

Prepared in cooperation with the Eugene Water and Electric Board

Evaluation of Passive Samplers for Long-Term Monitoring of Organic Compounds in the Untreated Drinking Water Supply for the City of Eugene, Oregon, September–October 2007

Scientific Investigations Report 2009–5178

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By Kathleen A. McCarthy, David Alvarez, Chauncey W. Anderson, Walter L. Cranor, Stephanie D. Perkins, and Vickie Schroeder

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KEN SALAZAR, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

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Conversion Factors, Datum, and Acronyms

Conversion Factors

Multiply	By	To obtain
Inch/Pound to SI		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
foot (ft)	0.3048	meter (m)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer (km)
square mile (mi ²)	2.590	square kilometer (km ²)
SI to Inch/Pound		
gram (g)	0.03527	ounce, avoirdupois (oz)
liter (L)	0.2642	gallon (gal)
liter (L)	33.81	ounce, fluid (fl. oz)
meter (m)	3.281	foot (ft)
millimeter (mm)	0.03937	inch (in.)

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

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L, parts per million), micrograms per liter (µg/L, parts per billion), nanograms per liter (ng/L, parts per trillion), or picogram per liter (pg/L, parts per quadrillion).

Datum

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Acronyms

CERC	Columbia Environmental Research Center
DEHP	Diethylhexylphthalate
EAFs	Exposure adjustment factors
EC10	Effective concentration dose of 10 percent
ECD	Electron capture detector
EEQ	Estradiol equivalent
EST	Environmental Sampling Technologies, Inc.
EWEB	Eugene Water and Electric Board
GC	Gas chromatograph
HBSLs	Health based screening levels
MDLs	Method detection limits
MQLs	Method quantification limits
MSD	Mass selective detector
PAHs	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ether
PCA	Pentachloroanisole
PCBs	Polychlorinated biphenyls
POCIS	Polar organic chemical integrative samplers
PRC	Performance reference compounds
SEC	Size exclusion chromatography
SPMDs	Semipermeable membrane devices
USGS	U.S. Geological Survey
YES	Yeast estrogen screen

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Evaluation of Passive Samplers for Long-Term Monitoring of Organic Compounds in the Untreated Drinking Water Supply for the City of Eugene, Oregon, September–October 2007

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Abstract

Two types of passive samplers, polar organic chemical integrative samplers (POCIS) and semipermeable membrane devices (SPMDs), were deployed at three sites in the McKenzie River basin during September–October 2007. The McKenzie River is the source of drinking water for the city of Eugene, Oregon, and the work presented here was designed to evaluate the use of POCIS and SMPDs as part of a long-term monitoring plan for the river. Various compounds were detected in extracts from the POCIS and SPMDs, indicating that some compounds of concern are present in the McKenzie River basin, including the intake for the drinking water plant. However, most concentrations were near the quantitation limits of the analytical methods used—generally at subnanogram per liter concentrations—and would not have been detectable with conventional water sampling and analysis methods. These results indicate that both POCIS and SPMDs are well suited to monitor organic compounds in the McKenzie River basin.

Introduction

The McKenzie River is the source of drinking water for approximately 200,000 people in the Eugene area of Oregon ([fig. 1](#)). To protect this critical resource, the Eugene Water and Electric Board (EWEB) completed a plan in August 2000 to protect the McKenzie River as the sole source of drinking water for its customers (Eugene Water and Electric Board, 2000). The overall goal of the source protection program is to “measure the balance between watershed health and human use over time and implement actions that maintain a healthy balance for production of exceptional water quality.” One component necessary to achieve this goal is monitoring water in the McKenzie River basin for the presence of anthropogenic organic contaminants.

Among the organic compounds of interest are those that may have significant ecological and(or) human-health consequences at concentrations that are orders of magnitude less than the detection limits associated with conventional water-sampling techniques. In addition, many compounds of interest may be present only during episodic events. As part of a U.S. Geological Survey (USGS)–EWEB cooperative study of water quality in the McKenzie River (U.S. Geological Survey, 2008), two types of passive samplers—polar organic chemical integrative samplers (POCIS) and semipermeable membrane devices (SPMDs)—were used to address these challenges. Both POCIS (Alvarez and others, 2004, 2007) and SPMDs (Huckins and others, 2006) are well suited to overcoming the difficulties of measuring low analyte concentrations and recording episodic analyte loading.

In order to evaluate the use of passive samplers in long-term monitoring for organic compounds in the McKenzie River basin, passive samplers were deployed at three sites in the basin for 35 days during September–October 2007. This report presents the design and results of this sampling effort.

Description of Study Area and Sampling Sites

The McKenzie River generally is considered to be a high-quality source of drinking water. The Oregon Department of Environmental Quality’s (2008) Oregon Water Quality Index rates the river’s water quality as excellent throughout the year. However, the basin includes managed forest land, agriculture, urban (residential) development, and a number of areas where septic systems are present in near stream alluvial aquifers. Each year, approximately 5–10 percent of the forest land is sprayed with chemicals (Lane Council of Governments, written commun., 2009). Agricultural activities include hazelnut orchards, blueberries, Christmas trees, peppermint, row crops, livestock, and pasturelands (Southern Willamette

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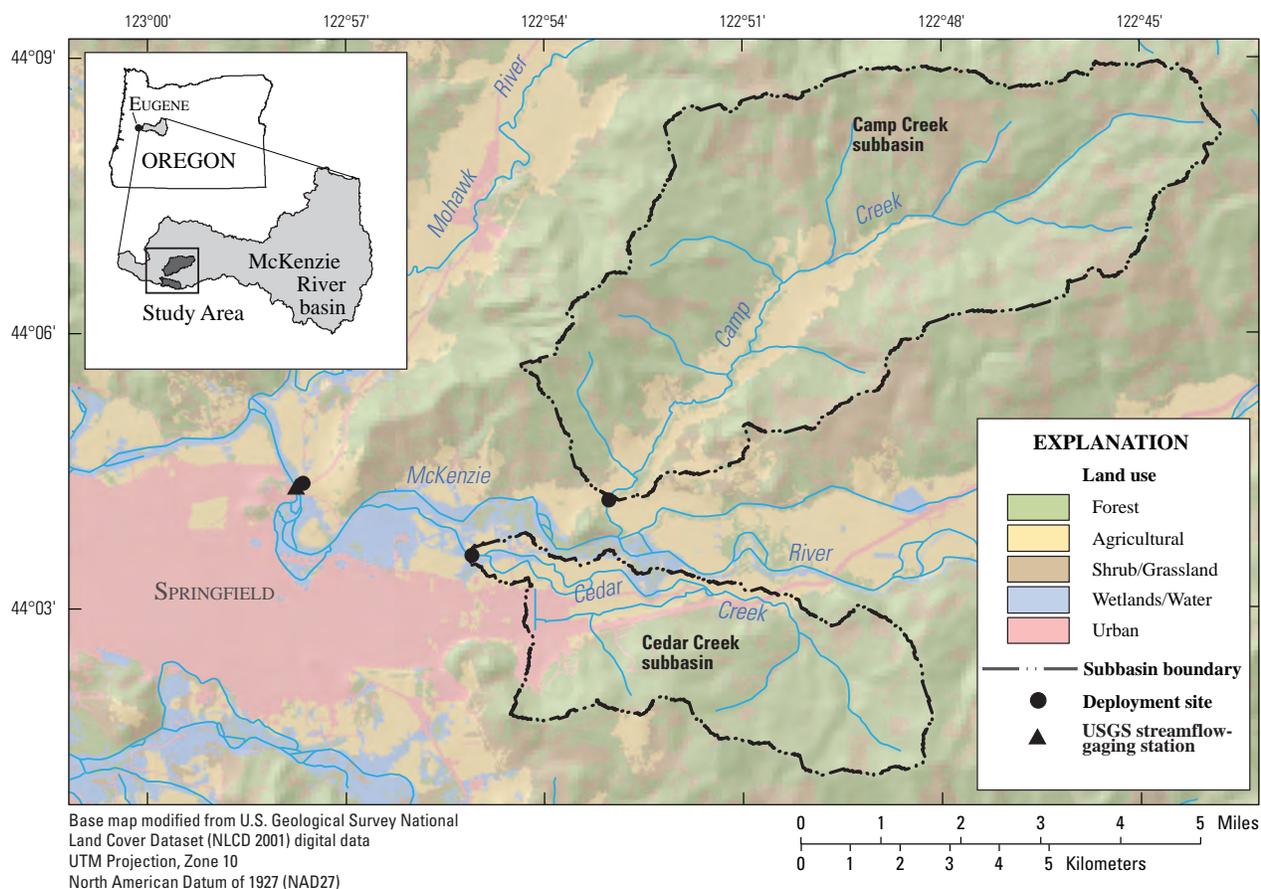


Figure 1. Locations of sites sampled using passive samplers in the McKenzie River basin, Oregon, September–October 2007.

Valley Local Advisory Committee, 2004), and chemical use associated with each of these land uses poses potential threats to the water quality in the river. During late September and early October 2007, passive samplers were deployed at three sites in the McKenzie River basin. The three sites include the inlet to EWEB’s drinking-water treatment plant and two upstream tributaries to the McKenzie River—Cedar Creek and Camp Creek (fig. 1).

The Cedar Creek and Camp Creek subbasins were selected for study because both include land-use activities that may be sources of organic contaminants to the McKenzie River. The Cedar Creek subbasin covers about 10 mi² and is approximately 60 percent forest (table 1). Less than 2 percent of the forest land in the Cedar Creek subbasin is sprayed with pesticides. Approximately 18 percent of the subbasin is used for agriculture and 15 percent is residential. The Camp Creek subbasin covers just over 26 mi² and also is approximately 60 percent forest and 18 percent agriculture. However, in contrast to the Cedar Creek subbasin, more than 10 percent of the forest land in the Camp Creek subbasin is sometimes sprayed with pesticides, and only about 2 percent of the subbasin is residential. Although there are widespread agricultural and residential uses of pesticides in both of these subbasins, the actual amounts of specific chemicals used are poorly documented.

Table 1. Land use in the Cedar Creek and Camp Creek subbasins and the McKenzie River basin, Oregon, 2008.

[Data sources: drainage area, Lane Council of Governments, written commun., 2009. Land use, 30-m 2001 National Land Cover Data, <http://www.epa.gov/mrlc/nlcd-2001.html>, accessed February 3, 2009]

Basin	Drainage area (mi ²)	Land use as a percentage of total subbasin area				
		Forest	Agriculture	Shrub and open grassland	Wetlands and open water	Urban
Cedar Creek subbasin	10.3	63	18	4.6	2.9	15
Camp Creek subbasin	26.2	61	18	20	0.01	2
McKenzie River basin	1,276	79	3.8	15	0.83	1.5

Study Methods

Field Sampling

At each of the three sites, POCIS and SPMDs were deployed in triplicate on September 11, 2007. Each sample set included 6 POCIS and 3 SPMDs. A triplicate sample set therefore consisted of 18 POCIS and 9 SPMDs. During the deployment and retrieval of samplers at each site, duplicate sets of field-blank samplers were exposed to the atmosphere to quantify sample contamination resulting from handling and exposure to the atmosphere.

The AQUASENSE-P POCIS and standard-configuration SPMDs used in this study were purchased from Environmental Sampling Technologies, Inc. (EST; St. Joseph, Missouri, <http://www.est-lab.com/index.php>). Two of the three SPMDs from each individual sample set and SPMDs from one of the field-blank sets for each site were fortified with performance reference compounds (PRCs; Huckins and others, 2006) during construction using a solution provided by U.S. Geological Survey's Columbia Environmental Research Center (CERC; Columbia, Missouri). The PRCs included the polychlorinated biphenyl (PCB) congeners PCB-14 and PCB-50, spiked at rates of 6.53 and 7.93 ng/SPMD, respectively, and the perdeuterated polycyclic aromatic hydrocarbons phenanthrene-d₁₀ and pyrene-d₁₀, spiked at rates of 457 and 524 ng/SPMD, respectively. Huckins and others (2002) provide a discussion of the theory and application of PRCs.

POCIS and SPMDs for deployment were premounted on deployment racks by the manufacturer (EST; St. Joseph, Missouri) and shipped under argon in sealed metal cans. POCIS and SPMDs were received 3 days prior to deployment and were refrigerated and then transported to the field on ice. In the field, POCIS and SPMDs were deployed in standard manufactured deployment canisters (EST; St. Joseph, Missouri).

At the EWEB drinking-water treatment plant, samplers were deployed inside a flowthrough chamber that received water directly from the plant's intake stream, prior to treatment. The chamber measured 6 ft in the direction of water flow by 1.5 ft in width by 2.0 ft in depth and was constructed of acrylic. Outflow from the chamber drained to the sewage system. At the Cedar Creek site (Cedar Creek at Saunders Road), samplers were suspended from a foot bridge on cables fitted with anchors. At the Camp Creek site (Camp Creek at Camp Creek Road Bridge), samplers were secured to metal fence posts driven into the streambed. At both stream sites, samplers were placed in the main flow channel.

One goal of this deployment was to capture water-quality information during a typical, early autumn storm-runoff period. The use of triplicate samplers and two field blanks at each site allowed for replication and allowed the option of staged retrieval. For example, if a significant rainfall event had occurred early in the deployment period, a subset of samplers could have been retrieved just after the rainfall event

and the remainder left in place for the full 35-day deployment period. Alternately, one set of samplers may have been left in place for later retrieval if a significant rainfall event had not occurred during the 35-day deployment period. A moderate rainfall event occurred during the 35-day deployment period and a staged retrieval was not necessary.

During deployments, water-temperature sensors (Onset Computer Corp., Pocasset, Massachusetts) were attached to deployment canisters, and water temperature was recorded at 10-min intervals over the entire deployment period to provide evidence that the canisters had remained submerged during the entire deployment period.

After the 35-day deployment period, POCIS and SPMDs were retrieved from the three sites on October 16, 2007, and shipped on ice to the laboratory at CERC for processing and analyses. At the laboratory, POCIS and SPMDs were stored at less than -20°C until processing began.

Laboratory Processing and Chemical Analyses

Because a staged retrieval was not necessary, only two of the three sets of samplers (referred to as A and B in tables) from each site were processed. The third set was archived by storing the passive samplers in the original shipping containers at less than -20°C.

Sequestered compounds were extracted from each POCIS and SPMD individually before designating extracts for specific processing and analysis procedures. Analyses for select agricultural pesticides and wastewater-indicator contaminants were performed on POCIS extracts along with screening for the total estrogenicity of sampled chemicals by the yeast estrogen screen (YES; Rastall and others, 2004; Alvarez and others, 2008a).

SPMDs were processed and analyzed for polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, total polychlorinated biphenyls (PCBs), the polybrominated diphenyl ether (PBDE) congeners 28, 47, 99, 100, and 153, and select wastewater-indicator chemicals.

The POCIS samples were prepared for analysis using published procedures (Alvarez and others, 2004, 2008a, 2008b). Chemicals of interest were recovered from the POCIS sorbent using 40 mL of methanol, with the exception of two POCIS from each deployment canister that were designated for wastewater-indicator chemical analysis. These two POCIS were extracted using 25 mL of an 80:20 volume-to-volume ratio of dichloromethane-to-methyl-tert-butyl ether solution. The liquid volume of each extract was reduced by rotary evaporation and filtered through 0.45 µm filter cartridges. From each deployment canister, the extracts from the two POCIS were composited into a single sample, thereby increasing the amount of chemical present in each sample to aid in detection. This resulted in separate 2-POCIS composite samples from each deployment canister for the agricultural pesticides, wastewater-indicator chemicals, and the YES assay.

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The procedures used for preparing SPMD samples for analysis were similar to previously published approaches (Petty and others, 2000; Alvarez and others, 2008a, 2008b). Briefly, the target analytes were recovered from the SPMDs by dialysis with hexane, followed by class-specific cleanup and analysis. One of the PRC-spiked SPMDs from each deployment canister was used for the analysis of PAHs; the other was used for chlorinated pesticide and total PCB measurements. The remaining SPMD from each deployment canister, which did not contain PRCs, was used for the analysis of wastewater-indicator chemicals.

Agricultural Pesticides

Details for the processing and analysis of POCIS for agricultural pesticides are reported by Alvarez and others (2008a). Briefly, the extracts were fractionated using size exclusion chromatography (SEC), followed by sample cleanup and enrichment by Florisil adsorption chromatography. Analysis was performed using an Agilent 6890 gas chromatograph (GC; Agilent Technologies, Inc., Wilmington, Delaware) coupled to a 5973N mass selective detector (MSD, Agilent Technologies, Inc., Palo Alto, California) with a HP-5MS [30 m × 0.25 mm inner diameter × 0.25 μm film thickness) capillary column (Agilent Technologies, Inc., Wilmington, Delaware). Instrumental parameters are described by Alvarez and others (2008a).

Wastewater-Indicator Chemicals

Analysis of wastewater-indicator chemicals was performed on raw POCIS extracts to maintain the integrity of such a diverse set of chemicals. SPMD dialysates required additional cleanup using SEC prior to analysis to remove matrix interferences such as co-extracted lipids and polyethylene waxes. Analyses were performed on the GC/MSD system previously described using a temperature program of injecting at 40°C, holding for 3 min, ramping up at 9°C/min to 320°C, and holding at 320°C for 3 min. Identification of the targeted chemicals was performed using full-scan mass spectrometry, and quantification was performed by selecting ions unique to each chemical. (Results of wastewater-indicator chemical analyses are presented here for POCIS extracts only. Results from SPMD extracts are available at http://or.water.usgs.gov/proj/EWEB/ww_spmd.pdf, accessed March 5, 2009.)

Yeast Estrogen Screen

The YES assay uses recombinant yeast cells transfected with the human estrogen receptor. Upon binding these cells to an estrogen or estrogen-mimicking chemical, a cascade of biochemical reactions occurs resulting in a color change that can be measured spectrophotometrically (Routledge and Sumpter, 1996; Rastall and others, 2004). POCIS extracts from each site were screened for total estrogenicity in

conjunction with a series of negative (solvent) and positive (17β-estradiol) controls (Rastall and others, 2004; Alvarez and others, 2008a). Estradiol equivalent factors (EEQ) for the samples were calculated to provide a relative measure of estrogenicity. The EEQ is an estimate of the amount of 17β-estradiol, a common natural hormone, that would be required to give a response equivalent to that of the complex mixture of chemicals sampled at each site. The measured responses were estimated at an effective concentration dose of 10 percent (EC₁₀); the weak response due to the estrogenicity of sampled chemicals made estimates at a greater dose impossible.

Polycyclic Aromatic Hydrocarbons

Following SEC, samples designated for PRCs and PAHs were processed using a tri-adsorbent column consisting of phosphoric acid silica gel, potassium hydroxide impregnated silica gel, and silica gel (Petty and others, 2000). The GC analyses for selected PAHs and PRCs were performed using the GC/MSD system previously described with the instrumental conditions as reported by Alvarez and others (2008a).

Chlorinated Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers

SPMD extracts used for the analysis of chlorinated pesticides, PCBs, and PBDEs were further enriched after SEC using a Florisil column followed by fractionation on silica gel (Petty and others, 2000). The first silica-gel fraction (SG1) contained greater than 95 percent of the total PCBs, hexachlorobenzene, heptachlor, mirex, and 40–80 percent of the p,p'-DDE when present in extracts. The second silica-gel fraction (SG2) contained the remaining 28 targeted chlorinated pesticides, less than 5 percent of the total PCBs (largely mono- and dichlorobiphenyl congeners), and the five PBDE congeners. Analysis of the silica-gel fractions were performed using a Hewlett Packard 5890 series GC equipped with an electron capture detector (ECD, Hewlett Packard, Inc., Palo Alto, California) and a DB-35MS (30 m × 0.25 mm inside diameter × 0.25 μm film thickness) capillary column (J&W Scientific, Folsom, California). Instrumental conditions for the analyses are reported in Alvarez and others (2008a).

Quality Control

Throughout the passive-sampler processing and procedural steps, a rigorous quality-control plan was used to ensure the reliability of the data obtained. In addition to the field-blank samplers, SPMD fabrication blanks were processed and analyzed to determine the presence of any contamination of the sampler matrix during construction in the laboratory and handling in the field. Matrix (fabrication and field) blanks for the passive samplers were processed and analyzed concurrently with the field deployed samplers.

Laboratory controls—such as reagent blanks, matrix blanks, surrogate recovery, and fortified matrix recovery checks—were included in the construction, deployment, and processing of the study samples. Instrument verification checks, reference standards, and positive and negative controls for the YES assay were used throughout the study. Detailed discussions on the benefits of each type of quality-control sample are reported in Huckins and others (2006) and Alvarez and others (2007).

Method detection limits (MDLs) and method quantification limits (MQLs) were estimated from low-level calibration standards as determined by the signal-to-noise ratio of the response from the instrumental analyses (Keith, 1991). The MDLs were determined as the mean plus three standard deviations of the response of a coincident peak present during instrumental analyses of laboratory and matrix blanks. The MQLs were determined as the greater of either the coincident peak mean from the analysis of laboratory and matrix blanks plus 10 standard deviations, or the concentration of the lowest-level calibration standard. In cases where no coincident peak was present, the MQL was set at the lowest-level calibration standard and the MDL was estimated to be 20 percent of the MQL. For reporting purposes, the MDLs and MQLs were expressed as the mass of chemical sequestered by a single sampler (ng/POCIS or ng/SPMD).

Throughout the passive-sampler processing and analysis steps, matrix spikes, and instrumental verification checks were used to monitor analyte recovery and chemical background contamination. Isotopically labeled surrogates of model compounds were used to allow for a rapid determination of results. A freshly prepared SPMD was fortified with ^{14}C -labeled phenanthrene (a common PAH) and processed concurrently with the remainder of the study SPMDs. A measured recovery following SEC cleanup of the ^{14}C -labeled phenanthrene of 87 percent (5.7 percent relative standard deviation, $n=2$) indicated acceptable performance of the dialysis and SEC processing steps. Recovery of chemicals processed by the SEC system were monitored using ^{14}C -labeled phenanthrene and averaged 93 percent with 1.3 percent relative standard deviation ($n=6$).

Surrogate spikes of many of the targeted chemicals were added to blank SPMDs and POCIS, in triplicate, which were then processed and analyzed concurrently with the field samples. Recoveries for most of the chemicals were within acceptable ranges and differences between replicates generally were less than 20 percent.

Estimation of Water Concentrations

The dissolved aquatic concentrations of analytes were estimated from SPMD concentrations using sampling rates and models provided by Huckins and others (2006) and site-specific exposure adjustment factors (EAFs) calculated from PRC data (Huckins and others, 2006; McCarthy, 2006, 2008).

Uptake of hydrophobic chemicals into SPMDs follows linear, curvilinear, and equilibrium phases of sampling (Huckins and others, 2006). Integrative (or linear) sampling is the predominant phase for compounds with $\log K_{ow}$ values greater than or equal to 5.0 and exposure periods of up to 1 month. During the linear-uptake phase the ambient chemical concentration (C_w) is determined by:

$$C_w = N / R_s t \quad (1)$$

where

- N is the mass of the chemical sampled by an SPMD,
- R_s is the site-specific SPMD sampling rate (volume/time), and
- t is the exposure time (time).

A key feature of the EAF is that it is relatively constant for all chemicals that have the same rate-limiting barrier to uptake, allowing PRC data to be applied to a range of chemicals. Previous data indicate that many chemicals of interest remain in the linear phase of sampling for at least 56 days (Alvarez and others, 2004, 2007); therefore, equation 1 was used to calculate estimates of dissolved aquatic concentrations.

Evaluation of Passive Samplers for Long-Term Monitoring of Organic Compounds

A period of moderate rainfall occurred during the passive sampler deployment period ([fig. 2](#)). Although this was a relatively small storm, it was preceded by an extended period of dry weather and was the first measurable runoff event of the autumn rainy season. The event produced a discernible increase in flow in the McKenzie River while the samplers were deployed ([fig. 2](#)).

Polar Organic Chemical Integrative Samplers

Chemical analyses.—The herbicide metolachlor, used for grass and broadleaf weed control in crops, was the only pesticide detected in extracts from the deployed POCIS ([table 2](#)). Metolachlor was detected in one of the samples from the treatment-plant inlet, but the detection was less than the MQL and metolachlor was not detected in the replicate sample ([table 2](#); column B).

Three wastewater-indicator chemicals were detected in deployed POCIS ([table 3](#)). Cholesterol, a sterol that is synthesized by animals and to a lesser degree by plants and fungi and is used as an emulsifying agent in cosmetics and pharmaceuticals, was quantified in one of the treatment-plant

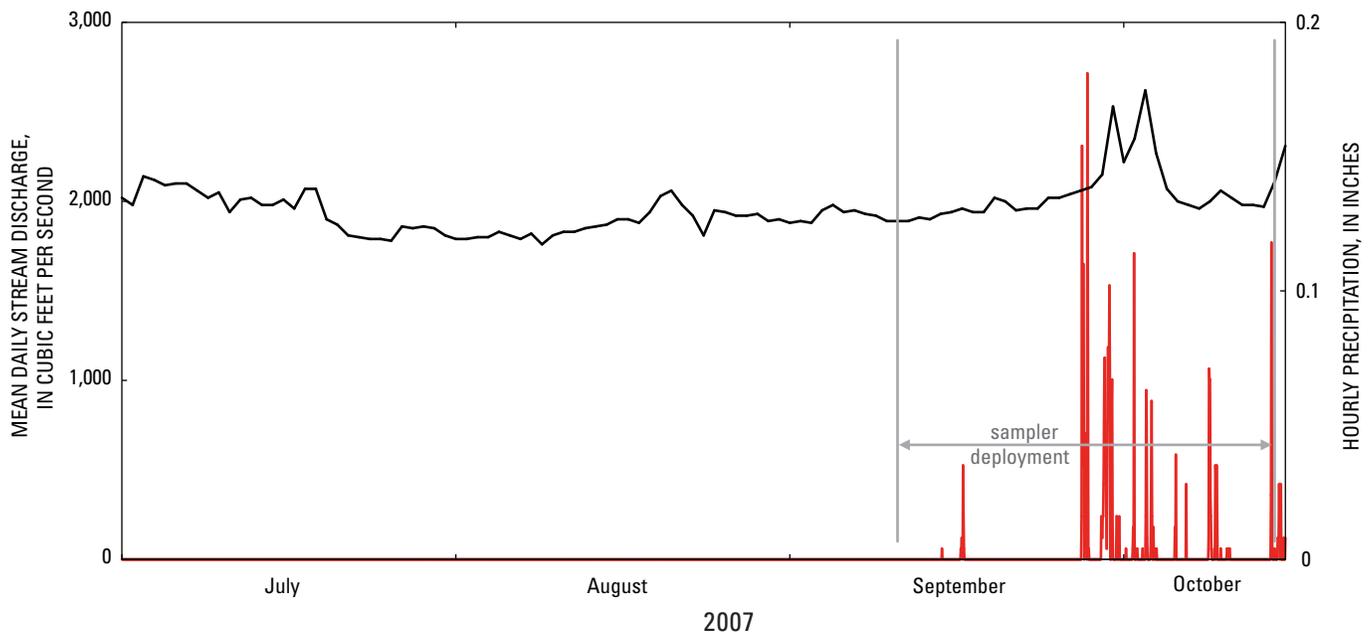


Figure 2. Mean daily stream discharge for the McKenzie River above Hayden Bridge, at Springfield, Oregon (black line), and hourly precipitation measured at Springfield (red line) for the period preceding and during the sampler deployment. Streamflow data are from USGS, station 14164900 McKenzie River above Hayden Bridge, at Springfield, Oregon; precipitation data are from Lane Regional Air Protection Agency.

inlet replicates and was detected but not quantified in one of the Camp Creek replicates. Diethyl phthalate, a widely used plasticizer and common background contaminant, was present at quantifiable levels in both treatment-plant inlet replicates and one of the Cedar Creek replicates. Another common plasticizer, diethylhexylphthalate (DEHP), was identified at a concentration less than the MQL in one of the treatment-plant inlet replicates.

Yeast Estrogen Screen.—Estrogenicity was not measurable in POCIS extracts from the treatment-plant inlet. Estrogenicity was measurable in samples from Cedar Creek and Camp Creek but at levels near the quantitation limit for this method (table 4). No estrogenic response was observed from any of the blanks, indicating that the sampler matrix and sample processing steps did not contribute to the total measured estrogenicity. The maximum estimated EEQ value of 0.06 ng/L was 130 times less estrogenic than the EC₁₀ concentration of 7.8 ng/L for the natural hormone 17 β -estradiol.

Most studies to date that have used the YES on POCIS extracts have been focused on effluents from wastewater-treatment plants or industrial processes, and data from relatively pristine streams are scarce. During a study to assess runoff from livestock operations, however, Matthiessen and others (2006) used YES on extracts from POCIS deployed at

sites upstream and downstream of the suspected sources of contamination. With the exception of one high outlier, YES results from their upstream (control) sites ranged from less than detection to 26.5 ng/L with a median EEQ of 0.4 ng/L. This median is approximately an order of magnitude greater than EEQ levels measured in Cedar and Camp Creeks.

Quality control.—The apparent lack of agreement between some replicate POCIS pairs is not an indication of poor data quality, but rather a manifestation of normal variability near method detection limits. With the exception of one unquantified detection of cholesterol in one of the treatment-plant inlet samplers, no pesticides, wastewater-indicator chemicals, or estrogenicity were detected in extracts from field-blank POCIS (appendix A, tables A1–A3).

Semipermeable Membrane Devices

Chemical analyses.—Several of the commonly identified PAHs were detected in the SPMDs deployed at each site (table 5). Fluorene, phenanthrene, fluoranthene, pyrene, chrysene, 1-methylfluorene, and 2-methylphenanthrene were detected at concentrations at or less than the MQL. These PAHs are common byproducts of combustion from sources such as wood smoke and automobiles.

Table 2. Concentrations of selected pesticides measured by polar organic chemical integrative samplers (POCIS) at three sites in the McKenzie River basin, Oregon, September–October 2007.

[A and B are replicate samples. MDL, method detection limit; MQL, method quantitation limit; “<,” compound not present at MDL; NQ, not quantified—compound detected at a concentration less than the MQL; detections are highlighted as bold type in shaded cells]

Pesticide	Concentrations, in nanograms of chemical per deployed POCIS						MDL	MQL
	Water-treatment plant inlet		Cedar Creek		Camp Creek			
	A	B	A	B	A	B		
EPTC	<4	<4	<4	<4	<4	<4	4	20
Desisopropylatrazine	<20	<20	<20	<20	<20	<20	20	100
Desethylatrazine	<20	<20	<20	<20	<20	<20	20	100
Trifluralin	<4	<4	<4	<4	<4	<4	4	20
Atraton	<4	<4	<4	<4	<4	<4	4	20
Simazine	<4	<4	<4	<4	<4	<4	4	20
Prometon	<4	<4	<4	<4	<4	<4	4	20
Dimethoate	<4	<4	<4	<4	<4	<4	4	20
Atrazine	<4	<4	<4	<4	<4	<4	4	20
Propazine	<4	<4	<4	<4	<4	<4	4	20
Terbuthylazine	<4	<4	<4	<4	<4	<4	4	20
Fonofos	<4	<4	<4	<4	<4	<4	4	20
Cyromazine	<20	<20	<20	<20	<20	<20	20	100
Diazinon	<4	<4	<4	<4	<4	<4	4	20
Metribuzin	<4	<4	<4	<4	<4	<4	4	20
Acetochlor	<4	<4	<4	<4	<4	<4	4	20
Methyl Parathion	<4	<4	<4	<4	<4	<4	4	20
Simetryn	<4	<4	<4	<4	<4	<4	4	20
Alachlor	<4	<4	<4	<4	<4	<4	4	20
Ametryn	<4	<4	<4	<4	<4	<4	4	20
Prometryn	<4	<4	<4	<4	<4	<4	4	20
Carbaryl	<4	<4	<4	<4	<4	<4	4	20
Terbutryn	<4	<4	<4	<4	<4	<4	4	20
Malathion	<4	<4	<4	<4	<4	<4	4	20
Metolachlor	NQ	<4	<4	<4	<4	<4	4	20
Chlorpyrifos	<4	<4	<4	<4	<4	<4	4	20
Dacthal	<4	<4	<4	<4	<4	<4	4	20
Pendimethalin	<4	<4	<4	<4	<4	<4	4	20
Fipronil	<4	<4	<4	<4	<4	<4	4	20
Ethopabate	<20	<20	<20	<20	<20	<20	20	100
Endosulfan I	<10	<10	<10	<10	<10	<10	10	50
Tetrachlorvinphos	<4	<4	<4	<4	<4	<4	4	20
Endosulfan II	<10	<10	<10	<10	<10	<10	10	50
<i>cis</i> -Permethrin	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	1.52	7.6
<i>trans</i> -Permethrin	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	0.96	4.8

Table 4. Relative estrogenic potential of chemicals sampled by polar organic chemical integrative samplers (POCIS) at three sites in the McKenzie River basin, Oregon, September–October 2007.

[A and B are replicate samples. EEQ, estimated estradiol equivalents as determined by the yeast estrogen screen; ng/L, estimated nanograms of 17 β -estradiol per liter of water which gives an equivalent response; ND, not determined - value was less than the 99-percent confidence interval of the negative (solvent) controls; detections are highlighted as bold type in shaded cells]

Water treatment plant inlet		EEQ, in ng/L			
		Cedar Creek		Camp Creek	
A	B	A	B	A	B
ND	ND	0.04	0.04	0.05	0.06

The persistent chlorinated pesticides dacthal, chlorpyrifos, trans-chlordane, and DDT, as well as pentachloroanisole (PCA), which likely results from the degradation of the pesticides pentachlorophenol and(or) pentachloronitrobenzene, were detected in SPMD extracts from each of the study sites (table 6). In addition, endosulfan was detected in both replicates from the Cedar Creek and Camp Creek sites. Hexachlorobenzene, trans-nonachlor, DDE, DDD, and dieldrin were detected in both replicates from the Cedar Creek site, and heptachlor epoxide was detected in both replicates from the treatment-plant inlet. With the exception of PCA, all detections were near or less than the MQL. PCA was detected at quantifiable concentrations in all samples. The concentrations of PCA were similar to or slightly higher than concentrations detected during multiple sampling periods in the Columbia Slough system in Portland, Oregon (McCarthy, 2006, 2008).

Quality control.—As with the POCIS data, the apparent lack of agreement between some SPMD replicates is not an indication of poor data quality and is common when compounds are detected at concentrations near method detection limits. Other than trace concentrations of 2-methylnaphthalene, fabrication and field-blank SPMDs were free from target PAHs and organochlorine compounds (appendix A, tables A4–A5).

Estimation of water concentrations.—Water concentrations estimated from SPMD data that were quantified (table 7) indicate that the compounds detected were

present in water at picogram-per-liter (parts per quadrillion) concentrations. For the compounds listed in table 7 for which health based screening levels (HBSLs) are available (Toccalino and others, 2008), the HBSLs were 4–6 orders of magnitude greater than the water concentrations estimated during this study.

Conclusions

The POCIS data indicate that cholesterol and diethyl phthalate likely are present in the waters sampled, but at concentrations that are near the quantitation limits of the available analytical methods.

Various PAHs and organochlorine compounds were detected in SPMDs from all sites. All these compounds were detected at concentrations near or less than the method quantification limit except for pentachloroanisole. Pentachloroanisole was measured at concentrations approximately an order of magnitude greater than the MQL at both Cedar Creek and Camp Creek sites and at somewhat more dilute concentrations at the treatment-plant intake.

The data presented here indicate that a number of compounds of concern are likely present in the McKenzie River basin, including at the intake for the Eugene Water and Electric Board drinking water plant, though generally at subnanogram per liter concentrations.

Results from this work indicate that both POCIS and SPMDs are well suited for monitoring organic compounds in the McKenzie River basin where organic compounds of interest are present at concentrations less than the detection limits of conventional sampling techniques. Passive samplers deployed at additional sites and during other streamflow conditions would provide further information on the sources of the organic compounds detected and how their concentrations may vary as hydrologic conditions change from low summer flow to high winter and spring flow.

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This project was a cooperative effort by USGS and EWEB, with active participation by personnel from both agencies. We are grateful for the cooperation of land owners who allowed access to their property.

Table 6. Concentrations of selected organochlorine pesticides, total polychlorinated biphenyls, and selected polybrominated diphenyl ethers measured by semipermeable membrane devices (SPMDs) at three sites in the McKenzie River basin, Oregon, September–October 2007.

[A and B are replicate samples. MDL, method detection limit; MQL, method quantitation limit; MQL, method quantitation limit; “<,” compound not present at MDL; NQ, not quantified—compound detected at a level less than the MQL; detections are highlighted as bold type in shaded cells]

Pesticides and compounds	Concentrations, in nanograms of chemical per deployed SPMD						MDL	MQL
	Water-treatment plant inlet		Cedar Creek		Camp Creek			
	A	B	A	B	A	B		
Organochlorine pesticides								
Trifluralin	NQ	<0.05	<0.05	<0.05	<0.05	<0.05	0.1	0.3
Hexachlorobenzene (HCB)	<0.62	NQ	NQ	NQ	<0.62	<0.62	0.6	1.8
Pentachloroanisole (PCA)	5.9	7.3	20	18	21	18	0.9	2.2
Tefluthrin	<3.8	NQ	<3.8	<3.8	<3.8	<3.8	3.8	8.1
<i>alpha</i> -Benzenhexachloride (<i>a</i> -BHC)	<1.9	<1.9	<1.9	<1.9	NQ	<1.9	1.9	2.5
Diazinon	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.3	1.3
Lindane	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	3.2	6.0
<i>beta</i> -Benzenhexachloride (<i>b</i> -BHC)	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	2.6	6.2
Heptachlor	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.2	1.0
<i>delta</i> -Benzenhexachloride (<i>d</i> -BHC)	NQ	<2.6	<2.6	NQ	<2.6	<2.6	2.6	3.4
Dacthal	<0.27	NQ	NQ	NQ	NQ	NQ	0.3	1.0
Chlorpyrifos	NQ	<0.53	<0.53	NQ	<0.53	NQ	0.5	1.5
Oxychlorane	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.2	1.0
Heptachlor Epoxide	NQ	NQ	<0.20	<0.20	<0.20	NQ	0.2	1.0
<i>trans</i> -Chlordane	NQ	NQ	NQ	NQ	NQ	1.9	0.7	1.2
<i>trans</i> -Nonachlor	<0.20	<0.20	NQ	NQ	<0.20	1.1	0.2	1.0
<i>o,p'</i> -DDE	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	2.2	5.6
<i>cis</i> -Chlordane	<1.2	<1.2	<1.2	<1.2	<1.2	NQ	1.2	3.0
Endosulfan	<0.20	<0.20	NQ	NQ	NQ	2.5	0.2	1.0
<i>p,p'</i> -DDE	<6.6	<6.6	NQ	NQ	<6.6	NQ	6.6	8.3
Dieldrin	<1.5	<1.5	NQ	NQ	<1.5	<1.5	1.5	3.0
<i>o,p'</i> -DDD	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.0	13.3
Endrin	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	1.1	3.4
<i>cis</i> -Nonachlor	NQ	<0.44	<0.44	<0.44	<0.44	<0.44	0.4	1.2
<i>o,p'</i> -DDT	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.2	1.0
<i>p,p'</i> -DDD	<2.9	<2.9	NQ	NQ	<2.9	<2.9	2.9	6.7
Endosulfan-II	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.2	1.0
<i>p,p'</i> -DDT	NQ	NQ	NQ	NQ	2.3	NQ	1.7	2.2
Endosulfan Sulfate	<0.20	<0.20	<0.20	<0.20	<0.20	NQ	0.2	1.0
<i>p,p'</i> -Methoxychlor	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	2.0	10.0
Mirex	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.2	1.0
<i>cis</i> -Permethrin	<18	<18	<18	<18	<18	<18	18.1	51.6
<i>trans</i> -Permethrin	<5.5	<5.5	<5.5	<5.5	<5.5	<5.5	5.5	16.5
Total polychlorinated biphenyls								
Total PCBs	<40	<40	<40	<40	<40	<40	40	200
Polybrominated diphenyl ethers								
PBDE-28	NQ	<0.46	<0.46	<0.46	<0.46	<0.46	0.5	1.0
PBDE-47	<3.6	<3.6	<3.6	<3.6	<3.6	<3.6	3.6	8.2
PBDE-99	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	2.1	3.7
PBDE-100	<.82	<.82	<.82	<.82	<.82	<.82	.8	2.3
PBDE-153	<.23	<.23	<.23	<.23	<.23	<.23	.2	1.0

Table 7. Dissolved water concentrations of select compounds estimated from semipermeable membrane devices (SPMDs) at three sites in the McKenzie River basin, Oregon, September–October 2007.

[A and B are replicate samples. Water concentrations were estimated from quantified SPMD data using methods described in the section, '[Estimation of Ambient Water Concentrations](#).' nd, not detected in passive sampler; NQ, not quantified--compound detected in passive sampler at a concentration less than the method quantitation limit; detections are highlighted as bold type in shaded cells; HBSL, health-based screening level (Toccalino and others, 2008)]

Compounds	Concentrations, in picograms per liter					
	Water treatment plant inlet		Cedar Creek		Camp Creek	
	A	B	A	B	A	B
Fluorene ¹	nd	nd	NQ	140	240	140
Chrysene ²	nd	nd	NQ	95	nd	nd
2-methylphenanthrene ²	nd	nd	NQ	100	190	96
Pentachloroanisole ²	18	65	130	170	370	150
<i>trans</i> -Chlordane ²	NQ	NQ	NQ	NQ	NQ	16
<i>trans</i> -Nonachlor ²	nd	nd	NQ	NQ	nd	13
Endosulfan ³	nd	nd	NQ	NQ	NQ	280
<i>p,p'</i> -DDT ⁴	NQ	NQ	NQ	NQ	41	NQ

¹ HBSL for fluorene is 300 micrograms per liter, more than 1 million times greater than the maximum concentration estimated from SPMD data during the current study.

² No toxicity data available.

³ HBSL for endosulfan is 40 micrograms per liter, more than 100,000 times greater than the maximum concentration estimated from SPMD data during the current study.

⁴ HBSL for *p,p'*-DDT ranges from 0.1 to 10 micrograms per liter, from 2,000 to more than 200,000 times greater than the maximum concentration estimated from SPMD data during the current study.

References Cited

- Alvarez, D.A., Cranor, W.L., Perkins, S.D., Clark, R.C., and Smith, S.B., 2008a, Chemical and toxicological assessment of organic contaminants in surface water using passive samplers: *Journal of Environmental Quality*, v. 37, p. 1024-1033.
- Alvarez, D.A., Cranor, W.L., Perkins, S.D., Schroeder, V.L., Werner, S.L., Furlong, E.T., and Holmes, John, 2008b, Investigation of organic chemicals potentially responsible for mortality and intersex in fish of the North Fork of the Shenandoah River, Virginia, during spring of 2007: U.S. Geological Survey Open-File Report 2008-1093, 16 p. Available at: <http://pubs.usgs.gov/of/2008/1093/>.
- Alvarez, D.A., Huckins, J.N., Petty, J.D., Jones-Lepp, T.L., Stuer-Lauridsen, F., Getting, D.T., Goddard, J.P., and Gravell, A., 2007, Polar organic chemical integrative sampler (POCIS), in Greenwood, R., Mills, G., and Vrana, B., eds., *Passive sampling techniques in environmental monitoring*, 48: Amsterdam, Elsevier, v. 48, p. 171-198.
- Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., and Manahan, S.E., 2004, Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments: *Environmental Toxicology Chemistry*, v. 23, p. 1640-1648.
- Eugene Water and Electric Board, 2000, Drinking water source protection plan: Eugene Water and Electric Board, Eugene, Oregon: Accessed June 17, 2009, at <http://www.eweb.org/public/documents/water/WaterProtectionPlan.pdf>.
- Huckins, J.N., Petty, J.D., and Booij, K., 2006, *Monitors of organic chemicals in the environment—Semipermeable membrane devices*: New York, Springer, 223 p.
- Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, Kees, Alvarez, D.A., Cranor, W.L., Clark, R.C., and Mogensen, B.B., 2002, Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices: *Environmental Science and Technology*, v. 36, no. 1, p. 85-91.
- Keith, L.H., 1991, *Environmental sampling and analysis—A practical guide*: CRC Press, Boca Raton, p. 101-113.
- Matthiessen, P., Arnold, D., Johnson, A.C., Pepper, T.J., Pottinger, T.G., and Pulman, K.G.T., 2006, Contamination of headwater streams in the United Kingdom by oestrogenic hormones from livestock farms: *Science of the Total Environment*, v. 367, no. 2-3, p. 616-630.
- McCarthy, K.A., 2006, Assessment of the usefulness of semipermeable membrane devices for long-term watershed monitoring in an urban slough system: *Environmental Monitoring and Assessment*, v. 118, no. 1-3, p. 293-318.
- McCarthy, K.A., 2008, Investigation of hydrophobic contaminants in an urban slough system using passive sampling—Insights from sampling rate calculations: *Environmental Monitoring and Assessment*, v. 145, no. 1-3, p. 31-47.
- Oregon Department of Environmental Quality, 2008, Oregon water quality index summary report, water years 1998-2007: Oregon Department of Environmental Quality, 14 p. Accessed June 18, 2009, at <http://www.deq.state.or.us/lab/wqm/docs/09-LAB-008.pdf>.
- Petty, J.D., Orazio, C.E., Huckins, J.N., Gale, R.W., Lebo, J.A., Meadows, J.C., Echols, K.R., and Cranor, W.L., 2000, Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants: *Journal of Chromatography A*, v. 879, issue 1, p. 83-95.
- Rastall, A.C., Neziri, A., Vukovic, Z., Jung, C., Mijovic, S., Hollert, H., Nikcevic, S., and Erdinger, L., 2004, The identification of readily bioavailable pollutants in Lake Shkodra/Skadar using semipermeable membrane devices (SPMDs), bioassays and chemical analysis: *Environmental Science and Pollution Research*, v. 11, no. 4, p. 240-253.
- Routledge, E.J., and Sumpter, J.P., 1996, Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen: *Environmental Toxicology and Chemistry*, v. 15, issue 3, p. 241-248.
- Southern Willamette Valley Local Advisory Committee, 2004, Southern Willamette Valley agricultural water quality management area plan: Salem, Oregon, Oregon Department of Agriculture, 72 p. Accessed June 17, 2009, at http://www.oregon.gov/ODA/NRD/docs/pdf/plans/sowlmt_04_pln.pdf.
- Toccalino, P.L., Norman, J.E., Booth, N.L., and Zogorski, J.S., 2008, Health-based screening levels: A tool for evaluating what water-quality data may mean to human health: U.S. Geological Survey, National Water-Quality Assessment Program, accessed March 16, 2009, at <http://water.usgs.gov/nawqa/HBSL/>.
- U.S. Geological Survey, 2008, McKenzie River, Oregon, source water quality protection: U.S. Geological Survey, 1 p. Accessed June 18, 2009, at <http://or.water.usgs.gov/proj/EWEB/>.

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Table A3. Relative estrogenic potential of chemicals sampled by field-blank polar organic chemical integrative samplers (POCIS) at three sites in the McKenzie River basin, Oregon, September–October 2007.

[EEQ, estimated estradiol equivalents as determined by the yeast estrogen screen; ng/L, estimated nanograms of 17 β -estradiol per liter of water which gives an equivalent response; ND, not determined - value was less than the 99-percent confidence interval of the negative (solvent) controls]

EEQ, in ng/L					
Water treatment plant inlet		Cedar Creek		Camp Creek	
Field blank		Field blank		Field blank	
1	2	1	2	1	2
ND	ND	ND	ND	ND	ND

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