

Prepared in cooperation with the Eugene Water & Electric Board

# **Time-Integrated Passive Sampling as a Complement to Conventional Point-in-Time Sampling for Investigating Drinking-Water Quality, McKenzie River Basin, Oregon, 2007 and 2010–11**

Scientific Investigations Report 2013–5215



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By Kathleen A. McCarthy and David A. Alvarez

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## Conversion Factors, Datums, and Abbreviations

SI to Inch/Pound

Multiply	By	To obtain
Length		
micrometer ( $\mu\text{m}$ )	0.0000397	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square centimeter ( $\text{cm}^2$ )	0.1550	square inch ( $\text{in}^2$ )
square kilometer ( $\text{km}^2$ )	0.3861	square mile ( $\text{mi}^2$ )
Flow rate		
cubic meter per second ( $\text{m}^3/\text{s}$ )	35.31	cubic foot per second ( $\text{ft}^3/\text{s}$ )

Temperature in degrees Celsius ( $^{\circ}\text{C}$ ) may be converted to degrees Fahrenheit ( $^{\circ}\text{F}$ ) as follows:

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

Concentrations of chemical constituents in water are given in nanograms per liter (ng/L) or picograms per liter (pg/L).

### Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

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

### Abbreviations

AgC	agricultural chemical
AIC	anthropogenic indicator compound
CERC	Columbia Environmental Research Center
D/F	dioxin and furan
DEHP	diethylhexylphthalate
DEP	diethyl phthalate
GC/MS	gas chromatograph/mass spectrometer
HCB	hexachlorobenzene
MDL	method detection limit
MQL	method quantitation limit
OHC	organohalogen compound
PAH	polycyclic aromatic hydrocarbon
PCA	pentachloronanisole
PCB	polychlorinated biphenyl
PDBE	polybrominated diphenyl ether
POCIS	polar organic chemical integrative sampler
QC	quality control
SEC	size-exclusion chromatography
SPMD	semipermeable membrane device
WWTP	wastewater treatment plant
YES	yeast estrogen screen

# Time-Integrated Passive Sampling as a Complement to Conventional Point-in-Time Sampling for Investigating Drinking-Water Quality, McKenzie River Basin, Oregon, 2007 and 2010–11

By Kathleen A. McCarthy and David A. Alvarez

## Abstract

The Eugene Water & Electric Board (EWEB) supplies drinking water to approximately 200,000 people in Eugene, Oregon. The sole source of this water is the McKenzie River, which has consistently excellent water quality relative to established drinking-water standards. To ensure that this quality is maintained as land use in the source basin changes and water demands increase, EWEB has developed a proactive management strategy that includes a combination of conventional point-in-time discrete water sampling and time-integrated passive sampling with a combination of chemical analyses and bioassays to explore water quality and identify where vulnerabilities may lie.

In this report, we present the results from six passive-sampling deployments at six sites in the basin, including the intake and outflow from the EWEB drinking-water treatment plant (DWTP). This is the first known use of passive samplers to investigate both the source and finished water of a municipal DWTP. Results indicate that low concentrations of several polycyclic aromatic hydrocarbons and organohalogen compounds are consistently present in source waters, and that many of these compounds are also present in finished drinking water. The nature and patterns of compounds detected suggest that land-surface runoff and atmospheric deposition act as ongoing sources of polycyclic aromatic hydrocarbons, some currently used pesticides, and several legacy organochlorine pesticides. Comparison of results from point-in-time and time-integrated sampling indicate that these two methods are complementary and, when used together, provide a clearer understanding of contaminant sources than either method alone.

## Introduction

The quality of drinking water in the United States has improved markedly since the implementation of the Safe Drinking Water Act by the U.S. Environmental Protection

Agency (EPA) (U.S. Environmental Protection Agency, 2012a), and regular monitoring of municipal water supplies throughout the country shows that many sources of public drinking water are of generally good quality. However, the production and use of anthropogenic substances is increasing, and conventional drinking water treatment was not designed to remove such contaminants. These circumstances, coupled with the growing sensitivity of analytical techniques, are raising awareness that many unregulated compounds are present throughout the environment (Benotti and others, 2009; Bigham, 2011; Sudhakaran and others, 2013). Additionally, there is evidence that some compounds—and especially mixtures of compounds—may be of concern at lower concentrations than previously thought (Altenburger and others, 2012; Birnbaum, 2012). Standard monitoring of drinking water may therefore be inadequate for understanding and proactively protecting drinking-water supplies in many places.

In addition to increasing chemical pressures on drinking water supplies, shifting populations, concomitant land-use changes, and changing climate are likely to put added stress on many municipal drinking-water supplies. This report presents a passive-sampler monitoring strategy designed to augment conventional monitoring for improving understanding of a municipal drinking-water supply. This is the first known application of passive-sampling technology to investigate the quality of both source and finished drinking water.

The Eugene Water & Electric Board (EWEB) supplies drinking water to approximately 200,000 people in Eugene, Oregon. The sole source of this water is the McKenzie River, a 138-km-long tributary of the Willamette River ([fig. 1](#)). Although the McKenzie River has consistently excellent water quality relative to established drinking-water standards throughout the year (Hubler and Merrick, 2012; U.S. Environmental Protection Agency, 2012b), the region is experiencing considerable growth. Therefore, EWEB has developed a proactive strategy for managing their source water. One part of this strategy is to use a combination of conventional point-in-time discrete water sampling and time-integrated passive sampling with a combination of

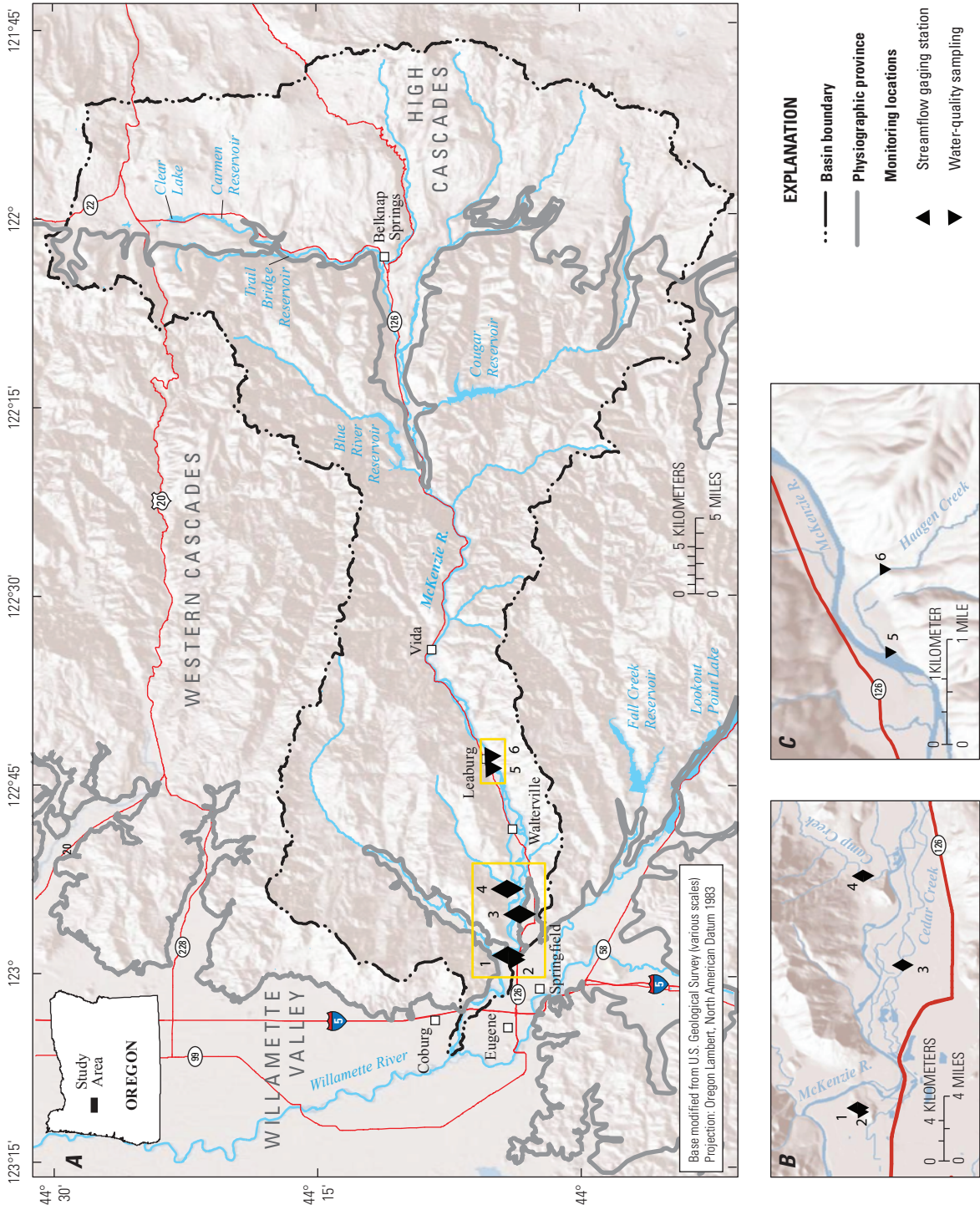


Figure 1. Study area and data-collection sites in the McKenzie River Basin, Oregon, 2007 and 2010–11.



chemical analyses and bioassays to explore water quality and identify potential vulnerabilities. Results from a conventional point-in-time water sampling study by the U.S. Geological Survey (USGS), done in cooperation with EWEB, are presented by Kelly and others (2012). This report (also a cooperative effort of USGS and EWEB) presents results from time-integrated passive sampling and the yeast estrogen screen (YES) bioassay.

## Study Area

The McKenzie River drains an area of approximately 3,400 km<sup>2</sup>. Several dams, reservoirs, and diversion canals are present in the basin for hydropower generation, flood control, and some irrigation. The upper basin is primarily timberland and includes areas of commercial forestry, where various pesticides are applied. The upper basin also contains several small communities. The lower basin supports moderate agricultural development—orchards, nurseries, row crops, and pasture. Residential density is greatest in the lower basin. The cities of Springfield and Eugene, Oregon ([fig. 1A](#)), near the mouth of the river, have a combined population of approximately 220,000 (U.S. Census Bureau, 2012).

The EWEB drinking-water treatment plant (DWTP) is located on the McKenzie River within the Springfield city limits. The treatment process includes disinfection with chlorine, coagulation and flocculation with alum, sedimentation, filtration, and pH adjustment with sodium hydroxide.

## Sampling Strategy

The sampling strategy for this study was designed to investigate the long-term quality of water entering and exiting the DWTP to complement a discreet, point-in-time monitoring program targeted largely at understanding acute conditions during storm events (Kelly and others, 2012). Time-integrated samples were collected at the intake (site 1, at USGS streamflow gaging station 14164900) and outflow (site 2, finished drinking water) from the DWTP and at four sites on three tributaries in the lower basin, upstream from the DWTP ([fig. 1B](#)). The tributary sites were selected because each subbasin includes land-use activities associated with organic contaminants. Previous monitoring indicates that the creeks are likely sources of these contaminants to the McKenzie River (Kelly and others, 2012). Additionally, Camp and Cedar Creeks are large tributaries to the lower basin and have considerable potential to affect the quality of the McKenzie River.

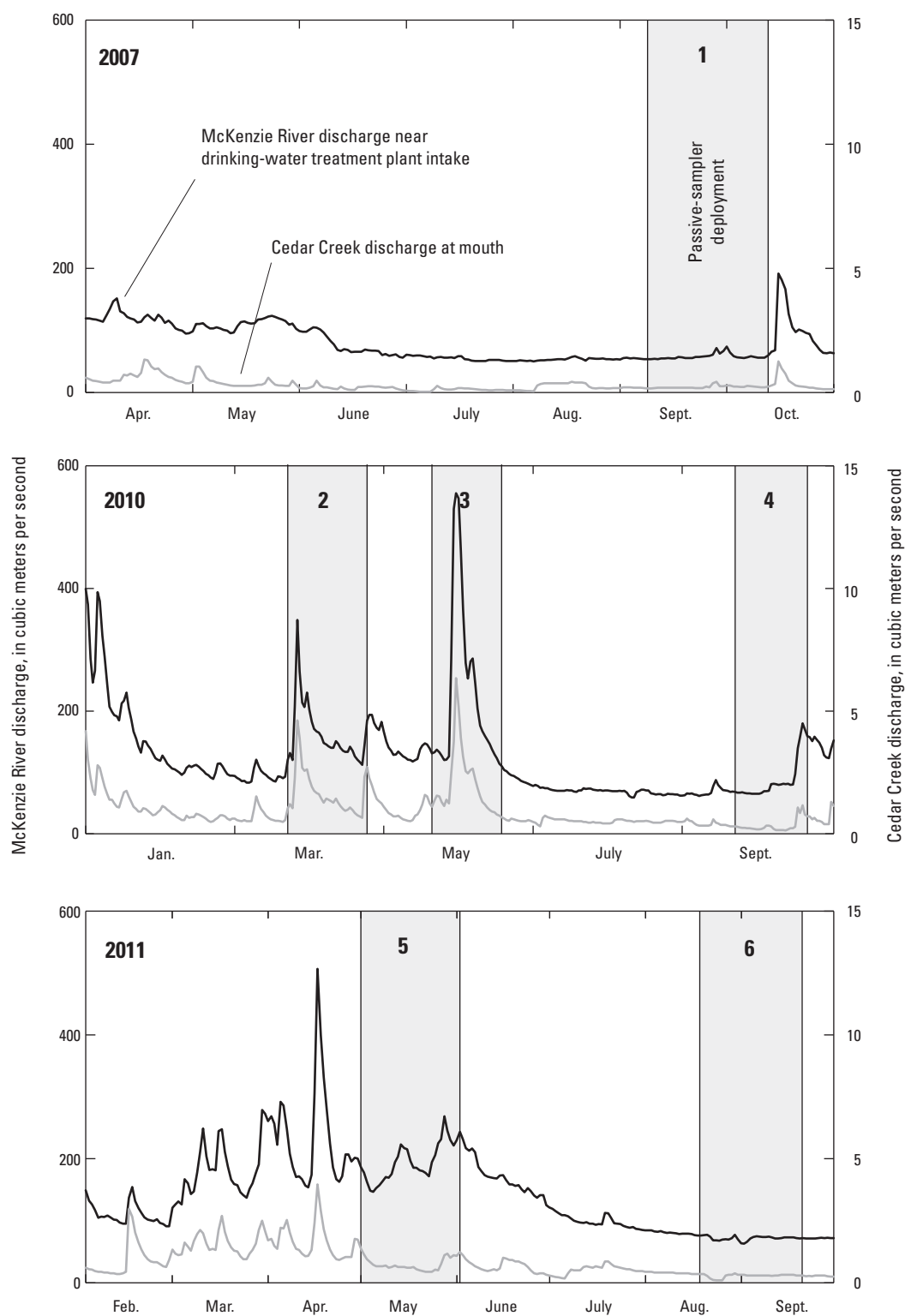
Sampling site 3 (USGS streamflow gaging station 14164700; [fig. 1B](#)) on lower Cedar Creek was selected to represent the effects of urban drainage. The headwaters of the Cedar Creek watershed are forested, but the lower part is

primarily urban residential. Most of the stormwater drainage from the eastern part of Springfield drains into Cedar Creek by way of three outfalls. During irrigation season, flows in Cedar Creek are augmented from a headgate on the McKenzie River upstream of the stormwater outfalls. Sampling site 4 (USGS streamflow gaging station 14164550; [fig. 1B](#)), near the mouth of the Camp Creek subbasin, was selected to represent the combined water-quality effects from managed forest and agriculture. The upper part of the Camp Creek watershed is predominantly forest land, some of which is sprayed periodically with pesticides. The lower altitudes of the watershed support moderate agricultural activity and some rural residences. The two sites on Haagen Creek (sites 5 and 6, [fig. 1C](#)) were selected to measure effects from septic system effluent. Most of the Haagen Creek watershed is forested, but residences are located along the lower reach of the stream. These residences use individual septic systems for wastewater disposal. The upper Haagen Creek site is upstream of these residences and the lower site is downstream of these residences.

Samples were collected during six periods that covered varying hydrologic conditions ([fig. 2](#)). The first sampling period, from mid-September to mid-October 2007, included a minor rain event after 3 months of low summer streamflow. The first sampling period in 2010 (2 in [fig. 2](#)), late March to late April, captured the first major spring runoff event. The late May to late June 2010 sampling period (3) included a large late-spring runoff peak and recession. The late September to late October 2010 sampling period (4) included the end of the seasonal low-flow period and the peak of the first moderate rain event of the autumn storm season. In 2011, the mid-April through mid-May sampling period (5) included the recession of a large spring storm event and two small rain events during the spring high-flow season. The last sampling period (6), from late August to late September 2011, captured late-summer low-flow conditions.

## Study Methods

The time-integrated (passive) sampling devices used in this study were semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCIS). The SPMD consists of a layflat low-density polyethylene tube containing a high purity lipid, triolein (460 cm<sup>2</sup> sampling surface area). SPMDs are used to sample dissolved neutral hydrophobic chemicals with log octanol-water partition coefficients ( $K_{ow}$ s) greater than 3 (Huckins and others, 2006). The POCIS contains a solid-phase extraction sorbent (Waters® Oasis® HLB) contained between two microporous sheets of polyethersulfone (0.1 µm, 41 cm<sup>2</sup> sampling surface area). The POCIS is designed to sample chemicals generally with log  $K_{ow}$ s greater than 3 (Alvarez and others, 2004). Use of the SPMD and POCIS samplers *in concert* provides a comprehensive approach to sampling trace concentrations of organic contaminants over time (Petty and others, 2004).



**Figure 2.** Discharge near the Eugene Water & Electric Board drinking-water treatment plant intake in the McKenzie River, and near the mouth of Cedar Creek, Oregon, 2007 and 2010–11.

For the 2007 deployment, POCIS and SPMDs were purchased from Environmental Sampling Technologies, Inc. (EST; St. Joseph, Missouri, <http://www.est-lab.com/index.php>) and were prepared for deployment at the U.S. Geological Survey (2013) Columbia Environmental Research Center (CERC). At CERC, SPMDs were fortified with phenanthrene-*d*<sub>10</sub>, pyrene-*d*<sub>10</sub>, and polychlorinated biphenyl (PCB) congeners 14, 29, and 50 as performance reference compounds. The use of performance reference compounds in SPMD field studies increases the accuracy of the estimates of ambient water concentrations because they correct for the site-specific variables such as water flow, temperature, and the buildup of a biofilm that can affect the rates at which chemicals are sampled (Huckins and others, 2006). For the 2010 and 2011 studies, the SPMDs and POCIS were obtained from CERC.

In the field, samplers were deployed in duplicate in protective canisters and left in place for approximately 1 month. At the DWTP intake and outflow, canisters were deployed in covered, flow-through tanks inside the DWTP. The stainless steel tanks (1.7-m long, 0.6-m wide, and 0.5-m deep) were designed and installed specifically for deploying passive samplers. At the tributary sites, canisters were deployed near the center of each stream. At each site, field blanks were exposed during both deployment and retrieval to account for potential contamination resulting from handling and exposure to the atmosphere during field operations. SPMDs and POCIS were shipped from the field on ice to CERC. At CERC, samplers were stored at less than -20°C until processing.

## Semipermeable Membrane Devices

SPMD extracts were analyzed for select polycyclic aromatic hydrocarbons (PAHs), organohalogen compounds (OHCs) including halogenated pesticides (HPs), polybrominated diphenyl ether (PBDE) congeners, total PCBs, and dioxins and furans (D/Fs).

Targeted chemicals were recovered from the SPMDs using the standard two-step dialysis into hexane. Dialysates were reduced in volume using rotary evaporation and high-purity nitrogen blowdown prior to fractionation using size-exclusion chromatography (SEC) to isolate the target chemicals from potential interferences. SPMD dialysates designated for PAHs underwent additional cleanup using a reactive tri-adsorbent gravity-flow chromatography followed by analysis using a gas chromatograph/mass spectrometer (GC/MS) in selected ion mode. SPMD dialysates designated for the analysis of OHCs were cleaned up using a gravity flow Florisil® chromatography column following SEC. ("Cleanup" is the process by which the target analyte is separated from nontarget molecules.) After Florisil, the samples were fractionated using neutral silica gel to separate the HPs and PBDEs from the PCBs. Analysis was performed using a gas chromatograph with an electron capture detector. SPMD dialysates designated for the analysis of D/Fs were cleaned

up using a reactive silica gel column prior to SEC. Following SEC, the D/Fs were isolated from potentially interfering chemicals, including PCBs, using porous graphitic carbon followed by fractionation on a basic alumina column. Analyses were performed using high resolution GC/MS (Gale, 2007).

## Polar Organic Chemical Integrative Samplers

POCIS extracts were analyzed for selected agricultural chemicals (AgCs), anthropogenic indicator compounds (AICs), pharmaceuticals, hormones, and relative estrogenicity (table 1). Detailed descriptions of processing methods have been reported in Alvarez and others (2008); McCarthy and others (2009); and Alvarez (2010).

Extraction solvents for the POCIS were selected on the basis of the targeted analytes. POCIS selected for the analysis of AICs were extracted with 80:20 methylene chloride:methyl-*tert*-butyl ether as this solvent mixture can be evaporated gently to prevent losses of some of the more volatile AICs. The remaining POCIS were extracted with methanol. All extracts were reduced in volume using rotary evaporation and high-purity nitrogen blowdown.

POCIS extracts selected for AgCs were cleaned up using a Florisil gravity-flow chromatography column followed by analysis using a GC/MS in selected ion mode (Alvarez and others, 2008). For the AICs, no cleanup of the extracts was done prior to GC/MS analysis due to the chemical diversity of this suite of target analytes.

Pharmaceuticals were measured in POCIS extracts using liquid chromatography/mass spectrometry (Furlong and others, 2008). Biogenic and synthetic hormones were analyzed in POCIS extracts using GC-tandem MS (Foreman and others, 2012). Total estrogenicity screening was performed on POCIS extracts using the *in vitro* yeast estrogen screen (YES). The YES provides a measure of the potential for a chemical or chemical mixture to mimic the natural estrogen, 17β-estradiol. This occurs through the reaction of estrogens and estrogen-mimics binding with an estrogen receptor on a yeast cell (Alvarez and others, 2008).

## Estimation of Time-Weighted Average Water Concentrations

The estimation of time-weighted average water concentrations of chemicals sequestered by the SPMD and POCIS requires knowledge of the sampling rate for each chemical along with the sampling duration. Using previously developed models (including online calculators) to calculate water concentrations from SPMD data (Huckins and others, 2006; Alvarez, 2010), data from the analysis of the performance reference compounds added to the SPMDs, and experimentally derived or theoretically estimated sampling rates, the bioavailable (by way of respiration from the dissolved phase) concentrations of targeted chemicals in the SPMD and POCIS can be estimated.

**Table 1.** Number of analytes detected in at least one replicate sample collected from the McKenzie River Basin, Oregon, 2007 and 2010–11.

[Total numbers of target analytes are shown in parentheses. **PAH:** polycyclic aromatic hydrocarbons measured by semipermeable membrane devices (SPMDs). **OHC:** organohalogen compounds (chlorinated pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers) measured by SPMDs. **A-I Chems:** anthropogenic indicator compounds measured by polar organic chemical integrative samplers (POCIS). **Ag Chems:** agricultural chemicals sampled by POCIS (includes both “ag chemicals” and “herbicides” analyte groups). **D/F:** dioxin and furan residues sampled by SPMDs. **Ho:** hormone residues sampled by POCIS. **Ph:** pharmaceutical residues sampled by POCIS. **Abbreviation:** EWEB, Eugene Water & Electric Board; –, no analysis]

Sampling period	EWEB drinking-water treatment plant intake (site 1)						
	PAH	OHC	A-I Chems	Ag Chems	D/F	Ho	Ph
1	(34)	(39)	(58)	(35)	—	—	—
	3	7	3	1	—	—	—
	(34)	(37)	(61)	—	—	—	—
2	8	13	0	—	—	—	—
3	6	4	2	—	—	—	—
4	7	26	2	—	—	—	—
5	(34)	(48)	(53)	(36)	(16)	(20)	(42)
	9	30	4	5	1	1	2
	6	5	31	7	2	1	0

Sampling period	EWEB drinking-water treatment plant finished water (site 2)						
	PAH	OHC	A-I Chems	Ag Chems	D/F	Ho	Ph
1	—	—	—	—	—	—	—
	—	—	—	—	—	—	—
	(34)	(37)	(61)	—	—	—	—
2	14	11	0	—	—	—	—
3	5	4	1	—	—	—	—
4	11	15	3	—	—	—	—
5	(34)	(48)	(53)	(36)	(16)	(20)	(42)
	3	13	7	1	1	1	1
	6	4	14	7	1	0	1

Sampling period	Cedar Creek (site 3)				Camp Creek (site 4)			
	PAH	OHC	A-I Chems	Ag Chems	PAH	OHC	A-I Chems	Ag Chems
1	(34)	(39)	(58)	(35)	(34)	(39)	(58)	(35)
	7	12	1	0	5	12	1	0
	(34)	(37)	(61)	—	(34)	(37)	(61)	—
2	—	—	—	—	—	—	—	—
3	11	15	2	—	16	26	0	—
4	—	—	—	—	—	—	—	—
5	(34)	(48)	—	(36)	(34)	(48)	—	(36)
	11	13	—	1	1	4	—	18
	6	5	10	—	1	4	—	0

**Table 1.** Number of analytes detected in at least one replicate sample collected from the McKenzie River Basin, Oregon, 2007 and 2010–11.—Continued

[Total numbers of target analytes are shown in parentheses. **PAH:** polycyclic aromatic hydrocarbons measured by semipermeable membrane devices (SPMDs). **OHC:** organohalogen compounds (chlorinated pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers) measured by SPMDs. **A-I Chems:** anthropogenic indicator compounds measured by polar organic chemical integrative samplers (POCIS). **Ag Chems:** agricultural chemicals sampled by POCIS (includes both “ag chemicals” and “herbicides” analyte groups). **D/F:** dioxin and furan residues sampled by SPMDs. **Ho:** hormone residues sampled by POCIS. **Ph:** pharmaceutical residues sampled by POCIS. **Abbreviation:** EWEB, Eugene Water & Electric Board; –, no analysis]

Sampling period	Lower Haagen Creek (site 5)			Upper Haagen Creek (site 6)		
	PAH	OHC	A-I chems	PAH	OHC	A-I chems
1	–	–	–	–	–	–
	(34)	(37)	(61)	(34)	(37)	(61)
2	13	21	1	4	19	0
3	18	25	2	18	19	3
4	–	–	–	–	–	–
	–	–	–	–	–	–
5	–	–	–	–	–	–
6	–	–	–	–	–	–

## Quality Control

Quality control (QC) samples for the SPMDs and POCIS consisted of fabrication blanks and field blanks intended to determine the presence of any contamination of the sampler matrix during construction in the laboratory, shipping, storage, and handling in the field. Laboratory controls such as reagent blanks, matrix blanks, surrogate recovery, and fortified matrix recovery checks were included with every processing set. Instrument verification checks, reference standards, and positive and negative controls for the YES assay were used. Specific details on the QC samples, including chemical residues detected in the blanks and procedural recoveries, are reported in McCarthy and others (2013).

Method detection limits (MDL) and method quantitation limits (MQL) were calculated from the blanks using methods described by Keith (1991). The MDL is defined as the mean of the response in the blanks plus three times the standard deviation of the blanks. The MQL is defined as the mean of the response in the blanks plus 10 times the standard deviation of the blanks. In cases where there were no detections in the blanks, the MQL was set at the level of the lowest calibration standard for the instrument and the MDL was set at 20 percent of the MQL.

Given the very low concentrations measured during this study, agreement between replicate pairs generally is satisfactory. In some cases, however, poor correlation between replicate pairs may have resulted from the relative

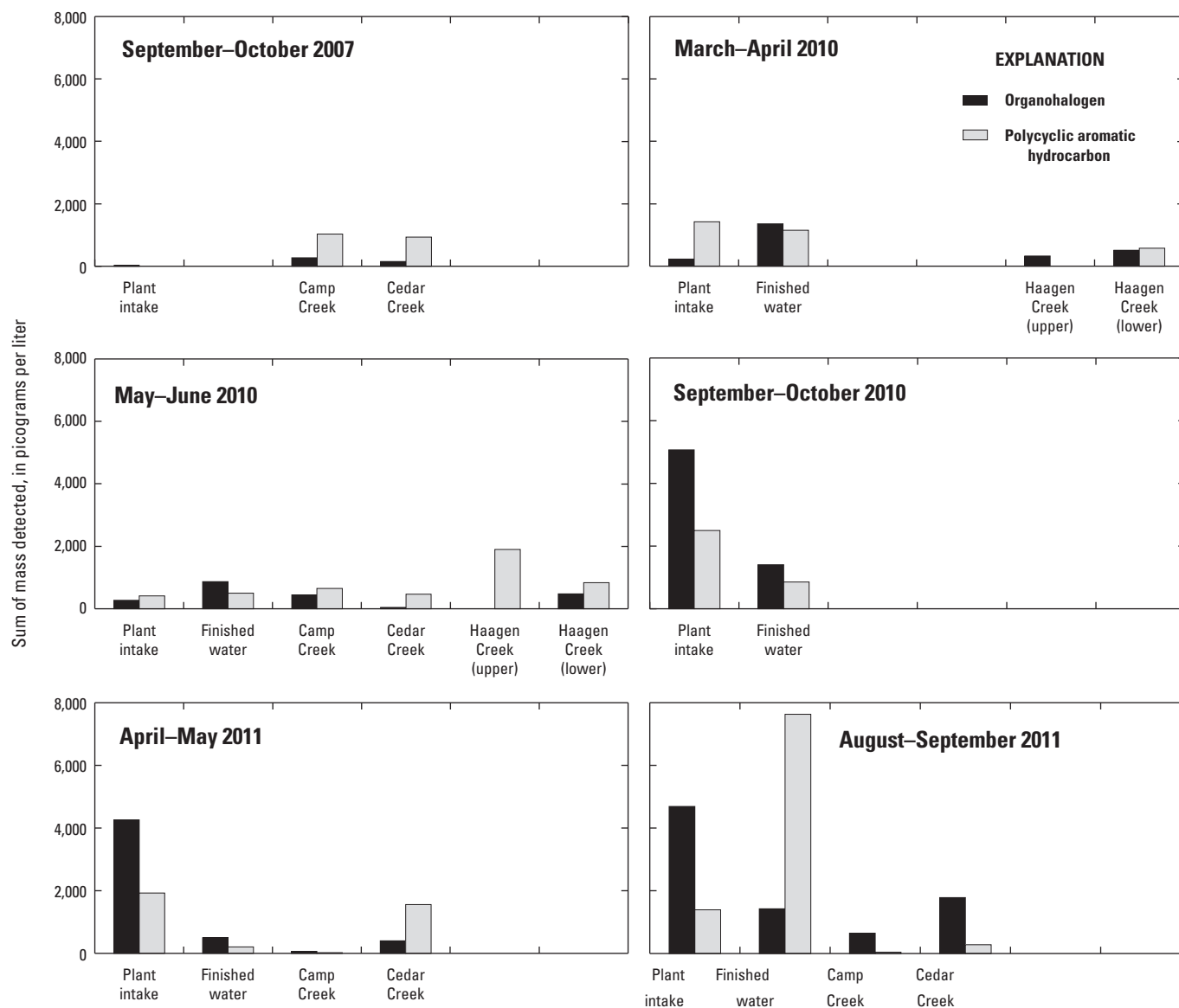
positions of the two sampler canisters. Even slight variations in absolute concentration across the flow field can become relatively important at the low concentrations measured during this study.

## Results

### Detections and Concentrations at Study Sites

During each of the six sampling periods, multiple analytes were detected at each site (table 1). However, concentrations were consistently low, generally in the picogram per liter range. Detailed analytical results from all six sampling periods are available in McCarthy and others (2013). The compound groups with the greatest number of compounds detected were the PAHs and OHCs (table 1; fig. 3). Compounds from each of these classes were detected at every site sampled during every sampling period.

Phenanthrene and fluoranthene were the most commonly detected PAHs. Common sources of PAHs such as these include engine combustion, wood smoke, and road runoff. The number of individual PAHs detected ranged from a single detection in Camp Creek during spring 2011 (sampling period 5) to 18 compounds detected at both Haagen Creek sites during late spring 2010 (sampling period 3) (table 1).



**Figure 3.** Sum of the mass of organohalogen compounds and polycyclic aromatic hydrocarbon compounds detected during each sampling period at selected sites in McKenzie River Basin, Oregon, 2007 and 2010–11. Estimated (less than method quantitation limit) and quantified values are included in sums. Sums are based on the average of two replicates; when a compound was detected in only one replicate, that single value was used. Only compounds that were targeted during all sampling periods are included; only detections that exceeded the maximum detection limit for all sampling periods are included.



Nearly all the PAH compounds detected were present at the picogram-per-liter level; however, in a few cases naphthalene, fluorene, phenanthrene, and fluoranthene were detected at concentrations greater than a nanogram per liter.

The most commonly detected OHCs were hexachlorobenzene (HCB) and pentachloroanisole (PCA). HCB was extensively used as a fungicide until 1965. Although HCB is no longer commercially produced, it is slow to degrade and is widely persistent in the environment (U.S. Environmental Protection Agency, 2012c). PCA is also ubiquitous in the environment. It is believed that PCA results from the degradation of compounds such as the pesticide and wood preservative pentachlorophenol (U.S. Department of Health and Human Services, 1993). Other OHCs detected frequently during the study include the herbicide dacthal, endosulfan sulfate (degradation product of the insecticide endosulfan, which is currently being phased out by the EPA), and the legacy insecticides chlordane, heptachlor, and p,p'-DDT as well as the DDT metabolites p,p'-DDE and o,p'-DDD. Historical commercial forestry practices in the basin are a likely source of some legacy insecticides (Moore and Loper, 1980).

Only a few AICs were detected during most sampling periods. These compounds are typically associated with discharge from wastewater treatment plants (WWTPs) and leaking septic systems, and there are no WWTPs upstream of the sites sampled. In Haagen Creek, where septic systems are present along the stream, septic effluent does not appear to be influencing stream water quality. Of the AICs targeted, only diethyl phthalate (DEP) and diethylhexyl phthalate (DEHP) were detected several times throughout the study. DEP and DEHP are common plasticizers and are regularly detected in the environment. Cholesterol also was detected several times, but because it is naturally present in many living organisms, its presence cannot necessarily be attributed to wastewater.

Estrogenic potential, as determined by the YES, was detected only in Cedar and Camp Creeks. In Cedar Creek, estrogenic potential was consistently detected and increased from less than 0.1 ng/L in 2007 to 0.8–1.0 ng/L during the last sampling period in 2011. During 2007 (sampling period 1), estrogenic potential was detected in Camp Creek at a level similar to Cedar Creek. During the last 2011 sampling period (6), estrogenicity in Camp Creek was detected at about one-half the level in Cedar Creek. No estrogenicity was detected in Camp Creek during the three 2010 sampling periods or during spring 2011 (sampling period 5).

By far the greatest number of AgCs were detected in Camp Creek during spring 2011 (sampling period 5) ([table 1](#)). This was the only spring sampling period when these analytes were targeted. No AgCs were detected in Camp Creek during the low-flow (late summer and autumn) deployments.

## Results from Drinking-Water Treatment Plant

In addition to phenanthrene and fluoranthene, the PAHs detected multiple times at the DWTP intake included 1- and 2-methylnaphthalene and pyrene. Fluorene and chrysene were detected at higher concentrations in finished water than at the intake during more than one sampling period. During summer 2011 (sampling period 6), PAHs (primarily phenanthrene, fluorene, and fluoranthene) in the DWTP finished water sample were detected at higher concentrations than in any other sample during the study. Construction and maintenance activities in the DWTP facility during this period may have contributed to the elevated PAH concentrations, but the source is not certain.

Of the 48 OHCs targeted for analysis over the course of the study, all but 4 (endosulfan-II, mirex, bifenthrin, and  $\lambda$ -cyhalothrin) were detected at least once at the intake to the DWTP. In addition to the OHCs, agricultural chemicals detected at the DWTP intake included the organophosphate insecticide diazinon and the herbicides metolachlor, dacthal, atrazine, triclopyr, imazapic, and 2,4-D. Pyrethroid insecticides detected at the intake included tefluthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin. Most of these herbicides and pyrethroid insecticides were targeted only during the 2011 sampling periods (5 and 6), but during those periods, their concentrations were the highest measured of the OHCs.

Caffeine was detected at the intake and in finished water during spring 2011, and again in the finished water during the late summer sampling period. Caffeine was the compound most frequently detected in the basin by Kelly and others (2012), which suggests this compound is ubiquitous. Erythromycin was also detected at the intake during spring 2011.

Octachloro-dibenzo-p-dioxin was detected in the intake and finished water during spring 2011 (sampling period 5). Octachloro-dibenzo-p-dioxin and octachlorodibenzofuran were detected at the intake, but not in finished water during late summer 2011 (sampling period 6). No other dioxin or furan congeners were detected.

The OHCs dacthal, chlorpyrifos, PCA, and PCBs, and the PAHs chrysene, fluoranthene, and phenanthrene were detected multiple times in the DWTP finished water. The concentrations of dacthal, chlorpyrifos, tefluthrin, alpha-benzenehexachloride, and PCBs were sometimes higher in finished water than at the DWTP intake, and chrysene was never detected at the intake. Additionally, the herbicides imazapic and 2,4-D, and octachloro-dibenzo-p-dioxin were each detected once in finished water.

None of the compounds detected in the DWTP finished water exceeded the EPA maximum contaminant levels (U.S. Environmental Protection Agency, 2009) ([table 2](#)).

**Table 2.** Concentrations of selected compounds measured at the Eugene Water & Electric Board drinking-water treatment plant compared with U.S. Environmental Protection Agency and Oregon Department of Environmental Quality criteria, McKenzie River Basin, Oregon, 2007 and 2010–11.

[**ODEQ criteria:** Oregon Department of Environmental Quality applies where fishing and domestic water supply are designated uses. **EPA MCL:** U.S. Environmental Protection Agency Maximum Contaminant Level. Values in bold are quantified concentrations greater than the method quantitation limit. Values in italics are estimated concentrations greater than the method detection limit (MDL), but less than the method quantitation limit. **Abbreviations:** DWTP, drinking water treatment plant; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; PCB, polychlorinated biphenyl; pg/L, picogram per liter; <, less than]

Compound	Environmental quality criteria					
	ODEQ criteria (pg/L)		EPA MCL (pg/L)			
Hexachlorobenzene	29		1,000,000			
Heptachlor	8		400,000			
Heptachlor Epoxide	4		200,000			
p,p'-DDE	22		no MCL			
p,p'-DDD	31		no MCL			
Total PCBs	6		500,000			

Compound	March 26–April 28, 2010						May 25–June 23, 2010					
	MDL (pg/L)	MQL (pg/L)	DWTP				MDL (pg/L)	MQL (pg/L)	DWTP			
			Intake		Finished water				Intake		Finished water	
			Replicate (pg/L)						Replicate (pg/L)			
			1	2	1	2			1	2	1	2
Hexachlorobenzene	2	8	14	<1.7	11	18	1	7	6	9	15	23
Heptachlor	2	8	<1.7	<1.7	5.5	9.1	1	7	17	28	20	29
Heptachlor Epoxide	20	60	<20	<20	25	35	16	64	<16	<16	<16	<16
p,p'-DDE	55	80	120	<55	<55	<55	18	100	61	88	37	63
p,p'-DDD	41	120	<41	<41	<41	<41	9	30	<8.8	<8.8	<8.8	<8.8
Total PCBs	240	2,100	430	<240	500	750	140	1,800	220	540	730	1,000

Compound	September 28–October 28, 2010						April 20–May 18, 2011					
	MDL (pg/L)	MQL (pg/L)	DWTP				MDL (pg/L)	MQL (pg/L)	DWTP			
			Intake		Finished water				Intake		Finished water	
			Replicate (pg/L)						Replicate (pg/L)			
			1	2	1	2			1	2	1	2
Hexachlorobenzene	39	60	<39	220	<39	41	2	9	14	12	13	11
Heptachlor	58	96	<58	250	<58	<58	8	15	10	13	<8.1	<8.1
Heptachlor Epoxide	21	28	23	110	27	61	31	45	55	63	<31	<31
p,p'-DDE	110	130	107	720	<110	41	17	36	50	39	32	29
p,p'-DDD	2	12	40	<2.4	22	42	2	9	4	5	<2.2	<2.2
Total PCBs	150	3,000	210	1,100	250	530	440	2,200	<440	<440	<440	<440

Compound	August 24–September 22, 2011					
	MDL (pg/L)	MQL (pg/L)	DWTP			
			Intake		Finished water	
			Replicate (pg/L)			
			1	2	1	2
Hexachlorobenzene	2	9	20	12	10	8
Heptachlor	53	120	61	54	<53	<53
Heptachlor Epoxide	290	700	<290	330	<290	<290
p,p'-DDE	84	230	<84	99	<84	<84
p,p'-DDD	2	9	<1.8	61	<1.8	<1.8
Total PCBs	440	2,200	<440	<440	<440	<440



However, in 2011, the EPA approved new human-health water-quality criteria developed by the Oregon Department of Environmental Quality (Oregon Department of Environmental Quality, 2011)—among the strictest criteria in the nation. The new ODEQ human-health criteria are based on high fish ingestion rates and apply to waters that serve as a source of fish and water; therefore, these criteria are not directly relevant for assessing EWEB drinking-water quality. Prior to the adoption of these new criteria, six HOCs were detected in the DWTP finished water at concentrations that would exceed these criteria (table 2). In most cases, the concentrations exceeding the criteria were less than method quantitation limits and were therefore estimated concentrations. In three cases, the exceedances occurred in only one of the two sample replicates. In only one case—heptachlor measured during the May–June 2010 deployment—were quantified exceedances measured in both sample replicates.

## Discussion

Because the sites sampled, the specific analytes targeted, and method detection and quantitation limits were not always consistent among sampling periods, general qualitative observations are discussed here rather than rigorous quantitative comparisons of the results from different sites and different sampling periods.

### Possible Sources of Contaminants

Several compounds were detected at all sites throughout the study, but concentrations of individual compounds were generally at the picogram-per-liter level, with a few detections at the nanogram-per-liter level. Both PAHs and OHCs were widely present and detected repeatedly. In addition to local sources, such as automobile combustion, wood burning, and runoff from forests, agricultural lands, roadways and residential areas, these compounds are known to be widely dispersed in the environment and can be transported over considerable distances in the atmosphere (Czuczwa and Hites, 1986; Hites, 2004; Shen and others, 2006; Zhang and Tao, 2009; Basis and Samara, 2012; Halse and others, 2012). Therefore, diffuse, ongoing pollution from atmospheric deposition and surface runoff is a likely source of these compounds at the low, persistent concentrations measured. Of particular importance, as water travels through the DWTP, it is exposed to the atmosphere in large open-air settling basins where atmospheric deposition can occur. This may account for some of the compounds detected in the finished water samples.

At the DWTP, the total mass of OHCs detected was markedly higher during each of the last three sampling periods than during the first three sampling periods (fig. 3).

Many more individual analytes were detected during the last three sampling periods, and analytes that had been detected in the first three sampling periods often were detected at higher concentrations during the last three sampling periods. The reason for this increase is not known, but many of the compounds involved are hydrophobic and tend to be associated with soil and sediment. Possible explanations include disturbances from landslides, logging operations, agricultural practices, in-stream construction projects, or reservoir operations that exposed previously buried soil or sediment that is now acting as an additional long-term source of contaminants.

The individual compounds detected in Cedar Creek pose no recognized threat at the concentrations measured. However, estrogenic potential was detected at this site during every sampling period and increased over the course of the study from less than 0.1 ng/L during the first sampling period to 1 ng/L during the last sampling period. This finding indicates that the synergistic effects of compounds present in Cedar Creek, including those not targeted during this study, produce estrogenic effects. Based on the limited number of sampling sites, these estrogenic effects may be attributable to stormwater drainage that flows into Cedar Creek from Springfield.

### Comparison of Conventional- and Passive-Sampling Results

Time-integrated passive-sampling methods, with their low detection limits, are a useful complement to conventional point-in-time sampling methods for monitoring organic contaminants. Especially when coupled with bioassays such as the YES used in this study, time-integrated samples can provide in-depth information on chronic water-quality conditions and potential biological implications (Kot and others, 2000; Vrana and others, 2005; Söderström and others, 2009; Emelogu and others, 2013).

A comparison of the results from this work with those from Kelly and others (2012) helps to illustrate the complementary nature of conventional- and passive-sampling methods. Although the dates of sample collection and the list of target analytes differed between the two studies, many analytes were common to both studies and a qualitative comparison of the two methods is worthwhile. From 2002 to 2010, Kelly and others (2012) collected conventional point-in-time samples from several sites throughout the McKenzie River Basin. Samples were collected primarily during storm events and were analyzed for various pesticides.

Prometon, diazinon, carbaryl, and chlorpyrifos were detected in conventional samples collected during storm events, but were not detected in passive samplers during the 2010 sampling periods that included storm events. This

suggests that although the average concentration over a 30-day deployment may be less than detection levels, compounds may occur in brief pulses at higher concentrations during individual storm events. During the spring 2011 passive-sampler deployment, which began during a storm recession and did not include any major storm events, several pesticides were detected by passive samplers in Camp Creek. This suggests that in Camp Creek, these compounds are not limited to short pulses during storm events. Diazinon in Camp Creek and 2,4-D and triclopyr at the DWTP intake were detected by passive- but not conventional-sampling methods; this may indicate that these compounds are present over extended periods, but at low concentrations. In contrast, triclopyr was detected in Camp and Cedar Creeks by both passive- and conventional-sampling methods, suggesting that this compound may be present at low concentrations over extended periods, as well as at somewhat higher concentrations during storm events.

Throughout their 8-year study period, Kelly and others (2012) sampled the DWTP intake 14 times and targeted more than 170 analytes. However, they detected only nine compounds at the intake, and most of these detections were at concentrations less than the laboratory reporting level. In contrast, many more compounds were consistently detected by passive samplers at the DWTP intake ([table 1](#)).

## Summary and Conclusions

Concentrations of individual compounds measured during this study were very low, generally at the nanogram-per-liter level; however, a large number of compounds were detected, and the data suggest that runoff from forested, agricultural, and residential areas, as well as atmospheric deposition, may be important sources of low-level contamination in both raw source water and finished drinking water in the McKenzie River Basin. Many compounds in current production are now dispersed widely in the environment, and legacy contaminants continue to be ubiquitous decades after their use was restricted or banned altogether. As a result, low concentrations of persistent chemicals may be present in water even in areas where there is only moderate agricultural activity, little industry, and no wastewater treatment facilities. This study has shown that time-integrated passive-sampling methods can be a useful complement to conventional point-in-time sampling methods for monitoring these contaminants. The addition of bioassays, such as the yeast estrogen screen (YES) used in this study, can provide further information on their potential biological effects.

As the U.S. Environmental Protection Agency and local authorities implement more stringent water-quality standards for toxic compounds at sub-nanogram per liter levels, passive samplers may be the most cost-effective, feasible means for monitoring these compounds.

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