Northeast River Basin Toxics Monitoring Summary

(Grande Ronde, John Day, Powder and Walla Walla River Basins)

February 2023

State of Oregon
DEQ Department of Environmental Quality

DEQ23-LAB-0004-TR
Version 1.0
Last updated: 02/03/2023

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Executive Summary

In 2016, the Oregon Department of Environmental Quality conducted water quality, sediment, and fish tissue sampling of 17 rivers and streams across the Grande Ronde, John Day, Powder and Walla Walla River basins. This sampling effort builds on previous sampling that DEQ conducted for the Toxics Monitoring Program between 2011 and 2012. The goals of this sampling – and of the Toxics Monitoring Program as a whole – are to gather information on chemicals of concern, identify their potential sources, make the information available to the public, and work with internal and external partners to reduce pollutant concentrations.

State of Oregon Department of Environmental Quality

DEQ staff collected water samples three times in 2016 at 20 locations across the four basins. Sediment samples were collected from the same 20 locations as the water samples. Fish tissue samples were collected at two locations in 2014 and four locations in 2016. Sediment and tissue sample collection occurred only once per location since the chemicals that can sequester to these media are more stable than in water and do not require frequent sampling. DEQ analyzed samples for nearly 500 chemicals from nine chemical groups including current-use pesticides, consumer use products, combustion by-products, dioxins and furans, flame retardants, industrial chemicals, legacy pesticides, polychlorinated biphenyls (PCBs), and metals. Across all media, 124 chemicals were detected. Among the most commonly detected chemicals were arsenic and DDT in water samples; metals and DDT in sediment samples; and metals and legacy pesticides in fish tissue samples.

Overall, 96% of the chemicals analyzed in the 2016 samples were undetectable or were detected only at concentrations below standards for the protection of aquatic life, wildlife, and human health. The Burnt River location upstream of Huntington WWTP (#33829) in the Powder Basin had the highest number of detections and standards exceedances in water. The exceedances included three DDT isomers and five metals (aluminum, inorganic arsenic, iron, selenium and thallium). Total DDT in sediment occurred at concentrations above the sediment bioaccumulation screening level at 80% of monitoring locations, with the highest concentrations occurring across the Walla Walla Basin. In tissue samples, mercury was the only chemical detected at concentrations that may pose a risk to human health. Concentrations at five of six locations exceeded the OHA screening level. This included both finfish and shellfish samples.

Based upon the 2016 results, DEQ staff selected 11 monitoring locations that will become a part of the Toxics Monitoring Program's trend network. Chemical detections, exceedances of applicable criteria, spatial

coverage, classification in the 2018/2020 Integrated Report, and the need for background or reference sites were all considered when selecting which monitoring locations to include in the statewide trend network. The Toxics Monitoring Program is working to establish a network that is sampled on a regular basis to establish trends rather than sampling each basin every five years as in previous efforts. This change in approach will help DEQ understand the broadest geographical area while maximizing limited lab and staff resources.

Data included in this toxics summary report were used in the 2022 Integrated Report, which reports the status of Oregon’s waters to EPA and informs other regulatory programs such as the total maximum daily load (TMDL), National Pollutant Discharge Elimination System (NPDES) and stormwater permitting programs. The data included in this report contributed to a number of assessment units being listed as impaired or not meeting their beneficial uses for certain chemicals. In addition, these data may be considered as part of the toxics reduction strategy, a cross media program that supports ongoing toxics reduction efforts within DEQ, and to prioritize drinking water source areas for other partnership programs.

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Introduction

In 2007, the Oregon Legislature funded the Oregon Department of Environmental Quality to begin the Statewide Water Quality Toxics Monitoring Program. The program identified four main goals:

1. Gather information to characterize the presence and concentration of chemicals of concern in Oregon's waters.

2. Use this information to identify potential sources of these chemicals.

3. Present and make data available for public benefit.

4. Work with DEQ internal groups, community groups, and Oregon citizens to identify opportunities to reduce these pollutants.

To achieve these goals, the DEQ Laboratory and Environmental Assessment Division (LEAD), with input from the Water Quality Program, developed a five-year monitoring plan. The initial phase of this plan followed a rotating basin approach to conduct reconnaissance sampling of the state's waters and was completed in 2013. DEQ LEAD published the water and fish tissue sampling results from this initial phase of sampling in two separate statewide reports (2015 Statewide Water Quality Toxics Assessment, 2017 Statewide Aquatic Tissue Toxics Assessment). The purpose of the current summary is to combine the sampling results from all media types collected in the Grande Ronde, John Day, Powder and Walla Walla River basins during the initial phase of Toxics Monitoring Program sampling in 2011/12 with the most recent phase, completed in 2016.

Throughout this summary, chemical concentrations are compared to media-specific water quality criteria, aquatic life benchmarks, or screening levels. Oregon's water quality standards for human health (Oregon Administrative Rules 340 Division 41) are designed to protect people who use the water as a primary drinking water source and consume fish or shellfish collected from waterbodies. These criteria assume a fish/shellfish consumption rate of 17.5 grams daily or twenty-three 8-ounce meals per month. DEQ is grateful for tribal input on exposure levels (CTUIR.)

Additionally, these criteria are intended to ensure that waterbodies support the beneficial use of "fishing" and that fish are safe to consume, rather than how much fish is safe to eat (DEQ 2017). Consequently, Oregon's criteria are more stringent than most other states' fish tissue standards and are protective of subsistence consumers. Oregon's human health criteria used in this assessment are generally lower (i.e., more stringent) than health standards set solely for drinking water consumption by EPA and others (i.e., Maximum Contaminant Levels or Health Based Screening Levels). Oregon's aquatic life criteria apply to waterbodies where the protection of fish and aquatic life is a beneficial use as outlined by the Oregon Administrative Rules (https://go.usa.gov/xyxSj). EPA's aquatic life benchmarks were developed for 635 current-use pesticides based on toxicity values supported by scientific studies. Comparing monitoring data with EPA's aquatic life benchmarks (EPA 2020) may help prioritize sites that need more investigation. These benchmarks were only used if DEQ has not established criteria for a particular chemical because the benchmarks have greater uncertainty than criteria.

For chemicals detected in sediment samples, the referenced screening levels estimate the likelihood that a chemical poses a threat to humans or wildlife as a result of eating fish, shellfish, or other aquatic organisms from a particular location (DEQ 2007). For chemicals detected in fish tissue samples, a combination of Oregon Health Authority (OHA) Fish Advisory Program screening levels and DEQ acceptable tissue levels were used to identify potential risk to human health via fish consumption. OHA screening levels identify concentrations of contaminants in fish below which are not expected to harm human health assuming a consumption rate of 17.5 grams daily or twenty-three 8-ounce meals per month (OHA 2022). DEQ acceptable tissue levels for humans are concentrations of bioaccumulative chemicals in fish tissue that are too low to cause adverse effects on humans that consume 17.5 grams of fish from the sampling locations per day (DEQ 2007). In all cases, if no DEQ criterion or screening level existed, then the lowest regional or national criterion or screening level was used to ensure a conservative report of exceedances across the basin for each media type. Pollutant-specific criteria, benchmarks and screening levels do not take into consideration the possible synergistic effect of multiple chemicals co-occurring in the environment.

The initial monitoring location selection process for the 2011 and 2012 sampling efforts focused on locations that integrate multiple watersheds within the basin. For the 2016 sampling effort, most monitoring locations were selected based on land use, proximity to point and non-point source pollution, and input from both local stakeholders and DEQ basin coordinators. Table 1 details the monitoring locations and matrices sampled during both sampling efforts. Figure 1 indicates the location and sampling effort of each monitoring location in each basin. Water samples were collected three times (May, August and October/November) in 2016, sediment and fish tissue samples were collected only once. Appendices A-C detail the detection results from both sampling efforts by media type.

Table 1. Northeast River Basin monitoring locations.

Station ID	Description	Basin	Matrices Sampled
10410	**Wallowa River at Minam**	**Grande Ronde**	**Water, Sediment**
10711	**Walla Walla River at Hwy 11**	**Walla Walla**	**Water, Sediment and Tissue**
10719	**Grande Ronde River at Hwy 82**	**Grande Ronde**	**Water[#], Sediment**
10720	**Grande Ronde River at Hilgard Park**	**Grande Ronde**	**Water***
10724	**Powder River at Hwy 86**	**Powder**	**Water***
11016	**South Fork John Day River at Dayville**	**John Day**	**Water***
11020	**John Day River ds of South Fork John Day**	**John Day**	**Water***
11386	**John Day River at Hwy 206**	**John Day**	**Water[#], Sediment**

11457	**Minam River at Minam**	**Grande Ronde**	**Water, Sediment**
11478	**John Day River at Service Creek**	**John Day**	**Water***
11494	**Burnt River at Snake River Road**	**Powder**	**Water***
11521	**Grande Ronde River at Peach Lane**	**Grande Ronde**	**Water#, Sediment and Tissue**
11647	**Grande Ronde River at Lower Cove Road**	**Grand Ronde**	**Water, Sediment**
11857	**Powder River at Snake River Road**	**Powder**	**Water#, Sediment**
23497	**Walla Walla River at OR/WA state line**	**Walla Walla**	**Water***
24135	**Clear Creek near Red Boy Mine**	**John Day**	**Water#, Sediment**
31987	**Canyon Creek at John Day City Park**	**John Day**	**Water#, Sediment**
31990	**John Day River at Clyde Holliday State Park**	**John Day**	**Water#, Sediment**
32010	**West Prong Little Walla Walla River**	**Walla Walla**	**Water, Sediment**
33084	**Little Walla Walla River**	**Walla Walla**	**Water, Sediment**
33829	**Burnt River upstream Huntington WWTP outfall**	**Powder**	**Water, Sediment and Tissue**
34238	**Bear Creek at Frontage Road**	**Grand Ronde**	**Water, Sediment**
34438	**Powder River downstream of Hudspeth Road**	**Powder**	**Water, Sediment**
36787	**Rock Creek at mouth**	**John Day**	**Water#, Sediment**
37118	**Middle Fork John Day River at Hwy 395 RM 25.4**	**John Day**	**Water***
37135	**North Fork John Day River at RM 73.2**	**John Day**	**Water***
37201	**Prairie Creek at Enterprise SW 2nd St.**	**Grand Ronde**	**Water, Sediment**
37424	**North Powder River near Pond #1**	**Powder**	**Water, Sediment**
37719	**John Day River at Burnt Ranch & Byrd's Point**	**John Day**	**Tissue**
37720	**John Day River at Cathedral Rock & Hwy 19**	**John Day**	**Tissue**
38510	**North Fork John Day River at Hwy 395 bridge**	**John Day**	**Water, Sediment**
38633	**Grande Ronde River at Red Bridge State Park**	**Grande Ronde**	**Tissue**

Note: Grey rows indicate locations that were included in the Toxics Monitoring Network. Pound signs (#) indicate replicate water samples collected during both sampling efforts. Asterisks (*) indicate locations sampled in 2011 or 2012 only.

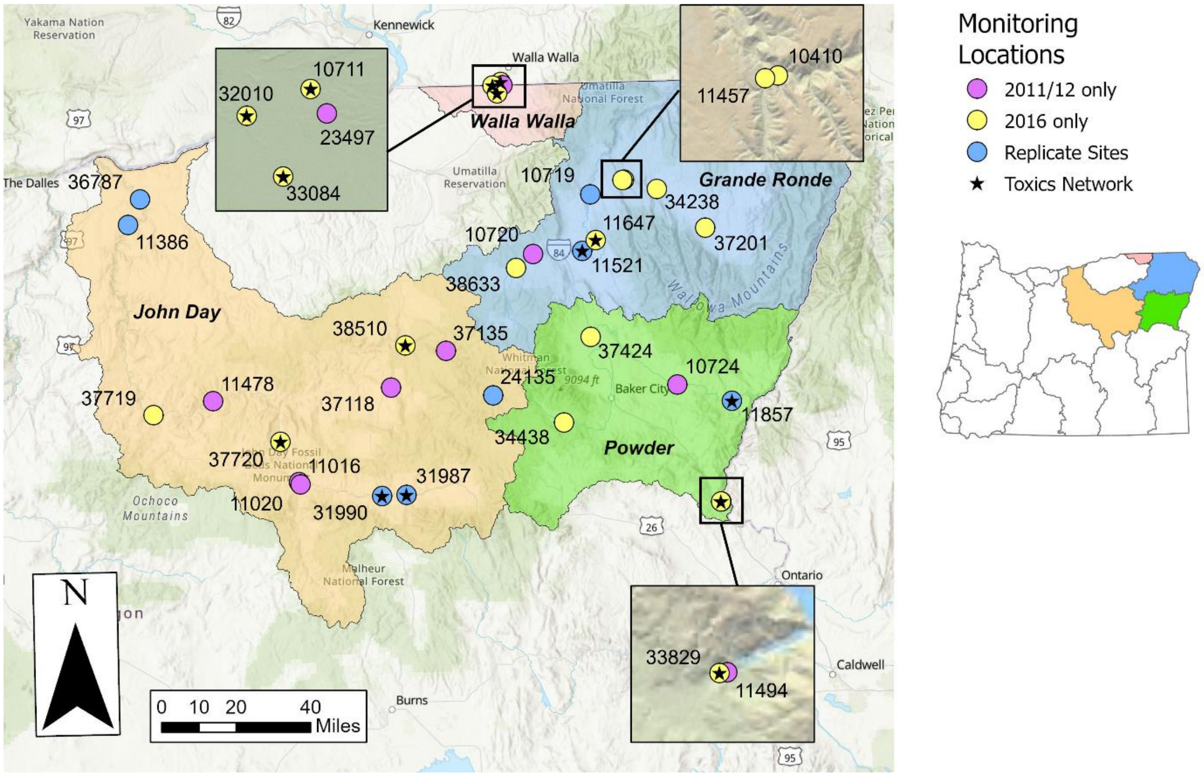

Figure 1. Map of the study area with monitoring locations by sampling effort. Visit the Water Quality Toxics Monitoring Program webpage for a map of the whole state.

Water Sample Results

Seasonality

In order to capture seasonal patterns in chemical transport and hydrologic differences, collection of water samples took place three times during each sampling year. These grab samples were collected from all monitoring locations over a weeklong period each spring (May), summer (Aug), and fall/winter (Sept-Oct). The sampling schedule was chosen to reflect the descending, low flow, and ascending phases of the hydrograph. The expectation being that the descending and ascending phases of the hydrograph capture when pesticide application may be occurring and thus sampling would capture concentrations via runoff. The low flow sampling effort is expected to capture pollutants at their most concentrated point given that less water may be flowing in the sampled water bodies during this period. As an example, Figure 2 shows the hydrograph of daily average flow at the USGS stream gauge (#14046500 – John Day River at Service Creek) near DEQ sampling location #11478 – John Day River at Service Creek. The figure is provided as an example only and is not intended to represent flow patterns at the locations sampled for this study.

Figure 3 shows the total number of chemicals detected by chemical group in each seasonal sampling event. This figure does not include chemicals not detected during the 2011/12 and 2016 sampling efforts. Detections of the four sterols are also not included in Figure 3 because detections occurred during each season. Detected concentrations do not indicate risk, only that the chemical was detected. Concentrations above applicable criteria, referred to exceedances, are specifically called out and may indicate a risk to human health or aquatic life. No clear seasonal patterns of the detected chemicals were evident when comparing the sampling efforts between years. More metals were detected during the 2016 spring sampling effort than during the 2011/12 spring sampling efforts; however, the 2016 samples were collected earlier in the season than the 2011/12 samples. The 2016 spring sampling event also potentially occurred during a period of increased flow, which may have influenced metals concentrations due to runoff from roadways and other impervious surfaces. A higher number of current-use pesticide detections occurred during the summer sampling effort in 2016 than during the summer sampling efforts in 2011/12. This may indicate a change in pesticide application timing or be a product of lower discharge at the time of sample collection in 2016 compared to 2011/12. Flows during sample collection in 2016 were 28 cfs or 70% less than flows during sample collection in 2011. Determining the potential reasons for these increases is difficult as the increases were not found consistently.

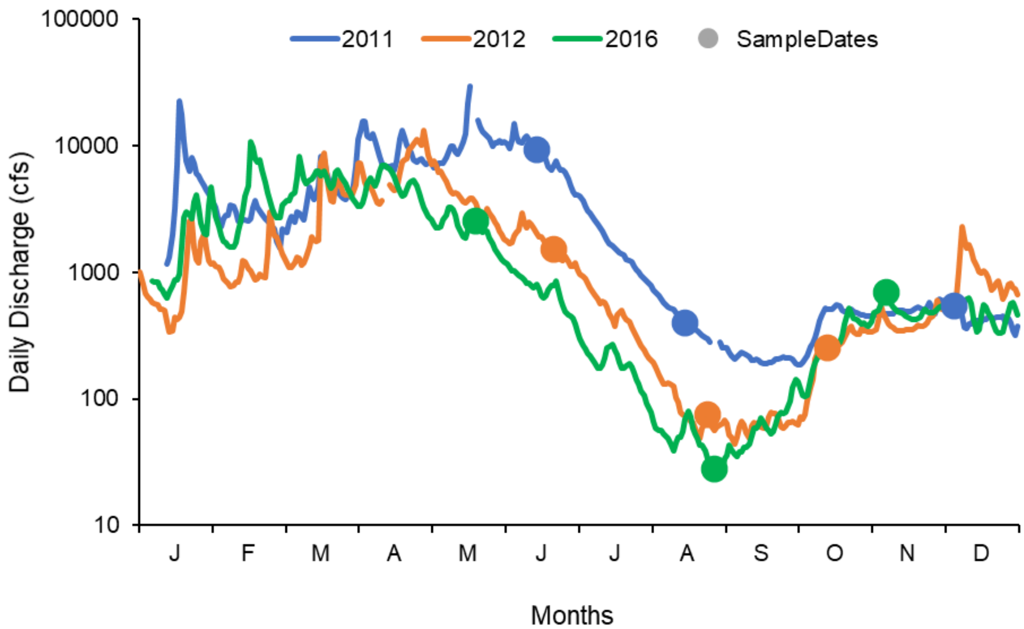

Figure 2. Hydrograph of daily average flow at the USGS stream flow gauge #14046500 – John Day River at Service Creek for the three years during which water samples were collected in the John Day River Basins. Circles indicate the sampling date for each year.

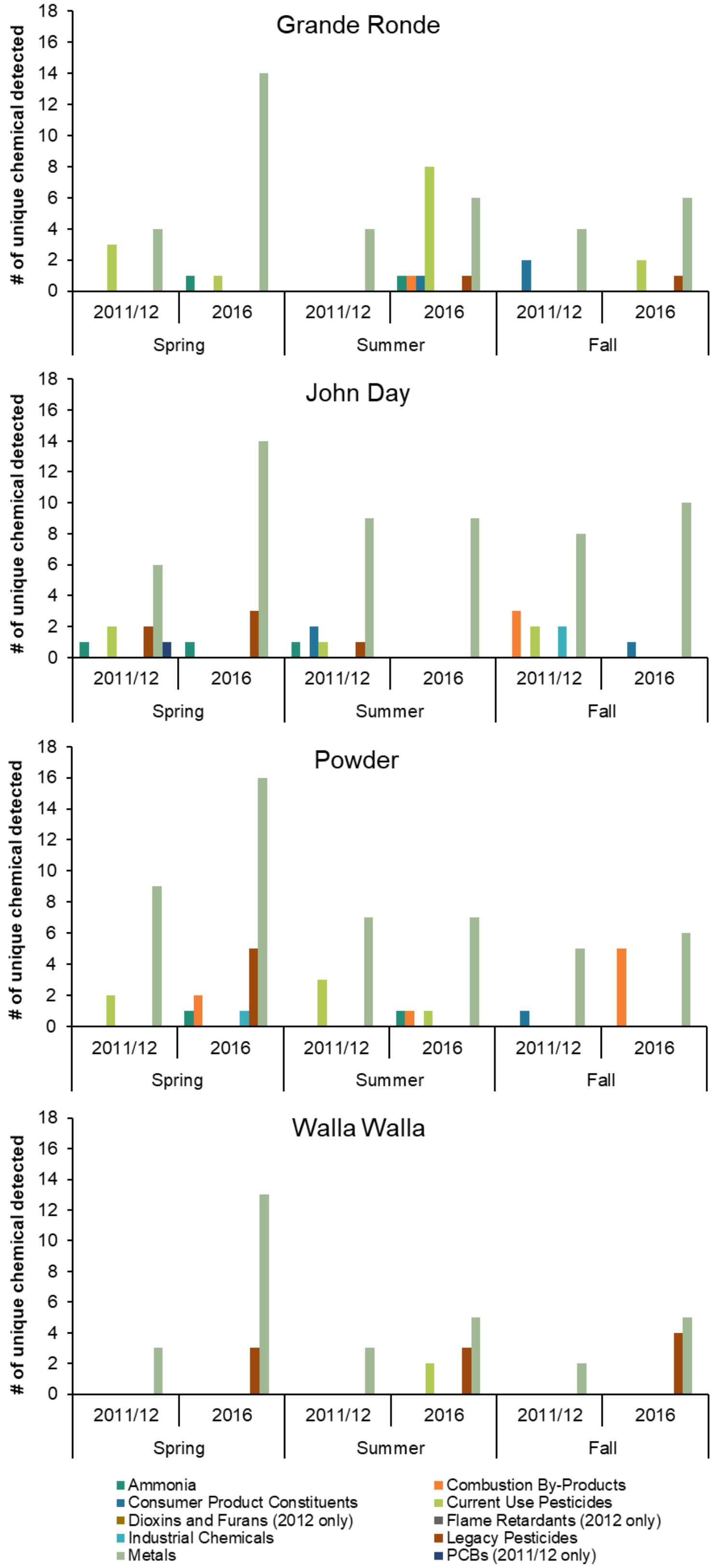

Figure 3. Seasonality of the total number of detections per chemical group in the John Day, Grande Ronde, Powder and Walla Walla River Basins by chemical group.

Seasonal samples collected during the 2016 effort contained an average of 26 total chemicals compared to an average of 17 total chemicals in 2011/12. The only analytical method used in 2016 that was not used in 2011/12 was for glyphosate (e.g., Roundup®) and its breakdown product aminomethylphosphonic acid (AMPA). These two chemicals were only detected once each in 2016. In 2011/12, DEQ ran two methods for current-use and legacy pesticides concurrently to validate an updated analytical method with lower detection limits. This updated method was adopted prior to the 2016 sampling efforts but did not influence differences in detection between the years because of its use in 2011/12.

Metals

This group includes all metals for which Oregon has existing water quality criteria. Metals can occur naturally or may be enriched or introduced by human activities. There are 16 metals included in this chemical group. Aluminum was added for the analysis of the 2016 samples, but all other metals were included in the 2011/12 sampling effort. Due to lab capacity, inorganic arsenic analysis was performed only at sites where total arsenic was at least half the inorganic arsenic criterion.

At the Burnt River location upstream of Huntington WWTP (#33829) in the Powder Basin, 15 metals were detected in water samples. This was the highest number of metals detected across all basins in this study and included five metals in exceedance of criteria. Metal concentrations also exceeded applicable criteria at three other locations in 2016 (Table 2). While this report recognizes exceedances of applicable criteria, not all metals listed in Table 2 are identified as impaired and needing a TMDL in the 303(d) list, which DEQ must report to EPA under the Clean Water Act. Requirements for listing waterbodies are outlined in the 2022 Assessment Methodology document (DEQ 2022). If a waterbody is impaired and in need of a TMDL, then a source assessment is likely to occur. At this stage, no source assessment has been conducted in the Burnt River.

Table 2. Metal concentrations exceeding applicable criteria in 2016. See Appendix A for concentrations and criteria.

Station	River Basin	Metal(s) Exceeding Criteria
Grande Ronde River at Lower Cove Road	**Grande Ronde**	**Iron**
Prairie Creek at Enterprise SW 2nd Street	**Grande Ronde**	**Iron**
Powder River downstream of Hudspeth Road	**Powder**	**Inorganic arsenic**
Burnt River upstream of Huntington WWTP outfall	**Powder**	**Aluminum, Inorganic arsenic, Iron, Selenium, Thallium**

Legacy pesticides

Pesticides are a broad class of chemicals that includes insecticides, herbicides and fungicides. Legacy pesticides refer to chlorinated insecticides, such as DDT, banned in the United States. Despite the ban, legacy pesticides and associated derivatives are frequently detected in water bodies across the state. Legacy pesticides are known to sequester in sediment where physical processes (e.g., photo-degradation by sunlight) or biological processes (e.g., bacterial metabolism) break parent pesticides down into different chemicals that may be more water soluble than the parent pesticide. Many legacy pesticides are also persistent, bioaccumulative and toxic. This means that the chemicals are resistant to degradation, can be stored in the bodies of living things, like fish or macroinvertebrates, and can be detrimental to the health of living things by increasing cancer risk or creating developmental problems.

Analysis of this chemical group included 32 chemicals in 2016. The list has remained largely the same since 2011. See Appendix B for a full analyte list. The highest number of unique chemicals detected (five) occurred again at the Burnt River upstream of Huntington WWTP location (#33829). Three of these detections exceeded DEQ human health criteria (4,4'-DDD, 4,4'-DDE, 4,4'-DDT) and contributed to total DDT exceeding the DEQ freshwater aquatic life chronic criterion. Exceedances of criteria do not always result in an impaired water designation under the Clean Water Act, as is the case for the concentrations detected in this section of the Burnt River (DEQ 2022).

Exceedances of DDT and its isomers or total DDT criteria occurred at four other locations across all basins. Dieldrin also exceeded its DEQ human health criterion at one location in the John Day Basin, Canyon Creek at John Day City Park (#31987). At the Little Walla Walla River location in the Walla Walla Basin, alpha-chlordane was detected but does not have an established criterion; however, the concentration of total chlordane, measured as the total concentration of chlordane compounds, exceeded its DEQ human health criterion. DEQ's Pesticide Stewardship Partnership Program is active in this watershed and is working with the Walla Walla Watershed Council to address this issue.

Methoxychlor was the only legacy pesticide detected that did not exceed the applicable criterion. Methoxychlor was detected at two locations, Grande Ronde River at Hwy 82 (#10719) and Burnt River upstream of Huntington WWTP (#33829). Methoxychlor was used as a replacement for DDT but was banned from use in the US in 2003 due in part to its toxicity to fish and aquatic invertebrates (ExToxNet 1996).

Current-use pesticides

Current-use pesticides include insecticides, herbicides and fungicides currently in use in the US. Chemicals in this group can enter surface waters from aerial drift, in surface runoff from agricultural fields, forests, urban lawns, and roadside spraying, or discharges from National Pollutant Discharge Elimination System (NPDES) permittees, among other sources. The analyte list for this chemical group changed slightly between the 2011/12 and 2016 with the addition of four chemicals in 2016: glyphosate and its breakdown product, aminophosphonic acid (AMPA), metsulfuron methyl and oxyfluorfen. All four chemicals were detected in 2016. The highest number of pesticides (five) were detected at the Grande Ronde River at Peach Lane location (#11521) in the Grande Ronde Basin.

The concentration of bifenthrin was above the EPA benchmark for aquatic invertebrates at the Grande Ronde River at Peach Lane location (#11521). Bifenthrin is an insecticide in the pyrethroid family that is highly toxic to fish, small aquatic organisms (Carpenter et al. 2016) and bees. This was the only current-use pesticide detected at a concentration over benchmarks across all basins.

Combustion by-products

Combustion by-products include polycyclic aromatic hydrocarbons (PAHs) and related compounds associated with the incomplete combustion of organic matter from automobiles, fossil fuel burning, woodstoves, and cigarette smoke, for example. They may enter the waterways as a result of air deposition or stormwater run-off from impervious surfaces, such as roads and parking lots.

Detections of combustion by-products occurred in water samples at two locations across all river basins in 2016. Dibenzofuran, which was added to the analysis in 2016, was detected at the Prairie Creek at Enterprise location (#37201) in the Grande Ronde Basin, and five compounds were detected at the Burnt River upstream of Huntington WWTP location (#33829). Dibenzofuran and phenanthrene do not have established criteria, while the other detected compounds did not exceed their criteria.

Consumer product constituents including pharmaceuticals

The laboratory analyzed water samples for 29 consumer product constituents including 16 pharmaceuticals in 2016. This is up slightly from 24 compounds included in the analysis of 2011/12 samples. Two compounds in this chemical group were detected in 2016. Diphenhydramine, an antihistamine used for allergy symptoms, was detected at two locations, Grande Ronde River at Peach Lane (#11521) and Grande Ronde River at Lower Cove Road (#11647). Caffeine was detected at the Rock Creek at mouth location (#36787) in the John Day Basin. Neither compound has an established human health or aquatic life criteria.

Dioxins and furans

Dioxins and furans share a similar chemical structure, persist in the environment, bioaccumulate in organisms, and can cause harm to humans and wildlife. Chemicals in this group can be produced as by-products during the manufacture of pesticides, bleached paper manufacturing, and as well as municipal and medical waste incineration and fossil fuel combustion. Wood stoves and forest fires are also potential sources of dioxins and furans in the environment (EPA 2015).

The chemical group was included in the analysis of samples collected in 2012; however, none were detected. For this reason, samples were not analyzed for dioxins and furans in 2016.

Flame retardants (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardants added to a variety of products such as laptops, automobiles, furniture and textiles. When these chemicals are released from products, they can enter the aquatic environment through air deposition, landfill leachate, and wastewater discharges. This chemical group does not include fire suppressing foams or chemicals used to fight wildfires.

The chemical group was included in the analysis of samples collected in 2012; however, none were detected. For this reason, samples were not analyzed for flame retardants in 2016.

Polychlorinated biphenyls (PCBs)

PCBs are a class of 209 industrial chemicals historically used as electrical insulating fluid in transformers and capacitors. The manufacture and use of PCBs were banned or limited in 1979 due to their environmental persistence and toxicity to humans and wildlife. However, low levels (below 50 mg/L) in products are not regulated and PCBs can be inadvertent by-products of some manufacturing processes, such as those associated with colorants.

The chemical group was included in the analysis of samples collected in 2011/12. PCB-209 was detected at the John Day River at Clyde Holliday State Park location (#31990). This PCB does not have an established criterion; however, total PCB concentration, measured as the sum of all PCB concentrations in one sample, was over the DEQ human health criterion. Samples were not analyzed for PCBs in 2016 because of the low number of detections in 2011/12.

Industrial chemicals and ammonia

This group of analytes includes a selection of chemical intermediates used in the production of pesticides, pharmaceuticals, rubber, consumer products, among other materials. The analysis in 2016 included 21 chemicals compared to 15 in 2012 and three in 2011.

Naphthalene, a PAH, often used as a chemical precursor, was detected at the Burnt River upstream of Huntington WWTP location (#33829) and was the only industrial chemical detected in 2016. There is no established criterion for naphthalene. Two industrial chemicals (2,4-dinitrotoluene and nitrobenzene) were detected at the North Fork John Day River at river mile 73.2 location (#37135) in 2012. Both concentrations were below Oregon’s human health criteria.

Ammonia is a naturally occurring compound commonly found in organic waste products and is included as an industrial chemical because of its use in fertilizers and dyes. While ammonia can be extremely toxic to aquatic organisms, the non-toxic form, ammonium, is also naturally occurring. The toxicity is dependent on pH and temperature. As pH and temperature increase, the presence of the toxic form of ammonia also increases. DEQ measures and reports total ammonia as N, which accounts for both forms. Total ammonia detections occurred at seven locations in 2016. Based on a calculation utilizing pH and temperature to determine the amount of ammonia present, the detected concentrations at Prairie Creek at Enterprise (#37201) in the

Grande Ronde Basin and the North Powder River near Pond #1 (#37424) locations exceeded the DEQ freshwater aquatic life chronic criterion.

Plant and animal sterols

The laboratory measured four plant and animal sterols across all basins. These sterols occur naturally in the environment but also may be enriched by humans and human activities, such as wastewater sources. None of the sterols detected currently have a screening level or water quality criteria. Additional work is required to fully evaluate these data and their implications and relationship to other chemicals.

The predominant source of the two plant sterols analyzed, beta-sitosterol and stigmastanol, is terrestrial plants. Other sources of these sterols may be industrial processes (wood pulping, food oils) and modern pharmaceutical supplements. Beta-sitosterol and stigmastanol were detected at all locations. Levels varied with the lowest concentrations detected at the Clear Creek near Red Boy Mine location (#24135) in the John Day Basin and the highest concentrations detected at the Burnt River upstream of Huntington WWTP (#33829) in the Powder Basin.

Measured levels of the animal sterols (cholesterol and coprostanol) varied across the basin with the lowest concentration of cholesterol detected at the Clear Creek near Red Boy Mine location (#24135) in the John Day Basin and the lowest concentration of coprostanol at the Minam River at Minam (#11457) location in the Grande Ronde Basin. The highest concentration of cholesterol was detected at the Burnt Creek upstream of Huntington WWTP (#33829) location and the highest concentration of coprostanol at the North Powder River near Pond #1 (#37424) location. While cholesterol is ubiquitous and found in a variety of different species, coprostanol is specific to fecal matter from humans and other mammals (e.g., cattle) as it is formed during digestion of cholesterol. The ratio of coprostanol to cholesterol may be used to evaluate contamination by human sewage. Ratios measured at all sites in this study were less than one, indicating that the source of coprostanol is likely biogenic (e.g., livestock) rather than an anthropogenic (e.g., human) source.

Sediment Sample Results

The Walla Walla River at OR/WA state line (#23497) location was the only location where a sediment sample was collected during the 2011/12 sampling effort, while sediment samples were collected from 20 locations in 2016. During both sampling efforts, a single composite sample was collected from each location. A composite sediment sample consists of multiple quantities of sediment from the monitoring location combined to meet the quantity requirements. Composite samples were then freeze-dried before analysis. One sample in 2016, Prairie Creek at Enterprise (#37201), encountered an error during the freeze-drying process and the results could not be reported.

Metals

Due to the difficulty in associating concentrations of metals in animals and fish with concentrations in sediment as well as the fact that metals occur naturally in the environment, detected concentrations were compared to background concentrations instead of screening levels (DEQ 2007). These background concentrations are intended for comparison use only as they are values representing the 90th or 95th percentile of regional soil samples.

Metals were detected in sediment at every monitoring location in 2016. The analysis included 16 metals. Fifteen metals were detected at two locations across all basins, the Clear Creek near Red Boy Mine location (#24135) in the John Day Basin and the Powder River downstream of Hudspeth Road location (#34438). No fewer than 10 of the 16 metals were detected at any site in 2016. Just four of the detected metals (arsenic, cadmium, lead, and mercury) have DEQ background concentrations. Selenium also has a DEQ background concentration; however, no detectable concentrations were found. The remaining metals do not have established background concentrations despite potential for bioaccumulation.

Arsenic concentrations at the Clear Creek at Red Boy Mine location (#24135) in the John Day Basin and Powder River downstream of Hudspeth Road location (#34438) were above the background concentration. Both locations are either a former mining location or downstream of a historic mining operation. Iron concentrations at the West Prong Little Walla Walla River (#32010) and Little Walla Walla River (#33084) locations were also above the background concentration. Elevation over these background concentrations does not indicate a potential health risk to humans or aquatic life, only that the concentration detected is higher than the concentration regularly detected in sediment across the region. Concentrations above the background concentrations may indicate an anthropogenic input of the metal. None of the cadmium or mercury detections were above the regional background concentrations. Metals were not included in the analysis of the sample collected in 2011.

Legacy pesticides

The analysis of sediment samples included 30 legacy pesticides in 2016. Across all basins, 25 chemicals were detected with the highest number (21 chemicals) detected at the Little Walla Walla River location (#33084). Of the detected chemicals, three have established bioaccumulation screening levels. Total chlordane and total DDT concentrations, both measured as the sum of the detected concentrations of parent and breakdown products in a single sample, were detected above the background screening levels at every location where they were detected. This includes six locations for total chlordane and 16 locations for total DDT. The total DDT concentrations detected in the Walla Walla Basin were substantially higher than those detected in the other three basins. The highest concentration, 236040 ng/kg, was detected at the Little Walla Walla River location (#33084), while the highest concentration detected outside the Walla Walla Basin was 1956 ng/kg at the John Day River at Clyde Holliday State Park location (#31990). Total DDT concentrations in water samples collected at the same locations across the Walla Walla Basin only marginally reflected the concentrations detected in the sediment samples (Figure 4). The impact ratio for total DDT concentrations at the West Prong Little Walla Walla River location (#32010) was nearly 2000 times higher in the sediment sample than in the water sample. While the impact ratio in the sediment sample at the Little Walla Walla River location (#33084) was near 6000 times higher than the impact ratio detected in the water sample. Both of these locations are irrigation ditches, which likely influenced these high concentrations.

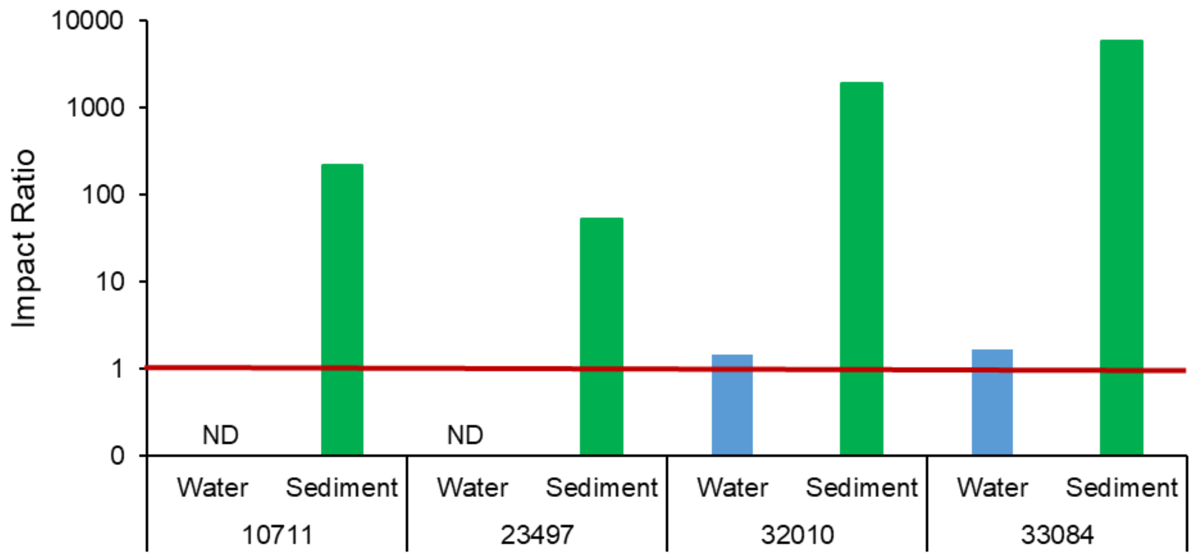

Figure 4. Impact ratios of total DDT concentrations detected in water and sediment samples collected in the Walla Walla Basin. The impact ratio is determined by dividing the concentration by the criterion. Values greater than one indicate a concentration that exceeds the criterion.

The third chemical with an established bioaccumulation screening level, hexachlorobenzene, was detected at two locations. Neither of the measured concentrations of hexachlorobenzene exceeded its screening level. The sediment bioaccumulation screening level represents the concentration at or below which a chemical would not be expected to affect the human population consuming more than 17 grams, about a tablespoon, of fish or shellfish per day from these waterways (DEQ 2007). In 2011, the analysis of the sediment sample included 25 legacy pesticides. See Appendix B for a full list of analytes. Six of these chemicals were detected, including hexachlorobenzene and five isomers or breakdown products of DDT. The total DDT concentration exceeded the bioaccumulation screening level but was substantially lower than the concentrations within the Walla Walla Basin in 2016.

Current-use pesticides

In 2015, DEQ monitored for a short list of current-use pesticides, most of which are pyrethroid pesticides because pyrethroid pesticides preferentially bind to sediment rather than dissolve into the water column. The non-pyrethroid pesticides analyzed for this study (chlorpyrifos, oxyfluorfen and trifluralin) have a similar affinity to partition to sediments as pyrethroids. These pesticides are usually sold as water soluble powders or granules under names like Lorsban®, Asana®, Goal® or Treflan®. DEQ detected chlorpyrifos at the Little Walla Walla River location

(#33084). This was the only detected current-use pesticide and it does not have a bioaccumulation screening level.

Amweg et al. (2006) identified toxicity units as a commonly used way to evaluate the toxicity of a chemical or chemicals in a sample. To calculate toxicity units, the concentration of the contaminant is first normalized to total organic carbon, then divided by the 10-day median lethal concentration (LC50) for *Hyalella azteca*, an aquatic invertebrate commonly used for acute toxicity tests. Normalization to total organic carbon is necessary in sediment samples because chemicals that partition to sediment are more likely to bind to the organic matter present. If the calculated toxicity units are greater than one, then the concentration of the chemical can be determined to be toxic. For the concentration of chlorpyrifos detected in the Little Walla Walla River, the calculated value was 0.18 toxicity units and would not be considered toxic to aquatic organisms. Current-use pesticides were not included in the analysis of the sediment sample collected in 2011.

Dioxins and furans

The analysis in 2011 included 16 compounds. Octachlorodibenzodioxin, or OCDD, was the only compound detected. The detected concentration was well below the established bioaccumulation screening level. Due to the low number of detections in 2011, dioxins and furans were not included in the analysis of sediment samples in 2016.

Polychlorinated biphenyls (PCBs)

PCBs were not included in the analysis of sediment samples in 2016. In 2011, the analysis included the full suite of 170 PCB congeners discernable by EPA analytical method 1668C. Twelve PCB congeners were detected in the sample and the total concentration exceeded the bioaccumulation screening level of 48 ng/kg. None of the other detected congeners have established screening levels.

Tissue Sample Results

Tissue sampling for this report occurred during two separate sampling efforts. In 2014, DEQ collected resident finfish, specifically Smallmouth Bass, *Micropterus dolomieu*, at two locations in the John Day Basin. These samples were collected with agency work on EPA's National Rivers and Streams Assessment. Resident fish were targeted to ensure that the fish lived in the general area of the monitoring location during their life. In 2016, DEQ chose to collect shellfish rather than finfish to capture a more accurate picture of the environment at the monitoring location given that shellfish occupy a lower trophic level than finfish. Signal crayfish, *Pacifastacus leniusculus*, were collected from four locations across the remaining basins. A duplicate sample was collected and analyzed for comparison at one location in the Walla Walla Basin. Finfish samples were analyzed as skinless fillets to match the OHA fish cleaning guidelines. Shellfish samples were shelled, homogenized and analyzed as whole-body samples. Table 3 provides information on the individuals included in each sample.

Table 3. Tissue sample composite information.

Station	Species	# individuals composited	Length / weight (mm / g)
Grande Ronde River at Peach Lane	Signal Crayfish	8	N/R
Grande Ronde River at Red Bridge State Park	Signal Crayfish	10	N/R
John Day River at Burnt Ranch and Byrd's Point	Smallmouth Bass	4	285/290, 265/210, 310/370, 295/310
John Day River at Cathedral Rock and Hwy 19	Smallmouth Bass	4	300/375, 235/165, 290/335, 245/245
Burnt River upstream of Huntington WWTP outfall	Signal Crayfish	10	N/R
Walla Walla River at Hwy 11	Signal Crayfish	7	N/R

Contaminant concentrations in this section were compared to OHA fish advisory program screening levels and DEQ acceptable tissue levels. OHA screening levels are based on a consumption rate of twenty-three 8-ounce meals per month or 17.5 grams per day (OHA 2022). The acceptable levels apply to humans consuming fish from a monitoring location. Concentrations of bioaccumulative chemicals below the acceptable tissue levels are not expected to cause adverse effects on the organisms consuming the fish (DEQ 2007). If a contaminant had more than one criterion or screening level, the lowest option was used to ensure a conservative report of exceedances across the basins.

Metals

The 2014 tissue samples were analyzed for the four metals that have established OHA screening levels or DEQ acceptable levels (arsenic, cadmium, mercury and selenium). The analysis of the 2016 tissue samples included five additional metals (chromium, cobalt, nickel, titanium and zinc) that do not have established screening levels.

Mercury was the most commonly detected metal during both sampling efforts. Concentrations in both fish samples in 2014, and four of the five crayfish samples in 2016 were above OHA's screening level. OHA has a statewide consumption advisory in place for mercury in bass (OHA 2016); however, the advisory does not extend to shellfish. Concentrations were higher in the fish samples than in the crayfish samples, which may reflect differences in diet, life cycle, or tissue type. A direct comparison cannot be made without crayfish samples from the John Day Basin. Mercury concentrations were relatively consistent across crayfish samples from the other three basins. Arsenic concentrations in all five crayfish samples in 2016 were above DEQ's acceptable tissue level. The maximum arsenic concentration was 0.33 mg/kg detected in samples from the Burnt River location upstream of the Huntington WWTP outfall (#33829). The average concentration was 0.24 mg/kg well above DEQ's acceptable tissue level for contaminants consumed by wildlife of 0.0062 mg/kg.

None of the other detected metal concentrations were above the applicable OHA screening levels.

Legacy pesticides

The list of legacy pesticides include in the analysis of the fish and crayfish samples were nearly identical. A total of 26 chemicals were included in 2016 with hexachlorobenzene the only chemical added between sampling efforts. Across all basins, 11 legacy pesticides were detected. The fish tissue sample from the John Day River at Cathedral Rock location (#37720) contained the highest number of legacy pesticide chemicals (10). The most chemicals detected in a crayfish sample (3) occurred at the Walla Walla River at Highway 11 (#10711). The most-detected legacy pesticide was 4,4'-DDE, which was detected in every sample regardless of basin or species. None of the detected chemicals were above the applicable OHA screening level.

Current-use pesticides

Few current-use pesticides show potential to sequester in tissue like legacy pesticides and thus were not included in either sampling effort.

Flame retardants (PBDEs)

Five PBDE congeners were detected in the fish samples collected in 2014. All five were occurred in the sample collected at the John Day River at Burnt Ranch and Byrd's Point location (#37719). Two were detected at the John Day River at Cathedral Rock and Hwy 10 location (#37720). Only one of the congeners has an established OHA screening level and both detected concentrations were well below the screening level. None of the crayfish samples had detectable concentrations of any of the included PBDE congeners.

Polychlorinated biphenyls (PCBs)

Twenty PCB congeners were detected in fish and crayfish samples across all basins. The highest number of detections occurred in the fish sample from the John Day River at Cathedral Rock and Hwy 10 location (#37720) with 19 different PCBs detected. In crayfish, the Grande Ronde River at Peach Lane location (#11521) had the highest number of detections with nine. None of the detected congeners have established screening values or criteria. Total PCB concentration has an OHA screening level, but all detected concentrations were well below the value.

Replicate Sampling Results

Sediment and tissue samples were not collected during the 2011/12 sampling effort, so this section only applies to water samples.

Water Sampling Results

The sampling protocols, analytical methods and detection limits largely remained the same between the two sampling efforts. In 2016, water samples were not analyzed for dioxins and furans, flame retardants, and PCBs, while glyphosate and aluminum, which were not analyzed in 2011, were added to the 2016 analysis. Replicate samples were collected at two locations in the Grande Ronde Basin, five locations in the John Day Basin, and one location in the Powder Basin. No replicate samples were collected in the Walla Walla Basin. Generally, the number of chemicals detected in water samples were higher across all three basins in 2016 compared to the 2011/12 sampling effort. Concentrations of chemicals detected during both sampling efforts were generally comparable with a few exceptions.

In the Grande Ronde Basin, bifenthrin, a current-use pesticide, was detected for the first time and the concentration exceeded the EPA aquatic life benchmark for aquatic invertebrates. This detection was one of five current-use pesticides detected at the Grande Ronde River at the Peach Lane location (#11521) in 2016 not detected during the initial sampling effort. Similarly in the John Day Basin, dieldrin, 4,4'-DDE and 4,4'-DDT were detected for the first time at the Canyon Creek at John Day City Park location (#31987), and the concentrations of each exceeded Oregon's human health criteria. In the Powder Basin, the concentration of iron detected at the Powder River at Snake River Road location (#11857) decreased from a value above Oregon's aquatic life criteria for freshwater in 2011 to a concentration safe for aquatic life in 2016. Appendix A contains a full comparison of concentrations and detections at replicate monitoring locations.

Summary and Recommendations

The analyte lists and analytical methods remained mostly consistent between the two sampling efforts for all four basins in this report. The main reasons for the increase in detections and exceedances that occurred in water samples between 2011/12 and 2016 are unclear, although historic mining operations and agricultural land use in the basins could have had an influence. The data from this report has been included in Oregon's Integrated Report, which DEQ submits to EPA every two years. The Integrated Report can identify waters as impaired and needing a TMDL or clean water plan.

For example, the Burnt River near Huntington is listed as impaired for inorganic arsenic and iron in the 2022 Integrated Report. These listings included the detected concentrations at Burnt River location upstream of Huntington WWTP (#33829) in 2016 and the Burnt River location at Snake River Road (#11494) sampled in 2011/12. These two sampling locations are less than 100 meters apart on either side of the WWTP outfall. Iron concentrations were over Oregon's freshwater aquatic life chronic criterion at both locations; however, the concentration detected upstream of the WWTP outfall in 2016 was nearly four times higher than the concentration detected downstream of the WWTP outfall in 2011/12.

The analysis of water samples collected across all four basins in 2016 detected 67 chemicals, eight of which were detected at concentrations above Oregon's human health criteria. These criteria are based on consumption of both water and organisms from the waterway. While some of the waterways sampled in this study provide drinking water to communities in these four basins, none of the detected chemicals exceeded the applicable drinking water-specific health standards set by EPA and others (i.e., Maximum Contaminant Levels or Health-Based Screening Levels.

Sediment samples collected in 2016 contained four chemicals (arsenic, total chlordane, total DDT and total PCBs) at concentrations above bioaccumulation screening levels or background concentrations. This accounts for 7% of the chemicals included in the analysis of the samples. Most of the chemicals were not detected or were detected at concentrations below applicable bioaccumulation screening levels. The high concentrations of total DDT detected in the Walla Walla Basin indicate that while the pesticide was banned from use in 1970 it is persistent in or still entering the river in some form and is a concern.

Across all four basins and regardless of tissue type, mercury was the only chemical that posed a potential risk to human health in sampled tissues. OHA has a statewide fish advisory and consumption guideline for mercury in place. This advisory does not specifically include crayfish; however, based on these data, consumption should be limited to less than the twenty-three 8-ounce meals per month used to calculate the OHA screening level. Further sampling in these basins may provide more insight into mercury concentrations and potential risk.

Eleven of the monitoring locations included in this study were selected for inclusion in the toxics monitoring network. Inclusion in the network should help create a clear picture of the influence of toxic chemicals at each monitoring location. Current plans are to collect water samples at these locations three times a year. Sediment and tissue sampling plans are still being developed at this time. Additional sampling may also help identify any potential trends emerging within the basin and will provide additional data for future source assessments.

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