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and the Bonneville Power Administration

Water-Quality Data, Columbia River Estuary, 2004-05

By Jennifer L. Morace



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Conversion Factors

Multiply	By	To obtain
Length		
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
Flow rate		
cubic meter per second (m ³ /s)	35.31	cubic foot per second (ft ³ /s)
cubic meter per second per square kilometer [(m ³ /s)/km ²]	91.49	cubic foot per second per square mile [(ft ³ /s)/mi ²]

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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) or micrograms per liter (μg/L).

Concentrations of chemical constituents on suspended sediment are given in micrograms per gram (μg/g).

Abbreviations

GC/MS	gas chromatography/mass spectrometry
MDL	method detection limit
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water Quality Assessment
NOAA Fisheries	National Oceanic and Atmospheric Administration (NOAA) National Marine Fisheries Service
NWQL	National Water-Quality Laboratory
OBW	organic blank water
OWSC	Oregon Water Science Center (USGS)
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
QC	quality control
RL	reporting limit
RM	river mile
RPD	relative percent difference
SPMD-	semipermeable-membrane device
STL	Severn Trent Laboratory
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Significant Findings

Water-column samples were collected monthly at the Columbia River at Warrendale (RM 141), Beaver Army Terminal (RM 54), and the Willamette River at Portland (RM 13) to characterize water-quality conditions in the Columbia River Estuary. To further characterize water-quality conditions during low- and high-streamflow conditions, seasonal samplings were performed in August 2004 and April and August 2005. These samplings included suspended-sediment and semipermeable-membrane device (SPMD) extract analyses and an expanded list of analytes, including wastewater compounds, pharmaceuticals, antibiotics, organochlorine compounds, polycyclic aromatic hydrocarbons (PAH), polybrominated diphenyl ethers (PBDE) and polychlorinated biphenyls (PCB). These additional samplings were performed at the three monthly sites as well as the Columbia River at Columbia City (RM 82) and near Point Adams (RM 4). The following significant findings have emerged from these data sets:

- None of the aquatic-life or human-health benchmarks based on the U.S. Environmental Protection Agency water-quality standards were exceeded in either the Columbia or Willamette Rivers at sampling sites in this study. It is important to note, however, that the majority of compounds measured in this study do not have standards established. Just because a compound is not addressed by a standard does not mean that its presence or measured concentrations are not of concern.
- Although concentrations of arsenic, chromium, copper, and lead were not present at levels of concern with regards to aquatic-life toxicity, sublethal effects and signs of endocrine disruption have been linked to low levels of these compounds. While chromium was only detected in the Willamette River, arsenic was found at higher concentrations in the Columbia River than in the Willamette River. The median copper concentration from each of the three monthly sampling sites was 1.0 microgram per liter, a level shown to have inhibitory effects on juvenile coho salmon.
- Concentrations of trace elements in the Columbia River near Point Adams were elevated when compared to concentrations further upstream in the main stem and the Willamette River.
- Of the 173 pesticides and degradation products analyzed, 29 were detected at least once, oftentimes with 2 or more compounds occurring in a sample together. Fourteen compounds were detected in the Columbia River, 25 in the Willamette River.
- The triazine herbicides atrazine and simazine were the most frequently detected pesticides, most often in the Willamette River.
- Eight of the 54 wastewater compounds analyzed were detected at least once, usually at trace levels. The known endocrine disruptor, bisphenol A, was detected in both the Columbia and Willamette Rivers, while the suspected endocrine disruptor, tri(2-chloroethyl)phosphate, was detected only in the Willamette River.

- Of the 24 pharmaceuticals analyzed, acetaminophen, a common analgesic, and diphenhydramine, a widely used antihistamine, were detected in the Columbia River.
- Three of the 49 antibiotics and degradation products analyzed were detected. Anhydroerythromycin, a degradation product of the antibiotic erythromycin, and trimethoprim, an antibiotic used both for people and in aquaculture, were detected at most sites during low-flow conditions, but at only one site during high-flow conditions.
- Even though organochlorine compounds on suspended sediment were monitored monthly at the Beaver Army Terminal site from May 2004 to April 2005, *p,p'*-DDT was detected only once in October 2004 at 0.02 micrograms per gram. No other organochlorine compounds were detected.
- During the seasonal samplings of suspended sediment at all four sites, no organochlorine compounds or PAHs were detected.
- Of the 11 PBDE congeners analyzed, all were detected on suspended sediment, usually in trace amounts. The only quantifiable concentrations were measured near Point Adams.
- Of the 209 PCB congeners analyzed, 102 were detected at some time on suspended sediment at the four sites, usually in trace amounts. A third of these detections were quantifiable at the Willamette River during the high-flow sampling. There were fewer PCB detections during the low-flow sampling than during the high-flow sampling.

Introduction

The Columbia River provides critical habitat for threatened and endangered salmonid species in the Pacific Northwest. Twelve stocks from this region are threatened or endangered, including Lower Columbia River Chinook and steelhead, Upper Columbia River Chinook and steelhead, Columbia River chum, Upper Columbia spring Chinook, Snake River spring/summer Chinook, Snake River fall Chinook, mid-Columbia River steelhead, Snake River steelhead, and Snake River sockeye. For at least some period of time, all of these stocks use the Columbia River Estuary for a migration corridor, and some stocks, such as the Lower Columbia River, Upper Columbia River, and Snake River fall Chinook, and Columbia River chum, use it for an extended period of rearing.

The Columbia River drains 259,000 square miles of the Pacific Northwest, and flows more than 1,200 miles from its headwaters in the Canadian Rockies of British Columbia, across the State of Washington, and along the border of Washington and Oregon to its mouth at the Pacific Ocean. This study focuses on the Columbia River Estuary, defined by the Clean Water Act as waters that are tidally influenced. This definition covers the lower 146 miles of the river, from Bonneville Dam to the mouth, and also includes the lower 26 miles of the Willamette River from Willamette Falls to its confluence with the Columbia River.

During their passage through and residence in the Columbia River Estuary, salmonids are exposed to a variety of environmental contaminants from numerous sources including municipal and industrial permitted discharges, atmospheric deposition, urban and industrial nonpoint pollution, accidental spills of oil and hazardous materials, and runoff from agricultural and forested areas (Fuhrer and others, 1996; Lower Columbia River Estuary Partnership, 1999). In addition to inputs from the Lower Columbia region, contaminants may also be transported to the estuary from areas of known sediment contamination above the Bonneville Dam, such as Lake Roosevelt (Bortleson and others, 1994), the Yakima River (Fuhrer and others, 2004), the Snake River (Clark and others, 1998), and in areas of sediment deposition behind the dams (U.S. Army Corps of Engineers, 2006).

Background

Earlier studies within the Columbia River Estuary have documented the presence of legacy pesticides and trace elements in water, suspended sediment, and streambed sediment (Fuhrer and others, 1996; Tetra Tech, Inc., 1996; McCarthy and Gale, 1999). Studies of contaminant residues in juvenile salmonids (Johnson and others, 2004) and osprey (Henny and others, 2003) clearly show that some legacy pesticides biomagnify and move up the food chain. Trace elements in the water column have been significantly enriched due to mining-related activities in the upper Columbia River Basin (Horowitz and others, 1999) and tributary inputs, most notably the Willamette River, in the lower basin. In addition to the inherent toxic properties of arsenic, cadmium, chromium, copper, lead, and mercury at threshold concentrations, even sublethal concentrations of some of these trace elements can inhibit sensory physiology, which is vital for the survival and migratory success of wild salmonids (Baldwin and others, 2003). Additionally, low levels of trace elements are beginning to be identified as endocrine disrupters that can cause embryonic and adult mortality in amphibians, birds, and fish.

Earlier studies of currently used hydrophilic pesticides show they are present at low levels and often in mixtures (Fuhrer and others, 1996). In particular, organophosphate and carbamate insecticides were detected at environmentally relevant concentrations in tributaries affected by agricultural and urban land uses and also in the main-stem Columbia River. This is of concern because they can desynchronize the reproductive physiology of prespawning adult salmonids and disable the olfactory

functions of the male salmonid, causing problems with alarm responses, prey capture, and homing (Scholz and others, 2000).

Little is known nationally, and no data are available locally, to describe adverse effects to salmonid populations from point and nonpoint source discharges of pharmaceuticals, antibiotics, hormones, and other organic wastewater contaminants. These contaminants were found in 80 percent of the 139 streams tested nationally in 1999–2000 (Kolpin and others, 2002). Of the 95 organic wastewater contaminants analyzed, fecal steroids, insect repellants, caffeine, antimicrobial disinfectants, fire retardants, and nonionic detergent metabolites were the classes detected commonly. Many of these contaminant classes pose developmental or toxic risks to salmonids.

Polybrominated diphenyl ethers (PBDEs) are man-made chemicals used as flame retardants in electronics, building materials, seat cushions, and clothing. Studies of salmon in the Great Lakes, where the most intensive research has been conducted to date, show that the average level of PBDE contamination is 80 parts per billion (Manchester-Neesvig and others, 2001). Concentrations of PBDEs in the upper Columbia River Basin's mountain whitefish were as high as 72 parts per billion and have increased 12-fold over the period 1992–2000, with a doubling period of 1.6 years (Rayne and others, 2003). PBDEs are similar toxicologically to polychlorinated biphenyls (PCBs), which have been measured in the tissue of juvenile salmon from the Columbia River Estuary at concentrations exceeding adverse-effects thresholds (Johnson and others, 2004).

Purpose and Scope

The mission of the Lower Columbia River Estuary Partnership is to preserve and enhance the water quality of the estuary to support its biological and human communities. The current understanding of the interactions and relative effect of toxic contaminants and conventional pollutants on salmonid life histories in the Columbia River Estuary is limited. Therefore, the Estuary Partnership, along with the USGS and NOAA Fisheries, designed the water-quality monitoring component of the Ecosystem Monitoring Project to help determine the role toxics may be playing in salmonid recovery in the estuary. The Ecosystem Monitoring Project has two main components—habitat monitoring, which involves field surveys and the development of an ecosystem-classification system, and water-quality monitoring, comprised of water-chemistry-data collection, juvenile salmonid sampling, and the creation of three models related to salmonid uptake, transport, and the ecological risk of toxics. USGS collected water-quality data and NOAA Fisheries sampled juvenile salmonids at co-located sites during the same time periods so that these data sets could be integrated to assess the effects of water-quality contaminants on salmonid growth, reproduction, and immune-system function. These data are also being used by NOAA Fisheries to develop and calibrate their models for the Columbia River Estuary.

This report describes the water-quality data collected by the USGS from 2004 through 05 as part of the Ecosystem Monitoring Project and attempts to quantify the spatial distribution and temporal variation of water-quality conditions, including contaminant concentrations, in water and suspended sediment in the Columbia River Estuary, and evaluate these water-quality conditions against aquatic-life standards and guidelines. The analytes to be measured in this study were selected because they are either known to be present in Columbia River salmonids at levels of concern; known to be present in salmonids, but not known if present at levels of concern; present in water at concentrations known to affect endocrine function in adult salmonids; or not previously measured in water, but if present, are of potential concern to salmonid populations.

Sampling Design and Methods

This study was designed to characterize water-quality conditions within the Columbia River Estuary through the analysis of water-column and suspended-sediment samples and semipermeable-membrane device (SPMD) extracts. Water-column and suspended-sediment samples were collected monthly at the Columbia River at Warrendale (river mile [RM] 141, site 1 on [fig. 1](#)), the Willamette River at Portland (Willamette RM 13, site 2), and the Columbia River at Beaver Army Terminal (RM 54, site 4) from May 2004 through April 2005 ([table 1](#)). To further characterize water-quality conditions, seasonal samplings of the water column, suspended sediment, and SPMDs were performed at these three sites as well as the Columbia River near Columbia City (RM 82, site 3) and the Columbia River near Point Adams (RM 4, site 5). The first of these seasonal samplings occurred in August 2004 during low-streamflow conditions, when contaminants from point sources, such as urban and industrial areas, and nonpoint sources, such as agricultural runoff, could have a greater impact on water-quality conditions and aquatic-life health because there is less water available in the rivers to dilute these contaminant inputs. The second seasonal sampling was scheduled to occur during high-streamflow conditions to characterize contaminants that may have accumulated in the river as a result of episodic storm events during the preceding winter, as well as contaminants that enter the river directly from overland runoff. Based on past hydrologic conditions, streamflow is expected to be elevated in the January–February time frame for the Willamette River due to winter storms and in the May–June snowmelt time period for the Columbia River. The winter of 2004–05, however, was unseasonably dry, and the first major precipitation occurred at the end of March 2005. Therefore, the high-streamflow seasonal sampling occurred in April 2005 for both the Columbia and Willamette River sites.

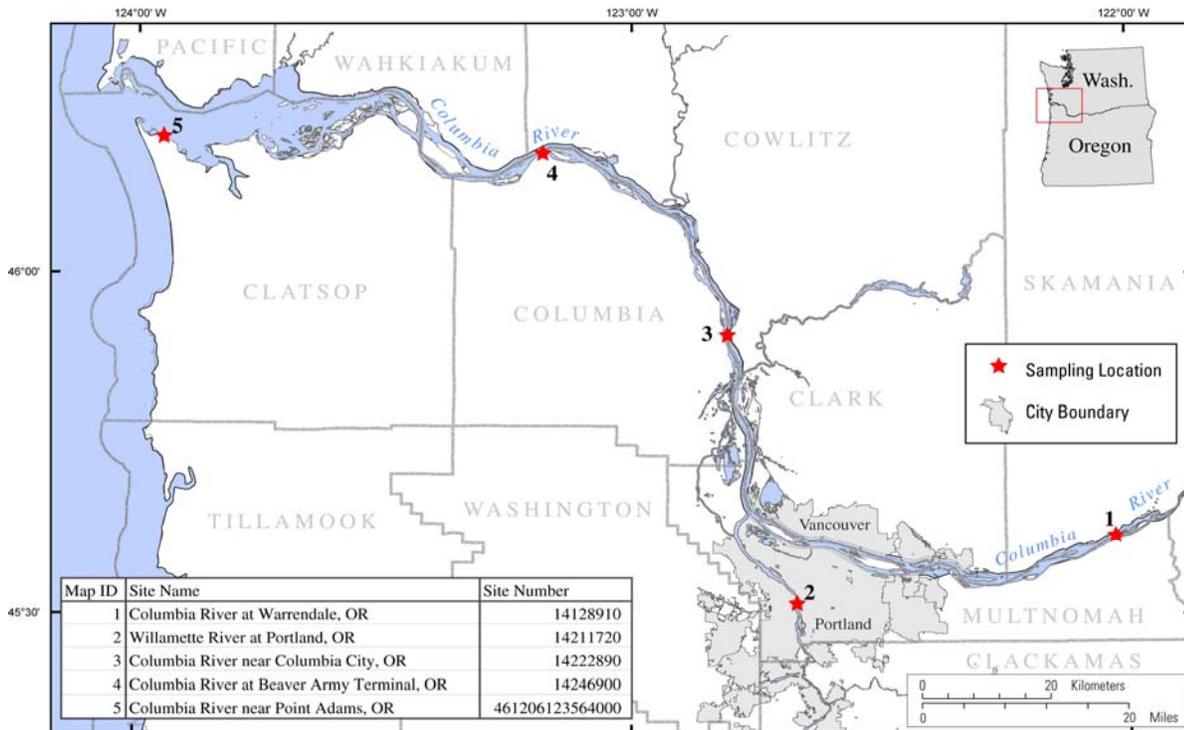


Figure 1. Map of water-quality sampling locations, Columbia River Estuary, 2004–05

Sample Collection and Laboratory Analysis

Monthly sampling

The monthly samples were collected at Columbia River at Warrendale (referred to in this report as Warrendale), the Willamette River at Portland (Willamette), and the Columbia River at Beaver Army Terminal (Beaver). These sites were chosen not only because of their locations, but also because they have historic data sets that make it possible to study changes in water quality over time. The USGS operates two programs that aim at characterizing water-quality conditions across the Nation. The National Stream-Quality Accounting Network (NASQAN) Program was designed to characterize the transport of sediment and contaminants in large-river systems, including the Columbia and Mississippi Rivers. The National Water-Quality Assessment (NAWQA) Program focuses on water quality in more than 50 major river basins and aquifers throughout the country. From 1974 through 2000, the Warrendale and Willamette sites were NASQAN sites. The Willamette site is a current (1991–present) NAWQA site, and the Beaver site is a continuing (1974–present) NASQAN site.

Samples were collected and analyzed for alkalinity, chlorophyll *a* and pheophytin A (table 2), nutrients (table 3), carbon species (table 4), trace elements (tables 5 and 6), biomass (tables 7 and 8), bacteria (table 9), suspended sediment, and a select listing of pesticides (table 10). An expanded listing of pesticides and degradation products (table 10), which were too cost prohibitive to analyze on a monthly basis, were analyzed quarterly. Samples from Beaver were analyzed for major ions (table 5) on alternating months as part of the NASQAN Program. In addition, field parameters (table 2), such as pH, dissolved oxygen, air and water temperatures, specific conductance, and turbidity, were measured using a multiprobe water-quality monitor that was calibrated in the field. At Beaver, suspended-sediment samples were collected monthly for the analysis of organochlorine compounds (DDT, endosulfan, etc.). Four times during the year, suspended-sediment samples were also analyzed for trace elements at all three sites.

Samples were collected using standardized depth- and width-integrating techniques and were processed and preserved using standard methods described in U.S. Geological Survey (1997–present). All samples were processed at the USGS Oregon Water Science Center (OWSC) in Portland, Oregon, prior to shipment to laboratories for analysis. Nutrient, chlorophyll *a* and pheophytin A (USEPA method 445.0), carbon species, major ion, and trace element samples were analyzed at the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado, according to methods described in Fishman (1993), Brenton and Arnett (1993), Patton and Truit (2000), U.S. Environmental Protection Agency (1993, 1997a, 1997b), Patton and Kryskalla (2003), Faires (1993), Garbarino (1999), Garbarino and others (2006), Fishman and Friedman (1989), and American Public Health Association (1998). The pesticide samples were also analyzed at the NWQL by gas chromatography/mass spectrometry (GC/MS) using methods O-1126-95 and O-1126-02 described by Zaugg and others (1995), Lindley and others (1996), and Madsen and others (2003). A full listing of all constituents analyzed for, reporting limits, and method numbers can be found in Appendix A. Suspended-sediment concentrations were determined at the Cascades Volcano Observatory Sediment Laboratory in Vancouver, Washington, according to Guy (1969). Biomass samples were sent to Aquatic Analysts in White Salmon, Washington, for algal identification and enumeration according to analytical procedures described by Jim Sweet (Aquatic Analysts, written commun., May 2004).

Unlike the depth- and width-integrated samples listed above, bacteria samples were collected as grab samples from the left and right banks and the center of flow at each site. The Oregon Department of Environmental Quality requested that these samples be collected, and coordinated the efforts for their

analysis at the Oregon Department of Health's laboratory in Portland, Oregon. From May through October 2004, *E.coli* bacteria concentrations were determined by method 9213D using membrane filtration, while from November 2004 through April 2005, *E.coli* and total coliform bacteria concentrations were determined by method 9223B using a 24-hour Quantitray approach (American Public Health Association, 1998). For the analysis of organochlorine compounds on suspended sediment, approximately 25 liters of water were collected at Beaver and then filtered through a 142-millimeter diameter, 0.7-micrometer pore-size glass-fiber filter at the OWSC laboratory. These filters containing the suspended sediment from the sample were then chilled and sent to Severn Trent Laboratories (STL) in West Sacramento, California, for sonication with hexane and methylene chloride. These samples were then analyzed by gas chromatography using method 8081A (US Environmental Protection Agency, 1996a). For the analysis of trace elements on suspended sediment, 100–200 liters of water were collected (based on the goal of collecting 1 gram or more of sediment mass) and sent to the Georgia Sediment Chemistry Laboratory in Atlanta for dewatering by flow-through centrifugation. Sample aliquots were then digested with a combination of hydrofluoric acid, perchloric acid, and aqua regia (a mixture of hydrochloric and nitric acids) and then analyzed by either atomic absorption spectrometry for silver, cadmium, and lead or inductively coupled plasma-atomic emission spectroscopy for all others (Horowitz and others, 2001).

Seasonal Samplings

Besides the three sites sampled monthly, two additional sites were added for the low-streamflow sampling in August 2004—the Columbia River near Columbia City (Columbia City) and the Columbia River near Point Adams (Point Adams). The Columbia City site is downstream of the Multnomah Channel and has historic water-quality (Fuhrer and others, 1996) and fish-tissue (Tetra Tech, 1996) data. The Point Adams site coincides with a NOAA Fisheries sampling location. Studies conducted by NOAA Fisheries have detected organochlorine compounds in salmonids in several locations throughout the estuary (Johnson and others, 2004). During the high-flow sampling in April 2005, the three monthly sites and Point Adams were sampled; however, Columbia City was not sampled due to limited funding.

Besides the constituents listed above for the monthly samples, samples were also collected for the analysis of an expanded listing of pesticides, degradation products, wastewater compounds (table 11), pharmaceuticals, and antibiotics (table 12). These samples were collected using depth- and width-integrating techniques and were filtered at the OWSC laboratory through a 142-millimeter diameter, 0.7-micrometer pore-size glass-fiber filter before they were sent off to the appropriate laboratories. The samples collected for additional pesticides were analyzed by high-performance liquid chromatography/mass spectrometry by method O-2060-01 at the NWQL (Furlong and others, 2001). Additional pesticides and degradation products (method O-2002-01) and wastewater compounds (method O-1433-01) were analyzed by GC/MS at the NWQL (Sandstrom and others, 2001; Zaugg and others, 2002). The pharmaceuticals were analyzed at the NWQL according to methods described by Cahill and others (2004), while the antibiotics were analyzed at the Organic Geochemist Research Laboratory in Lawrence, Kansas, according to methods described by Michael Meyer (written commun., August 2006). Both the pharmaceutical and antibiotic samples were analyzed by liquid chromatography/electrospray ionization-mass spectrometry.

SPMDs were deployed and suspended-sediment samples were collected during the high-flow sampling in April 2005 and during a low-flow sampling in August 2005 at the three fixed sites and Point Adams. SPMDs are passive samplers that concentrate trace levels of hydrophobic organic contaminants. They are sometimes referred to as "virtual fish" because they can mimic the bioconcentration of organic contaminants in the fatty tissues of fish. SPMDs are pieces of low-density

polyethylene lay-flat tubing with 10-angstrom-diameter cavities that are designed to sample the dissolved, or readily bioavailable, organic contaminants present in the water (Huckins and others, 2006). They complement traditional water-quality and fish-tissue monitoring because sampling occurs continuously during deployment and thus captures the daily range of contaminant concentrations.

At the time of SPMD deployment, 100 to 120 liters of water were collected using depth- and width-integrated sampling techniques, and then filtered through a 142-millimeter diameter, 0.7-micrometer pore-size glass-fiber filter at the OWSC laboratory in four batches of 25 to 30 liters each. These filters containing the suspended sediment from each sample were then chilled and sent to STL for analysis. After about 35 days of deployment, the SPMDs were sent to Environmental Sampling Technologies in St. Joseph, Missouri, for cleaning and extraction. The dialysates from these SPMDs and the suspended-sediment samples were analyzed for four different groups of compounds: organochlorine compounds, polyaromatic hydrocarbons (PAHs), a selected group of 11 PBDE congeners¹ (table 13), and all 209 PCB congeners (table 14). The filters analyzed for organochlorine compounds (method 8081A) and PAHs (method 8270C SIM) went through sonication with hexane and methylene chloride followed by analysis by gas chromatography (US Environmental Protection Agency, 1996a; 1996b). The organochlorine compounds were detected using electron capture detectors, while the PAHs were detected by mass spectrometry. The filters analyzed for PBDEs (method 1614) and PCBs (method 1668) went through a soxhlet extraction with toluene and were analyzed by high-resolution GC/MS (U.S. Environmental Protection Agency, 1999; 2006a).

Reporting of Data

When an analyte is measured in a laboratory, it is either detected or not detected. When it is not detected, it is reported as “censored,” or less than the reporting limit (RL). This does not mean that the analyte is not present; it simply means that it could not be detected in this sample with these conditions. It may be present, but at a concentration lower than the instrument can measure. Likewise, the presence of other material or analytes in the sample may be causing interference, preventing the analysis of the analyte in this sample. Or, it may not be present at all. If, however, the analyte is detected, it may be reported in several ways. If it is detected at a concentration above the RL, then the value is simply reported at the concentration measured. If the analyte is a poor performer (long-term variability or poor recovery) in laboratory performance samples or if matrix problems cause interference for that analyte in a sample, the measured concentration may be qualified as an estimated (“E”) value.

The concentration may also be reported as an estimated value if the analyte is detected at a concentration below the RL but above the method detection limit (MDL). The MDL is a statistically derived minimum concentration that can be measured with a 99% confidence of being greater than zero (Childress and others, 1999). Therefore, there is a less than 1% chance that an analyte will be reported as a false positive or, in other words, that the concentration was reported but the analyte was not present. If the analyte is detected at a concentration below the MDL, then, in this report, the value is shown as an “M,” indicating that the presence of the analyte was verified, but that the concentration was too small to be quantified. For some analyses, such as the pharmaceuticals and antibiotics, too few data have been collected to establish an MDL; therefore concentrations detected below the RL are reported as “M.” The

¹ In chemistry, the term congener refers to one of many variants or configurations of a common chemical structure. For example, PBDEs and PCBs occur in 209 different forms, or congeners. Each congener has two or more bromine or chlorine atoms located at specific sites on the PBDE or PCB molecule, respectively.

NWQL reevaluates the RL and MDL values every year and adjusts them as needed based on the laboratory performance data. Because of these adjustments, there may be multiple RLs shown for a given analyte (appendix [table A4](#)).

The data from STL for the suspended-sediment samples and SPMD extracts were reported as the mass of the given analyte detected in the sample. For the suspended-sediment samples, the mass of a given compound was divided by the number of liters filtered to obtain a concentration of the analyte in the water column. The concentration of the analyte in water (micrograms per liter) was then divided by the concentration of suspended sediment in the water column (milligrams per liter) and the appropriate conversion factors were applied to achieve the concentration of the analyte on suspended sediment (micrograms per gram) for the sample. RLs to be used for this study were derived by doubling either the highest value reported in a laboratory blank or trip blank, or the MDL supplied by STL if there were no detections for that analyte in any blanks (tables [A8](#) and [A9](#)). The SPMD data will be reported and interpreted in a future report.

Quality Assurance

Quality assurance is the analysis of quality-control (QC) data as a means to assess potential contamination and variability associated with sampling and laboratory techniques. QC samples for this study included field and trip blanks, replicate environmental samples, field-matrix spikes, surrogates, and a standard-reference sample, as well as internal laboratory QC data. The number and types of QC samples were distributed evenly throughout the sampling period, with more QC samples directed towards analyses that are not as well established for these sites, like chlorophyll and bacteria ([table 15](#)). The results of all of these QC samples ([Appendix B](#)) were used to assess the environmental data, and other data users are urged to do the same.

Types of Quality-Control Samples Used

Field blanks are performed by passing a volume of contaminant-free water (organic blank water [OBW], deionized distilled water, or inorganic blank water, depending upon the analyses being performed) through all sampling and processing equipment that an environmental sample would contact. The results of field blanks can be used to assess contamination issues associated with cleaning, sampling, processing, or transporting the sample. The field blanks prepared for the analysis of organic compounds on suspended sediment were performed slightly differently. The water was filtered directly from the original OBW bottle to minimize some of the sources of contamination, and test primarily the analytical procedure. In April 2005, 4 liters of OBW were filtered for each grouping of compounds and one filter was sent in for each sample. It was realized that the reporting limits for this blank sample would not be similar to the environmental sample because the mass of compound would be divided by only 4 liters, whereas the environmental samples usually involved 25 to 30 liters of water being filtered. Therefore, in August 2005, 24 liters of OBW were filtered onto 6 filters for each compound grouping in an effort to more directly mimic the actual processing procedures.

Replicate environmental samples test for precision, which is a measure of the variability between two or more samples. Replicate samples in this study were collected by splitting the sample collected during processing into two samples to be providing to the analyzing laboratory, rather than by collecting two or more concurrent samples in the field. These replicate samples measure the variability of the processing techniques and the laboratory precision, but are not designed to measure field-sampling variability. One exception to this is for the analysis of pharmaceuticals in filtered water, where limited funding was directed at field-matrix-spike samples instead.

Field-matrix spikes were performed by adding a known amount of a spike solution with a known concentration to an environmental replicate sample. Field spikes were performed for all analyses for which spiking solutions were readily available (all pesticide and wastewater-compound analyses in filtered water). Spike recoveries were calculated and used to identify which compounds consistently under or over report the actual concentrations or which compounds were variable in their recoveries. Internal lab spikes were also performed for all analyses. These results help the lab determine how the different methods are performing and were used when needed to examine the data in this study.

Surrogate compounds are expected to behave similarly to the target analytes and are used to monitor the method's performance for the target analytes they represent. Surrogate compounds are added to the sample at the lab and are analyzed as part of the list of analytes. The NWQL uses the surrogate recoveries to assess problems associated with individual samples or sets of samples, but also uses long-term surrogate recoveries to assess long-term analytical precision.

One standard-reference sample for the analysis of nutrients in water was prepared during this study. A sample of known nutrient concentrations (analyzed multiple times to determine a most probable value and the expected range) was sent to NWQL along with the routine environmental samples. Standard reference samples do not come in contact with sampling or processing equipment; therefore, the results are used to assess analytical accuracy only.

Results of Quality-Control Data

Contamination of samples is not considered a problem for this study. There were no detections for chlorophyll *a*, pesticides, bacteria, biomass, or antibiotics in any of the field blanks. There were but a few analytes with detections in the field blanks (appendix [table B1](#)), and they were all at levels that did not warrant concern with respect to the environmental detections. Two wastewater compounds, phenol and benzophenone, have been removed from consideration for this study because of concern over detections in the blanks (Zaugg and Leiker, 2006). Phenol is a chronic contaminant at NWQL, and the majority of the field blanks for this study also had detections at a significant level. Benzophenone is a compound with known field contamination consistency, and the field blanks for this study confirmed this.

When comparing differences in concentrations from different sites or different times, the analytical and environmental variability must be considered. Examining environmental replicate data can help to quantify this variability. Relative percent difference (RPD) values, which provide a measure of how well the concentrations from two samples agree, were calculated for all environmental replicate data pairs. The RPD is calculated as the absolute difference between two values, normalized to the average value, and expressed as a percentage:

$$RPD \equiv \left| \frac{(Value1 - Value2)}{(Value1 + Value2)/2} \right| \times 100 \quad (1)$$

An RPD close to zero shows good agreement between the sample results.

Environmental replicate results indicate generally good agreement for most compound concentrations (appendix [tables B2–B6](#)). The RPDs for the nutrient, carbon, major ion, and trace element analyses were generally low, usually less than 10 percent. There was one replicate pair of samples for trace-element analysis from Warrendale in November 2004 that had some higher RPDs, particularly for aluminum, copper, and zinc. After determining the error bars for each questionable concentration by using the NWQL's internal QC data, it was found that the replicate results were within acceptable agreement. This example portrays the variability that can be associated with the trace-

element analyses. The suspended-sediment, chlorophyll *a*, pheophytin A, and pesticide and degradation product analyses generally had higher and more variable RPDs. This indicates that there is more inherent variability occurring in the analytical process for these compounds.

Field-matrix spike recoveries for the pesticides, degradation products, and wastewater compounds were calculated to evaluate the effectiveness and variability of the analyses. Most compounds had spike recoveries within the desired range of 60 to 140 percent. When examining only analytes that were detected in this study (appendix [table B7](#)), the majority of the analytes had recoveries distributed closely around 100 percent. A few analytes, however, had lower recoveries—the sulfonyl urea herbicide metsulfuron methyl; the degradation products 1-naphthol, CIAT, and OIET; and the known endocrine disruptor, bisphenol A. Most of these analytes have shown poor recoveries in the internal lab spikes as well.

The standard-reference sample that was prepared at the Warrendale site in April 2005 for the analysis of low-level nutrient concentrations in water agrees very well with the established concentrations for the reference material (appendix [table B8](#)).

Comparison of Data to Water-Quality Standards

Water-quality data collected during this study were screened against USEPA ambient water-quality criteria for the protection of aquatic life and human health (U.S. Environmental Protection Agency, 2006b) and USEPA primary drinking-water regulations and human-health advisories (U.S. Environmental Protection Agency, 2004) to identify compounds that may require further study. All USEPA ambient water-quality criteria are nonenforceable benchmarks that provide the basis for Oregon and Washington State standards. None of the USEPA benchmarks were exceeded in either the Columbia or Willamette Rivers at locations measured in this study. It is important to note, however, that the majority of compounds measured in this study do not have water-quality standards established. Just because a compound is not addressed by a standard does not mean that its presence or measured concentrations are not of concern.

Water-quality data collected in this study cannot be evaluated against most standards for the States of Oregon (Oregon Department of Environmental Quality, 2004) and Washington (Washington State Department of Ecology, 2003) because most standards are not based on instantaneous data, but rather are based on multiday average concentrations. These standards can, however, be used as benchmarks for comparison. The State of Oregon has total maximum daily loads (TMDLs) established for the Columbia River for dioxin and total dissolved gas, neither of which were measured in this study. The State of Oregon standards for *Escherichia coli* bacteria and total dissolved solids were not exceeded. The Washington Administrative Code standards for bacteria are based on fecal coliform bacteria, which were not measured as a part of this study, and the standards for turbidity were not exceeded. The dissolved oxygen and pH standards for both Oregon and Washington have many conditions built into them—designated use (aquatic life, recreation, water supply), spawning area and type of aquatic life present—making it difficult to determine if exceedances were measured or not.

Discussion of Selected Results

Although concentrations of arsenic, chromium, copper, and lead ([table 5](#)) were not present at levels of concern with regards to aquatic-life toxicity, sublethal effects and signs of endocrine disruption have been linked to low levels of these compounds (Kaltreider and others, 2001; Orazio, 2004). While chromium was only detected in the Willamette River, arsenic was found at higher concentrations in the

Columbia River than in the Willamette River. The median copper concentration from each of the three monthly sites was 1.0 microgram per liter, a level shown to have inhibitory effects on juvenile coho salmon (Baldwin and others, 2003). Concentrations of most trace elements were elevated near Point Adams when compared to the concentrations further upstream in the main stem and in the Willamette River.

Of the 173 pesticides and degradation products analyzed, 29 were detected at least once, oftentimes with 2 or more compounds occurring in a sample together (table 10). Fourteen compounds were detected in the Columbia River, 25 in the Willamette River. There were also many more occurrences of these compounds in the Willamette River. The triazine herbicides, atrazine and simazine, were the most frequently detected pesticides, most often in the Willamette River.

Eight of the 54 wastewater compounds analyzed were detected at least once, usually at trace levels. The known endocrine disruptor, bisphenol A, was detected in both the Columbia and Willamette Rivers, while the suspected endocrine disruptor, tri(2-chloroethyl)phosphate, was detected only in the Willamette River.

Of the 24 pharmaceuticals analyzed, acetaminophen, a common analgesic, and diphenhydramine, a widely used antihistamine, were detected in the Columbia River (table 12). Three of the 49 antibiotics and degradation products analyzed were detected. Anhydroerythromycin, a degradation product of the widely used antibiotic erythromycin, was detected at all four sites where it was measured in August 2004 during low-flow conditions, but at none of the sites in April 2005 during high-flow conditions. Likewise, trimethoprim, an antibiotic used both for people and in aquaculture, was found at most sites in August but at only one site in April.

Even though organochlorine compounds were monitored monthly on suspended sediment at Beaver from May 2004 to April 2005, p,p'-DDT was detected on suspended sediment only once in October 2004 at 0.02 micrograms per gram. No other organochlorine compounds were detected. During the seasonal samplings of suspended sediment at all four sites, no organochlorine compounds or PAHs were detected. Of the 11 PBDE congeners analyzed, all were detected on suspended sediment, usually in trace amounts (table 13). The only quantifiable concentrations were measured near Point Adams. Of the 209 PCB congeners analyzed, 102 were detected at some time on suspended sediment at the four sites, usually in trace amounts (table 14). A third of these detections were quantifiable at the Willamette River during the April sampling. There were fewer PCB detections during the August low-flow sampling than during the April high-flow sampling.

This report presents the water-quality data collected by USGS from 2004–2005, and complements the juvenile-salmonid data collected by NOAA Fisheries as part of the Lower Columbia River Estuary Partnership's Ecosystem Monitoring Project. NOAA Fisheries also created three models related to salmonid uptake, transport, and the ecological risk of toxics, and calibrated these models based on the water-quality and salmonid data sets. The synthesis of these data sets and models will be presented in a future report. The SPMD data, as well as a discussion of their relevance and a comparison to other SPMD and aquatic-life data sets, will also be presented in a future report.

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Appendix A. Methods, Reporting Limits, and Analyte Information.

(Click on link to open table.)

[Table A1. Reporting limits and methods for the carbon and nutrient species analyzed, Columbia River Estuary, 2004–05](#)

[Table A2. Reporting limits and methods for the major ions, metals, and trace elements analyzed in filtered water, Columbia River Estuary, 2004–05](#)

[Table A3. Reporting limits for the trace elements analyzed on suspended sediment, Columbia River Estuary, 2004–05](#)

[Table A4. Reporting limits, sampling frequency, use, and class for pesticides and degradation products analyzed in filtered water, Columbia River Estuary, 2004–05](#)

[Table A5. Reporting limits and possible uses or sources of wastewater compounds analyzed in filtered water, Columbia River Estuary, 2004–05](#)

[Table A6. Reporting limits, drug name, and class for pharmaceuticals analyzed in filtered water, Columbia River Estuary, 2004–05](#)

[Table A7. Reporting limits for antibiotic compounds analyzed in filtered water, Columbia River Estuary, 2004–05](#)

[Table A8. Derived reporting limits for organochlorine compounds, polycyclic aromatic hydrocarbons, and polybrominated diphenyl ethers analyzed on suspended sediment, Columbia River Estuary, 2004–05](#)

[Table A9. Derived reporting limits for polychlorinated biphenyls \(PCBs\) analyzed on suspended sediment, Columbia River Estuary, 2004–05](#)

Appendix B. Quality-Assurance Data

(Click on link to open table.)

[Table B1. Summary of field-blank detections, Columbia River Estuary, 2004–05](#)

[Table B2. Environmental replicate results for suspended-sediment, chlorophyll *a*, and pheophytin A analyses, Columbia River Estuary, 2004–05](#)

[Table B3. Environmental replicate results for carbon analyses, Columbia River Estuary, 2004–05](#)

[Table B4. Environmental replicate results for nutrient analyses, Columbia River Estuary, 2004–05](#)

[Table B5. Environmental replicate results for major ion, metal, and trace-element analyses, Columbia River Estuary, 2004–05](#)

[Table B6. Environmental replicate results for pesticides, wastewater compounds, antibiotics, and degradation products, Columbia River Estuary, 2004–05](#)

[Table B7. Field-matrix spike recoveries for detected pesticides and degradation products and wastewater compounds, Columbia River Estuary, 2004–05](#)

[Table B8. Standard-reference sample prepared for low-level nutrient analyses, Columbia River Estuary, 2004–05](#)