, 2000) because of the large number of sediment sections that failed to meet the regional Puget Sound suitability guidelines for open-water disposal and because sediment chemistry concentrations of toxic constituents were poorly related with the occurrence of toxicity end points (U.S. Navy, 1999).

As early as 1997, coordination began between planning efforts for clean-up of the marine sediment and construction activities designed to improve the home port capabilities of the shipyard. With the need for navigational dredging of marine sediment within OU B Marine, plans for a confined aquatic disposal (CAD) site were developed in 1999. In the design of a CAD, a pit is dug in the subtidal sediment of an estuary and the contaminated sediment is placed in the pit. After dredging and dredge disposal are complete, the pit is covered with a thick cover of clean, coarse sediment. Disposal of dredge spoils from the most contaminated sediment of the BNC also were to be confined in the CAD under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

The Record of Decision for OU B Marine (U.S. Environmental Protection Agency, 2000) indicated that fish tissue contaminated with PCBs posed an unacceptable risk to subsistence seafood harvesters. Consumption of older rockfish with high THg concentrations also was identified as a possible human health risk. Because the marine area off OU A is not part of the working waterfront of the BNC, capping of this subtidal contaminated sediment with clean sediment was selected as a remedy to isolate living marine resources from the contaminated sediment. A thick cap was placed over the most contaminated sediment near the shoreline and a thin cap was placed over most of the contaminated sediment off OU A. The assumption underlying the placement of a thin cap over the less contaminated sediment was that the thin cap would isolate living marine resources from contamination until such time that natural sedimentation of clean sediment (enhanced natural recovery) would permanently bury the contaminated sediment. Higher than expected results of PCB analyses of sediment collected around the CAD Pit in 2001 and in state-owned aquatic lands (SOAL) in 2003 led to additional thin caps being placed on the periphery of the CAD pit (U.S. Navy, 2004).

The Record of Decision provides for post-remediation monitoring to be used in reviews every 5 years to assess the effects of the initial and subsequent remedial actions. The Long-Term Monitoring Program (LTMP) examines the marine sediment and natural resources in Sinclair Inlet and in the groundwater resources of OU A, OU B, and OU NSC. Beginning in 2003, the LTMP examined the concentrations of PCBs and THg in sediment in 72 cells of a 500-ft sampling grid within the boundary of the BNC and 32 cells of a 1,500-ft sampling grid in Sinclair Inlet outside of the BNC boundary on a biennial basis. In addition, the cap of the CAD pit was examined in 2003 and 2005, as well as a ring of 15 cells of uncapped sediment around the CAD pit, called the CAD Pit Apron. In 2004 (U.S. Navy, 2004), the boundary of OU B Marine was extended to include State owned aquatic lands (southeast protrusion of the Navy confined aquatic disposal pit in fig. 3).

The LTMP continues to monitor groundwater for THg in unfiltered water, other dissolved metals, and organic contaminants in five wells installed during the Remedial Investigation and five new wells installed in 2004 within close proximity to the shoreline. The PCB and THg concentrations in composites of English sole were measured in 2003 and 2007 to assess impacts of contamination on human health. In the second 5-year review (U.S. Navy, 2007), mercury contamination in marine sediment and groundwater continued to be a concern.

The ENVironmental inVESTment (ENVVEST) project was developed between Federal, State, and local partners to specifically address the development of total maximum daily loads for the Sinclair-Dyes Inlet watershed adjacent to PSNS & IMF. The Final Project Agreement was signed in September 2000 (Washington State Department of Ecology, 2011b). The ENVVEST project assessed the sources and impacts of fecal coliform (FC) pollution within the inlets (May and others, 2005); developed a watershed-receiving water model of FC pollution, fate, and transport to support the total maximum daily load assessment of FC loading (Johnston and others, 2009a); assessed the sources of contamination, including Hg, from watershed and stormwater runoff as a function of upstream land use and cover (Brandenberger and others, 2007; May and others, 2007); and evaluated chemical contaminant levels in demersal fish and invertebrates in Sinclair Inlet and other areas of the Puget Sound (Johnston and others, 2007).

After the USGS marine sampling was completed, the ENVVEST project initiated an ambient monitoring program (Johnston and others, 2009b) with the following objectives: (1) establish a baseline for assessing continuous process improvement of shipyard operations and other sources of contamination into Sinclair and Dyes Inlets, (2) provide data for validation of proposed mixing zones and model verification, (3) obtain data and information on toxicity of effluents and receiving waters for NPDES permit requirements for the PSNS&IMF, and (4) develop procedures needed to meet ambient monitoring requirements. Additionally, Brandenberger and others (2010) evaluated the atmospheric deposition of selected metals (including Hg), PAHs, PBDE, and biomarkers to assess potential inputs of combustion-derived constituents to the Puget Sound airsheds.

Methods

Equipment

Equipment for sampling dry docks between December 2007 and February 2009 and monitoring wells in January and February 2008 was acid cleaned at the USGS Washington Water Science Center (WAWSC) in Tacoma, Washington, as described by Lewis and Brigham (2004). Laboratory reverse osmosis (RO) water was processed through an Elga (High Wycombe, United Kingdom) Centra™ unit that contained 5 µm and 1-µm prefilters, a carbon filter, RO cartridge, ultraviolet chamber, and 0.2-µm filter, before passing through a deionizing cartridge unit and being distributed to the laboratory faucets and point-of-service units in a continuously recirculating loop. Water for cleaning was taken from an Elga Purelab® point-of-service unit supplied with water from the Centra™ unit.

The only exceptions to these procedures were that the polytetrafluoroethylene (PTFE) tubing was acid cleaned at room temperature, filtered water for analysis of FTHg by the USGS National Water Quality Laboratory (NWQL) was collected in glass bottles, and unfiltered water for PTHG analyses was collected in high-density polyethylene (HDPE) bottles between December 2007 and February 2008.

From March 2008 to August 2009, all equipment for sampling of groundwater, dry docks, steam plant, streams, stormwater drains, and marine water column (including the PTFE and fluorocarbon polymer (FP) tubing and PTFE sampling ports) was hot acid cleaned at the USGS Wisconsin Mercury Research laboratory (WMRL) in Middleton, Wisconsin, by following the procedures described by Lewis and Brigham (2004), as were C-Flex™ peristaltic tubing and the cartridge filters (Meissner ALpHA CMF0.45-442) by using cold acid cleaning. Quartz fiber filters (QFF) were precombusted at the WMRL. Savillex perfluoroalkoxy copolymer (PFA) filtering towers and FP bottles for FTHg and FMHg samples, 5-L FP bottles for compositing the wastewater effluent samples, 50-mL FP centrifuge tubes and plastic utensils for processing porewater samples, FP floating stirring bar, FP syringe tips for the incubation experiments, and the 500-mL FP beakers for tumbling-core experiments were hot acid cleaned at the WMRL. Sterile polyethylene terephthalate copolyester G (PETG) bottles were used for collection of unfiltered water. The rubber core caps; HDPE bottles for analysis of nutrients and total metals; and acrylic parts, such as the square liners for the box corer, the circular core lines for the incubation and redox cores, and the incubation core tops, were cleaned in cold acid at the WAWSC.

Watershed Sources Project Sampling Methods

Groundwater

In January–February and April 2008, water-level elevations; field measurements for dissolved oxygen (DO), pH, specific conductance, salinity, and turbidity; and concentrations of FTHg. PTHg, and total suspended solids (TSS) from discreet samples were measured in the three waterfront OUs for 12 wells (fig. 4, locations listed in appendix A–Basewide Wells). In a subset of samples, methylmercury and selected constituents were measured in April and June 2008. Two wells (OUBT-715R and OUBT-722) and five temporary piezometers also were sampled during two tidal studies in May and June 2008 (fig. 4).

Basewide Wells

The construction details and physical measurements of monitoring wells in OU A, OU B Terrestrial, and OU NSC are listed in appendix A–Basewide Wells. Upon removing the well cover at each well location at the BNC, any water in the well cavity around the polyvinylchloride (PVC) casing was bailed first manually and then completed with a peristaltic pump dedicated for bailing. The bailing peristaltic pump also was operated during the sampling if the water level in the well cavity began to rise.

After the water level was measured, a 1-foot long, dense PTFE sampling port secured to a well-specific length of ¼-in. PTFE tubing was lowered into the PVC casing to the middle of the screened interval of the well, and field parameters of the groundwater were monitored while purging. The upper open end of the ¼-in. PTFE tubing was inserted into C-Flex™ tubing at the inlet side of the pump and secured with zip ties. A disposable piece of C-Flex™ tubing was added to the pump C-Flex™ tubing with an HDPE connector sealed in plastic to keep the outlet side of the pump C-Flex™ tubing clean during purging and monitoring of field parameters. The pump C-Flex™ tubing was threaded through the peristaltic pump, and the outlet side of the disposal piece of C-Flex™

tubing was connected to a flow chamber of a data sonde (Yellow Springs Instruments (YSI), Yellow Springs, Ohio) equipped with temperature-compensated sensors. Purging of the well occurred at approximately 300 mL/min, while continuously monitoring field parameters (temperature, specific conductance, pH, and DO) and measuring turbidity by discrete samples from the outlet of the flow-through chamber by using a Hach 2100P portable turbidimeter. Samples for chemical constituents were collected after approximately three casing volumes of water were purged from the wells and after allowing pH, specific conductance, and DO to stabilize within 0.1 unit, 5 percent, and 0.3 mg/L, respectively. The specific conductance sensor was checked daily with standard reference solutions; the pH sensor was calibrated daily with two pH standards; and the DO sensor was calibrated daily by using the water-saturated air method and occasionally verified with zero DO solution. The turbidimeter was calibrated weekly with primary standards and daily with secondary standards.

After purging and measurement of field variables, the disposable piece of C-Flex™ tubing and HDPE connector were removed, and the clean end was inserted into a filter inside a plastic sampling chamber to minimize contamination. A bagged, cleaned cartridge filter connected to a 3-in. piece of ¼-in PTFE tubing with a PFA fitting (female ¼-in. threaded to ¼-in. tube) was brought into the sampling chamber and connected to the C-Flex™ tubing. The bottle for the FTHg sample (acid-cleaned 250-mL glass in January–February and 500-mL FP in April) was unbagged and rinsed three times with filtrate from the cartridge filter within the sampling chamber. During this process, the person sampling was wearing polyethylene gloves and a Tyvek laboratory frock to minimize ambient contamination, while an assistant held the cartridge filter through the plastic bag in a manner in which the outlet of the cartridge filter would not touch any surfaces. After rinsing, filtered water for analysis of FTHg was collected. A backup FTHg sample was collected in a similar manner. In April 2008 at five wells as part of the methylmercury survey task, additional filtrate was collected in a 250-mL FP bottle for analysis of FMHg. The cartridge filter was then disconnected from the pump C-Flex™ tubing and the PFA fitting was removed from the cartridge filter. Unfiltered water was collected in the sampling chamber in two 1-L PETG bottles for analysis of PTHg at the WMRL and one 1-L HDPE bottle for a TSS measurement that was processed in the WAWSC laboratory at the end of the day. Raw and filtered samples were placed over ice in a cooler and transported to the WAWSC.

For the five wells sampled in April 2008 (OUA-206, OUB-718, OUB-722, OUB-724, OUNSC-380) as part of the methylmercury survey tasks (appendix A–Base-Wide Wells), analytes included FMHg, and selected constituents [total particulate carbon and nitrogen (TPCN), DOC, nutrients (ammonia, nitrite, nitrate, orthophosphate and silica) and redox-sensitive species (sulfide, ferrous iron, filtered total iron and manganese]. Three nitrogen species (nitrite, nitrate, and ammonium) also are redox-sensitive species. Sulfide concentrations were measured in the field immediately after the field parameters stabilized by using a colorimetric methylene-blue indicator method according to the Hach Method 8131 (Hach Company, 2003a) and by using a Hach Model 2010 spectrophotometer, a procedure equivalent to USEPA method 376.2 (U.S. Environmental Protection Agency, 1978). Then, concentrations of ferrous iron were measured in the field by using a colorimetric 1,10 phenanthroline indicator method following the Hach Method 8146 (Hach Company, 2003b; adapted from American Public Health Association, 1980) and by using the Hack Model 2010.

A 0.45-µm pore-size, 25-mm diameter disk Millex-HV membrane filter (Millipore, New Bedford, Maine) was connected to the C-Flex™ in the sampling chamber after all mercury samples were taken. Samples for determination of filtered total iron and total manganese were filtered into 125-mL polyethylene (PE) bottles, acidified in the field with nitric acid to a pH of less than 2. Samples for determination of nutrients were filtered through the same 0.45-µm membrane filter into 65 mL PE bottles. The disk filter was removed and raw water was collected into three 1-L baked amber glass bottles for TPCN and DOC. Because 9 of the 11 wells contained seawater, samples for major ions were not collected. Similar to the mercury samples, raw and filtered samples were transported to the WAWSC, where the samples for total metals were shipped on ice to the USGS NWQL in Lakewood, Colorado, and the nutrient samples were frozen and shipped to the University of Washington (UW) Chemical Oceanography Laboratory in Seattle, Washington.

Tidal Studies

On May 6, 2008, groundwater at well OUBT-722 was sampled, and water levels in the well and in Sinclair Inlet were monitored over an approximate 14-hour period. Tides ebbed from +1.7 to –3.1 m, and flooded back up to +1.7 m. Groundwater samples were collected at about 2-hour increments from two or three depths in well OUBT-722: from near the bottom of the screened interval, from the middle of the screened interval or at the water table (whichever was lowest), and from near the water table when it was above midscreen. Samples were filtered and analyzed for mercury concentrations at the NWQL, and salinity was measured in unfiltered samples in the field. Water levels in the well were periodically measured with a steel tape, water levels in Sinclair Inlet were periodically measured with a surveyor's level and rod, and the difference between well and inlet water levels were periodically measured by using a manometer board. All water-level data were converted to a common datum (NGVD 29) for direct comparison. Groundwater from the newly installed nearby well 715R was sampled twice. Nutrients, TPCN, and redox-sensitive constituents were analyzed in a single sample from well 715R, and in eight samples at well OUBT-722.

Additional data were collected during June 4–5, 2008, at well OUBT-722 to gain further insight into mercury migration in groundwater in the vicinity. Again, groundwater in well OUBT-722 was sampled, and water levels in the well and Sinclair Inlet were monitored over an approximate 30-hour period that included two ebb cycles with tidal changes greater than 5 m. Twenty-five groundwater samples were collected at about 1-hour increments from near the fluctuating water table in well OUBT-722. The samples were filtered and analyzed for mercury concentrations at the NWQL, and specific conductance was measured in unfiltered samples in the field. Three times during the sampling, duplicate samples were collected for a laboratory intercomparison exercise between NWQL and WMRL. Water levels in the well were periodically measured with a steel tape, and the difference between well and Sinclair Inlet water levels were periodically measured by using a manometer board.

Additionally, five temporary piezometers were installed within the intertidal zone and were sampled at about 1-hour increments. All piezometers were constructed of 2-m long sections of 2-in. outside diameter marine-grade stainless steel. The bottom 5 cm were crimped and holes were drilled in the lower 0.35 m of each pipe for an open interval of about 0.3 m. The piezometer tops were threaded and 1.1-m extensions made of standard schedule-80 steel were added to facilitate sampling at higher tides. The piezometers were hand driven until refusal. Samples pumped from the piezometers were filtered and analyzed for mercury concentrations at the WMRL, or specific conductance and temperature was measured in the field from unfiltered samples. Water levels in the piezometers were periodically measured with a steel tape, and the difference between piezometer and Sinclair Inlet water levels was periodically measured by using a manometer board.

At least one PTHg and TSS sample from each of the five piezometers and at least one FMHg sample from each of the five piezometers was collected.

Industrial and Municipal Sources

Three outfalls from dry dock relief drainage systems at the BNC (appendix A– Industrial & Municipal Sources) were sampled by the USGS from December 2007 through June 2008 as well as the effluent from the BNC steam plant. The first sample at each dry dock system consisted of a grab sample collected at the level of the sump and a composite sample that was collected from a composite sampler three floors above. In both cases, the collection of a composite sample was discontinued because of a faint smell of hydrogen sulfide, indicating possible methylation of mercury in the riser between the level of the sump and level of the composite sampler. All subsequent samples from dry docks were grab samples collected at the sump level. Dry dock 6 was sampled by using a PTFE sampling port connected to ¼-in. PTFE tubing that was lowered into a metal standpipe through the ceiling of the sump well, allowing sampling similar to that previously described for monitoring wells. Dry Docks 4 and 5 were sampled by connecting a PTFE reducing coupler (5/8 to ¼-in.) directly to the plumbing of the discharge pipe of the well sump, thus eliminating the need for a peristaltic pump. Samples from the steam plant mixing well were collected by using a PFTE sampling port connected to ¼-in. PTFE tubing that was lowered into the effluent holding tank, allowing sampling similar to that previously described for monitoring wells. In all cases, sample collection and processing procedures were similar to the manner described for monitoring wells once the sample lines were connected. During the April 2008 sampling, samples for FMHg and selected constituents (TPCN, nutrients, and redox-sensitive species) were collected as part of the methylmercury survey.

Samples of treated wastewater effluent were collected during April, July, and August 2008 from the City of Bremerton wastewater treatment plant, which discharges to Sinclair Inlet, and from the West Sound Utility District, which discharges just outside the boundary of the Sinclair Inlet study area (appendix A–Industrial & Municipal Sources). Four to five 1-L grab samples were collected from the final effluent flow stream of each treatment plant by plant personnel at regular intervals during the 8-hr day shift by using 1-L PETG bottles held in a plastic holder attached to a swing pole. After transporting the grab samples to WAWSC at the end of the day shift, the 1-L bottles were composited into a 5-L FP bottle. The composite sample was then split out into five equal volumes for processing of (1) FTHg, FPTg, FMHg, (2) major ions, filtered nutrients, and filtered total iron and manganese, (3) DOC and TPCN, (4) TSS, and (5) extra water if needed. Measurements of specific conductance, pH, and turbidity were obtained from one of the splits of the composite sample.

Surface Water

As part of the methylmercury survey of the Watersheds Project, four streams discharging to Sinclair Inlet and one stream discharging to marine waters adjacent to Sinclair Inlet (fig. 5, appendix A–Surface Water) were sampled by USGS twice during 2008. Sampling and processing techniques were similar to those for groundwater sampling for which FMHg was collected. Modifications from the groundwater sampling include the following: (1) field parameters were monitored by placing the YSI data sonde in the stream instead of pumping water to a flow chamber, (2) the ¼-in. PFA sampling tubing was inserted directly into the centroid of flow without a sampling port, and (3) field measurements of sulfide and ferrous iron were not made in these open-flow channel streams. After pumping native stream water through the PFA sampling tubing for about 5 minutes, FTHg and FMHg samples were collected through a Meissner cartridge filter and

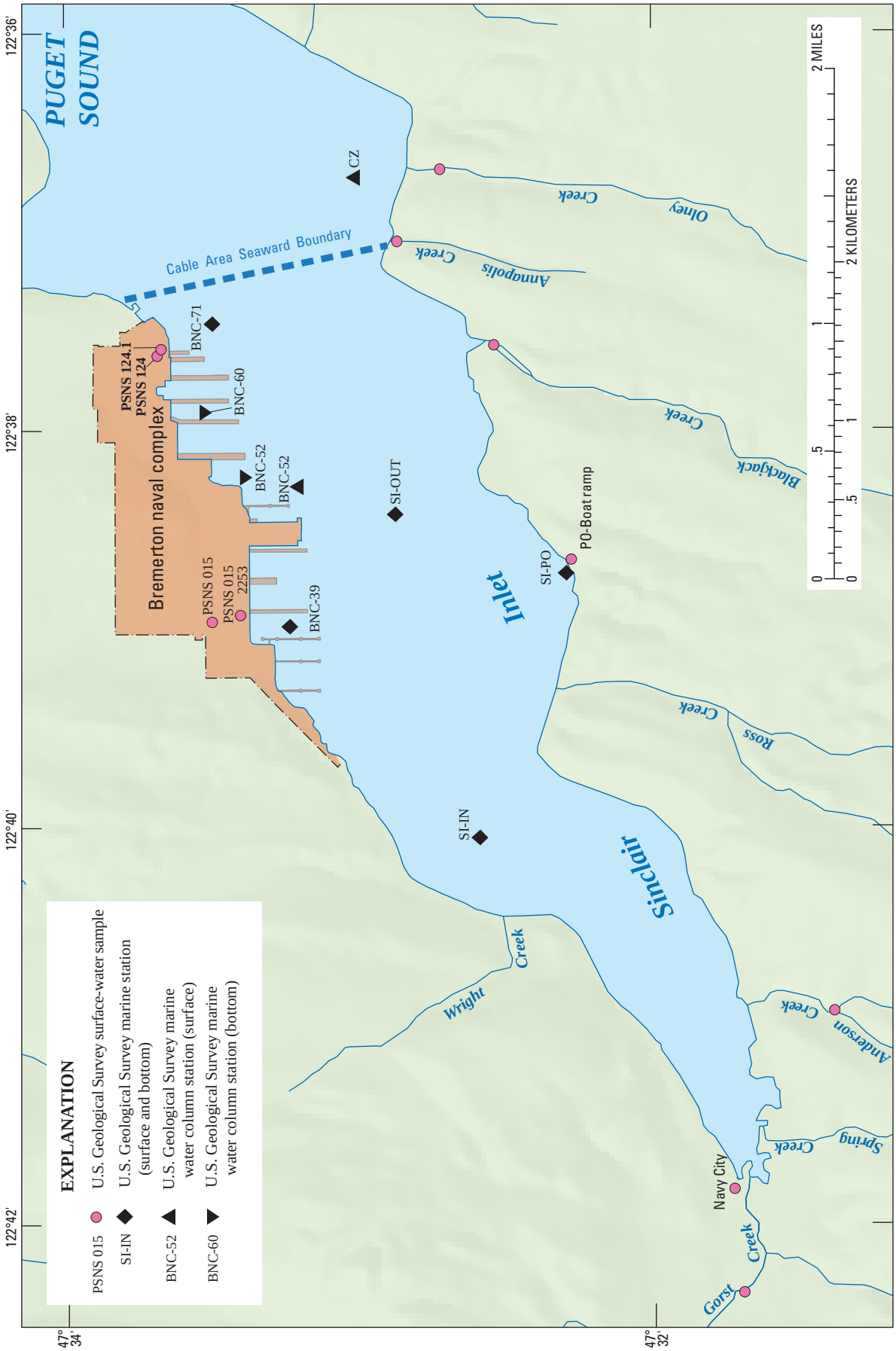

Figure 5. Location of stream, stormwater, and marine water column stations sampled, Sinclair Inlet drainage basin, Washington, 2008–10.

into FP bottles. The Meissner cartridge filter was removed and raw water for PTHg analysis was collected in 1-L PETG bottles. Filtered samples for analysis of major ions, nutrients, and total iron and manganese were filtered through 0.45-µm pore size, 25-mm diameter, Millex disk filters in field-rinsed PE bottles. Filtered samples for the analysis of cations and total iron and manganese were collected into acid-rinsed, 250-mL PE bottles and acidified with nitric acid to a pH less than 2. Filtered samples for the analysis of major anions were collected in 250-mL PE bottles, and for the analysis of nutrients were collected in amber 250-mL PE bottles and then chilled over ice. Raw water for DOC and TPCN was collected in baked glass bottles for laboratory processing.

Samples from one drainage system discharging into marine water adjacent to Sinclair Inlet (fig. 2), three stormwater drains on the BNC, and two drainage systems discharging to Sinclair Inlet (fig. 5, appendix A–Surface Water) were collected during a major rain event on January 7, 2009 (0.6 cm on January 6, and 4.0 cm on January 7), as part of the methylmercury survey. The stormwater drains on the BNC were sampled by using the techniques described for sampling groundwater. The three drainage outfalls outside of BNC were sampled in a manner similar to the stream sampling.

On December 29, 2009, and March 31, 2010, grab samples for FTHg were taken from stormwater drain vault PSNS015 (2253) on the BNC during the ebbing tidal period to examine the effects of saltwater leakage from the stormwater drain into the contaminated soils of Site 2 of the Initial Assessment Study (URS Consultants, Inc., 1991). A YSI data sonde and sampling port were deployed into the stormwater drain. The water velocity was measured at the center of the drain pipe by using a Price-type AA current meter (Rantz and others, 1982). Filtered grab samples for FTHg were taken during the ebbing cycle in the same manner described for the tidal cycle study at well OUBT-722. The individual grab samples were sent to the NWQL for analysis. An equal-volume composite of each of the grab samples on each day was collected in a 2-L PETG bottle in the field and processed in the WAWSC laboratory for FTHg analysis by both the NWQL and WMRL, for PTHg analysis by the WMRL, and for TSS by WAWSC. On December 19, 2009, rain started falling 4 hours into the ebbing tide. When salinity of the drain water started to decrease just as the top of the stormwater drain became visible, operations were terminated after collecting six grab samples for FTHg and the composite sample. On March 31, 2010, lighter rain fell with minor decreases in salinity and 10 grab samples were collected for FTHg and the composite sample.

An assessment of the quality of the data for all parameters measured in association with the Watershed Sources Project can be found in appendix B.

Methylation and Bioaccumulation Project Sampling Methods

Marine Sediment

Sediment was sampled at three Puget Sound stations, in representative bays (Liberty Bay, Holmes Harbor, and Budd Inlet) (figs. 1, 2, and appendix A–Marine Sediment Stations), three stations in greater Sinclair Inlet (SI-SI-PO, SI-IN, SI-OUT), and three BNC stations (BNC-39, BNC-52, and BNC-71) during August 2008 (figs. 3 and 4). Because a variety of different sediment samples were collected at each site, the vessel used for sampling was anchored during the operation. Bottom sediment and overlying water were collected by using a 13.5 × 13.5 × 23-cm deep box corer (Wildlife Supply Company, Buffalo, New York) connected to a winch cable that was allowed to fall to the bottom. Upon retrieval of the box corer, the collected sediment was inspected for an intact sediment-water interface free from turbidity and disturbance. The overlying height of water of an intact core was between 5 and 15 cm, and the sediment surface was not steeply angled or cracked. Sediment cores with at least 10 cm of overlying water were subsampled for incubation experiments (described later in this report). For intact cores with less than 10 cm of overlying water, the top 2 cm of sediment was sampled for the following: (1) analyses of physical characteristics; species of mercury, iron, and sulfur; and methylation rates by the USGS National Research Program (NRP), Menlo Park, Calif., (2) analyses of mercury species by WMRL, (3) sediment tumbling-core experiments, and (4) extraction of porewater for the analysis of (a) mercury species by the WMRL; (b) DOC by NRP, Boulder, Colorado, (c) redox-sensitive species described below. Figure 6 provides a flow diagram describing the many different samples collected at each station. Box core samples that were turbid, overly full, did not have at least 5 cm of overlying water, or leaked out during retrieval were not used. If the sediment sample was intact, the box corer was transferred to the extruder for subsampling.

During February, June, and August 2009, similar procedures were used to collect sediment at SI-PO, SI-IN, SI-OUT, BNC-39, BNC-60, and BNC-71. With the assessment of total mercury in BNC sediments reported in Paulson and others (2009), it became clear that station BNC-52 did not represent conditions of the central PSNS & IMF and the bottom-water and sediment sampling station was shifted to station BNC-60. In addition, sediment was collected at 14 other stations to provide a broad-scale understanding of the seasonal methylation potential in the top 2 cm of sediments (appendix A–Marine Sediment Stations). Because only two box cores were needed at these 14 stations, the vessel did not anchor during sediment sampling. The geographical distribution of these stations was approximately evenly divided between the BNC and greater Sinclair Inlet, except in February 2009, when only four stations were occupied in greater Sinclair Inlet. Three additional stations were sampled in February 2010 to provide a broader geographical range of environment conditions during winter.

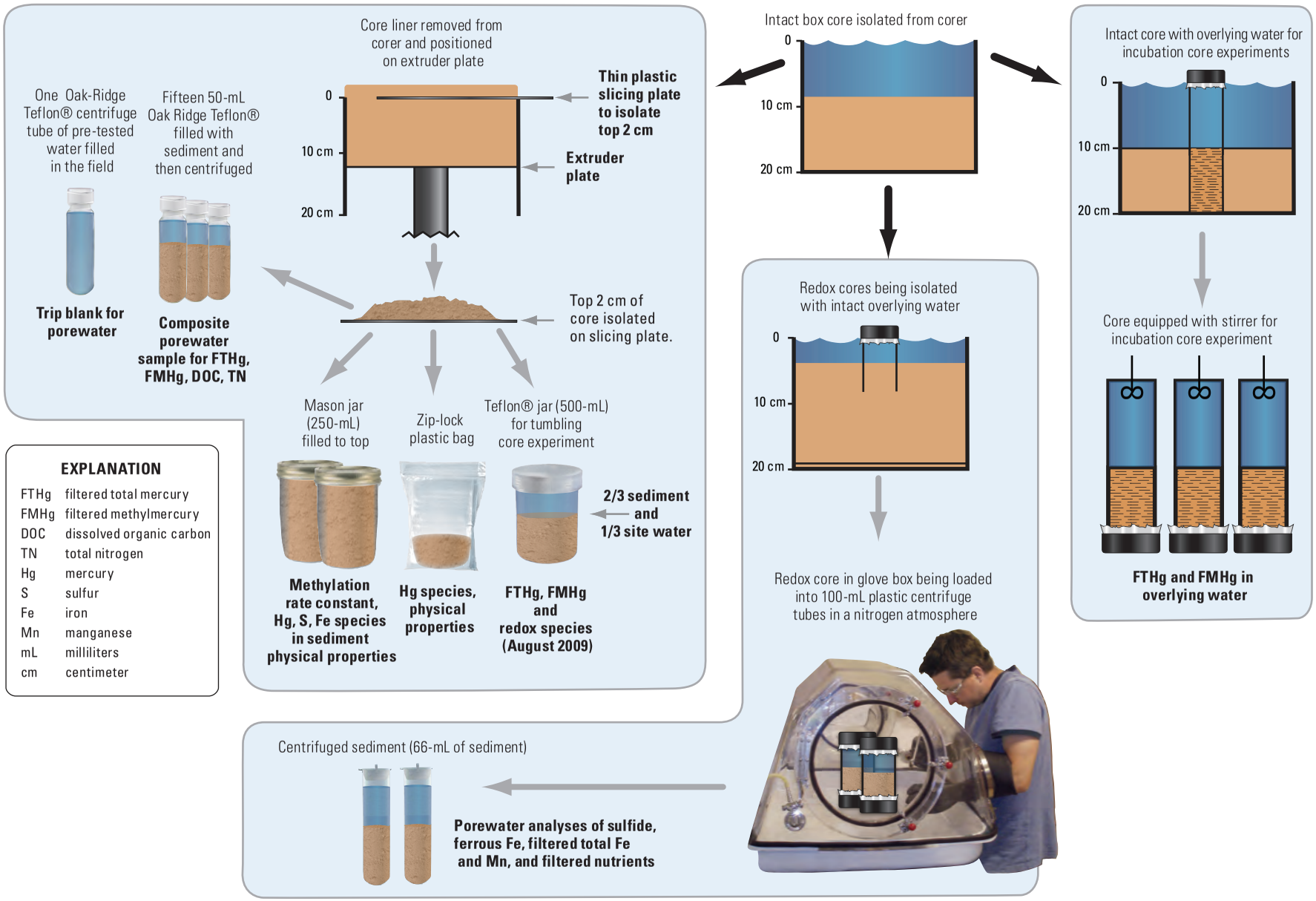

Figure 6. Sediment methylation potential, porewater analyses, tumbling-core experiments and incubation experiments.

Incubation Cores (>10 cm overlying water)

Intact cores with overlying water were collected for core incubation experiments from which the benthic flux of porewater constituents can be estimated from the change of concentration with time. For box cores that were deemed suitable for incubation cores (minimum of 10 cm of overlying water), an open, 16- to 20-cm long, 7.5-cm diameter, circular core liner was driven by hand through the overlying water, positioning it just below the surface of the water contained in the square acrylic sleeve of the box corer. A 5-cm square of Parafilm® was placed over the top opening of the tube, sealing in its contents. The seal was reinforced with a rubber core cap, making sure that no air became trapped. The box core containing the isolated, intact core was then positioned onto the extruder plate, taking care not to disturb the sediment water interface throughout this process.

The square acrylic sleeve was slowly lowered on the extruder; water and excess sediment that was not contained in the incubation subsample was removed. Excess Parafilm® on the extruder plate that was not under the circular core was folded up the side of the core liner. The bottom of the incubation tube was sealed by gently sliding the incubation core with the 5×5-cm piece of Parafilm® off the extruder plate into a second bottom rubber core cap. The taut Parafilm® stretched across the bottom of the circular core liner also prevented sediment from sliding down the core liner as the bottom rubber core cap was inserted onto the core liner. The tube was then rinsed with laboratory water and stored upright in a cooler on top of wet ice for transport to the WAWSC. In August 2008, one incubation core was collected and four incubation cores were collected at each station in 2009 to perform three incubation experiments (appendix A–Incubation Experiments).

Sediment Cores (<10 cm overlying water)

Cores for Redox-Sensitive Species in Porewater

Sample collection for redox-sensitive constituents was similar to that described for the incubation cores with the exception that the length of circular core liner was between 8 and 10 cm. This shorter, circular core liner was pressed into the sediment so that 2 cm or less of water remained above the sediment core. The top of the core liner was sealed with Parafilm® and a rubber core cap. Like the incubation cores, the box corer was positioned onto the extruder plate, the water outside the circular core liner drained, and then the square acrylic sleeve slid through the sediment core. Because the bottom of the redox core was positioned at mid-depth in the free standing sediment column, the circular core was slid to the outside of the sediment column, and the bottom sealed with a piece of Parafilm®. The bottom piece of Parafilm® was folded onto the side of the circular core liner, rinsed with laboratory water, and sealed with a rubber core cap. Two short intact cores were collected at each station for evaluation of redox-sensitive constituents of porewaters that included (1) total iron and manganese by the NWQL, (2) nutrients by the UW Chemical Oceanography Laboratory, and (3) ferrous iron and sulfide by the WAWSC.

Sediment in the Top 2 Centimeters

For sediment sampling of the top 2 cm, the box corer was positioned on the extruder plate as described previously without inserting the circular core liner. The square acrylic core sleeve was slowly lowered by the extruder plate first draining the overlying water and then exposing surface sediment. A 2-cm plastic measuring tool was placed on the lip of the sleeve to determine when 2 cm of surface sediment had been exposed. A 20-cm, square sheet of thin plastic was slid through the exposed sediment over the top lip of the square acrylic sleeve to slice the top 2 cm of sediment, while an individual scooped the sediment away from the cutting edge by using a small plastic scraper. After the forward edge was clear, the large sheet was slid farther into the extruded sediment, and this process was repeated until the entire top 2 cm of sediment was on the large plastic sheet. This upper 2 cm of sediment was collected (1) in glass mason jars for analyses of physical characteristics; species of mercury, iron, and sulfur; and methylation rates by NRP, (2) in plastic bags for analyses of mercury species by WMRL, and (3) in 500-mL PFA beakers for tumbling-core experiments by the WAWSC, and (4) in 50-mL centrifuge tubes for porewater analyses of FTHg and FMHg by the WMRL and DOC by NRP, Boulder Colorado The short exposure of the sediment to the atmosphere is not thought to cause significant changes in parameters being measured in the sediment.

For each of two replicate cores at each station, a glass mason jar was overfilled with sediment from the plastic sheet by using plastic utensils for assessment of methylation potential. The lid (without the threaded ring) was placed on top of the jar and pressed, forcing air and excess sediment out of the jar. While holding the lid firmly in place, the threads of the jar were carefully rinsed. The lid was secured to the jar with the threaded ring and the seal of the ring was reinforced with Parafilm®. The jars were placed in plastic shipping protectors, double bagged, and chilled over ice in the field.

In August 2008, subsamples of sediment for the mason jars and the plastic bags were not necessarily taken from the same box core. Sediment bags and mason jars were stored over wet ice until returning to field laboratories in the evening. The contents of the jars were homogenized and subsamples of STHg and SMHg were taken. The composited NRP samples and the two WMRL sample bags for analyses of STHg and SMHg were frozen the evening of the day that the samples were collected. In June and August, sediment placed in the two plastic bags for WMRL was taken from the same two box cores used to fill the mason jars for NRP, and the WMRL bags were frozen immediately over dry ice in the field.

At the six seasonal stations (SI-IN, SI-OUT, SI-PO, BNC-39, BNC-60, BNC-71) in February, June, and August 2009, the top 2 cm of sediment from a box core was used for the tumbling-core experiment (appendix A–Tumble Cores). After the box core lid was removed, a preweighed, 500-mL FP beaker was filled with about 150 mL of seawater overlying the box core. The sediment in the box core was then processed as above by draining the excess water over the core and collecting the top 2 cm of sediment on the plastic sheet. Sediment from the plastic sheet was then used to fill the last one-third of the FP beaker and the threaded beaker lid was sealed, bagged, and stored over ice. The convergence zone (CZ) station (fig. 3) located in the convergence zone of Sinclair Inlet, Port Orchard Passage, and Rich Passage (fig. 2) contained sediment too coarse to obtain box cores. To provide some assessment of the mercury release from sediments at the CZ station, the top 2 cm of sediment was collected by a weighted Van Veen sampler for tumbling-core experiments. In February 2009, a regular bottom-water sample from site Convergence Zone-Bottom (CZ-BOT) was collected to use as a substitute for overlying water for the tumbling-core experiment, while water overlying the sediment in the Van Veen sampler was used in tumbling-core experiments for June and August 2009.

Sediment from the top 2 cm was isolated for porewater analyses on the thin plastic sheet as above and packed into the centrifuge tubes by using plastic funnels and PTFE spatulas. A total of fifteen 50-mL, Oak Ridge-type, FP centrifuge tubes were packed with surface sediment. For each of the nine stations in August 2008, and the six stations in February, June, and August 2009, multiple box cores were dedicated to filling centrifuge tubes. If three or fewer centrifuge tubes needed to be filled, sediment remaining on the thin sheet from other box cores used to fill mason jars was packed into the remaining few centrifuge tubes. After each tube was filled, a 3×10-cm piece of Parafilm® was placed firmly on the top of the centrifuge tube with a gloved thumb, and the threads of the tube were rinsed over the side. The cap was placed on the tube, and the Parafilm® was used to seal the threads of the tube to limit contamination and oxidation. In August 2008, June 2009, and August 2009, pretested blank water was used to fill a random centrifuge tube at each station, which was then sealed. The 16 centrifuge tubes were then double bagged and placed over ice in the field. In August 2009, 30 centrifuge tubes were collected at station BNC-39 for replicate porewater analysis. All porewater samples were analyzed for FTHg, FMHg, and DOC.

An assessment of the quality of the data for all measured parameters associated with sediment collected for the Methylation and Bioaccumulation Project can be found in appendix C.

Marine Water

Sampling of the marine water column (fig. 5) supported the Methylation and Bioaccumulation Project. At approximately monthly intervals between August 2008 and August 2009, except for December 2008, near-surface seawater was collected from three stations in Sinclair Inlet (BNC-52, SI-PO, SI-Inner) and the CZ station located in the convergence zone of Sinclair Inlet, Port Orchard Passage, and Rich Passage (appendix A–Water Column Stations). For the BNC-52 station, surface water and zooplankton were sampled along the outside of the security fence.

From August to November 2008, the vertical profiles of temperature, salinity, and dissolved oxygen were measured at discrete depths determined from marks on a line supporting a YSI data sonde. Starting in January 2009, an SBE 19plus (Seabird Electronics., Inc., Bellevue, Wash.) conductivity, temperature, and depth (CTD) sensor package recorded the profile of depth, salinity, temperature, DO, turbidity, and fluorescence.

Water-quality sampling equipment of marine waters consisted of a clean, PFA tubing attached to a PTFE sampling port and C-Flex® tubing that extended over the side of a small boat. The short section of C-Flex® tubing was attached to a peristaltic pump positioned on the boat rail. After purging the sampling port and tubing with native seawater, while motoring slowly during the zooplankton tows, the following samples were collected in order:

- 2-L PETG bottles for Hg.
- Seawater filtered through Pall Aqua-Prep 0.45-µm pore size, 79-mm diameter, polyester polysulfone disk filter for nutrients and total metals (acidified in the field).
- Amber bottles for TCPN.
- Amber bottles for chlorophyll.
- Amber bottles for carbon (C) and nitrogen (N) isotopes on suspended matter.

During four intensive seasonal sampling events (August 2008, February 2009, June 2009, and August 2009), near-bottom water (appendix A–Water Column Stations) was collected at stations SI-Inner and SI-PO from a larger boat used for sediment sampling. All near-bottom sampling of water was completed before sediment sampling at a station began. Bottom water at station CZ-BOT was collected only in February. At station BNC-52 in August 2008, the bottom water and sediment were sampled inside the security zone. Similar to the change of station for sediment sampling, bottom-water sampling was shifted to station BNC-60. Near-surface water and near-bottom water (fig. 5) also were collected at a central Sinclair Inlet station (SI-Outer,) and BNC stations BNC-39 and BNC-71.

The sampling for TSS evolved over the course of the 13-month study as sampling artifacts were discovered and the importance of obtaining accurate calculated concentrations of PTHg and PMHg on the suspended solids became more evident. Concentrations of PTHg, PMHg, and other particulate constituents on the particles can be calculated indirectly by dividing the concentrations of the particulate constituent in the water column (mass of constituent/volume) by the TSS concentration (TSS mass/volume) to produce a calculated concentration of the constituent in solid phase (mass of constituent/mass particulate solids). For August and September 2009 sampling, water for PTHg and PMHg was sampled in one PETG bottle at the beginning of the sampling sequence, and water for TSS was sampled in a separate HDPE bottle after pumping 11-L of raw surface water in nine bottles and filtering water for nutrients and total metals. The results of the near-bottom-water sample collected at BNC-71 on August 18, 2008, suggested the probability of temporal biasing of TSS concentrations. As a result of the extended time to collect water, changes of constituents, especially TSS, in the water column can easily bias the calculated concentration of a constituent on particles. To minimize effects of temporal changes in the water column on the calculated concentrations of PTHG and PMHg on particles, the TSS concentration was measured in the bottle in which PTHg and PMHg samples were obtained starting in October 2009, as was the TSS concentration measured in the bottle in which the duplicate PMHg was obtained. Upon review of data in March 2009, it was noticed that not enough water was being filtered to generate detectable concentrations of PMHg. Therefore, starting in April 2009, a new sample scheme using three 2-L bottles was initiated to collect larger masses of particulates.

Zooplankton

Zooplankton collections were made at the same time as the monthly water sampling. On each sampling date, one vertical plankton tow was taken for quantitative analysis at each station by using a 0.5-m diameter, 0.1-mm mesh plankton net with an attached TSK (Tsurumi Seiki Co., Ltd., North Bend, Wash.) flowmeter. The net was lowered to the bottom, depth was recorded, and the net was pulled to the surface at a speed of approximately 0.5 m/s. Samples were fixed in 10-percent (volume/volume, (v/v)) buffered formalin solution. Between three and six additional vertical hauls were made with the 0.1-mm mesh net, and several vertical hauls were made with a 0.75-m diameter, 0.253-mesh plankton net, in order to collect live material. The number of hauls conducted depended on the density of organisms observed in the samples. Live hauls were placed on ice in 1-gallon glass jars. Live samples were returned to the UW School of Aquatic Fisheries and Sciences laboratory and immediately sorted for whole community and species-specific zooplankton, and later sent to the National Research Laboratory in Menlo Park, California, for mercury analyses. An assessment of the quality of the data for all measured parameters associated with samples collected from the marine water column for the Methylation and Bioaccumulation Project can be found in appendix D.

Laboratory Processing

Watershed Sources Project

Mercury

Upon returning to the WAWSC laboratory within 6 hours of collection, water samples from wells, dry docks, steam plant, and streams, filtered through the Meissner cartridge filters for FTHg and FMHg analyses, were acidified with 20 mL of 6 molar (M) hydrochloric acid (HCl) per liter of sample provided by the WMRL in a laminar flow hood and shipped dry to the WMRL. Samples for the analysis of particulate mercury were processed as described by Lewis and Brigham (2004). A PETG bottle containing unfiltered water was weighed and filtered through a prebaked quartz fiber filter (QFF) that was loaded in a Savillex PFA filtering tower. The filtering assembly was connected by PFA tubing to a vacuum filtering flask connected to a vacuum pump outside the laminar flow hood. After shaking the bottle, the filtering tower was filled with water until all the water in the bottle was filtered. The QFF was removed from the filtering tower by using Tefzel® tweezers, placed in a stackable PFA petri dish, and covered by a second PFA petri dish. The empty bottle was reweighed and the weight of the filtered volume was calculated by difference. After repeating this procedure for all samples, the stacked petri dishes were secured with tape, bagged in plastic, frozen, and shipped to the WMRL over dry ice for PTHg analyses.

FTHg, FMHg, and PTHg samples were processed from the same PETG bottle containing raw water collected from the wastewater composite samples and stormwater samples collected in January 2009. Within a laminar flow hood, an open 500-mL FP bottle for FTHg was placed in a plastic vacuum desiccator with a ¼-in. tubing fitting on top that connected to the Savillex FP filter tower containing a QFF, and vacuum was applied to the vacuum desiccator. The PETG bottle containing the raw water was weighed and the raw water was filtered through the QFF until the 500-mL FP bottle was filled. The vacuum on the desiccator was released slowly and the 500-mL FP bottle was capped and bagged. A 250-mL FP bottle for FMHg was placed in the desiccator and filtering continued until the filter clogged. The 250-mL FP bottle was removed from the desiccator, capped, and bagged. The QFF was removed by using Tefzel® tweezers and placed in a stackable PFA petri dish. After all samples were filtered, FTHg and FMHg samples were acidified in the laminar flow hood and shipped to the WMRL. The stacked petri dishes were shipped as mentioned above to the WMRL.

For the December 2009 and March 2010 PSNS015 composite stormwater, FTHg and PTHg were processed as above. For each sampling trip, samples of FTHg from the composite were sent to both NWQL and WMRL as an interlaboratory comparison exercise. The PTHg sample for each composite was sent to WMRL over dry ice.

Total Suspended Solids

Each lot of the 100 Nuclepore™ 0.4-µm pore size, 47-mm diameter, polycarbonate filters in a box were placed in individual covered polystyrene petri dishes, labeled, and preweighted on a 6-place balance (precision of 0.001mg) after eliminating static with an ionizing bar. The filters weigh about 15 mg. Five filters were retained as reference filters (Sackett, 1975).

A bottle containing the unfiltered water for total suspended solids concentrations was weighed. A drain disk was placed on the base of a polysulfonate plastic filter holder to distribute the vacuum across the entire surface of the filter, and the base was sealed into a glass vacuum Erlenmeyer flask with a rubber stopper. A water trap was placed between the Erlenmeyer flask and the pump to protect the pump in case the Erlenmeyer flask overflowed through the side arm. A preweighed polycarbonate filter was placed in the center of the filter holder and sealed with a 300-mL plastic reservoir column. Additions of decreasing volumes of gently shaken sample were added to the reservoir column until the filter began to clog or the entire sample was filtered. The volume of each addition was reduced such that all water in the reservoir could be filtered in less than about 20 minutes. Once an aliquot of water was added to the reservoir column, that aliquot was completely filtered. If the filter clogged before the aliquot was filtered, the filter was discarded and the process was restarted with smaller aliquots. After the last aliquot, the bottle with any remaining sample was reweighted. After all liquid in the reservoir passed through the filter, the inside of the reservoir was rinsed with filtered Purelab® laboratory water. The top of the filter holder was removed and the outside of the filter was rinsed with Purelab® laboratory water (about 1–2 mL) three times under vacuum to remove any accumulated salt. The vacuum was released and the filter was placed in a plastic petri dish. After loosely applying the cover to the petri dish, it was placed in a desiccator under vacuum. After 2 weeks, the petri dishes were removed from the desiccator and the cover sealed prior to weighing. The mass of the suspended solids on the filter was determined by differences between the weight of the specific filter after filtering and the preweight. The difference between the weight of unused reference filter that was reweighed on the day that sample filters were weighed and the initial preweighed weight was used to assess changes in weight due to atmospheric humidity differences, calibration of the balance, and to calculate the reporting level. During the initial testing of the procedure, the weight difference for four unused reference filters was 0.01 and 0.03 mg for the fifth filter. The variance of this difference was 0.01 mg and resulted in a reporting level of 0.03 mg.

Carbon and Nitrogen

Water for total particulate carbon and nitrogen (TPCN) and dissolved organic carbon (DOC) analyses were filtered at the WAWSC within 5 hours of collection. The three 1-L sample aliquots were filtered through 0.45-µm pore size, 25-mm diameter, baked glass-fiber filters in a PFA filter holder (Wilde and others, 2004), and the material retained on the three filters was used for the analysis of TPCN. The filtrate (125 mL) was collected into a baked, glass bottle and acidified with HCl for analysis of DOC.

Methylation and Bioaccumulation Project

Marine Sediment

Sediment subsamples were taken in the laboratory under anoxic conditions (in a nitrogen gas (N_2)-flushed glove bag) from less than 1 to 7 days following field collection. Sediment was initially transferred from the two mason jars from each station into plastic bags to facilitate homogenization. Analysis of sediment subsamples from the composite sample from the two mason jars included (a) bulk density, porosity, and organic content (all three taken from a single subsample), transferred into an acid-cleaned glass screw-top vial and refrigerated; (b) acid volatile sulfur (AVS), subsampled (1.5 g) into acid-cleaned glass crimp vials, preserved with 5.0 mL of a 10-percent (weight/volume, (w/v)) zinc-acetate (anoxic) solution, homogenized, and stored frozen (August 2008 only); (c) total reduced sulfur (TRS), subsampled (1.5 g) into acid-cleaned glass crimp vials, preserved with 5.0 mL of a 10-percent (w/v) anoxic zinc-acetate solution, homogenized, and stored frozen; (d) iron speciation, subsampled into acid-cleaned glass crimp vials and stored frozen; (e) mercury speciation (STHg, SMHg, and sediment "reactive" mercury ($Hg(II)_R$)) stored frozen; and (f) microbial MHg production potential (3.0 g in triplicate per site) stored refrigerated until the following day. In addition, sediment pH and oxidation-reduction potential (E_H) were measured on subsamples taken the day of laboratory subsampling.

Sediment "reactive" mercury ($Hg(II)_R$) is methodologically defined as the fraction of total Hg(II), which has not been chemically altered (for example, digested, oxidized, or chemically preserved apart from freezing), that is readily reduced to elemental Hg^0 by an excess of stannous (tin) chloride ($SnCl_2$) over a defined (short) exposure time. This operationally defined parameter was developed as a surrogate measure of the fraction of inorganic mercury [Hg(II)] that is most likely available to Hg(II)-methylating bacteria responsible for MHg production (Marvin-DiPasquale and others, 2009). For STHg, SMHg, and $Hg(II)_R$ quantification, sediment collected in the field was stored chilled, transported to NRP laboratory (Menlo Park, California) over ice within 3 days, subsampled under anaerobic conditions, and preserved frozen (-–80 °C) until analysis.

Several precautionary measures were made to minimize changes in redox-sensitive sediment geochemistry between the time of field collection and subsequent subsampling and analyte-specific preservation. Precautions included (a) minimum achievable holding times prior to subsampling, (b) completely filling glass mason jars with sediment, and (c) cold storage (on wet ice or refrigerated) during the holding period. Even with these precautions, some changes in redox chemistry may have occurred during the holding period and sample processing.

Porewaters

Mercury and Dissolved Organic Carbon

After returning dockside (August 2008) or to the WAWSC laboratory within 6 hours (February, June, and August 2009), the sixteen 50-mL, Oak Ridge-type, FP centrifuge tubes, in which the closures were sealed with Parafilm®, were loaded into a centrifuge containing eight stainless steel sleeves in two batches for each station. The sediment was centrifuged at 2,000 revolutions per minute (rpm) for 20 minutes.

In August 2008, the centrifuge tube blank (containing blank water) from each station was filtered in the field in a portable laminar flow hood through a new QFF in the filtering tower that was set up to filter the porewater sample from the same station. Before the filter tower was used to filter the porewater sample, blank water for each station was filtered through the filter tower into a 500-mL FP containing the nine-station composite filtered blank water sample. Thus, the composite filtered blank-water sample came in contact with nine QFF filters and nine filtering towers, which probably overestimated the contamination from a single filter and tower used for samples. In June and August 2009, blank waters in the 50-mL Oak Ridge-type FP centrifuge tubes from each station were filtered through a single QFF and tower assembly that was double bagged after use with each of the six stations. Similar to the August 2008 porewater blank, the filtrate of the blank water was composited into a single 500-mL FP bottle. In August 2008, some of the FP centrifuge tubes, included those used for blank water, were cold-acid cleaned overnight.

After centrifugation, the centrifuge tubes were brought back to the field laminar flow hood (August 2008) or to the laboratory laminar flow hood (2009), the Parafilm® seal broken, and the supernatant filtered through a QFF held in a filtering tower into a 500-mL FP bottle in the vacuum desiccator. If the filter clogged, the tower assembly was removed from the desiccator and a new QFF was inserted into the tower. Filtering of porewater continued until supernatant in the 15 centrifuge tubes was filtered. About 20–30 mL of the composite porewater sample was poured into a baked, 60-mL glass bottle for analysis of DOC, total nitrogen (TN), and ultraviolet (UV) absorbance if the unfiltered sample did not become cloudy due to precipitation of ferrous iron. The composite porewater in the FP bottle was acidified with HCl after all FTHg samples for the day were filtered. For the replicate analysis of porewater, 15 centrifuge tubes were randomly selected from the 30 tubes of sediment collected at the station for the first porewater composite, and the remaining 15 centrifuge tubes were used for the replicate composite sample. Porewater DOC measurements and Ultraviolet (UV) absorbance was measured with a Shimadzu elemental analyzer by following methods of Weishaar and others (2003).

Reduction-Oxidation Sensitive Constituents

The two redox cores were clamped to a ring stand and placed in a glove bag in the field during August 2008 or in a glove box in the laboratory during February, June, and August 2009. The following items also were placed in the glove bag or box were (1) tubing attached to the outside N_2 gas line, (2) a 500-mL vacuum reservoir attached to a hand pump and a suction tube, (3) 100-mL centrifuge tubes marked at 66 mL, (4) three 100-mL centrifuge tubes with covers in a test tube rack, (5) three plastic square spoons, and (6) several pieces of 3×10-cm Parafilm®. In August 2008, the glove bag was compressed around the equipment to the smallest volume without jeopardizing the core samples. The glove bag was filled with nitrogen (N_2) until the bag bulged slightly, and N_2 gas was allowed to flow for 5 minutes through the opening seal that was broken. The process of compressing, filling the glove bag, and purging was repeated twice. After the bag was filled for the third time, the open centrifuge tube was purged by inserting the tubing connected to the N_2 gas line into the centrifuge tube. The rubber cap and Parafilm® were removed from the top of the core liner. Water over the sediment was removed through the suction tube by hand pumping the vacuum reservoir. After overlying water was removed, the surface of the sediment was evenly scooped into the centrifuge tube by using a square spoon, and the centrifuge tube was tapped on the floor of the glove bag to knock the sediment to the bottom of the tube. When the tube was filled with 66 mL of sediment (2 cm deep by 33 cm^2 opening of the core liner), the cap was placed on the centrifuge tube and sealed with Parafilm®. The process of removing overlying water and filling the centrifuge tube was repeated with the other one to three redox cores in the glove bag. The glove bag was opened up and the centrifuge tubes were centrifuged at 2,000 rpm for 20 minutes. During February, June, and August 2009, equipment was loaded into the glove box and the box was purged with N_2 gas for about 20 minutes.

After centrifugation, the centrifuge tubes were opened in air, and the supernatant was quickly pulled into an all-plastic syringe through a 10-cm long, FP syringe tip to minimize oxidation of reduced species. Immediately after isolating the unfiltered porewater in the syringe, sulfide concentrations were measured in one analytical batch containing the duplicate

porewater samples processed each day from either the one station sampled outside Sinclair Inlet in August 2008 or two stations sampled in Sinclair Inlet in 2008 and 2009. Porewater was volumetrically diluted by a factor of 4 with N_2-purged, laboratory water in 6-mL rectangular plastic cuvettes. In some instances when a strong sulfide odor was noticed in the field, duplicate porewater samples from a station also were diluted by a factor of 1:36 in a second dilution. Sulfide was measured by using Hach Method 8131as described in the basewide groundwater sampling method section. For sulfide and ferrous iron measurements, a Hach Model 2010 spectrophotometer was used in August 2008, and a Hach Model DR 2400 spectrophotometer was used in 2009 with the specified 3.6-mL, square cuvettes. Ferrous iron concentrations were then measured by using Hach Method 8146, described in the basewide groundwater sampling method section, at a nominal dilution of about 4. In some cases, a second analytical batch of sulfide and ferrous iron measurements were performed with differing dilutions from full strength (1:1) to 1:36, based on the results of the initial measurements. Because sulfide and ferrous iron concentrations are used qualitatively to assess redox state and were not calibrated against diluted sulfide and ferrous iron standards, measurements are not adjusted for dilution, and actual measurements are reported at the specified dilutions in the results tables.

After all spectrometric measurements were completed, the syringe tip was removed and replaced with a 0.45-µm, 25-mm, Millex disk filter. The remaining porewater was filtered into a 15-mL, HCl-cleaned, HDPE bottle, and volume permitting, into a second 15-mL bottle for analysis of nutrients. Because the high salt content of the porewater requires significant dilution at the laboratory for the measurement of iron and manganese, a diluted porewater sample was sent to the laboratory to conserve limited porewater volume. A 100-µL aliquot of the porewater sampled from the original 15-mL bottle was pipetted into a second 15-mL, HCl-cleaned, HDPE bottle containing 10 mL of 1-percent nitric acid. The nutrient samples were frozen and sent to the UW Chemical Oceanography Laboratory. The diluted samples for iron and manganese were sent to the NWQL. Concentrations of diluted samples and concentrations and reporting levels adjusted by a factor of 100 are reported in the results tables. In February, June, and August 2009, the centrifuged sediment from both redox cores from each of the stations was sent to the NWQL for analysis of TOC.

A field duplicate core was processed at most stations. Laboratory quality assurance (QA) procedures included zeroing the spectrometer on blank water for each analytical run and replicate measurements of porewater at the same and differing dilutions. Analysis of filtering blanks and laboratory duplicates of filtered porewater were performed for nutrients and total iron and manganese.

Incubation Core Experiments

As a pilot study in August 2008, single cores at nine stations (appendix A–Incubation Experiments) were incubated, in a manner similar to Hammerschmidt and Fitzgerald (2008), except where noted, by using a floating stir bar suspended with an FP cord through a hole in a polycarbonate core cap. A floating stir bar is a stirring bar positioned in an open circular cage made of PFA rods that connect into circular disks on the top and bottom. For the core incubation experiments conducted in 2009, the top disk of the FP floating stir bar was carefully press fitted into the indentation in the polycarbonate caps by using a metal needle-nose pliers that was covered with a plastic bag to prevent any metal contamination of the polycarbonate cap assembly. The assembly was bagged and weighed with the tare weight set to the weight of the bag. All processing of open bottles, and cores and equipment exposed directly to the overlying water occurred inside the laminar flow hood. Three 2-L bottles of bottom water were sequentially filtered into a 1-L FP bottle as described for processing of water column samples and placed back into their original collection bottles after rinsing the bottle with Purelab® laboratory water. The replacement water was stored in the refrigerator when not in use.

The three core samples with the best volume-to-sediment ratio from each of the six stations in February, June, and August 2009 (appendix A–Incubation Experiments) were selected from the four cores that were returned to the laboratory and labeled as Core A, Core B, and Core C. The weight of each core sample and the assembled polycarbonate cap assembly was recorded along with the start time of the experiment. The core was placed in the clean room laminar flow hood before removing the rubber core cap and Parafilm®. Station-specific C-Flex® tubing, outfitted with a syringe tip, was placed two-thirds down into the overlying water of the core. About two-thirds of the overlying water was filtered into a 125-mL or 250-mL FP bottle by pumping water through the syringe tip into a Savillex PFA filtering tower holding a QFF, which resulted in nonstandard sample volumes for WMRL analyses. The preweighed polycarbonate cap was then placed on the incubation core, and the weight of the partially filled core and time were recorded. In order to preserve the sediment water interface, the core liner was refilled very slowly with replacement water from a station-specific 500-mL bottle. However, sometimes the bacterial mat or fluff layer was disturbed, but the overlying water became clear within minutes. The weight of the refilled core and time were recorded after each refilling of the core liner.

The rubber core cap and Parafilm® were patted with laboratory tissue, and their combined weight was recorded to allow the weight datum of the original weight to be converted to the datum of the core with the polycarbonate cap assembly. The weights of the partially filled core and the

refilled core were used to calculate an expected concentration from which FTHg and FMHg release rates can be calculated. The incubation core was then placed into an incubator set to temperatures simulating the conditions of the station sampled. A magnet attached to a motor (10 rpm) was placed into an indentation in the outside of the polycarbonate core to rotate the floating stir bar to simulate gentle mixing conditions. In February 2009, a number of malfunctions were noted, including the loosening of the connection between the motor and magnet, which stopped the floating stir bar causing it to disengage from the core cap and fall into the sediment. After all cores were processed for the day, the overlying water was filtered into an FP bottle and preserved with 20 mL of 50-percent HCl (v/v) per liter of sample.

On days 1, 2, and 3 of the incubation experiment, the weight was recorded initially to determine the amount lost due to evaporation or leakage, which was usually less than 10 g (about 10 mL). The procedure for filtering and preserving two-thirds of the overlying water and refilling the core with replacement water while recording weights at each step was repeated on days 1, 2, and 3. On the last day immediately after taking the last sample of overlying water, a DO concentration of overlying water of a subset of cores was measured by using 0–1 mg/L R-7501 CHEMets (Chemetrics, Calverton, Virginia) and 0–12 mg/L R-7512 CHEMets. The entire volume of the overlying water was removed on the last day, rather than refilling the core liner, and the sediment core with the cap assembly was weighed. This final weight of only the sediment and core assembly allowed calculation of the water remaining in the partially filled core each day. At the end of the experiments, filtered overlying water from each of the three cores from a station were shipped to the WMRL for analysis of FMHg and FTHg, if the volume in the same bottle permitted.

Besides triplicate incubation cores at most of the six seasonal stations, QA included several control experiments where a core liner with a polycarbonate bottom plug was filled with Purelab® laboratory water and the release of FTHg and FMHg was measured. In addition, the chilled filtered replacement water was preserved as a check on changing FTHg and FMHg of the replacement water.

A laboratory water blank was analyzed in June 2008 and January 2009 to verify the effectiveness of the in-house cleaning methods of acrylic and polycarbonate equipment (appendix D– Laboratory Blanks). The results of the total filtered mercury and the filtered methylmercury were below or near the reporting level, indicating the labware used in the incubation study was free from contamination.

Tumbling-Core Experiments

The sediment slurries (2/3 sediment and 1/3 station water) in preweighed, 500-mL FP beakers were weighed. The bagged beaker was secured to a 1-m diameter wheel that was rotated at 7 rpm for 15 minutes to allow mixing of porewater and added water. The beakers were taken off the wheel and the slurry was allowed to settle. Depending on the consistency of the overlying water, it was either filtered directly through a QFF or filtered through a QFF after centrifugation in 50-mL, Oak Ridge-type, FP centrifuge tubes that had been cold-acid cleaned. The beaker was reweighed, and filled to the rim with replacement water prepared for the incubation experiments. The beaker was sealed, reweighed, bagged, and secured to the wheel, where it was rotated for 2 days at room temperature. Similar to the initial measurements at 15 minutes, the slurry was allowed to settle and the overlying water was filtered through QFF with and without centrifugation. The mass of dry solids in the beaker during the experiment was used to calculate the ratio of solids to liquid. All solid material contained in the beaker between 15 minutes and 2 days was carefully retained. A tray was used when pouring the overlying water into the centrifuge tubes. The contents of the beaker were dried at 60°C along with any filters used to filter the final supernatant. The solids in the centrifuge tubes were first scraped and then rinsed into the beaker, requiring multiple drying sessions. The weight of the dry solids during the experiment was calculated as:

$$\text{(Weight of dried sediment, filters and beaker)} - \text{(number of filters} * 0.2\text{ g)} - \text{beaker weight.} \quad (1)$$

The weight of the liquid during the experiment was calculated as:

$$\text{(Weight of experimental slurry)} - \text{(weight of solids as calculated in eq. 1).} \quad (2)$$

In February, DO concentrations in overlying water from three tumbling cores were measured by using 0–12 mg/L R-7512 CHEMets immediately after withdrawing sample for FTHg and FMHg. In August 2009, the overlying water was processed for redox-sensitive species described for the porewater sampling.

Marine Water Column

Mercury

Processing of all water column samples for FTHg, FMHg, PTHg, and PMHg occurred in a laminar flow hood, either in the field (August 2008) or in the laboratory (October 2008–September 2009). In August and

September 2009, FTHg, FMHg, PTHg, and PMHg samples were processed from one 2-L PETG sample of raw seawater and the replicate PMHg was processed from a 1-L PETG bottle of raw seawater. An open 500-mL FP bottle for receiving the FTHg sample was placed in a plastic vacuum desiccator with a ¼-in. tube fitting on top that connected to the Savillex FP filter tower containing a QFF, and vacuum was applied to the vacuum desiccator. The PETG bottle containing the raw seawater was weighed and approximately 1,000 mL of seawater (volume recorded) was filtered through the QFF for PTHg overflowing the 500-mL FP bottle in the desiccator. The vacuum on the desiccator was slowly released and the bottle was capped and bagged. The QFF for PTHg was removed by using FP tweezers and placed in a stackable FP petri dish. A new QFF for analysis of PMHg was loaded into the filtering tower and a 250-mL FP bottle for FMHg was placed in the desiccator. Vacuum was applied to the desiccator and filtering continued until the filter clogged. The 250-mL FP bottle was removed from the desiccator, capped, and bagged. The QFF was removed by using Tefzel® tweezers and placed in a stackable FP petri dish. After all samples were filtered, FTHg and FMHg samples were acidized in the laminar flow hood and shipped to the WMRL. The stack of petri dishes containing the QFFs were secured with tape, bagged in plastic, frozen, and shipped to the WMRL over dry ice.

Continuous data review as part of the quality assurance program revealed that temporal changes in TSS concentrations during the duration of some sampling events likely caused temporal bias in several parameters associated with particulate matter, especially the concentration of THg of suspended solids (as mg/kg). Beginning in November 2008, about 300 mL of raw seawater was left in the 2-L PETG bottle measurement for TSS measurements after processing FTHg, FMHg, PTHg, or PMHg from the same bottle. Likewise, about 300 mL of raw seawater was left in the 1-L bottle used to process the replicate PMHg sample for a corresponding measurement of TSS from the same bottle. This procedure resulted in field duplicates of TSS for every sample in which replicate PMHg samples were collected.

Continuous review of the analytical data also indicated that a significant number of PMHg concentrations were less than the detection limit, possibly indicating that an insufficient volume of water was filtered through some of the QFF used for analysis of PMHg samples. Therefore, starting in April 2009, three 2-L bottles of raw seawater were collected, which allowed the following processing scheme:

- Bottle A: FTHg, PTHg, TSS.
- Bottle B: FMHg, PMHg, TSS.
- Bottle C: Duplicate PMHg, TSS.

When all FTHg and FMHg samples for the day were processed, all samples were acidified with 20 mL of 6-M HCl per liter with one individual handling the acid bottle and the measuring FP vial and another handling the sample bottles.

Total Suspended Solids

Processing of seawater through preweighed, 0.4-µm-pore size, 47-mm-diameter, polycarbonate filters was performed in a manner similar to that described for terrestrial samples. Blank water for field-filtering blanks was processed through six filters. Duplicate samples from the same bottle were processed to provide 65 duplicate samples. Because of a major phytoplankton bloom in August 2009, which resulted in filters clogging after filtering less than 100 mL, three or four samples were taken from five bottles. Although only one field duplicate was taken in each of August 2008 and September 2009, the revisions of the sampling plan starting in November 2008 resulted in field replicates at any station at which replicate PMHg samples were taken. Although seawater remained in the PETG bottles used to process mercury samples in January 2009, they were not filtered in a timely manner and no TSS data are available.

Phytoplankton and Suspended Solids

As described in the section on processing terrestrial samples, seawater was processed for analyses of TCPN and DOC in a mobile laboratory in August 2008 and at the WAWSC between September 2008 and August 2009. Duplicate chlorophyll samples were filtered within 2 hours of collection onto precombusted, 25-mm-diameter, glass fiber filters (GFF nominal pore size of 0.7 µm), frozen on dry ice, and then later stored at –80 °C.

To elucidate the food quality of the suspended particulate material and its trophic relationship to zooplankton, samples of suspended solids and zooplankton were analyzed for stable isotopes. Stable nitrogen isotope ratios ($\delta^{15}N$) provide a spatially and temporally integrated measure of trophic relationships in a food web (that is, primary producers → invertebrates → fish) because $\delta^{15}N$ becomes enriched by 2.5–5 per mill between prey and predator (Peterson and Fry, 1987). Stable carbon isotope ratios ($\delta^{13}C$) tend to show little or no enrichment (<1 ‰) with each trophic level, but can identify contributions of different foods (that is, carbon sources), if foods have distinct isotopic signatures (France, 1995).

The 25-mm-diameter filters holding suspended solids were subsampled with a 6.3-mm-diameter hole-punch (two per 25-mm filter). To prepare suspended solids samples for isotopic analysis, subsampled filters were moistened with Milli-Q® water (about 100 µL), and fumed overnight in a desiccator with concentrated HCl to remove carbonates. The

following morning subsamples were dried in an oven at 60°C for 1 hour and then cooled in a desiccator. The subsamples from each 25-mm filter were then loaded into tin capsules and held in a desiccator until analyzed for carbon and nitrogen isotopes. To calculate particulate organic carbon and nitrogen per unit volume, the area of the punches (62.4 mm^2) was first divided by the area of the 25-mm filter that was holding suspended solids (339.8 mm^2) and then divided by the total volume of water that was filtered onto the 25-mm filter.

Zooplankton

Live samples were returned to the laboratory and immediately sorted for whole community and species-specific zooplankton samples for mercury analyses. Material from the 0.1 mm mesh net was used for obtaining "whole community" samples: for these samples, zooplankton were first separated from phytoplankton as much as possible by swirling aliquots of the sample in a petri dish, causing heavier diatoms to separate from the lighter zooplankton. Representative samples of the zooplankton were then moved by using plastic forceps onto 0.073-mm mesh pieces of net and concentrated for freezing and later analysis. When approximately 10–12 mg wet weight of organisms were obtained, they were placed on a small sheet of FP paper (about 5 × 8 mm), put into labeled 1.5-mL centrifuge tubes, and frozen for later analysis.

The 0.253-mm mesh samples were used to obtain individuals of larger species for analysis. The most abundant organism was used (for example, *Acartia* sp.). If possible, the same species was used across all sampling stations for a given date, but this was often not possible because of low numbers of the chosen organism at one or two stations. Individual species were collected by pipette from the sample jar, placed on 0.073-mm mesh pieces of net, and individually sorted from there until approximately 10–12 mg wet weight of a given species was obtained; they were then frozen as with the whole community samples. Vertical hauls that had been fixed in the field were quantitatively subsampled if necessary in the laboratory, by using a Hensen's Stempel pipette to obtain approximately 200 of the most abundant taxon. Plankton taxa were enumerated and all adult copepods were identified to genus or species.

Composite samples of zooplankton representing either the whole community or individual species were freeze-dried (Virtis Genesis 35EL) prior to processing for stable isotope and MHg analysis. Zooplankton samples for stable isotopes were weighed out by using a microbalance (1–2 mg) and packed into tin capsules.

Laboratory Analyses

Water Samples

Mercury

FTHg in samples from the outfalls of the dry dock relief drainage systems between December 2007 and February 2008, from all monitoring wells in January and February 2008, from wells 722 and R715R in May and June 2008, and from stormwater from PSNS015-2253 in December 2009 and March 2010 were analyzed at the NWQL by cold vapor atomic fluorescence spectrometry (CVAFS) by using the method of Garbarino and Damrau (2001). The reporting level is 0.01 µg/L (or 10 ng/L). Total mercury in filtered water (FTHg) in all other samples was measured by the WMRL using the EPA method 1631, revision E (U.S. Environmental Protection Agency, 2002) that includes oxidation, purge and trap, desorption, and cold vapor atomic fluorescence spectrometry (CVAFS). Methylmercury in filtered water (FMHg) is first distilled to reduce matrix affects, then ethylated and trapped onto reaction traps (DeWild and others, 2002). The mercury species were thermally desorbed, separated by gas chromatography, and analyzed by CVAFS. Quality assurance included frequent recalibration of the instrument, numerous laboratory blanks, replicate analysis of every sample (except where noted in the volume-limited samples), several matrix spikes during the run, and quality control standards that are independent of the standards used for calibration. The reporting levels for FTHg and FMHg are 0.04 ng/L.

Analysis of total mercury in suspended solids (PTHg) and sediment (STHg) are prepared by room-temperature acid digestion and oxidation with aqua regia followed by overnight heating (50°C) in a 5-percent (w/v) bromine monochloride solution to ensure complete oxidation (Olund and others, 2004). The solution is analyzed by CVAFS. The reporting level of STHg is 6 ng/g. The method detection limit of PTHg is 0.059 ng of mercury per filter.

Analysis of methylmercury in suspended solids (PMHg) and sediment (SMHg) are prepared by extraction with potassium bromide, copper sulfate, and methylene chloride (DeWild and others, 2004). The methylmercury is solvent extracted with methylene chloride and back extracted in water by evaporation of the methylene chloride. The methylmercury is then analyzed in a manner similar to the ethylation, chromatographic separation, and analysis by CVAFS. The reporting level for SMHg is 0.08 ng/g. The method detection limit of PTHg is 0.01 ng of mercury per filter.

Quality assurance included frequent recalibration of the instrument, numerous laboratory blanks, replicate analysis of selected samples, matrix spikes, and/or analysis of certified reference materials (CRM), if available (U.S. Geological Survey Mercury Research Laboratory, 2008).

Carbon and Nitrogen

Stream, stormwater, and wastewater effluent samples were analyzed at the NWQL by colorimetry for filtered orthophosphate, ammonia, and nitrate-plus-nitrite nitrogen (Fishman, 1993). Dissolved organic carbon was analyzed by ultraviolet (UV)-promoted persulfate oxidation and infrared spectrometry by using the methods of the U.S. Environmental Protection Agency (1997). Particulate total carbon and total nitrogen were measured by U.S. EPA method 440.0 (U.S Environmental Protection Agency, 1997).

The UW Chemical Oceanography Laboratory analyzed groundwater, dry dock discharges, and steam plant effluents as part of the methylmercury survey of terrestrial sources and all marine water column samples. Nitrate and nitrite were analyzed by following the method of Armstrong and others (1967), and ammonia was analyzed by following the method of Slawyk and MacIsaac (1972). Orthophosphate was analyzed by following a modification of the procedure of Bernhardt and Wilhelms (1967), and silicate was analyzed by following the method of Armstrong and others (1967).

Metals and Major Ions

Major ions and total iron and manganese in streams, stormwater, and waste water were analyzed at the NWQL by ion chromatography and inductively coupled plasma-optical emission spectrometry (ICP-OES) methods (Fishman and Friedman, 1989; Fishman, 1993). Total iron and manganese in groundwater, dry dock discharges, porewaters, and marine surface water collected in 2008 were analyzed by ICP-OES. Total manganese in saline water samples collected in 2009 were analyzed by using inductively coupled plasma-mass spectrometry (ICP-MS) by Garbarino and others (2006). Reporting levels of total iron and manganese were adjusted to higher values as a result of the significant dilution of seawater samples required to conduct ICP analyses.

Chlorophyll

Chlorophyll *a* concentrations were determined fluorometrically from the 25-mm filters (Holm-Hansen and Riemann, 1978) within 6 months of collection by the NRP in Menlo Park, California. The reporting level was 0.1 µg/L, and values under 1.0 µg/L were qualified as estimated.

Marine Sediment Samples

Physical Properties

The bulk density, dry weight, porosity, and organic content of sediment were taken in sequence from a single sediment subsample, and assayed by the NRP laboratory (Menlo Park, California) as previously described by Marvin-DiPasquale and others (2008).

Mercury

For analysis of STHg by NRP, 0.2–1.0 g of thawed sediment (exact weight measured) was initially digested with aqua regia (2 mL concentrated nitric (HNO_3) and 6 mL concentrated HCl) in FP digestion bombs overnight at room temperature by following standard USGS method (Olund and others, 2004), with modifications to the sample digestion. Subsequently, 22 mL of 5-percent bromine monochloride was added to each sample, which was then heated to 50 °C in an oven overnight. Once cooled, a 5-mL subsample was transferred into a precombusted glass container. The digestate was analyzed on an Automated Mercury Analyzer (Tekran® Model 2600, Tekran, Inc., Canada), according to U.S. EPA Method 1631, Revision E (U.S. Environmental Protection Agency, 2002). This method is based on the $SnCl_2$ reduction of ionic mercury [Hg(II)] to gaseous mercury [Hg^0], trapping Hg^0 on gold sand, thermal desorption, and quantification of Hg^0 via CVAFS. The method detection limit at the level of the Tekran analyzer was 0.05 ng/L of aqueous digest, giving a sediment dry weight detection limit of approximately 0.5 ng/g (as run), depending on the wet sediment mass digested and its water content. The reporting limit is 1 ng/g dry weight.

Upon thawing, whole sediment subsamples (about 2–5 g, exact weight recorded) for reactive mercury ($Hg(II)_R$) were mixed with 10 mL of 0.5-percent HCl (anoxic) (v/v) and again preserved frozen at –80 °C. Subsequently, these diluted subsamples were again thawed and assayed as previously described by Marvin-DiPasquale and Cox (2007). Each analytical batch of $Hg(II)_R$ samples was accompanied by the analysis of the following minimum of QA samples: a) one analytical duplicate and b) four ‘bubbler’ blanks. These blanks consisted of anoxic 0.5-percent HCl (v/v) solution only plus the $SnCl_2$ reductant, and were treated in the same way as an environmental sample (that is, 15-minute purge and trap). Any Hg^0 that was subsequently collected on the gold trap was assayed, and the average blank value for all four bubblers was subtracted in the calculation of environmental sample concentrations. Typically, the amount of Hg in bubbler blanks was less than the level of detection. The method detection limit at the level of the bubbler is approximately 0.05 ng of $Hg(II)_R$ (absolute), giving a dry sediment detection limit of approximately 0.01 ng/g dry weight (as run), depending on the actual mass assayed and its water content. The reporting limit for this parameter is 0.1 ng/g dry weight.

Upon thawing, sediment for SMHg analysis was first subsampled (0.5–1.0 g wet weight) into plastic centrifuge tubes and extracted with 2 mL of 2-percent (w/v) solution of potassium hydroxide (KOH) in methanol in a 60 °C oven for 4 hours (Xianchao and others, 2005). After cooling, 8 mL of laboratory water was added to each centrifuge tube. The contents of each tube were then homogenized via vortex stirring and stored frozen (–80 °C) until further processing. Upon thawing, samples were centrifuged at 4,000 rpm for 15 minutes. A 0.15-mL aliquot of the extractant

was subsampled into a trace-metal-free glass I-Chem™ vial. The vial was nearly filled with laboratory water, the pH was adjusted to 4.9 by using acetate buffer, and an ethylated agent (sodium tetraethyl borate) was added. The vial was then topped off with laboratory water, capped with an FP septa screw-top cap, and shaken. MHg was converted within the vial to volatile methyl-ethyl-mercury, which was subsequently analyzed on an MERX automated MHg analysis system (Brooks Rand Laboratories, Seattle, Washington) by using CVAFS detection. Calibration standards were prepared from a National Institute of Standards and Technology (NIST)-certified, commercially obtained mercuric chloride ($HgCl_2$) standard. The method detection limit at the level of the MERX analyzer was approximately 0.4 pg of MHg (absolute), giving a dry sediment detection limit of approximately 0.01 ng/g (as run), depending on the actual mass assayed and its water content. The reporting limit for this parameter is 0.1 ng/g dry weight.

Methylmercury Production Potential

Methylmercury production potential (MPP) rate experiments were carried out by the NRP laboratory and were quantified for the 0–2 cm surface sediment samples (collected during August 2008, February, June, and August 2009, and February 2010) by using a stable isotope incubation assay, initiated the day after subsampling in the laboratory (1–8 days following field collection). Three subsamples of sediment (3.0 g wet weight) per site were transferred into 13-cm^3 sealed serum vials, which were crimp-sealed with an FP-lined stopper. The vial headspace was then flushed with N_2 gas and the samples were stored in the refrigerator at 5 °C overnight. The following morning, prior to stable isotope amendment, the samples were allowed to preincubate for approximately 2 hours in an incubator maintained at a temperature within 1 °C of the average field temperature for all samples collected on a given field trip. An isotopically enriched solution of inorganic mercury ($^{200}HgCl_2$) was then injected (0.1 mL) through the septa of each vial for a final amendment concentration of approximately 50–60 ng of $^{200}Hg(II)$ per g of sediment (wet weight). The samples were vortexed for 1 minute each immediately following the isotope amendment. One of the three samples per set was immediately flash frozen in a mixture of dry ice and ethanol. This sample represented the killed control. The remaining two samples per set were returned to the incubator, where they remained for 4–5 hours, after which they too were flash frozen in dry ice and ethanol. The samples were stored at –80°C until further processing.

The isotopically enriched methylmercury ($M^{200}Hg$) produced from the $^{200}Hg(II)$ during the incubation was extracted into 25-percent (wt/v) KOH/methanol solution by a method modified from Xianchao and others (2005). Upon thawing, a subsample (0.5–1.0 g wet weight) was removed from each serum vial and transferred into a 15-mL plastic centrifuge tube. An internal standard of isotopically enriched $M^{199}Hg$ was added (0.15 ng) to each tube, followed by 2 mL of 25-percent (w/v) KOH/methanol solution. After tightly capping, each centrifuge tube was vortexed for 1 minute and then placed in a 60 °C oven for 4 hours. After cooling to room temperature, 8 mL of laboratory water was added to each centrifuge tube, which was then shaken to mix, and stored frozen at –80°C until further processing.

The $M^{200}Hg$ was subsequently quantified by a modified version of the ethylation assay (Bloom, 1989), coupled with ICP-MS (Hintelmann and others, 1995; Hintelmann and Evans, 1997). Upon thawing, 1 mL of the 25-percent (w/v) KOH/methanol extract was transferred to a glass bubbler containing 100 mL of anoxic laboratory water and 4 mL of citrate buffer. Ethylating agent (tetraethyl borate) was added (100 µL) and the mixture was shaken and allowed to react for 15 minutes prior to purging with argon gas for an additional 20 minutes. Volatile ethylated mercury species were trapped on a carbon trap (Carbotrap®) that was in-line with the bubbler gas outflow. After purging, the gas in-flow was diverted directly to the carbon traps which were flushed and dried for an additional 7 minutes to remove any water vapor. Each carbon trap was then removed from the bubbler and placed onto a separate gas-flushing rig, where the ethylated mercury species were desorbed from the carbon trap by heating, separated via gas chromatography, and sent through the ICP-MS (Perkin-Elmer DRC II). Calibration standards were prepared with both nonenriched MHg and istopically enriched $M^{199}Hg$, and were assayed in the same way as the samples. Excess $M^{200}Hg$ (above natural abundance levels) produced during the sediment incubation was quantified based on the calibration standards and the recovery of the internal standard ($M^{199}Hg$) added during the KOH/methanol extraction step. Any excess $M^{200}Hg$ measured in the killed controls was subtracted from the incubated samples. A Pseudo first-order rate constant for $^{200}Hg(II)$-methylation (k_{meth}, units = 1/d) was then calculated from the 'kill-corrected' incubated samples as previously described for the radiotracer $^{203}Hg(II)$-methylation assay (Marvin-DiPasquale and others, 2003).

Daily MPP rates (units = ng/g dry sediment/d) are then calculated as:

$$MPP = Hg(II)_R - Hg(II)_R \bullet EXP(-k_{meth} \bullet t), \qquad (3)$$

where t = 1.0 day and $Hg(II)_R$ is the independently measured situ concentration of inorganic 'reactive' mercury (in units of: ng/g dry weight), as described above. The reporting limit for this assay is 0.0015 per day (1.5×10^{-3}/d), which was partially determined by the results of the killed controls. Quality assurance included (a) analytical duplicates, and (b) the use of internal standards ($Me^{199}Hg$, as described above).

Sulfur Species

Sediment subsamples (approximately 1.5 g, exact weight recorded) collected for AVS (August 2008 only) and TRS analysis were preserved with the addition of 0.5 mL of 10-percent (w/v) zinc-acetate solution and stored frozen (–80 °C) in crimp-sealed serum vials under anoxic conditions. Analysis of both AVS and TRS was described by Marvin-DiPasquale and others (2008). The typical detection limits for both AVS and TRS assays is approximately 1 nanomole per milliliter at the level of the spectrophotometric analysis, with reporting limits of 0.1 and 1 micromole per gram dry sediment, respectively.

Iron Species

Sediment sub-samples collected for Fe-speciation analysis were preserved by freezing (-80°C) in crimp sealed serum vials under anoxic conditions. Three Fe-fractions (acidextractable ferrous iron (Fe(II)AE), amorphous (poorly-crystalline) ferric iron (Fe(III)a), and crystalline ferric iron (Fe(III)c) were assayed by the NRP laboratory (Menlo Park, Calif.) as previously described (Marvin-DiPasquale and others, 2008). The typical detection limit for each Fe-fraction is approximately 0.02 µg/ml at the level of the spectrophotometric analysis. The reporting limits are 0.01 mg Fe per gram dry sediment for all three fractions. Quality assurance included: (a) analytical duplicates, (b) matrix spikes and (c) method blanks. Calibration standards (FeSO4) were prepared using analytical grade reagent in 0.25 M hydroxylamine-HCl.

Zooplankton

Taxonomy

Zooplankton sorting and taxonomy was conducted by the Wetland Ecosystem Team within the School of Aquatic and Fishery Science at the University of Washington. Species and bulk zooplankton identification and sorting was conducted by trained technicians under low power magnification.

Mercury

Methylmercury concentrations in whole community and species-specific zooplankton samples were determined by the U.S. Geological Survey Mercury Laboratory (Menlo Park, California). Subsamples of freeze-dried zooplankton (whole community and species specific) were weighed out by using a microbalance (1–2 mg) into 1.5 mL acid-washed centrifuge tubes. Methylmercury was extracted from the samples by adding 200 µL of 25-percent (w/v) KOH/methanol to the centrifuge tubes. The sample and extractant were homogenized by vortexing and then samples were heated in an oven at 60 °C for a total of 4 hours with samples being vortexed once after 2 hours. Digested samples were cooled and stored frozen (–80 °C) until analysis. On the day of analysis, samples were thawed and 8 µL of low-DOC laboratory water was added to each centrifuge tube. The samples were then homogenized by vortexing and then centrifuged at 4,000 rpm for 15 minutes to compress pellet the remaining solid material into a pellet. A 0.15-mL aliquot of the extractant was subsampled into a trace-metal-clean glass I-Chem™ vial along with a drop (about 25 µL) of a silica-based antifoaming agent. The vial was nearly filled with laboratory water, the pH was adjusted to 4.9 by using acetate buffer, and an ethylated agent (sodium tetraethyl borate) was added. The vial was then topped off with laboratory water, capped with an FP septa screw-top cap, and shaken. MHg was converted within the vial to volatile methyl-ethyl-mercury, which was subsequently analyzed by MERX Automated Methyl Mercury Analytical System Brooks Rand Laboratories, Seattle, Washington) by using CVAFS detection. Each batch of analytical samples was accompanied with analysis of the minimum following QA samples: (a) two certified reference materials–National Research Council Canada (NRCC) DORM-2 dogfish muscle and NIST-Research Material 2890 Mussel Tissue, (b) one matrix spike sample, (c) one analytical duplicate, and (d) one method blank.

Stable Isotopes

Carbon and nitrogen stable isotopes were measured in frozen zooplankton and particulate matter samples by the University of California at Davis Stable Isotope Facility (2011) by following established methods. Particulate matter samples were evaluated in triplicate, and zooplankton replication depended upon organism availability, but ranged from 2 to 5 per sampling event. Isotope ratios of C and N of the suspended solids and zooplankton were determined at the Stable Isotope Facility, University of California, Davis, by using a Europa Scientific Hydra 20/20 continuous flow isotope ratio mass spectrometer in conjunction with a Europa ANCA-SL elemental analyzer to convert organic C and N into CO_2 and N_2 gas. Nitrogen isotope samples were standardized against N_2 in air as follows:

$$\delta^{15}N‰ = [(Rsample/Rstandard)-1] \times 1\,000, \qquad (4)$$

where $R = {}^{15}N/{}^{14}N$, and where ‰ is used to indicate parts per thousand. A similar relation for $\delta^{13}C$ ($R = {}^{13}C/{}^{12}C$) was used to standardize carbon isotope samples against Vienna Pee Dee Belemnite.

Quality Assurance and Assessment of Data

Quality assurance (QA) samples for both laboratory and field procedures were collected. Laboratory quality assurance samples included instrumental blanks, blind blanks, laboratory replicates, recovery of continuous calibration verification standards (CCV), laboratory control samples (LCS), digestion checks (DIGCHK), third party controls (TPC), matrix spikes (MS), duplicate matrix spikes and reference materials (certified reference materials (CRM); standard reference material (SRM); standard reference sample (SRS)). The CCVs are analyzed frequently within a run to provide evidence of long-term instrument stability (Maloney, 2005). DIGCHKs were used to evaluate the digestion of samples for the analyses of total nitrogen in filtered and unfiltered water. For the purpose of this report, laboratory replicates are samples taken from the same container during post-sampling processing or in the analytical laboratory.

Field QA samples included analysis of source water from WAWSC and blank water processed through equipment in the field, field replicates taken in different bottles from the water body, submission of double blind standard SRS samples and CRM samples, and interlaboratory comparisons.

QA results for the Watershed Sources Project are listed in appendix B. Similar types of laboratory and field quality assurance for the Methylation and Bioaccumulation Project are listed in appendix C for sediment and appendix D for marine water. The assessment of related data for internal consistency is one of the first steps in interpreting field data and is beyond the scope of this data report. Checks for internal consistency may reveal discrepancies other than revealed by assessment of laboratory and field data for a specific constituent.

Data

Tables 1–10 indicate the titles of the specific worksheets in appendixes E–J that contain the different types of data.

Watershed Sources Project

The type and number of samples collected during the Watershed Sources Project are summarized in table 1. The concentrations of FTHg, PTHg, TSS, and elevations from the BNC wells, including the May and June tidal studies and in discharges from industrial and municipal sources (dry dock, steam plant, and wastewater treatment plants), streams, and stormwater are presented in appendix E. The type and number of samples collected during the survey of methylmercury are summarized in table 2. The FMHg and selected constituents in samples from the BNC groundwater, industrial and municipal sources, streams, and stormwater are presented in appendix F.

Methylation and Bioaccumulation Project

The number and types of data collected from sediment, porewaters, and incubation experiments, as part of sediment sampling during August 2008 are summarized in table 3 and presented in appendix G. The biological monthly sampling, seasonal intensive surface- and bottom-water sampling, CTD profiles of field parameters, taxonomy of zooplankton species, and species-specific methylmercury concentrations collected as part of the water column sampling in August, September, and October 2008 are summarized in table 4 and the data are presented in appendix G. Data from Puget Sound representative bays Holmes Harbor, Liberty Bay and Budd Inlet are only found in appendix G. The data for sediment and water column sampling during November 2008, January, February, and March 2009, and February 2010 are summarized in tables 5 and 6 and are presented in appendix H. Similar data collected in April, May, and June 2009 are summarized in tables 7 and 8 and the data are presented in appendix I. Tables 9 and 10 summarize the data collected in July and August 2009 and presented in appendix J.

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Table 1. Study sites and numbers of samples for filtered and particulate mercury and selected constituents collected during the Watershed Sources Project, Sinclair Inlet, Washington.

[NWQL, U.S. Geological Survey (USGS) National Water Quality Laboratory; WMRL, USGS Wisconsin Mercury Research Laboratory; WAWSC, Washington Water Science Center; YSI, Yellow Springs Instruments; NA, not applicable; –, not analyzed]

Watershed project study sites	Number of sampling events	Measurements		Method for collecting field parameters			NWQL	WMRL		WAWSC	Title of worksheet containing data	
		Water level	Discharge/ velocity	Flow-through YSI sonde system	Discrete aliquots	Immersion in water body	Filtered total mercury	Filtered total mercury	Particulate total mercury	Total suspended solids	Discrete sample data	Continuous record of field parameters by flow-through YSI sonde system
Groundwater in the Bremerton naval complex												
Base-wide	22	22	NA	X			11	11	22	21	Appendix E: Basewide GW	
May tidal study	19	11	NA	X			19	–	10	10	Appendix E: May tidal discrete; May and June tidal water levels	Appendix E: May tidal continuous
June tidal study, Wells 722	26	30	NA	X			25	–	1	–	Appendix E: June tidal discrete; May and June tidal water levels	Appendix E: June tidal continuous
June piezometer study	45	NA	NA		X		–	45	9	9	Appendix E: June piezometers, June piezometer water levels	
Permitted sources												
Dry dock composite samples	2	NA	NA		X		2	–	2	2	Appendix E: Industrial and municipal sources	
Dry dock grab samples	12	NA	NA	X			4	8	12	12	Appendix E: Industrial and municipal sources	
Steam plant	4	NA	NA	X			–	4	4	4	Appendix E: Industrial and municipal sources	
Wastewater treatment plant	6	NA	NA		X		–	6	6	6	Appendix E: Industrial and municipal sources	
Surface water												
Streams	10	NA	10			X	–	10	10	10	Appendix E: Streams	
Stormwater	6	NA	NA	X			–	6	6	6	Appendix E: Stormwater	
PSNS015 composites	2	NA	NA				2	2	2	2	Appendix E: PSNS015 composites	
PSNS015 Ebb tide study	10	NA	9		X		10	–	–	–	Appendix E: PSNS015 tidal study	Appendix E: PSNS015 tidal study
Total number of discrete samples		63	19				73	92	84	82		

Table 2. Study sites and numbers of samples for filtered methylmercury and selected constituents collected during the Watershed Sources Project, Sinclair Inlet, Washington.

[UW, University of Washington; WMRL, Wisconsin Mercury Research Laboratory; –, not analyzed]

Watershed project study sites	Number of sampling events	WMRL	National Water Quality Laboratory				Washington Water Science Center		UW Oceanography Laboratory	Title of worksheet containing data
		Filtered methyl-mercury	Total particulate carbon and nitrogen	Major ions	Nutrients	Trace metals	Sulfide	Ferrous iron	Nutrients	
Groundwater in the Bremerton naval complex										
Base-wide	5	5	5	–	–	5	5	4	5	Appendix F: Base-wide groundwater
May tidal study	9	–	9	–	–	1	1	1	3	Appendix F: May tidal study
June piezometer study	6	6	–	–	–	–	–	–	–	Appendix F: June piezometers
Industrial and municipal sources										
Dry dock grab samples	3	2	2	–	–	2	3	2	2	Appendix F: Industrial and municipal sources
Steam plant	1	1	1	–	–	1	1	–	1	Appendix F: Industrial and municipal sources
Wastewater treatment plant	6	6	6	4	6	6	–	–	–	Appendix F: Industrial and municipal sources
Surface water										
Streams	10	10	10	10	10	10	–	–	–	Appendix F: Streams
Stormwater	6	6	6	6	6	6	–	–	–	Appendix F: Stormwater
Total number of discrete samples		36	39	20	22	31	10	7	11	

Table 3. Numbers and types of samples collected during August 2008 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.

[**National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, sediment total filtered mercury; SMHg; sediment methylmercury; UW, University of Washington; –, not analyzed]

Type of sample station	Number of sites	National Research Program							Title of worksheet containing data
		Sediment physical characteristics	Mercury species in sediment	Methylation rate constants	Iron species in sediment	Sulfur species in sediment	Dissolved organic carbon in porewater	Ultraviolet absorbance in porewater	
Seasonal sediment sampling (August 2008)									
Sediment	9	9	9	9	9	9	–	–	Appendix G: Sediment-Aug-08
Porewaters	9	–	–	–	–	–	9	9	Appendix G: Porewater-Aug-08
Incubation experiments (August 2008)									
Representative bays	3	–	–	–	–	–	–	–	Appendix G: Representative Bays-INC-Aug-08
Sinclair Inlet	3	–	–	–	–	–	–	–	Appendix G: SI-INC-Aug-08
Bremerton naval complex	3	–	–	–	–	–	–	–	Appendix G: BNC-INC-Aug-08
Total number of discrete samples		9	9	9	9	9	9	9	

Type of sample station	Number of sites	Wisconsin Mercury Research Laboratory			
		Sediment physical characteristics	Mercury species in sediment	Filtered total mercury	Filtered methyl-mercury
Seasonal sediment sampling (August 2008)					
Sediment	9	9	9	–	–
Porewaters	9	–	–	9	9
Incubation experiments (August 2008)					
Representative bays	3	–	–	5	6
Sinclair Inlet	3	–	–	7	7
Bremerton naval complex	3	–	–	9	9
Total number of discrete samples		9	9	30	31

Table 3. Numbers and types of samples collected during August 2008 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.—Continued

[**National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, sediment total filtered mercury; SMHg; sediment methylmercury; UW, University of Washington; –, not analyzed]

Type of sample station	Number of sites	Washington Water Science Center		UW chemical oceanography nutrients	National Water Quality Laboratory	Title of worksheet containing data
		Unfiltered ferrous iron	Unfiltered sulfide		Filtered total manganese	
Seasonal sediment sampling (August 2008)						
Sediment	9	–	–	–	–	Appendix G: Sediment-Aug-08
Porewaters	9	11	15	16	15	Appendix G: Porewater-Aug-08
Incubation experiments (August 2008)						
Representative bays	3	–	–	–	–	Appendix G: Representative Bays-INC-Aug-08
Sinclair Inlet	3	–	–	–	–	Appendix G: SI-INC-Aug-08
Bremerton naval complex	3	–	–	–	–	Appendix G: BNC-INC-Aug-08
Total number of discrete samples		11	15	16	15	

Table 4. Numbers and types of samples collected during summer and fall 2008 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.

[CTD, conductance, temperature, depth; DOC, dissolved organic carbon; TSS, total suspended solids; UC; University of California; UW, University of Washington; YSI, Yellow Springs Instruments; –, not analyzed]

Type of sample station	Number of sites	National Research Program		Wisconsin Mercury Research Laboratory				Washington Water Science Center	UW Chemical Oceanography		National Water Quality Laboratory		
		Chlorophyll in water column	Methyl-mercury in bulk zooplankton	Particulate total mercury	Particulate methyl-mercury in solids	Filtered total mercury	Filtered methyl-mercury	Total suspended solids	Salinity	Nutrients	Filtered total manganese	DOC in the water column	Particulate carbon and nitrogen
Biological monthly sampling													
Surface (August 2008)	7	7	20	8	15	8	8	7	4	7	7	7	7
Surface (September 2008)	4	4	12	8	8	5	5	4	4	4	3	3	3
Surface (October 2008)	4	4	12	4	8	4	4	8	4	4	4	4	4
Intensive (August 2008)													
Surface water	2	–	–	2	4	2	2	2	2	–	2	2	3
Bottom water	9	–	–	10	9	10	10	10	6	9	9	8	8
Total number of discrete samples		15	44	32	44	29	29	31	20	24	25	24	25

Table 4. Numbers and types of samples collected during summer and fall 2008 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.—Continued

[CTD, conductance, temperature, depth; DOC, dissolved organic carbon; TSS, total suspended solids; UC; University of California; UW, University of Washington; YSI, Yellow Springs Instruments; –, not analyzed]

Type of sample station	Number of sites	UC Stable Isotope Laboratory		Title of worksheet containing data	CTD profiles	Title of worksheet containing data	UW Wetland ecosystem team		Title of worksheet containing data	National Research Program
		Carbon and nitrogen isotopes in TSS	Isotopes in zoo-plankton		Measured field parameter method		Zoo-plankton concen-tration	Tax-onomy		Specific species in which methylmercury was measured [stations (with number of samples) found in appendix G: Species-MHg-Aug-Oct-08]
Biological monthly sampling										
Surface (August 2008)	7	21	18	Appendix G: BIO-Aug-Sept-08	YSI Sonde	Appendix G: CTD-Representative Bays-Aug-08; CTD-SI-BNC-Aug-08	7	7	Appendix G: TAX-Aug-Oct-08 Appendix G: TAX-Aug-Oct-08 Appendix G: TAX-Aug-Oct-08	*Acartia* sp. [BI(2), LB(3), 52(1), *Evadne* sp. [HH(22), Out(1), IN(1)], *Paracalanus* sp. [CZ(2)].
Surface (September 2008)	4	12	12	Appendix G: BIO-Aug-Sept-08	YSI Sonde	Appendix G: CTD-Sept-08	4	4		*Calanus* sp. [CZ(1), 52(1)], *Cragon* sp. [CZ(3), 52 (3)], *Paracalanus* sp. [CZ(3), IN(3), PO(3), 52(3)], *Pleopis polyphemoides* [IN(2)].
Surface (October 2008)	4	12	11	Appendix G: BIO-Oct-08	YSI Sonde	Appendix G: CTD-Oct-08	4	4		*Acartia* sp. [IN(3), PO(4), 52(3)], *Corycaeus* sp. [CZ(3)], *Cragon* sp. [SI(3)].
Intensive (August 2008)										
Surface water	2	–	–	Appendix G: Intensive-Aug-08	YSI Sonde	Appendix G: CTD-Representative Bays-Aug-08; CTD-SI-BNC-Aug-08	–	–		
Bottom water	9	–	–	Appendix G: Intensive-Aug-08	YSI Sonde	Appendix G: CTD-Representative Bays-Aug-08; CTD-SI-BNC-Aug-08	–	–		
Total number of discrete samples		45	41				15	15		

Table 5. Numbers and types of samples collected during winter 2009–10 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.

[A complete description of station names and field identifiers is shown in appendix A. **National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, sediment total filtered mercury; SMHg; sediment methylmercury; THg, Sediment total filtered mercury; SMHg, Sediment filtered methylmercury; DOC, dissolved organic carbon; SI, Sinclair Inlet, BNC, Bremerton naval complex; Fe, iron; Mn, manganese; –, not analyzed]

Type of sample station	Number of sites	National Research Program									Title of worksheet containing data
		Sediment physical characteristics	Mercury species in sediment	Methylation rate constants	Total mercury in sediment	Methy-mercury in sediment	Iron species in sediment	Sulfur species in sediment	DOC in porewater	Ultraviolet absorbance in porewater	
Seasonal sediment sampling (Winter 2009–10)											
Sediment	23	23	23	20	23	23	23	23	–	–	Appendix H: Sediment-Feb-09-10
Porewaters	6	–	–	–	–	–	–	–	6	6	Appendix H: Porewater-Feb-09
Incubation experiments (Winter 2009–10)											
SI-PO	1	–	–	–	–	–	–	–	–	–	Appendix H: SI-PO-INC-Feb-09
SI-OUT	1	–	–	–	–	–	–	–	–	–	Appendix H: SI-OUT-INC-Feb-09
SI-IN	1	–	–	–	–	–	–	–	–	–	Appendix H: SI-IN-INC-Feb-09
BNC-39	1	–	–	–	–	–	–	–	–	–	Appendix H: BNC-39-INC-Feb
BNC-60	1	–	–	–	–	–	–	–	–	–	Appendix H: BNC-60-INC-Feb-09
BNC-71	1	–	–	–	–	–	–	–	–	–	Appendix H: BNC-71-INC-Feb-09
Tumbling core experiments (Winter 2009–10)											
	7	–	–	–	–	–	–	–	–	–	Appendix H: Tumble-Hg-Feb-09
Total number of discrete samples		23	23	20	23	23	23	23	6	6	

Table 5. Numbers and types of samples collected during winter 2009–10 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.–Continued

[A complete description of station names and field identifiers is shown in appendix A. **National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, sediment total filtered mercury; SMHg; sediment methylmercury; THg, Sediment total filtered mercury; SMHg, Sediment filtered methylmercury; DOC, dissolved organic carbon; SI, Sinclair Inlet, BNC, Bremerton naval complex; Fe, iron; Mn, manganese; –, not analyzed]

Type of sample station	Number of sites	Wisconsin Mercury Research Laboratory					Washington Water Science Center		UW Chemical Oceanography	National Water Quality Laboratory	
		Sediment physical characteristics	Mercury species in sediment	Methyl-mercury in sediment	Filtered total mercury	Filtered methyl-mercury	Unfiltered ferrous iron	Unfiltered sulfide	Nutrients	Filtered total metals (Fe and Mn)	Organic carbon in sediments
Seasonal sediment sampling (Winter 2009–10)											
Sediment	23	–	–	–	–	–	–	–	–	–	–
Porewaters	6	–	–	–	6	6	12	12	12	11	11
Incubation experiments (Winter 2009–10)											
SI-PO	1	–	–	–	12	12	–	–	–	–	–
SI-OUT	1	–	–	–	12	12	–	–	–	–	–
SI-IN	1	–	–	–	10	10	–	–	–	–	–
BNC-39	1	–	–	–	12	12	–	–	–	–	–
BNC-60	1	–	–	–	8	8	–	–	–	–	–
BNC-71	1	–	–	–	12	12	–	–	–	–	–
Tumbling core experiments (Winter 2009–10)											
	7	–	–	–	14	14	–	–	–		
Total number of discrete samples	42	–	–	–	86	86	12	12	12	11	12

Table 6. Numbers and types of samples collected during winter 2008–09 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.

[CTD, conductance, temperature, depth; DOC, dissolved organic carbon; TSS, total suspended solids; UC; University of California; UW, University of Washington; YSI, Yellow Springs Instruments; –, not analyzed]

Type of sample station	Number of sites	National Research Program		Wisconsin Mercury Research Laboratory				Washington Water Science Center	UW Chemical Oceanography		National Water Quality Laboratory		
		Chlorophyll in water column	Methyl-mercury in bulk zooplankton	Particulate total mercury	Particulate methyl-mercury in solids	Filtered total mercury	Filtered methyl-mercury	Total suspended solids	Salinity	Nutrients	Filtered total man-ganese	DOC in the water column	Particulate carbon and nitrogen
Biological monthly sampling													
Surface (November 2008)	4	4	12	4	6	4	4	8	4	4	4	4	4
Surface (January 2009)	4	4	12	4	8	4	4	–	4	4	4	4	4
Surface (February 2009)	4	4	12	4	8	4	4	8	2	4	4	4	4
Surface (March 2009)	4	4	12	4	8	4	4	8	4	4	4	4	4
Intensive (February 2009)													
Surface water	4	–	–	4	4	4	4	6	3	3	3	3	3
Bottom water	6	–	–	6	8	6	6	14	7	6	6	6	6
Total number of discrete samples		16	48	26	42	26	26	44	24	25	25	25	25

Table 6. Numbers and types of samples collected during winter 2008–09 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.—Continued

[CTD, conductance, temperature, depth; DOC, dissolved organic carbon; TSS, total suspended solids; UC; University of California; UW, University of Washington; YSI, Yellow Springs Instruments; –, not analyzed]

Type of sample station	Number of sites	UC Stable Isotope Laboratory		Title of worksheet containing data	CTD Profiles	Title of worksheet containing data	UW Wetland Ecosystem Team			National Research Program
		Carbon and nitrogen isotopes in TSS	Isotopes in zoo-plankton		Measured field parameter method		Zoo-plankton concen-tration	Tax-onomy	Title of worksheet containing data	Specific species in which methyl-mercury was measured [stations (with number of samples) found in appendix H: Species-MHg-Nov-08 Jan-Mar-09]
Biological monthly sampling										
Surface (November 2008)	4	12	12	Appendix H: BIO-Nov-08 Jan-Mar-09	YSI Sonde	Appendix H: CTD-Nov-08	4	4	Appendix H: TAX-Nov-08 Jan-Mar-09	*Acartia* sp. [IN(3), PO(3), 52(4)], Corycaeus sp. [CZ(3)]
Surface (January 2009)	4	12	12	Appendix H: BIO-Nov-08 Jan-Mar-09	YSI Sonde	Appendix H: CTD-Jan-09	4	4		*Acartia* sp. [IN(3), PO(3), 52(3), CZ(3)], Calanus sp. [CZ(1)], Paracalanus spp. [CZ(1)]
Surface (February 2009)	4	12	12	Appendix H: BIO-Nov-08 Jan-Mar-09	Seabird 19+	Appendix H: CTD-Feb-09	4	4		*Acartia* sp. [IN(3), PO(3), 52(3), CZ(3)]
Surface (March 2009)	4	12	11	Appendix H: BIO-Nov-08 Jan-Mar-09	Seabird 19+	Appendix H: CTD-Mar-09	4	4		*Acartia* sp. [IN(3), PO(3), 52(3), CZ(3)]
Intensive (February 2009)										
Surface water	4	–	–	Appendix H: Intensive-Feb-09	Seabird 19+	Appendix H: CTD-Feb-09	–	–		
Bottom water	6	–	–	Appendix H: Intensive-Feb-09	Seabird 19+	Appendix H: CTD-Feb-09	–	–		
Total number of discrete samples		48	47				8	16		

Table 7. Numbers and types of samples collected in June 2009 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.

[A complete description of station names and field identifiers is shown in appendix A. **National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, Sediment total filtered mercury; SMHg, Sediment filtered methylmercury; DOC, dissolved organic carbon; SI, Sinclair Inlet, BNC, Bremerton naval complex; Fe, iron; Mn, manganese; –, not analyzed]

Type of sample station	Number of sites	National Research Program								Wisconsin Mercury Research Laboratory			
		Sediment physical characteristics	Mercury species in sediment	Methylation rate constants	Total mercury in sediment	Methyl-mercury in sediment	Iron species in sediment	Sulfur species in sediment	DOC in porewater	Sediment physical character-istics	Mercury species in sediment	Filtered total mercury	Filtered methyl-mercury
Seasonal sediment sampling (June 2009)													
Sediment	20	20	20	20	20	20	20	20	–	20	20	–	–
Porewaters	6	–	–	–	–	–	–	–	6	–	–	6	6
Incubation experiments (June 2009)													
SI-PO	1	–	–	–	–	–	–	–	–	–	–	9	9
SI-OUT	1	–	–	–	–	–	–	–	–	–	–	9	9
SI-IN	1	–	–	–	–	–	–	–	–	–	–	12	11
BNC-39	1	–	–	–	–	–	–	–	–	–	–	12	12
BNC-60	1	–	–	–	–	–	–	–	–	–	–	11	11
BNC-71	1									–	–	12	12
Tumbling core experiments (June 2009)													
	7	–	–	–	–	–	–	–	–	–	–	14	14
Total number discrete samples		20	20	20	20	20	20	20	9	20	20	85	84

Table 7. Numbers and types of samples collected in June 2009 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.—Continued

[A complete description of station names and field identifiers is shown in appendix A. **National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, Sediment total filtered mercury; SMHg, Sediment filtered methylmercury; DOC, dissolved organic carbon; SI, Sinclair Inlet, BNC, Bremerton naval complex; Fe, iron; Mn, manganese; –, not analyzed]

Type of sample station	Number of sites	Washington Water Science Center		UW Chemical Oceanography	National Water Quality Laboratory		Title of worksheet containing data
		Unfiltered ferrous iron	Unfiltered sulfide	Nutrients	Filtered total metals (Fe and Mn)	Organic carbon in sediments	
Seasonal sediment sampling (June 2009)							
Sediment	20	–	–	–	–	–	Appendix I: Sediment-June-09
Porewaters	6	12	12	12	12	12	Appendix I: Porewater-June-09
Incubation experiments (June 2009)							
SI-PO	1	–	–	–	–	–	Appendix I: SI-PO-INC-June-09
SI-OUT	1	–	–	–	–	–	Appendix I: SI-OUT-INC-June-09
SI-IN	1	–	–	–	–	–	Appendix I: SI-IN-INC-June-09
BNC-39	1	–	–	–	–	–	Appendix I: BNC-39-INC-June-09
BNC-60	1	–	–	–	–	–	Appendix I: BNC-60-INC-June-09
BNC-71	1	–	–	–	–	–	Appendix I: BNC-71-INC-June-09
Tumbling core experiments (June 2009)							
	7	–	–	–	–	–	Appendix I: Tumble-Hg-June-09
Total number discrete samples		12	12	12	12	12	

Table 8. Numbers and types of samples collected during spring 2009 (April to June) for the Methylation and Bioaccumulation Project in association with the water column sampling program, Sinclair Inlet, Washington

[DOC, dissolved organic carbon; TSS, total suspended solids; –, not analyzed]

Type of sample station	Number of sites	National Research Program		Wisconsin Mercury Research Laboratory				Washington Water Science Center	UW Chemical Oceanography		National Water Quality Laboratory		
		Chlorophyll in water column	Methyl-mercury in bulk zooplankton	Particulate total mercury	Particulate methyl-mercury in solids	Filtered total mercury	Filtered methyl-mercury	Total suspended solids	Salinity	Nutrients	Filtered total manganese	DOC in the water column	Particulate carbon and nitrogen
Biological monthly sampling													
Surface (April 2009)	4	4	12	4	8	4	4	12	4	4	4	4	4
Surface (May 2009)	4	4	12	4	8	4	4	12	4	4	4	4	4
Surface (June 2009)	4	4	10	4	8	4	4	11	4	4	4	4	4
Intensive (June 2009)													
Surface water	3	3	–	4	3	5	4	6	3	3	3	3	4
Bottom water	6	–	–	6	4	6	6	12	6	6	6	6	6
May time series													
May time series	4	–	–	40	–	–	–	40	–	–	–	–	–
Total number of discrete samples		15	34	62	31	23	22	93	21	22	21	22	22

Table 8. Numbers and types of samples collected during spring 2009 (April–June) for the Methylation and Bioaccumulation Project in association with the water column sampling program, Sinclair Inlet, Washington.—Continued

[DOC, dissolved organic carbon; TSS, total suspended solids; –, not analyzed]

Type of sample station	Number of sites	UC Stable Isotope Laboratory		Title of worksheet containing data	CTD Profiles	Title of worksheet containing data	UW Wetland Ecosystem Team		Title of worksheet containing data	National Research Program
		Carbon and nitrogen isotopes in TSS	Isotopes in zoo-plankton		Measured field parameter method		Zooplankton concentration	Tax-onomy		Specific species in which methylmercury was measured [stations (with number of samples) found in appendix I: Species-MHg-April-June-09)
Biological monthly sampling										
Surface (April 2009)	4	12	12	Appendix I: Bio-April-June-09	Seabird 19+	Appendix I: CTD-April	4	4	Appendix I: TAX-April-June-09	*Acartia* sp. [CZ(1), PO(3), 52(3), IN(3)], *Pseudocalanus* sp. [CZ(1)].
Surface (May 2009)	4	12	12	Appendix I: Bio-April-June-09	Seabird 19+	Appendix I: CTD-May	4	4	Appendix I: TAX-April-June-09	*Acartia* sp. [CZ(1), PO(2), 52(3), IN(3)], *Evadne* sp. [CZ(2)].
Surface (June 2009)	4	12	10	Appendix I: Bio-April-June-09	Seabird 19+	Appendix I: CTD-June	4	4	Appendix I: TAX-April-June-09	*Acartia* sp. [PO(3), 52(3)], *Evadne* sp. [CZ(1), IN(3)], *Polychaete sp.* [CZ(5), IN(1)].
Intensive (June 2009)										
Surface water	3	–	–	Appendix I: intensive-June	Seabird 19+	Appendix I: CTD-June	–	–		
Bottom water	6	–	–	Appendix I: intensive-June	Seabird 19+	Appendix I: CTD-June	–	–		
May time series										
May time series	4	–	–	Appendix I: May Time Series	Seabird 19+	Appendix I: CTD-May Time Series	–	–		
Total number of discrete samples		36	34				12	12		

Table 9. Numbers and types of samples collected in August 2009 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.

[A complete description of station names and field identifiers is shown in appendix A. **National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, Sediment total filtered mercury; SMHg, Sediment filtered methylmercury; DOC, dissolved organic carbon; SI, Sinclair Inlet, BNC, Bremerton naval complex; Fe, iron; Mn, manganese; –, not analyzed]

Type of sample station	Number of sites	National Research Program						Wisconsin Mercury Research Laboratory			
		Sediment physical characteristics	Mercury species in sediment	Methylation rate constants	Iron species in sediment	Sulfur species in sediment	DOC in porewater	Sediment physical characteristics	Mercury species in sediment	Filtered total mercury	Filtered methyl-mercury
Seasonal sediment sampling (August 2009)											
Sediment	20	20	20	20	20	20	–	–	20	–	–
Porewaters	6	–	–	–	–	–	6	–	–	6	6
Incubation experiments											
SI-PO	1	–	–	–	–	–	–	–	–	11	11
SI-OUT	1	–	–	–	–	–	–	–	–	12	12
SI-IN	1	–	–	–	–	–	–	–	–	12	12
BNC-39	1	–	–	–	–	–	–	–	–	12	12
BNC-60	1	–	–	–	–	–	–	–	–	12	12
BNC-71	1	–	–	–	–	–	–		–	12	12
Tumbling core experiments											
	7	–	–	–	–	–	–	–	–	14	14
Total number of discrete samples		20	20	20	20	20	6	–	40	91	91

Table 9. Numbers and types of samples collected in August 2009 for the Methylation and Bioaccumulation Project associated with the sediment sampling program, Sinclair Inlet, Washington.—Continued

[A complete description of station names and field identifiers is shown in appendix A. **National Research Program:** Sediment physical characteristics—Percentage dry weight, loss on ignition, bulk density, porosity, total fines. Mercury species in sediment—STHg, SMHg, and reactive inorganic mercury. **Wisconsin Mercury Research Laboratory**: Sediment physical characteristics—Percentage dry weight, loss on ignition. Mercury species in sediment—STHg and SMHg. STHg, Sediment total filtered mercury; SMHg, Sediment filtered methylmercury; DOC, dissolved organic carbon; SI, Sinclair Inlet, BNC, Bremerton naval complex; Fe, iron; Mn, manganese; –, not analyzed]

Type of sample station	Number of sites	Washington Water Science Center		UW Chemical Oceanography	National Water Quality Laboratory		Title of worksheet containing data
		Unfiltered ferrous iron	Unfiltered sulfide	Nutrients	Filtered total metals (Fe and Mn)	Organic carbon in sediments	
Seasonal sediment sampling (August 2009)							
Sediment	20	–	–	–	–	12	Appendix J: Sediment-Aug-09
Porewaters	6	12	12	12	12	–	Appendix J: Porewater-Aug-09
Incubation experiments							
SI-PO	1	–	–	–	–	–	Appendix J: SI-PO-INC-Aug-09
SI-OUT	1	–	–	–	–	–	Appendix J: SI-OUT-INC-Aug-09
SI-IN	1	–	–	–	–	–	Appendix J: SI-IN-INC-Aug-09
BNC-39	1	–	–	–	–	–	Appendix J: BNC-39-INC-Aug-09
BNC-60	1	–	–	–	–	–	Appendix J: BNC-60-INC-Aug-09
BNC-71	1	–	–	–	–	–	Appendix J: BNC-71-INC-Aug-09
Tumbling core experiments							
	7	6	7	7	7	–	Appendix J: Tumble-Hg-Aug-09
Total number of discrete samples		18	19	19	19	12	

Table 10. Numbers and types of samples collected in summer 2009 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.

[DOC, dissolved organic carbon; TSS, total suspended solids; –, analyzed]

Type of sample station	Number of sites	National Research Program		Wisconsin Mercury Research Laboratory				Washington Water Science Center
		Chlorophyll in water column	Methyl-mercury in bulk zooplankton	Particulate total mercury	Particulate methyl-mercury in solids	Filtered total mercury	Filtered methyl-mercury	Total suspended solids
Biological monthly sampling								
Surface (July 2009)	4	4	12	4	8	4	4	12
Surface (Aug 2009)	4	4	12	4	9	5	5	14
Intensive (August 2009)								
Surface water	3	3	0	4	3	3	3	6
Bottom water	6	0	0	6	6	7	7	13
Total number of discrete samples		11	24	18	26	19	19	45

Type of sample station	Number of sites	UW Chemical Oceanography		National Water Quality Laboratory			UC Stable Isotope Laboratory		Title of worksheet containing data
		Salinity	Nutrients	Filtered total manganese	DOC in the water column	Particulate carbon and nitrogen	Carbon and nitrogen isotopes in TSS	Isotopes in zoo-plankton	
Biological monthly sampling									
Surface (July 2009)	4	4	4	4	4	4	12	12	Appendix J: Bio-July-Aug-09
Surface (Aug 2009)	4	4	5	4	5	5	12	12	Appendix J: Bio-July-Aug-09
Intensive (August 2009)									
Surface water	3	3	3	3	3	3	3	–	Appendix J: Intensive-Aug-09
Bottom water	6	6	6	7	7	7	–	–	Appendix J: Intensive-Aug-09
Total number of discrete samples		17	18	18	19	19	27	24	

Table 10. Numbers and types of samples collected in summer 2009 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.—Continued

[DOC, dissolved organic carbon; TSS, total suspended solids; –, analyzed]

Type of sample station	Number of sites	CTD Profiles		UW Wetland Ecosystem Team			National Research Program
		Measured field parameter method	Title of worksheet containing data	Zooplankton concentration	Taxonomy	Title of worksheet containing data	Specific species in which methylmercury was measured [stations (with number of samples) found in appendix J: Species-MHg-July-Aug-09)]
Biological monthly sampling							
Surface (July 2009)	4	Seabird 19+	Appendix J: CTD-July-09	4	4	Appendix J: TAX-July-Aug-09	*Evadne nordmanni* [PO(3), IN(3), 52 (3)], *Paracalanus* spp. [CZ(3)].
Surface (Aug 2009)	4	Seabird 19+	Appendix J: CTD-Aug-09	4	4	Appendix J: TAX-July-Aug-09	*Cragon* sp. [CZ(3)], *Evadne nordmanni* [CZ(3), PO(2)], *Paracalanus* sp. [IN(3), 52(3)].
Intensive (August 2009)							
Surface water	3	Seabird 19+	Appendix J: CTD-Aug-09	–	–		
Bottom water	6	Seabird 19+	Appendix J: CTD-Aug-09	–	–		
Total number of discrete samples				8	8		

Table 10. Numbers and types of samples collected in summer 2009 for the Methylation and Bioaccumulation Project associated with the water column sampling program, Sinclair Inlet, Washington.—Continued

[DOC, dissolved organic carbon; TSS, total suspended solids; –, analyzed]

Type of sample station	Number of sites	UC Stable Isotope Laboratory		Title of worksheet containing data	CTD profiles	Title of worksheet containing data	UW Wetland Ecosystem Team		Title of worksheet containing data	National Research Program
		Carbon and nitrogen isotopes in TSS	Isotopes in zoo-plankton		Measured field parameter method		Zoo-plankton concen-tration	Tax-onomy		Specific species in which methylmercury was measured [stations (with number of samples) found in appendix G: Species-MHg-Aug-Oct-08]
Biological monthly sampling										
Surface (July 2009)	4	21	18	Appendix G: BIO-Aug-Sept-08	YSI Sonde	Appendix G: CTD-Representative Bays-Aug-08; CTD-SI-BNC-Aug-08	7	7	Appendix G: TAX-Aug-Oct-08	*Acartia* sp. [BI(2), LB(3), 52(1), *Evadne* sp. [HH(22), Out(1), IN(1)], *Paracalanus* sp. [CZ(2)].
Surface (Aug 2009)	4	12	12	Appendix G: BIO-Aug-Sept-08	YSI Sonde	Appendix G: CTD-Sept-08	4	4	Appendix G: TAX-Aug-Oct-08	*Calanus* sp. [CZ(1), 52(1)], *Cragon* sp. [CZ(3), 52 (3)], Paracalanus sp. [CZ(3), IN(3), PO(3), 52(3)], *Pleopis polyphemoides* [IN(2)].
Intensive (August 2009)										
Surface water	3	12	11	Appendix G: Intensive-Aug-08	YSI Sonde	Appendix G: CTD-Representative Bays-Aug-08; CTD-SI-BNC-Aug-08	–	–		
Bottom water	6	–	–	Appendix G: Intensive-Aug-08	YSI Sonde	Appendix G: CTD-Representative Bays-Aug-08; CTD-SI-BNC-Aug-08	–	–		
Total number of discrete samples		45	44							

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Appendix A: Tables Describing Water and Sediment Sampling Stations and Fequency of Sampling for the Watershed Sources and Methylation and Bioaccumulation Projects, Sinclair Inlet, Washington

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix B: Quality Assurance and Assessment of Data Collected for Watershed Source Project

By K.L. Scholting, T.G. Sabin, J.M. Ogorek, C.D. Thompson, J.R. Dobbs, and K.A. Krogslund

Filtered Mercury

The USGS NWQL analyzed THg from (1) dry dock samples from December 2007 to February 2008, (2) groundwater samples from 11 wells in January 2008, (3) groundwater from well OUBT-722 in May and June during the tidal study, and (4) stormwater samples from PSNS 015-2253 in December 2009 and March 2010. As part of a QA assessment, the concentrations of total mercury in filtered water (20 ng/L) and the solids (0.53 mg/kg) obtained from the cavity of well OUBT-722 were measured and showed that the previously high concentrations of mercury in groundwater from well OUBT-722 were not a result of ground-level contamination through the well cavity. The WMRL analyzed dry dock, groundwater samples after March 2008, five stormwater samples other than PSNS015, and all samples from streams and wastewater treatment plants. In addition, interlaboratory comparison exercises were conducted for three OUBT-722 well samples and composite samples for two PSNS 015-2253 ebbing tidal study.

For the 6 months in 2008 during which samples from this project were analyzed at the NWQL, 171 instrument blanks were performed with a median value of –0.017 ng/L and an RPDev of 0.98 ng/L (appendix B–Laboratory Blanks). Prior to sampling in 2007, WAWSC Purelab® laboratory water used for rinsing equipment did not contain detectable total mercury concentrations (10 ng/L), as measured by the NWQL. Between December 2007 and June 2008, when WAWSC Purelab® was used for rinsing field equipment for the Watershed Sources project, FTHg in WAWSC Purelab® laboratory water was less than 0.04 ng/L (appendix B–Mercury Field Blanks). From March 2008 through January 2009 during which the WMRL analyzed samples for FTHg, the FTHg concentrations in two field blanks collected in March and April 2008 by using pretested water obtained from the WMRL were 0.08 and 0.09 ng/L. The concentrations of two field blank water samples collected during the June tidal study were 0.11 and 0.28 ng/L, while the one field blank sample collected during the July 2008 stream sampling was 0.33 ng/L (appendix B–Mercury Field Blanks).

The median percent recoveries of FTHg of CCVs, third party controls, and SRS analyzed by the NWQL ranged between 94.6 and 104.8 percent for concentrations ranging from 14 to about 100 ng/L (appendix B–Laboratory Standards). The median percent recoveries of 1 ng/L (n = 6), 2.5 ng/L (n =14), and 5 ng/L (n = 6) matrix spike samples analyzed by the WMRL were 100.5, 100.3, and 98.9, respectively. The recoveries of 50 measurements of a 5.0 ng/L CRM standard by the WMRL ranged between 4.77 and 5.48 ng/L with a median recovery of 100.0 percent.

The recoveries of one blind SRS submitted from WAWSC and analyzed by each of the laboratories was within the deviation of the most probable value (MPV) (appendix B–Mercury SRMs). In an interlaboratory comparison exercise between the NWQL and the WMRL during the June tidal study, the relative percentage difference (RPD) of three samples ranged between 0.7 and 2.9 percent for samples ranging in mean concentration from 103.5 to 2,070 ng/L (appendix B–Interlaboratory Comparison). The RPD of FTHg analysis from the composite bottle collected on March 31, 2010, performed by the NWQL and WMRL was 16.2 percent. The analyses of FTHg filtered from the same bottle of composited grab samples collected from PSNS015 on December 29, 2009, showed a considerable discrepancy between the results of the NWQL (<10 ng/L) and the results of the WMRL (34.9 ng/L). Except for the concentrations of PTHg and TSS collected from the same composite bottle, all FTHg results from the December 29, 2009, exercise are disregarded because of this discrepancy in FTHg results and the effects of rain and decreasing salinity on the interpretation of the data.

The RPD of six field duplicates from well OUBT-722 during the January–February 2008 groundwater sampling and the tidal studies of May and June, 2008, analyzed by the NWQL ranged between 4.2 and 65 percent (appendix B–FTHg Field RPD). This sample with the 65 RPD was taken during a time when the FTHg concentration decreased by a factor of 2 within 1 hour. The median RPD of the other five duplicates was 8.2 percent. The reporting level of the NWQL was not sufficient to measure FTHg in the dry dock samples and most of the wells sampled in January 2008 were qualified, but the quality of the FTHg analyses of samples from well OUBT-722 by the NWQL was good.

Duplicate laboratory analyses of FTHg in all samples are performed by the WMRL and results with RPD greater than 10 percent are flagged as estimated. The median RPD for analysis of 12 field duplicate samples of groundwater, steam plant, and wastewater treatment plant effluent water by the WMRL was 12.6 percent. The maximum RPD of 51 percent was measured for a field duplicate at an average

FTHg concentration of 0.46 ng/L collected from Anderson Creek in July 2008. Because the field blank value measured during the July stream sample was comparable to the FTHg concentrations of the five stream samples and because of the high RPD for the one pair of field duplicate samples, the FTHg concentrations for the five streams collected in July are qualified as estimated.

In addition, the RPDs of six field duplicate samples from the piezometers (T-1to T-4) with average FTHg concentrations ranging between 0.38 and 2.24 ng/L ranged between 8 and 18 percent. Ten FTHg concentrations (appendix E–June Piezometers) were flagged as estimated because they were less than twice the highest field filtering blank of 0.28 ng/L (appendix B–Mercury Field Blanks). One of the two replicate samples with the lowest RPD (8 percent) was associated with the duplicate pair with the lowest average FTHg concentration (0.38 ng/L) (appendix B–FTHg field RPD). Although one field filtering blank for the tidal study was higher than desired (0.28 ng/L) (appendix B–Mercury Field Blanks), the quality of the FTHg concentrations of samples from the dry docks, steam plant, wells, piezometers, wastewater treatment plants, and the stream in May that were analyzed by the WMRL was deemed adequate.

Particulate Total Mercury

The WMRL analyzed all particulate samples on quartz fiber filters for particulate total mercury. The daily detection limits of mass were calculated as three times the standard deviation (SD) of the mass of THg measured from seven unused filters. The detection limit of each sample (ng/L) was calculated by dividing the daily detection limit (ng) by the volume of sample filtered (L). The mean determination of daily detection limits (n = 3) was 0.030 ng, with a maximum of 0.157 ng. No field blanks for PTHg were collected for the Watershed Sources Project.

Laboratory QA for PTHg includes 17 MS samples with a spike concentration ranging from 7.2 to 10.2 ng/L with median recovery of 94.3 percent. Twenty analyses of SRM IAEA-433 (International Atomic Energy Agency, Vienna, Austria) ranged from 135.8 to 273.5 ng/g (certified value of 168 ng/g) with a median recovery of 91.9 percent (appendix B–Laboratory Standards).

Aliquots of varying masses of the SRM IAEA-405 (certified concentration of 810 mg/kg) were loaded onto three filters and two aliquots of the CRM PACS-3 (National Research Council of Canada, Ottawa, Canada) (certified concentration of 3.04 mg/kg) was loaded onto filters. Each aliquot was weighed on a polycarbonate filter and transferred to the PFA filtering tower containing a QFF filter overlain with laboratory water (appendix B–Mercury SRMs). The water was then filtered and the tower rinsed down with source water before the filter containing the wet SRM was removed to a PFA petri dish. After the transfer of the four aliquots, a small amount of dust was observed on the white tissue under the filtering flask used with the filtering tower suggesting that not all the weighed SRM was transferred to the tower, possibly due to the static repulsion of the filtering tower. The samples were shipped to the WMRL as environmental samples with fictional reported volumes. The recovery of the SRM IAEA-405 ranged between 81.3 and 111.2 percent, whereas the recovery of the two CRM PACS-2 aliquots were 65.6 and 74.5 percent. Because it is not known whether the low recoveries were caused by the loss of mass during the transfer to the filtering tower or in the laboratory, or incomplete dissolution of the sample, this procedure was discontinued.

The RPD of field duplicate samples of the effluent from the steam plant ranged from 3.7 to 8.8 percent in which average PTHg concentrations were about 24 and 33 ng/L (appendix B–PTHg RPD). The RPD of PTHg concentrations for two sets of stream field duplicates collected in May and July 2008 with concentrations less than 1 ng/L was 28 percent. The RPD of West Sound WWTP field duplicate samples, which had an average PTHg concentration of 10 ng/L, was 46 percent.

Particulate total mercury and TSS were only measured in groundwater wells to provide a calculated measure of total mercury in unfiltered groundwater that could be compared to a direct measurement of total mercury in unfiltered groundwater for regulatory purposes and was not used in calculations of mercury flux to Sinclair Inlet. For groundwater samples from well OUBT-722 with the highest average PTHg concentration of 57 ng/L, the RPD for analyses of field duplicates was 1.8 percent. The higher RPD between field replicates of stream and wastewater particulate total mercury in comparison to BNC sources probably was a result of lower concentrations and more variable TSS concentrations.

Filtered Methylmercury

The concentration of FMHg in the field blank water was less than the reporting level of 0.04 ng/L (appendix B–Mercury Field Blanks). Duplicate laboratory analyses of FMHg in all samples are performed by the WMRL, and results with RPD greater than 10 percent are flagged as estimated. Two of the four pairs of field duplicate samples were less than or near the reporting level of 0.04 ng/L (appendix B–FMHg Field RPD). The RPD of field duplicates with an average concentration within a factor of 3 (0.085 ng/L) of the reporting level was 35 percent. The concentrations of duplicate samples of a wastewater treatment plant effluent were identical (0.15 ng/L) within the level of significant figures reported. Although high RPD were observed at concentrations near the reporting level, the quality of data is sufficient to rank the sources of methylmercury in waters discharging to Sinclair Inlet.

Total Suspended Solids

Quality control measures included laboratory replication (duplicate measurements from the same bottle) and field replication (duplicate measurements from water collected in two bottles from the field). The median RPD of six surface water laboratory duplicate samples taken for the same bottle was 7.8 percent and ranged between 0.7 percent measured in a steam plant effluent and 26.3 percent measured in a wastewater effluent (appendix B–TSS RPD). The RPD of three surface water field duplicates ranged between 8.9 and 13.4 percent. The RPD of surface water duplicates was acceptable given the likely variability in the TSS of permitted sources.

The RPD of laboratory and field replicates for groundwater was generally higher than surface water samples with a maximum of 89.2 percent for duplicate measurement of well OUBT-722 water in February 2008. The RPD of two dry dock samples were 15.5 and 19.1 percent. Although the RPD of TSS values was high, particulate material in the groundwater wells is not considered in the project's calculations of mercury transport to Sinclair Inlet. Particulate total mercury and TSS were only measured to provide a measure of total mercury in unfiltered groundwater that could be compared to direct measurement of total mercury in unfiltered groundwater for regulatory purposes.

Metals and Major Ions

As part of the methylmercury survey and the tidal studies, DOC and a number of redox-sensitive species, nutrients in filtered and unfiltered water, and C and N of solids were determined primarily by the NWQL. The laboratory quality control measures of these ancillary parameters included laboratory blanks and standards. Field quality assurance included one field equipment blank and one field duplicate sample for both a groundwater and a stream sample. Major ions were measured in nonsaline that included streams, wastewater effluents, and stormwater. The groundwater and dry dock samples were saline, and the discussion of the quality of nutrient analysis in marine water will be addressed in the section Methylation and Bioaccumulation.

The median laboratory blank for total iron and manganese for the duration of the project was 0.322 and 0.031 µg/L, respectively (appendix B–Laboratory Blanks). The mean concentrations of instrument blanks and blind blanks for nitrate and ammonia were less than 0.001 mg/L as N, and the mean concentration for the orthophosphate was 0.002 mg/L as phosphorous (P). For TPCN, 51 instrument blanks were performed with a median value of 0.007 and 0.003 mg/L for total carbon and nitrogen, respectively. Except for a small concentration of silica in the groundwater sample, all parameters measured in the field blank water were less than or just slightly greater than the reporting level (appendix B–Ancillary Field Blanks).

The median recovery of total iron in CCV standard at a concentration of 500 µg/L was 99 percent, whereas the median recovery of total manganese in a 250 µg/L CCV standard was 101.0 (appendix B–Laboratory Standard). The median recovery of DOC from four ranges of CCV (4–33.9 mg/L), from a TPC (5 mg/L) and blind SRS (ranging in concentrations from 1.5 to 12.7 mg/L), ranged between 93.9 and 103.1 percent, with the maximum RSD of the recovery being 6.2 percent. The median recovery for orthophosphate, nitrite, and CCV standards for ammonia were 103.0, 100.0, and 98.0 percent, well within control limits. The median recovery for the third party controls (TPC) were best for the highest concentration range, but even the lowest concentration range had acceptable recoveries of 98.9, 102.3, and 91.3 percent, for orthophosphate, nitrite, and ammonia, respectively. A low level (<1 mg/L) blind SRS and TPC for unfiltered total nitrogen deviated the most from their true values with RSDs of 9.2 and 3.9, respectively. The remaining QA nutrient standards all had recoveries of 100 ± 10 percent. The median recovery of a TPCN CCV standard (70 mg/L as C and 10 mg/L as N) was 100.0 percent.

The RPD of groundwater duplicate analyses of total Fe and Mn, dissolved nutrients, and TCPN taken at well OUBT-724 (appendix B–Ancillary Field RPD) generally fell within the acceptable range of less than 10 percent or were less than the reporting level, except for ammonia at 23.9 percent and nitrate plus nitrite at 30.2 percent. The high variability in the ammonia and the nitrate plus nitrite probably reflects the nature of the groundwater, which has both sea water and freshwater components because it is adjacent to the intertidal zone of Sinclair Inlet. The RPDs of duplicate analyses of a stream sample (Anderson Creek on July 15, 2008) of all parameters were less than 10 percent or were less than the reporting level, except for an RPD of 26.2 percent for chloride.

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix C. Quality Assurance and Assessment for Marine Sediment Collected for the Methylation and Bioaccumulation Project

By Carter, B., Sabin, T.G., Ogorek, J.M., Thompson, C.D., Agee, J.L., Sheibley, R.W., and Krogslund, K.A.

Physical Properties

Duplicate measurements (dry weight, loss on ignition, bulk density, porosity) on composite sediment of the top 2 cm of sediment from every station collected during February and August 2009 and about 15 percent of the samples collected during August 2008 and June 2009 (56 total duplicate samples in appendix C–Physical Characteristics) were conducted for the percentage of dry solids, loss on ignition, bulk density, and porosity. The median relative percentage deviations (RPDev defined as 100* error/mean) of porosity were 0.3, 1.2, 0.3 percent and identical values down to the reporting level, respectively, while the maximum RPDev were 7.0, 20.0, 6.4, and 10.6 percent, respectively. Duplicate samples of total fines were measured in about 15 percent of the composited sediment samples throughout the project (29 total duplicate samples, appendix C–Total Fines) with a median RPDev of 1.3 percent and a maximum RPDev of 7.7 percent.

Total Mercury

Duplicate measurements of STHg concentrations in about 10 percent of the composited samples from two box cores at each station were performed by NRP (appendix C–STHg Intralaboratory). In August 2008, STHg was measured by the WMRL in laboratory duplicates taken from each of two separate box cores at BNC-39 and two separate box cores at BNC-71, which also allowed measurement of variability both within box cores (laboratory replication of dependent samples) and between box cores (field replication of independent samples) at both stations. In June and August 2009, field replicates of STHg were measured at every station by WMRL.

Wisconsin Mercury Research Laboratory

Laboratory quality assurance for STHg by the WRML included analyses of two SRMs, recovery of matrix spikes, and triplicate laboratory analyses of field samples. The median recoveries of IAEA-405, IAEA-433, and the matrix spikes were 97.1, 84.8, and 98.5 percent, respectively (appendix C–Laboratory Standards). The median RPDev of 10 laboratory triplicate analyses was 3.1 percent, with the maximum RPDev of 17.4 percent for the June 2009 sample from BNC-19 (appendix C–STHg Intralaboratory).

WMRL analyzed field replicate aliquots collected directly from the same box core four times in August 2008, which resulted in RPDs ranging between 1.9 and 6.4 percent. The RPD of two samples collected in August 2008 from different box cores and analyzed by WMRL ranged from 5.2 to 8.0 percent. In June and August 2009 at every station, WMRL analyzed samples from two box cores. The median RPD for these field replicates analyzed by WMRL was 10.4 percent, with a range from 0.4 to 118.6 percent. The station with the highest RPD (BNC-61) was located in the area in which the U.S. Navy LTMP also measured high variability (Paulson and others, 2009).

National Research Program

Each analytical batch of sediment samples analyzed for STHg by the NRP was accompanied by the analyses of the following minimum of QA samples: (a) one method blank, (b) one certified reference material, (c) one matrix spike sample, and (d) one analytical duplicate. Calibration standards were prepared from an NIST-certified commercially obtained mercuric chloride standard. The average (± standard error) recovery of the certified reference material (IAEA 405, estuarine sediment, THg certified value = 0.81 µg/g was 93 ± 2 percent, n = 8 in appendix C–Laboratory Standards). The average matrix spike recovery was 95 ± 3 percent (n = 9). The NRP analyzed duplicate aliquots of sediment composited from the two mason jars between August 2008 and 2009, and the RPD for laboratory duplicates ranged from 0.2 to 34.0 percent with a median RPD of 3.0 percent in appendix C–STHg Intralaboratory).

Interlaboratory Comparison

In August 2008, NRP, WMRL, and WAWSC staff collected sediment from all nine stations. Sediment was initially field chilled and subsequently (within 12 hrs) homogenized, subsampled, and frozen. Both NRP and WMRL laboratories assayed sample splits from different box cores for THg. In the assessment of the interlaboratory comparison, the station average concentration from the individual duplicate sample for each station (appendix C–STHg Interlaboratory) was then compared to the one STHg concentration taken from an aliquot of the NRP composited sample. The relative

percentage difference for the interlaboratory comparison is defined as the percentage difference of the NRP value relative to the WMRL value (appendix C–STHg-Interlaboratory). Negative relative percent difference values indicate NRP value was lower than the WRML and positive relative percent difference values indicate that NRP values were higher than the WMRL average concentrations. For the August 2008 sample set (n = 9), the median relative percent difference of THg was –45.4 percent and ranged from –79.5 to +9.3 percent. This range of interlaboratory variation is not surprising given (a) the small sample size (n = 9) for August 2008 interlaboratory comparison, (b) the variability in field replicates for the 2009 data set assayed by the WMRL for sediment THg (RPD range = 0.4 to 118.6 percent, n = 40, appendix C–STHg Intralaboratory), (c) the variability between laboratory duplicates from homogenized sediment by NRP (RPD range = 0.2–34 percent, n = 8), and (d) the small masses of material used for the THg assay (for example, 0.2–1.0 g) relative to the mass of material collected (for example, about 20 g).

During June and August 2009, WAWSC staff collected paired interlaboratory samples for NRP and WMRL laboratories from each of duplicate box cores. The two samples for WMRL were field frozen and analyzed separately, whereas the samples for NRP were initially chilled, shipped to the NRP laboratory, homogenized into one composite, subsampled (1–7 days after field collection), and then refrozen. Over the 2009 dataset, the median relative percent difference was –11.8 percent (appendix C–STHg Interlaboratory), much closer to a value of zero indicating no interlaboratory basis. The relative percent difference ranged from –65.1 to +44.1 percent (n = 40). Six of the seven pairs with an relative percent difference greater than 25 percent were collected from the BNC, and the station (BNC-61) with the two highest absolute values of relative percent difference (–65.0 and –56.0) was located in the area in which the U.S. Navy LTMP also measured high variability (Paulson and others, 2009). Thus, the observed level of interlaboratory variability likely reflects the combined effects of (a) the small sample mass for the analysis, (b) the natural variability in the THg content of sediment subsamples that may have not completely homogenized, and (c) minor differences in laboratory procedures, such as assaying whole wet sediment (NRP) versus freeze-dried sediment (WMRL).

Reactive Mercury

Reactive mercury ($Hg(II)_R$) was measured in the composited samples from two box cores from about 25 percent of the stations by NRP (appendix C–Reactive Mercury). The median RPDev of assays of $Hg(II)_R$ concentrations in duplicate aliquots of 18 composited samples was 7.7 percent, with the RPDev ranging from the reporting level of 0.1 nanogram per gram dry weight (ng/gdw) to 21.4 ng/gdw.

Methylmercury in Sediment

Duplicate measurements of SMHg concentrations in about 15 percent of the composited samples from two box cores at each station were performed by NRP (appendix C–SMHg Intralaboratory). In August 2008, SMHg was measured by the WMRL in laboratory duplicates taken from a single box core from four separate box cores at BNC-39 and BNC-71, which also allowed measurement of field replication. In June and August 2009, field replicates of SMHg were measured at every station by WMRL.

Wisconsin Mercury Research Laboratory

Laboratory quality assurance for SMHg by the WRML included analyses of four standards ranging in concentration from 0.12 ng/g (SRM IAEA-433) to an average value of about 14.9 ng/g (LCS QC1238, Resource Technology Corporation, Laramie, Wyo.; appendix C–Laboratory Standards). For the three standards with an SMHg concentration greater than 0.5 ng/g, the median recovery ranged from 100.8 to 106.1 percent. In contrast, the median recovery of the SRM IAEA-433 was 72.5 percent. The median RPDev for five triplicate analyses of subsamples from a single box core was 23.9 percent, and ranged from 9.0 to 54.8 percent (BNC-71 PW; appendix C– SMHg Intralaboratory).

The RPD of four duplicate aliquots from the same box core were analyzed in 2008 and ranged from identical values to the level of reporting to 25.3 percent. The RPD of average values from two different box cores were 4.9 and 22.4 percent. The median RPD of the 40 duplicate samples collected in 2009 was 33.7 percent and the range spanned from identical values to the reporting level of reporting to 140 percent.

National Research Program

Each batch of analytical samples was accompanied with analysis of the minimum following QA samples: (a) one method blank, (b) one certified reference material sample, (c) one matrix spike sample, and (d) one analytical duplicate. Calibration standards were prepared from a crystalline methylmercury chloride and compared to a separate, commercially available MHg standard solution. The average (± standard error) recovery of the certified reference material (IAEA 405, estuarine sediment, MHg certified value = 5.49 ng/g) was 102 ± 3 percent (n = 12) (appendix C–Laboratory Standards). The average matrix spike recovery was 84 ± 3 percent (n = 23). The average RPD for duplicate spike analyses was 4.7 ± 1.3 percent (n = 13). The median RPD of 12 laboratory duplicates was 7.8 percent and ranged from identical values to the level of reporting to 19.4 percent (appendix C–SMHg Intralaboratory).

Interlaboratory Comparison

In August 2008, NRP and WMRL staff collected sediment for different box cores from all nine stations. Sediment was initially field chilled for up to 12 hours. Each laboratory assayed sample splits for SMHg (appendix C–SMHg Interlaboratory). The WMRL then froze the aliquot from the box core in plastic bags. The contents of the two jars for the NRP were homogenized, subsampled, and frozen. During June and August 2009, WAWSC staff collected paired interlaboratory samples for NRP and WMRL laboratories from each of duplicate box cores. The two samples in plastic bags for WMRL were frozen in the field and analyzed separately while the samples for NRP were initially chilled, shipped to the NRP laboratory, homogenized into one composite, subsampled (1–7 days after field collection), and then refrozen.

For the August 2008 sample set, the median relative percent difference of SMHg analysis was –19.3 and ranged from the NRP laboratory value being 40.8 percent less than the WMRL value to 63 percent greater than the WMRL value. Over the 2009 dataset, the SMHg analysis of the NRP laboratory ranged from 4.4 percent less than and 760 percent greater than the result of the WMRL (median of 63.2 percent, n = 40), with the relative percent difference of 10 pairs greater than 100 percent. This range of interlaboratory variation is not surprising given (a) the small sample size (n = 9) for August 2009 interlaboratory comparison, (b) the variability in field duplicates (n = 2 from different box cores) for the complete dataset assayed by the WMRL for SMHg (RPD range = 0–140 percent, median = 33.7 percent, n = 40) (appendix C–SMHg Intralaboratory), and (c) the small masses of material used for the SMHg assay (for example, 0.2–0.6 g) relative to the mass of material collected. Thus, the observed level of interlaboratory variability likely reflects the combined effects of the natural variability in SMHg content of the subsamples that were used for this intercomparison, and the fact that the samples were either not completely homogenized or were not from the same box core.

The difference also could potentially reflect differences in field and laboratory procedures. In 2009, the SMHg samples for WMRL were field frozen, while the NRP samples where chilled, shipped, subsampled 1–7 days later, and then frozen. The WMRL assayed sediment for SMHg by using dichloromethane extraction, back-extraction into water, and finally ethylation, GC-separation, and ICP-MS detection with mercury isotope dilution. In contrast, the NRP laboratory used a KOH/methanol extraction with subsequent quantification by ethylation, GC-separation, and CVAFS detection. The latter approach may be affected from inhibition of the ethylation step in high sulfide sediments. Post-assay data analysis indicated a strong negative relationship (least squares regression $R^2 = 0.83$) between the absolute difference in SMHg concentration measured by the two laboratories (NRP - WMRL) and the concentration of acid volatile sulfur (AVS) (data not shown) for the August 2009 dataset. This suggests that in sediment samples with high AVS concentrations, the NRP laboratory underestimated the actual SMHg concentration by as much as 30 percent.

Methylmercury Production Potential

Quality assurance included(a) killed controls (as described above), (b) analytical duplicates, (c) the use of internal standards ($Me^{199}Hg$, as described above), and (d) calibration standards. Methylation rate constants of ^{200}Hg were measured for duplicate aliquots of composited sediment at a reporting level of 0.5×10^{-3}/d. The median RPDev of duplicate measurements of methylation rate constants of ^{200}Hg was 28.5 percent and RPDev ranged from 0.7 to 85.0 percent (appendix C–Methylation Rate Constants).

Sulfur Species

Quality assurance included the following: (a) method blanks that determine the reporting level, (b) matrix spikes, and (c) laboratory replication of the analyses of duplicate composited samples. There is no certified reference material for either the AVS or total reduced sulfur (TRS) in sediment. The average matrix spike recovery was 78 ± 12 percent (n = 3) and 100 ± 3 percent (n = 10) for AVS and TRS, respectively (appendix C–Laboratory Standards). Acid volatile sulfur was measured only in August 2009, and the RPDev of the duplicate measurements of sediment from one of the nine stations was 5.3 percent (appendix C–Reduced Sulfur). TRS was measured during four seasonal sediment collections in 2009 and 2010, and TRS was measured in duplicate samples in about 15 percent of composited samples. The RPDev of total reduced sulfur in duplicate aliquots of composited samples ranged from 0.6 to 12.3 percent, with a median RPDev of 5.8 percent.

Iron Species

Ferrous iron, amorphous ferric iron, and crystalline ferric iron were analyzed in replicate samples in about 15, 10, and 10 percent, respectively, of composited samples from two box cores at each station (appendix C–Iron Species). The median RPDev of duplicate analyses were 1.1, 0.8, and 8.3, respectively.

Organic Carbon

Although loss on ignition measurements were conducted on all sediment samples, STHg in sediment in Sinclair Inlet are highly correlated with organic carbon measured by direct elemental analysis (Paulson and others, 2009). Centrifuged sediments collected from two separate box cores at six stations each in February, June, and August 2009 were analyzed for organic carbon. The RPD of organic carbon results ranged from identical to the reporting precision levels of 0.1 weight percent carbon to 5.5 percent with a median RPD of 4.0 percent (appendix C–Organic Carbon in Sediments).

Porewater

Compositing of filtered blank water poured into a 50-mL, Oak Ridge-type, FP centrifuge tube at each station for analysis of FTHg and FMHg was performed in August 2008, June 2009, and August 2009 (appendix C–Porewater Blanks). Two of the FMHg concentrations in the porewater filtering blanks were less than the reporting level of 0.04 ng/L, while the third was 0.05 ng/L. Although the porewater filtering blanks for FTHg in June and August 2009 were 0.41 and 0.18 ng/L, respectively, the porewater filtering blank processed in August 2008 was 1.44 ng/L. This larger FTHg in August 2008 probably was a result of a difference in processing of the blank water that overestimated the blank contribution. Before the filter/tower combination was used for porewater sampling in August 2008, the blank water from each station was passed through the new QFF filter and tower in the field and then composited into a single 500-mL bottle. Thus, the filtered composite water processed in August 2008 was exposed to nine QFF/tower combinations instead of the one QFF/tower combination to which a normal sample would be exposed. In contrast, a single QFF and filtering tower was dedicated to processing porewater blank water in the laboratory in June and August 2009. Dividing the August 2008 porewater filtering blank (1.44 ng/L) by the 9 (number of filter/tower combinations) yields 0.16 ng/L per filter/tower combination, which is similar to the 0.18 for August 2009. Another possible reason for the high FTHg concentration of the filtering blank is that the porewater was processed onshore in a portable laminar flow hood in August 2008 as opposed to the laboratory laminar flow hood in June and August 2009. In addition, some of the 50-mL, Oak Ridge-type, FP centrifuge tubes used at the end of the August 2008 collection were cleaned in cold acid while the centrifuge tubes used in February, June, and August 2009 were hot acid cleaned at the WMRL. Correcting the August 2008 procedure for overestimating contamination for a single sample by using multiple filters and towers in producing the blank water, an average per filter/tower porewater filtering blank of 0.35 ng/L was calculated with an RSD of 0.11 ng/L. This resulted in a reporting level or MDL of 0.59 ng/L, which was less than twice the higher per filter/tower porewater filtering blank of 0.41 in June 2009 (appendix C–Porewater Blanks). All porewater FTHg concentrations were greater than 0.82 ng/L.

One field duplicate set of porewater samples for analysis of FTHg, FMHg, and DOC was performed at station BNC-39 by compositing porewater from two different sets of 15 centrifuge tubs (appendix C–Porewater Metal Replicates). The RPD for the field composited duplicates was 28.9, 2.2, and 8.9 percent, respectively. Field replicates of redox cores were taken at 25 of the 27 stations visited. Sulfide concentrations were measured in two porewater samples from redox cores at the same dilution and five samples at different dilutions (appendix C–Porewater Sulfide). Nutrient analyses of filtered supernatant from replicate redox cores were performed for 31 of the 52 porewater sampling events (appendix C–Porewater Nutrient Replicates). Analyses of two laboratory duplicates of diluted total Fe and Mn in filtered supernatant were analyzed in August 2008 (appendix C–Porewater Metal Replicates).

Incubation and Tumbling-Core Experiments

Quality control procedures included running triplicate core incubation experiments for 17 of the 18 stations sampled in 2009 with samples collected on 3 consecutive days for each core experiment. During the August 2008 pilot study, incubation cores were sampled on two consecutive days from single cores from four of the nine stations. In 2009, the filtered seawater used as replacement water for the incubation cores from each station was analyzed for FTHg and FMHg concentrations at the end of the experiment to test for methylation in the unacidified chilled seawater held in PETG bottles.

To test for contamination of THg and FMHg from the core liner or cap assembly, seven control incubation experiments with Purelab® water held in core incubation assemblies were conducted in August 2008, and April, July, and August 2009 (appendix C–Incubation Blanks). After 2 days in August 2008, the FTHg concentrations of Purelab® water left in the incubation core was 0.71 ng/L. In 2009, the largest increase in FTHg of Purelab® water left in stirred cores was 0.29 ng/L (July 24–27, 2009). Two tumbling-core control experiments in the PFA beakers were conducted in May 2010 and showed an average FTHg increase of 0.04 ng/L over the 0.22 ng/L in Purelab® water. Only two of the nine samples taken from the incubation control experiments had FMHg concentrations greater than 0.1 ng/L.

Eight FTHg samples analyzed on September 29, 2009, from the June 2009 incubation experiments were rejected by the WMRL because the concentration values

could not be verified because the sample volumes for these nonstandard-volume samples could not be recovered at the time of the laboratory verification. The project accepted the original values because (1) three incubation samples from BNC-60 Core A with high FTHg concentrations (16.8–20.3-ng/L; appendix I–BNC-60-INC-Jun-09) were verified by high FMHg concentrations (16–18 ng/L) derived from a procedure that was completely independent of the lost sample volume for FTHg, (2) the FTHg in the overlying water of BNC-71 Core A on day 0 (appendix I–BNC-71-INC-Jun-09) was consistent with the FTHg concentrations of BNC-71 Cores B and C on day 0, (3) the FTHg concentrations for the other four samples from random cores (BNC-60, BNC-39, and SI-PO) were consistent with the results of the other samples from the individual core, as well as other cores from the same station, and (4) all FTHg concentrations were greater than the corresponding FMHg concentration. A limited number of FTHg and FMHg concentrations measured during the February and June incubation core experiments were rejected and are shown in appendix C–Incubation Rejections.

Data are available for download at http://pubs.usgs/gov/ds/658/

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Appendix D. Quality Assurance and Assessment for Marine Water Column Samples Collected for the Methylation and Bioaccumulation Project

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Filtered Total Mercury and Methylmercury

Concentrations of FTHg in Purelab® water used for cleaning acrylic and polycarbonate equipment were near or less than the reporting level (appendix D–Mercury Field Blanks). Field contamination was evaluated by pumping pretested blank water samples through near-surface and near-bottom sampling ports, FP tubing, C-Flex tubing into a PETG bottle and then filtering the water in a Savillex filter tower in a laminar flow hood in the field (August 2008) or in the WAWSC laboratory (September 2008–August 2009). The concentration of FTHg in filtered field blank water ranged from 0.05 to 0.13 ng/L, with a median of 0.08 ng/L. All concentrations of FMHg in filtered field blank water were less than the reporting level of 0.04 ng/L. Laboratory notes taken during laboratory filtering of the four surfaces samples collected in November 2008 indicated that several protocols were not followed and included (1) raw water samples in PTEG bottles were not bagged in the refrigerator prior to filtering, (2) the PFA towers on the filtering assembly were acid cleaned, but not with hot acid, and (3) an alternative stopcock on the filtering desiccator was used. Because any one of these actions could facilitate secondary contamination of FTHg, the FTHg concentrations for November 2008 were rejected.

The median RPD for FTHg concentrations in four field replicates in near-surface marine water was 14.5 percent and the RPD ranged from identical values of 0.43 ng/L to 23.5 percent for a sample with an average concentration of 0.51 ng/L (appendix D–Mercury Field Replicates). The RPDs of FTHg in two near-bottom marine water replicates were 16.5 and 69 percent. FMHg concentrations in two of the five field replicates were at or less than the reporting level of 0.04 ng/L. The RPD of FMHg in field replicates for one bottom-water and two surface-water samples ranged from 42.4 to 113 percent.

Particulate Total Mercury and Methylmercury

All concentrations of PTHg and PMHg in field blanks were less than the reporting level, which varied with the volume of water filtered (appendix D–Mercury Field Blanks). The RPD of two field replicates of PTHg in surface water in June and August 2009 were 6.9 and 25.3 percent (appendix D–Mercury Field Replicates). Because samples for PTHg and TSS analysis were taken from the same bottle, the concentration of THg on the suspended solids (ng/mg or mg/kg) can be calculated by dividing PTHg (ng/L) by TSS (mg/L) without bias of temporal changes in the field. The RPD of the calculations of concentration of total mercury on the suspended solids from replicate bottles for these two sites was 11.9 percent for BNC-39-SURF in June 2009 and 12.4 percent for BNC-52-SURF in August 2009. However, the RPD of laboratory replicates of TSS from the same bottles of BNC-52-SURF water in August 2009 (range of 16.3–85.7 percent in appendix D–TSS Replicates) during an algal bloom suggests that uncertainty in calculation of THg concentrations on the suspended solids may be controlled by the TSS measurement. The RPD of field replicates of PTHg collected in August and September 2008 ranged from 24.4 to 86 percent (appendix D–Mercury Field Replicates). BecauseTSS samples were collected in bottles separate from the PTHg bottles, the effect of TSS variation within bottles could not be evaluated in August and October 2008. The variability of FTHg in bottom water is higher than that of the surface water. When FMHg is detected, the variability of FMHg is high both near the bottom and in surface water collected during the zooplankton tows. The variability of PTHg is high (up to a RPD of 86 percent), but calculations of the concentrations of total mercury on the suspended solids suggest that variability is due more to the variability in TSS concentrations than on the amount of PTHg content of the suspended solids.

MHg concentrations of solids are not affected by field contamination (appendix D–Mercury Field Blanks). Duplicates of PMHg were performed at most stations (appendices G–J) and the assessment of field variability is beyond the scope of this report. Most PMHg samples were analyzed between August 27, 2008, and November 20, 2009, during which the median recovery for SRM IAEA-405 (5.04 ng/g) was 103.8 percent (range: 78.6–122.2 percent) (appendix D–Laboratory Standards). Two samples from BNC-71 collected in August 2009 were analyzed in 2010 with the much lower SMHg concentration SRM IAEA-433 standard (MPV of 0.17 ng/g) because of new stocks of SRM IAEA-405 from IAEA were not available. The recovery of the SRM IAEA-433 for the batch in which the BNC-71 were analyzed averaged 39.6 percent The results of these two samples were qualified.

All samples collected during April 2009 and the 16 replicate field samples collected between May and August 2009 were analyzed on March 25, 2010, along with a liquid laboratory control standard (LCS) that would

not reflect analytical bias that might arise during the solid digestion process. The recovery of the liquid LCS averaged 111.1 percent. In August 2010, WMRL analyzed aliquots from the bottle of SRM IAEA-405 from which WAWSC produced the double blind SRM submission for the Watersheds Project and recovery averaged 113.7 percent (range: 104.8–122.6 percent). Thus, the low recovery of SRM IAEA-433 analyzed in 2010 related to the changing standard.

Because the samples analyzed on March 25, 2010, were not accompanied by a solid SRM, the filters analyzed on March 25, 2010 (Rep 2 in appendix D–Particulate Methylmercury), were compared to the corresponding samples analyzed in 2009 (Rep 1) to assess if analytical bias between the 2009 and 2010 analyses could be detected relative to the considerable sampling variability of the duplicate field samples. The concentrations of PMHg analyzed on March 25, 2010, were significantly higher ($p = 0.005$) than those analyzed in 2009 with median percent difference of +40.8 percent and a range from -40.9 to +146.2 percent. Because some of the variability of PMHg (in ng/L) between sets of duplicate samples analyzed on different days also may be a result of differing TSS concentrations in the replicate sample bottles, especially during bloom condition, the difference in methylmercury concentration of the particles (PMHg/TSS with both measurements coming from the same PETG bottle) also was examined. The median relative difference of methylmercury analyzed on March 25, 2010, relative to the corresponding replicate samples analyzed in 2009 was +16.6 percent, which was not significant ($p = 0.24$) while the range in relative difference ranged from –54.2 to +208.8 percent (appendix D–Particulate Methylmercury). Given these results, the date of analysis does not appear to bias the results for PMHg.

Total Suspended Solids

In 2009, five samples of blank water were pumped through sampling ports, FP tubing, C-Flex tubing, and into a PETG bottle (appendix D–Filtering Blanks). The filled PETG bottle was brought back to the laboratory and the water filtered. The weight variation ranged from –0.02 mg (loss of 0.02 mg) to + 0.01 mg. The average weight was 0.01 mg with 1 SD of 0.01 mg. The reporting level of TSS based on 3 SDs is 0.03 mg, which is the same as the reporting level based on reweighing unused filters. TSS concentrations were measured in replicate laboratory aliquots (n = 2–4) from 70 bottles (appendix D–TSS Replicates), particularly when sampling algal blooms and filters clog after filtering little volume (as few as 100 mL). The median RPD was 13.3 percent and ranged from 0.9 to 103.5 percent. Laboratory replicates for TSS were taken primarily during algal blooms, and five of the 10 results with RPD greater than 40 percent were obtained from samples collected during the algal bloom in July and August 2009.

Nutrients and Particulate Carbon and Nitrogen

Nutrients collected from the marine water column and porewaters were analyzed by the UW Chemical Oceanography Laboratory. Concentrations were reported to 0.1 µg/L (or 0.0001 mg/L). Six filtering blanks using either Millipore® Millex® or Pall® AquaPrep™ filters (appendix D–Filtering Blanks) and 14 matrix spike samples (appendix D–Nutrients TPCN Mn Replicates) were collected. The mean concentrations of filtering blanks for ammonia and nitrite were less than 0.001 mg/L as N, and the mean concentration for orthophosphate was 0.0001 mg/L as P. The filtering blanks for nitrate were consistently about 0.002 mg/L as N, whereas two of the six blanks for silicate were greater than 0.03 mg/L as silicon dioxide (SiO_2) and the remaining four near or less than the detection limit. The reporting level for each constituent (appendix D–Filtering Blanks) was based on the mean concentration plus three times the SD of the six filtering blank results.

The median recovery of orthophosphate, nitrite, and nitrate in 14 seawater samples spiked at concentrations less than 0.06 mg/L were 102.0, 100.0, and 100.0 percent, respectively (appendix D–Laboratory Standards). The median recovery of seawater spiked at orthophosphate concentrations of up to 0.06 mg/L as P and nitrate concentrations up to 0.5 mg/L as N were 100.0 percent. The median recovery of 12 samples of seawater spiked at concentrations of silicate up to 4.5 mg/L as SiO_2 was 99.7 percent, whereas the median recovery of two samples at higher concentration was 100.0

Concentration of TPCN in the four filtering blanks (Purelab® water filtered through the GFF) were less than the respective reporting levels, as was the particulate nitrogen (appendix D–Filtering Blanks). The concentrations of DOC in Purelab® water passed through the GFF ranged from estimated values of 0.3–0.4 mg/L.

Manganese

Total Mn in seawater collected in August 2008 was analyzed by ICP-OES, and QA data are grouped together with the QA data for terrestrial samples taken between May and August 2009. Total Mn in marine water column samples collected in 2009 was analyzed by ICP-MS. The median instrument blank for total Mn in 2009 was 0.005 µg/L, while the median of 32 blind blanks was 0.007 µg/L (appendix D–Laboratory Blanks). The four field filtering Purelab® blanks were significantly diluted along with the analytical run of seawater samples and ranged from an estimated value of 1.5 µg/L to a value less than 4 µg/L (appendix D–Filtering Blanks). The recovery of independent laboratory control samples was 97.0 and 95.0 percent for 25 and 250 µg/L standards, respectively (appendix D–Laboratory Standards).

Chlorophyll

The quality assurance data presented here summarizes replicate chlorophyll values collected during the duration of the project. This summary includes a slight variation in the chlorophyll processing methods. Earlier in the project, larger volumes (100–200 mL) of water was collected in separate bottles and filtered separately to generate unique sample replicates. As significant "patchiness" of phytoplankton abundance was observed during sampling events and was somewhat reflected in the CTD profiles, it was decided that the collection and processing of larger volumes of sample water, in separate bottles, may be contributing to elevated variability. Therefore, a modification was made to filter smaller volumes of water, approximately 40 mLs, from a common sampling container, to generate the replicate samples. This change in methods resulted in two groups of chlorophyll data from a QA perspective; replicates from separate collection bottles and replicates taken from a common collection bottle. The details of the variance of these replicate values are presented in appendix D–Chlorophyll Replicates. Overall, the RSD of the replicate values was fair to good with median and mean RSD of 8.6 and 12.9 percent, respectively, for replicates from separate bottles, and 14.6 and 15.5 percent for median and mean RSD for replicates from the same bottle. However, there was occasionally high variability within a given set of sample replicates; with RSD values as high as 48.9 and 40.4 percent for the separate and common collection bottle groupings, respectively. Two points should be considered regarding this high variability. Although not significant, there was an increased tendency to have elevated variability between replicates as the mean concentration decreased. For example, three of the four field replicate samples with RSDs greater than 40 percent had mean chlorophyll values less than 6 mg/L. Secondly, in a detailed U.S. EPA method review of fluorescence determination for chlorophyll *a* (Arar and Collins, 1997), the RSD of chlorophyll replicate measurement from pure algal culture was never less than 14.6 percent, and was commonly in the 20–30 percent range. Despite this variability, clear differences between seasons and locations are evident and the information is useful as a relative measure of primary production.

Zooplankton

Taxonomy

Quantitative zooplankton samples were checked for accuracy in classification following initial quantification by a senior taxonomist (J. Cordell), who examined all samples for accurate identification of those taxa that were identified to the species level. Only one case of a consistent identification error was discovered; where two larvacean species were counted as one. Samples were reanalyzed by the senior taxonomist to correct this error.

Methylmercury

Quality assurance was evaluated in the zooplankton tissue analysis through the use of five types of reference samples: laboratory blanks (n = 30), laboratory duplicates (n = 10), and matrix spiked samples (n = 19), laboratory control samples, and certified reference materials (n = 60). For a nominal zooplankton sample mass of 0.002 g, the mean laboratory blank was 0.10 ± 0.06 ng/gdw (appendix D–Laboratory Blanks). The daily detection limit for zooplankton tissue was calculated to be 0.28 ng/gdw for the period of these analyses. The median recovery of matrix spikes was 101.3 percent with a median RPD of 11 percent for duplicate matrix spikes (appendix D–Laboratory Standards). The percent recovery of 18 LCS CFWR 4/23/02 ranged from 83.9 to 115 percent. The median percent recoveries for the two CRMs were 101 and 103.8 percent.

Stable Isotopes

Carbon and nitrogen stable isotopes were measured in frozen zooplankton and particulate matter samples by the University of California at Davis Stable Isotope Facility (2011) by following established methods (see section, Methods). Nitrogen isotope samples were standardized against N_2 in air, and carbon isotope samples standardized against Vienna Pee Dee Belemnite (appendix D–Laboratory Standards). Instrument precision for carbon analysis was excellent for both the CRM NIST 1547 (peach leaves and the internal UC Davis LCS G-7 (nylon); which was less than 0.2 ‰ for both (‰ is used to indicate parts per thousand). Performance with the nitrogen standards was more variable, with nitrogen analysis of the peach leaves as excellent, at less than 0.15 ‰, while the internal nylon LCS was more variable at less than 0.7 ‰.

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Appendix E. Data Tables of Total and Particulate Mercury and Selected Constituents for Freshwater Inputs to Sinclair Inlet and Vicinity, Water Sources Project, Sinclair Inlet, Washington

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix F. Data Tables of Methylmercury and Selected Constituents for Freshwater Inputs to Sinclair Inlet and Vicinity, Watershed Sources Project, Sinclair Inlet, Washington

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix G. Data Tables of Total Mercury, Methylmercury, and Selected Constituents in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Summer 2008

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix H. Data Tables of Total Mercury, Methylmercury, and Selected Constituents in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Fall 2008

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix I. Data Tables of Total Mercury and Methylmercury, and Selected Constituents, in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Winter 2008–10

Data are available for download at http://pubs.usgs/gov/ds/658/

Appendix J. Data Tables of Total Mercury, Methylmercury, and Selected Constituents in Marine Sediments and Porewaters of Sinclair Inlet, Methylation and Bioaccumulation Project, Sinclair Inlet, Washington, Spring 2009

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