

# **Water Resources Research Institute Annual Technical Report FY 2003**

## **Introduction**

In 2003, Oregon's Center for Water and Environmental Sustainability (CWEST) focused efforts on three programs:

- 1) The Water Resources Program administers interdisciplinary and multi-agency watershed education and water resources research programs in Oregon and the Pacific Northwest.
- 2) The Groundwater Cleanup and Hazardous Substance Outreach Program studies public perceptions of cleanup strategies and provides information to communities affected by hazardous waste sites and groundwater contamination.
- 3) The Sustainable University Program promotes and facilitates a wide range of interdisciplinary research, information dissemination, and project and agency coordination related to natural resources and environmental sustainability.

During FY 2003 the Center for Water and Environmental Sustainability (CWEST) program included four new research and information transfer projects funded by the USGS 104B program and four projects that were carried over from the previous year.

CWEST also sponsored and/or participated in a wide variety of educational and outreach activities including five conferences, numerous workshops, the Fall Water Resources Seminar Series, the graduate minor in water resources, research internships for undergraduate and graduate students, and educational websites.

## **Research Program**

For Fiscal Year 2003 CWEST supported projects examining issues of long-term water management with a focus on creating sustainable solutions that balance stewardship of the resource with economic viability for local communities. CWEST sought projects that would increase knowledge about how resource demands and supplies can be balanced for the long term.

# Investigation of Nitrate Transport Across the Willamette Silt of the Southern Willamette Valley

## Basic Information

<b>Title:</b>	Investigation of Nitrate Transport Across the Willamette Silt of the Southern Willamette Valley
<b>Project Number:</b>	2003OR29B
<b>Start Date:</b>	2/15/2003
<b>End Date:</b>	2/14/2004
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 4th and 5th
<b>Research Category:</b>	Ground-water Flow and Transport
<b>Focus Category:</b>	Groundwater, Nitrate Contamination, Management and Planning
<b>Descriptors:</b>	Nitrate Contamination, Willamette Silt, Ground-water
<b>Principal Investigators:</b>	Roy Haggerty

## Publication

- 1.

### Problem and Research Objectives:

Nitrate in groundwater in Oregon's SWV has been a concern for several years, with more than 7% of domestic wells in 2001 reporting concentrations exceeding the USEPA's Maximum Contaminant Level of 10 ppm [Aitken *et al.*, 2003]. However, not all groundwater is equally affected, due to differences in land use, agricultural practices, and particularly geology. The Willamette Silt, which overlies much of the Willamette Aquifer, acts as a hydraulic barrier to nitrate transport and, more importantly, acts as a natural biogeochemical "reactor-bed" for denitrification. Prior work [Iverson and Haggerty, 2002; Iverson, 2002] in the Northern Willamette Valley shows that nitrate does not penetrate beyond a redox front in the Silt approximately 25 ft below ground surface, providing very effective protection to the Aquifer. Across the Willamette Valley wherever the Willamette Aquifer is overlain by the Willamette Silt nitrate concentrations are generally low [see data in Hinkle, 1997, p. 23]. The SWV has been more susceptible to groundwater contamination than the Northern Valley even though the Willamette Silt is also the surface unit in much of the Southern Valley.

Few studies have attempted to characterize and quantify the nitrate attenuation capacities of geologically young aquitards even though the phenomenon has been noted previously. Our objectives were (1) to quantify critical nitrate-attenuating geochemical characteristics of the Willamette Silt in the SWV, including nitrate concentrations, pH, and at selected sites manganese, organic matter, and ferric and ferrous iron; (2) to map the reduced zone of Willamette Silt that is correlated with the attenuation of nitrate; and (3) to propose a geochemical model for denitrification in these sediments.

### Methods, Procedures, and Facilities:

Continuous core samples were taken at 30 sites in the SWV with the ODEQ push-probe rig. Nitrate and pH profiles were taken at all sites and manganese and organic matter measurements were taken at selected sites. Cores were stored on dry ice in the field, and then taken back to the lab to be stored in a freezer until they could be sampled for chemical analysis. Chemical analyses were performed by Central Analytical Laboratories on the Oregon State University campus. Locations and thickness of Willamette Silt were compared to USGS data and found to be in agreement without much new location information. Maps of the reduced zone of Willamette Silt were produced for the SWV, and using data collected previously and data from the Oregon Department of Geology and Mineral Industries (Ian Madin, pers. comm., 2003) a map of the reduced zone in the Northern Willamette Valley was also created. The majority of cores obtained are stored in a freezer at Oregon State University for use in future research.

### Principal Findings and Significance:

Our study suggests that nitrate attenuation is strongly correlated with a reduced zone of Willamette Silt that is present in much of the Northern Willamette Valley but that is present in only a small area in the SWV. The reduced zone is geochemically important because of the reduced iron it contains. It is this reduced iron that seems to be the geochemical barrier to nitrate transport in the Willamette Valley. Carbonate minerals appear just below the top of the reduced zone and are visually identifiable from the blue-gray color, differentiating it from the red-brown oxidized silt above. Nitrate and nitrite, where they were found in detectable quantities just above the reduced zone, reached non-detect levels just below the redox boundary. The redox boundary, as identified by the color change, sharp increase in pH, and in some locations by dominant valence state of iron, was usually found only in Willamette Silt thicker than 5.2 m (17 ft).

Biological denitrification tests in the Northern Valley turned up no significant denitrification potential, leading us to believe that chemical reduction by reduced iron is the main mechanism of nitrate attenuation in the Willamette Silt.

Biological denitrification, often suggested as the principal method of nitrate attenuation in shallow sediment, was found not to be a factor in our study. Instead, chemical denitrification by reduced iron appears to be the main mechanism of nitrate reduction in the Willamette Silt. The blue-gray color of the reduced silt acts as a visual marker for the geochemical boundary, allowing groundwater resource managers to easily identify areas likely to be resistant to nitrate loading from readily available sources such as domestic well logs. Mapping of the reduced zone of Willamette Silt in the Southern Valley increases the data available for Willamette Valley groundwater resource managers such as the Oregon Department of Environmental Quality.

Publications: We intend to submit a manuscript, now in draft form, to *Ground Water*.

Student Support (# and degree level): 3 students, all MS

Arighi, Louis, Quantification of the Nitrate Attenuation Capacity of Low-Permeability Missoula Flood Deposits in the Willamette Valley of Oregon, MS in Geology, Dept. of Geosciences, Oregon State University, Corvallis, Oregon. Defended April, 2004. Grant provided major support for this thesis.

Craner, Jeremy. Tentative title: Regional Flow Model of the Southern Willamette Valley Groundwater Management Area. MS in Geology, in progress. Grant provided minor support in aspects relating to nitrate transport data collection.

Mutti, Glenn. Tentative title: Nonpoint Source Nitrogen Dynamics in the South Willamette Valley, Oregon. MS in Geology, in progress. Grant to provide nitrate sample support in Southern Willamette Valley.

### References

Aitken, G., J. Arendt, and A. Eldridge, Southern Willamette Valley Groundwater Assessment 2000-2001 Nitrate Study, pp. 37 p. plus appendices, Oregon Department of Environmental Quality, Salem, Oregon, 2003.

Hinkle, S.R., Quality of shallow ground water in alluvial aquifers of the Willamette Basin, Oregon, 1993-95, 48 p., US Geological Survey, Portland, Oregon, 1997.

Iverson, J., Investigation of the Hydraulic, Physical, and Chemical Buffering Capacity of Missoula Flood Deposits for Water Quality and Supply in the Willamette Valley of Oregon, MS thesis, Oregon State University, Corvallis, Oregon, 2002.

Iverson, J., and R. Haggerty, Investigation of the hydraulic, physical, and chemical buffering capacity of Missoula Flood Deposits for water quality and supply in the Willamette Valley of Oregon, in *9th Annual Meeting, Cordilleran Section, Geological Society of America*, pp. A-109, Geological Society of America, Corvallis, Oregon, 2002.

# Discharge, source areas, and water ages of spring-fed streams and implications for water management in the McKenzie River basin

## Basic Information

<b>Title:</b>	Discharge, source areas, and water ages of spring-fed streams and implications for water management in the McKenzie River basin
<b>Project Number:</b>	2003OR37B
<b>Start Date:</b>	2/15/2003
<b>End Date:</b>	2/14/2004
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 5th
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Water Quantity, Surface Water, Hydrology
<b>Descriptors:</b>	Streamflow source areas, water age, springs, Cascade Mountains
<b>Principal Investigators:</b>	Gordon Grant

## Publication

### Problem and Research Objectives:

The McKenzie River basin provides habitat for endangered and threatened fish species, contains federal and private dams for flood control and hydroelectric power generation, and supplies drinking water to Eugene, Oregon's second largest city. In low flow periods, the McKenzie provides a disproportionate share of water to the Willamette Valley, where 70% of the Oregon's population lives (PNWERC, 2002). Recently released climate modeling (Service, 2004) suggests that declining Cascades snowpacks over the next 50 years will exacerbate demand for limited water resources.

Despite the importance of the McKenzie River's water to the region's quality of life, geologic and climatic controls on patterns of streamflow have been poorly understood. The watershed of the McKenzie River, which is tributary to the Willamette River (Figure 1), lies primarily within two distinct geologic provinces: the High and Western Cascades. Preliminary hydrograph analyses indicated that High Cascades streams show much more uniform flow and temperature through time compared to Western Cascades streams (Tague and Grant, 2004). Many High Cascades streams are also sourced in springs, while Western Cascades streams are dominated by water from shallow-subsurface flow through the soil. These differences have significant implications for water quantity and quality in headwater streams and for larger rivers, such as the McKenzie and Willamette, where both High and Western Cascades streams contribute to flow.

This project represents a systematic attempt to quantify volumes, sources, and ages of streamflow in the McKenzie River basin. The overall goal of the project was to provide a more complete picture of flow contributions to the McKenzie River, for use in planning the sustainable long-term water management of the basin. The work was focused around four objectives:

- 1) Obtain continuous discharge records for large spring-fed streams in the McKenzie River basin
- 2) Identify, map, and obtain point discharge measurements for additional springs in the basin
- 3) Use isotopic information to constrain residence times and recharge source areas of the springs
- 4) Discuss implications of spring-fed streams for management of water resources in the McKenzie basin.

### Methods, Procedures, and Facilities:

#### **1) Obtain continuous discharge records for large spring-fed streams in the McKenzie River basin**

Tru-track capacitance rod water stage and temperature recorders were installed on 13 streams in the McKenzie River watershed during July 2003, as shown in Figure 2. Stage and temperature measurements were taken at 15 minute to 1 hour intervals, and continue to operate past the ending date of this grant. These streams included 8 spring-fed streams, 4 runoff-dominated streams, and 1 ephemeral spring-fed stream. The selected spring-fed streams included all of the major ungauged springs that are tributary to the McKenzie River. Runoff-dominated streams were selected because they were tributary to or provided a reference site in close proximity to spring-fed streams.

By wading and using a Marsh-McBirney flow meter, discharge measurements were made at a variety of stages in order to develop rating curves for each site, following standard USGS procedures. These curves allow interpolation from stage to discharge and result in daily hydrographs for the streams. Discharge was directly measured between 4 and 18 times at each site, depending on flow variability. Despite repeated measurements, peak flows had to be extrapolated from the rating curve for each site. Where there is not sufficient confidence in such extrapolations, hydrographs are truncated in high flow periods. Rating curve refinement is continuing to date.

#### **2) Identify, map and obtain point discharge measurements for additional springs in the basin**

Topographic maps indicated the presence of other springs in the McKenzie River watershed, for which no discharge measurements existed. Several of these springs were visited and one-time discharge measurements were made during the summer of 2003. Additionally, in early and late August, discharge was measured at all tributaries flowing from High Cascades geology between the headwaters of the McKenzie River and the junction with the South Fork of the McKenzie.

#### **3) Use isotopic information to constrain residence time and recharge source areas for springs**

In mountainous regions, the isotopic composition of precipitation varies in systematic way with elevation. The isotopic composition of spring water can be projected to the elevation at which precipitation has a comparable composition. Water samples were collected from springs at approximately monthly intervals, and analyzed by Anne Jefferson at Lawrence Livermore National Laboratory under the supervision of Dr. Tim Rose. Isotopic composition of spring water was compared to a published altitude-isotope relationship for the Oregon Cascades (Ingebritsen et al., 1994). In March 2004, after most of the

year's snow had fallen, snow cores were collected from sites at 814 to 1729 m elevation for calibration of the altitude-isotope curve to the McKenzie region. These samples are awaiting analysis.

One liter water samples were collected in mid-November 2003 for tritium concentration analysis, from which groundwater age can be estimated. Water samples were taken from Roaring Spring, Lost Spring, Olallie North and South Springs, and Great Spring. Tritium was not analyzed for Tamolitch Spring groundwater, because of possible effects of spilling upstream at Carmen Reservoir during October 2003. Samples were sent to the University of Waterloo (Canada) Environmental Isotope Laboratory for analysis by standard procedures. Data from these samples will be used to guide selection of more refined measures of groundwater age in the summer of 2004.

#### **4) Discuss implications of spring-fed streams for management of water resources in the McKenzie Basin**

Patterns of groundwater discharge and recharge have impacts on how flow is regulated at dams along the mainstem and tributaries of the McKenzie River, how stream habitat is monitored and managed, and the quality of water of recreation, habitat, and drinking water uses. Synthesis of objectives 1-3 allows discussion of implications for water resources in the McKenzie basin. Conversations with Forest Service hydrologists from the Willamette, Mount Hood, and Umpqua National Forests also generated examination and discussion of regional-scale significance of spring-fed streams.

##### Principal Findings and Significance:

#### **1) Obtain continuous discharge records for large spring-fed streams in the McKenzie River basin**

Considerable differences were observed between the hydrographs of spring-fed and runoff-dominated streams in the McKenzie River watershed (Figure 3). The difference between peak flow discharges and low flow discharges on spring-fed streams was a factor of 1.5 to 2.7, whereas for runoff-dominated streams peak flows were approximately 30 to 1000 times greater than low flows. Hydrographs of spring-fed streams also showed little recession during the summer, as compared to those of runoff-dominated streams. Comparison of flows from summer 2003 to spot discharge measurements in 2001-2002, and to irregular measurements from the 1910-1926 (Stearns, 1929) suggests that springs have less interannual variability than runoff-dominated streams.

Two major peak flow events are represented in the gauging record: December 13-14, 2003 and January 29, 2004. The spring-fed streams exhibit a delayed peak flow compared to runoff-dominated streams, and this cannot be completely explained by elevation or watershed area. For example, all four runoff-dominated streams had their peak flow on January 29, 2004, but the spring-fed streams reached their peak flows on January 30-31.

There were also differences in behavior among spring-fed streams (Figure 4). Anderson Creek showed almost no response to rain events, while the bigger spring-fed streams showed some responsiveness. Some of this responsiveness may be due to gauging location, as the Roaring and South Fork sites are downstream of runoff-dominated tributaries. Furthermore, springs feeding the same creek exhibited different dynamics during the summer period, as illustrated below.

Olallie North Branch rises through July and August and drops off in September, while downstream on Olallie Creek, below the confluence of the north and south branches, Olallie Creek exhibits a slight recession throughout the summer. This recession is similar to the stage record at Olallie South Branch (not shown), which contributes most of the flow to Olallie Creek. Thus, although the two branches are sourced in springs less than 1 km apart, they function differently.

Between August 15 and September 15, 2003, the north spring on Roaring River dropped from supplying 29% of the water in the river at Road 19 to providing only 23% of the water. This decrease in relative contribution cannot be explained by increased flow from runoff-dominated streams, because, as exemplified by McBee, their flow decreased by half. Consequently, increased flow from Roaring Spring (south branch) or another unidentified spring must account for the discharge measured at Road 19.

White Branch Creek, as measured near its confluence with Lost Creek, appears to be controlled by an ephemeral spring (Figure 5). It exhibits markedly different discharge dynamics than either spring-fed or runoff-dominated streams, despite its spatial proximity to perennial Lost Spring. The stream had a very steep recession in July-August and again in March, each time resulting in a completely dry channel. The stream did not respond to the December 13-14 peak flow event, and exhibited a 5-day delay in peak flow for the end of January event. Throughout the vagaries in discharge, water temperature remained nearly constant between 6.5 and 6.7°C, within the range exhibited by Lost Spring. Only when discharge was below  $\sim 0.1 \text{ m}^3/\text{s}$  did significant temperature fluctuations occur.

Water temperature trends also exhibited differences between spring-fed and runoff-dominated streams (Figure 6). Temperature measured directly at springs was nearly constant throughout the year, while streams showed fluctuations due to cooling or heating from the surrounding air mass. However, spring-fed streams showed much smaller variation in temperature both seasonally and daily than did runoff-dominated streams.

## **2) Identify, map and obtain point discharge measurements for additional springs in the basin**

During August 5-7 and again August 26-28, 2003, discharge measurements were made on High Cascades tributaries to the McKenzie River (Figure 7). Discharge of the McKenzie River at Vida was 50.7 m<sup>3</sup>/s on August 7, 2003. According to our measurements, 42.3 m<sup>3</sup>/s, or 83%, of this flow came from spring-fed streams. By combining locations from this project and the USGS, 49.4 m<sup>3</sup>/s, or over 97% of the flow in the McKenzie River was measured, despite ignoring most tributaries flowing from Western Cascades geology. Reservoir supplementation accounted for ~10% of the flow at Vida. Without this supplementation, spring-fed streams would comprise 93% of the flow in the McKenzie River.

These measurements indicated that all major springs discharging into the McKenzie were accounted for in the above gauging scheme. Some small springs discharge water to the surface where it quickly infiltrates back into the ground (e.g., Beeler), while other springs discharge into closed basins (e.g., Linton), where their water either evaporates or recharges the groundwater system. There is also considerable accretion of groundwater along the mainstem of the McKenzie River between Clear Lake and Carmen Reservoir. Discrete springs are found at the base of Koosah Falls and multiple small springs flow into Carmen Reservoir.

## **3) Use isotopic information to constrain residence time and recharge source areas for springs**

Spring water samples plot substantially to the right of the altitude-isotope curve for the west side of the Oregon Cascades (Figure 8). This suggests that groundwater aquifers are recharging at higher elevations (1300 to 1800 m) than they are discharging (600 to 1200m). The recharge elevations for the springs are concordant with the elevation of substantial young lava fields between McKenzie and Santiam Passes. Springs providing flow to tributaries of the South Fork of McKenzie also recharge in this elevation range, despite less aerially extensive young lavas. Recharge elevations estimated by this method represent precipitation-weighted averages and have an error of  $\pm 60$  m due to analytical uncertainty, plus some uncertainty associated with the meteoric water line.

This analysis also suggests that some springs may derive their water from the same source, while others have unique recharge areas and flow paths. Lost Spring and White Branch have similar isotopic compositions, and thus are likely drawing from the same aquifer or recharging their aquifer in comparable areas. Conversely, Olallie North Spring and Olallie South Spring have dissimilar compositions, indicating that their flow paths and recharge areas are distinct. This is supported by the differing flow dynamics of each spring, as discussed earlier. Roaring Spring and Roaring North Spring appear to share similar recharge areas. Furthermore, recharge elevations inferred by isotopic methods infer that topographic watersheds may not be providing evenly distributed recharge to the groundwater system. In at least one case, the inferred average recharge elevation is greater than the maximum elevation in the topographic watershed, requiring significant recharge from outside the topographic watershed.

Mean residence time of groundwater, or groundwater age, can be estimated from tritium (<sup>3</sup>H) concentrations in the spring water, by comparing the spring tritium levels to a record of atmospheric tritium levels over time. Tritium values for the five sampled springs ranged between 2.9 and 6.1 TU (Table 1). Preliminary analysis indicates that these values correspond to the 5-10 year age range. Based on this method, Great Spring may have a non-unique young residence time solution. Despite their difference in recharge elevations and flow dynamics, Olallie North and South Springs have similar discharge water with similar residence times.

## **4) Discuss implications of spring-fed streams for management of water resources in the McKenzie Basin**

The following significance discussion subsumes the findings of this objective.

### **Significance**

Spring-fed streams are by far the dominant source of streamflow in the McKenzie River at Vida, and this flow is sourced from less than 10 areas in the watershed. Most of these springs occur on federal land, requiring local and federal water resources agencies to cooperate in their management and protection. One important management objective might be to maintain high water quality of the spring-fed streams up to and beyond National Forest boundaries, so that the environmental attributes of springs themselves are not compromised by direct tapping for clean water supplies. While spring-fed streams provide more



consistent flow than do runoff-dominated streams, they do experience higher flows in response to rain and rain-on-snow events. Thus, adequate gauging of these systems is still important for reservoir management planning. A small number of discharge measurements might be sufficient to characterize summer streamflows in spring-fed streams, but winter flows cannot be assumed to be static. Furthermore, differences in flow dynamics between spring-fed streams, even those in close proximity to each other, preclude generalizing measurements from one spring system to others.

Stream temperature, an important habitat criterion for bull trout and other species, is generally lower and more stable in spring-fed streams than runoff-dominated streams, suggesting that conservation efforts for some species might be concentrated in spring-fed streams.

Recharge elevations are significantly higher than spring locations and suggest some discordance between recharge areas and topographic watersheds. Furthermore, the effects of human activities and natural disturbances in recharge areas on spring water quantity and quality are not well understood. These findings emphasize the importance of further investigation into recharge area geometry, the question of whether specific portions of the landscape provide a disproportionate share of recharge to the groundwater system, and what effects human activities in source areas may have on streamflow and water quality.

Mean residence times in the range of 5-10 years imply that the groundwater system is being actively recharged, probably in balance with the amount discharged at springs. This suggests that spring water may be susceptible to contamination by atmospheric deposition or chemical spills in recharge areas. Contamination of spring water may appear several years after a spill and the effects may last several years. Finally, a change in the overall amount of precipitation falling on the Cascades would probably have an impact on spring discharge within a few years, but a change in seasonality or form of precipitation may be less significant for spring-fed streams than for runoff-dominated streams.

Because of their importance to summer streamflow, water quality, and habitat in the McKenzie River basin, water resources decision-making must differentiate between spring-fed and runoff-dominated streams. This will require cooperation between local and federal organizations, continued assessment of long-term behavior of spring-fed streams in light of climate variability and change, and more investigation into how human and natural impacts on recharge areas could affect groundwater quantity and quality.

#### **Invited talks on McKenzie River springs, given by Gordon Grant:**

US Forest Service Fish and Wildlife meeting, Eugene, OR 5/1/03  
H.J. Andrews Long Term Ecological Research Network Science Hour, Corvallis, 6/6/03  
McKenzie Watershed Council, Eugene, OR 6/12/03  
Klamath River Watershed Council, Arcata, CA 6/18/03  
Middle Fork Willamette Watershed Council, Lowell, OR, 6/18/03  
National Council on Air and Stream Improvement Workshop, H.J. Andrews, 7/18/03  
Bureau of Land Management National Advisory field trip, Blue River, OR, 7/30/03  
Willamette Riverkeeper field trip, Albany, OR 9/9/03  
Geological Society of America National Meeting, Seattle, WA 11/3/03  
Oregon Public Broadcasting, Oregon Field Guide, 11/20/03, 11/23/03  
Willamette Technical Advisory Group, Salem, OR 12/3/03  
South Santiam Watershed Council, Lebanon, OR 1/21/04  
OSU Science Connection, Portland, 3/11/04  
Santiam Fish and Game Commission, Lebanon, OR 4/2/04  
National Public Radio, "Earth and Sky", 4/27-28/04

#### Student Support (# and degree level):

This project involved one Ph.D. student (Anne Jefferson, OSU Geosciences), who oversaw execution of the project, including conducting field and laboratory work and data analysis. An M.S. student (Michael Farrell, SDSU Geography) and a Ph.D. student (Josh Wyrick, OSU Civil Engineering) were supported as field assistants and were involved with stream temperature analysis.

#### Figures

Figure 1. The McKenzie River watershed in the context of Willamette River basin streams and reservoirs.  
Figure 2. Location map of springs and discharge measurement sites in the McKenzie River basin.

- Figure 3. Daily average discharge of spring-fed and runoff-dominated streams between July 9, 2003 and April 12, 2004. Hydrographs are truncated at the last data download date or where there is missing data or low confidence in extrapolated discharge values.
- Figure 4. Daily hydrographs of spring-fed streams in the McKenzie River basin. Lines represent daily average flow estimated from stage-discharge relationships, while points represent single discharge measurements.
- Figure 5. Discharge and water temperature of White Branch Creek near Highway 242. White Branch had no water in its channel from August 19 to October 25, 2003 and from March 16, 2004 until the end of the grant period.
- Figure 6. Water temperature histories of springs (dashed lines), spring-fed streams (blue colors), and runoff-dominated streams (green colors). Water temperature at springs measured by Hobo Water Temp Pro sensors, and in streams, temperature was measured using Hobo or Trutrack sensors.
- Figure 7. Sources of water to the McKenzie River during low flow (measured August 5-7, 2003).
- Figure 8. Average isotopic composition of spring water compared to spring elevation. Mean recharge elevation can be determined by projecting isotopic composition onto the meteoric water line.
- Table 1. Tritium values for spring water samples collected November 15-17, 2003. One tritium unit (TU) is equal to 3.149 picocuries/L or 0.11815 Becquerels/L.

#### References Cited

- Ingebritsen, S.E., Mariner, R.H. and Sherrod, D.R., 1994. Hydrothermal systems of the Cascade Range, north-central Oregon. U.S. Geological Survey, Professional Paper 1044-L: 86 pp.
- PNWERC, 2002. Willamette River Basin Planning Atlas: Trajectories of environmental and ecological change. Oregon State University Press, Corvallis, OR, 178 pp.
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- Tague, C. and Grant, G.E., 2004. A geological framework for interpreting the low flow regimes of Cascade streams, Willamette River Basin, Oregon. *Water Resources Research*, 40(4): W04303 10.1029/2003WR002629.

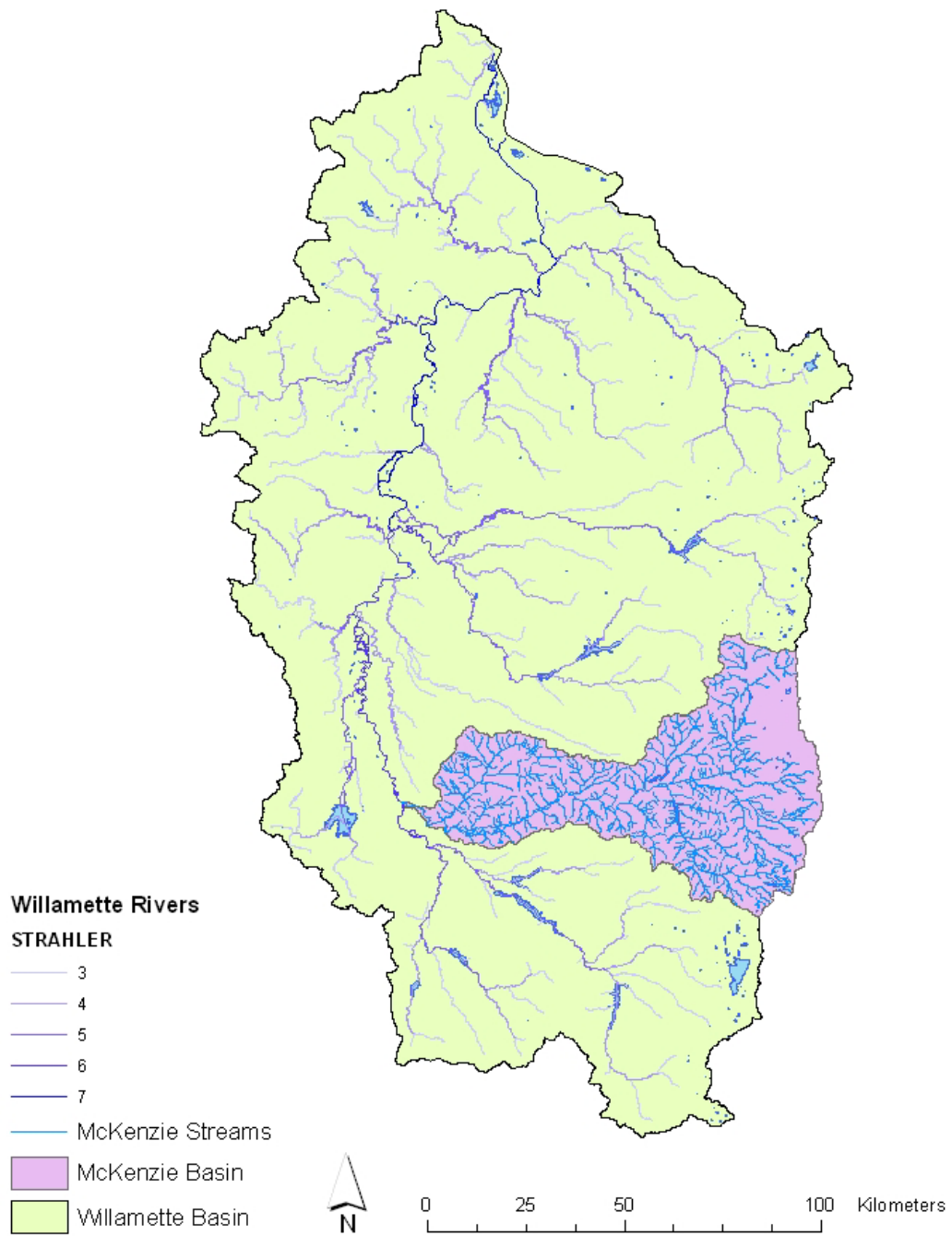


Figure 1. The McKenzie River watershed in the context of Willamette River basin streams and reservoirs.

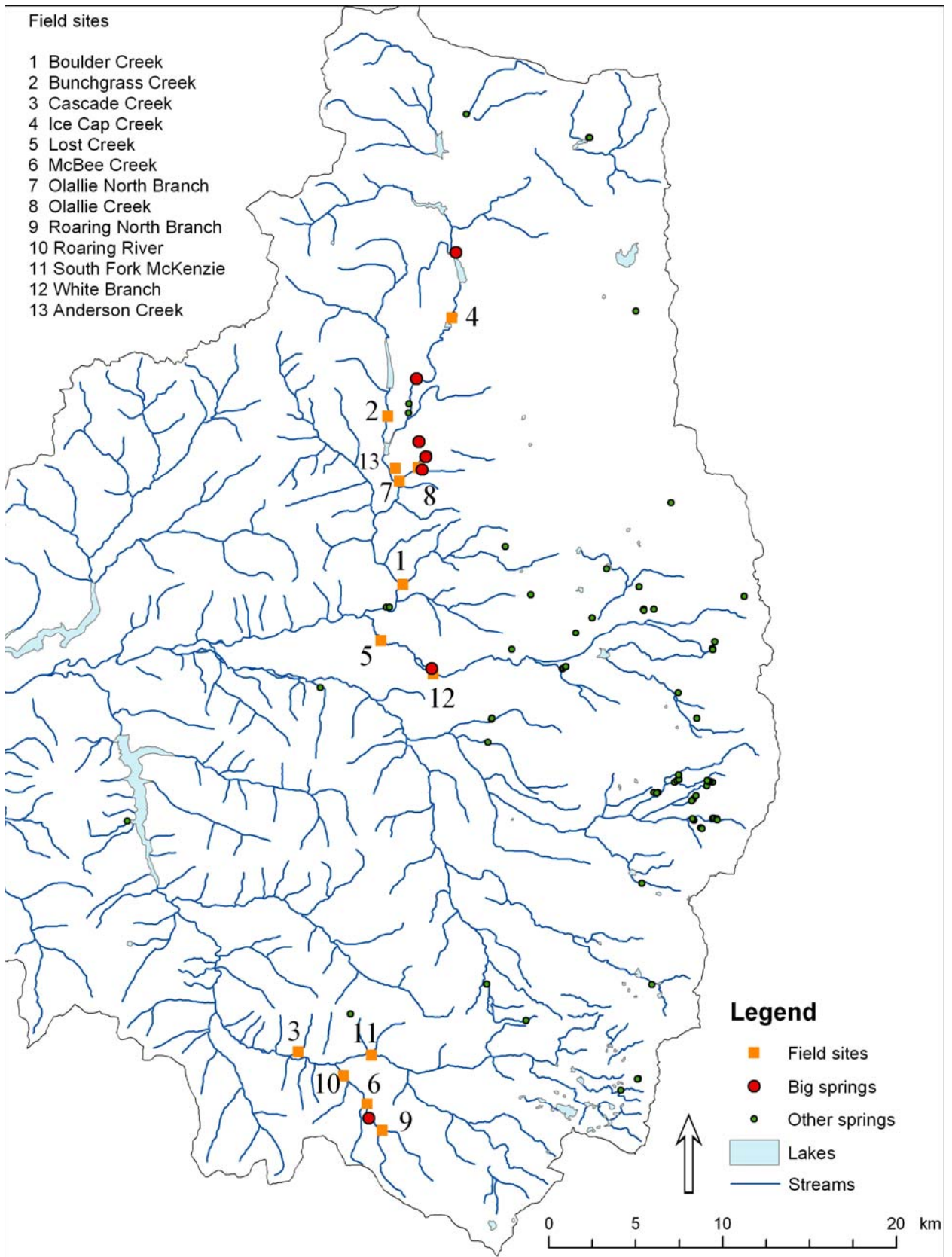


Figure 2. Location map of springs and discharge measurement sites in the McKenzie River basin.

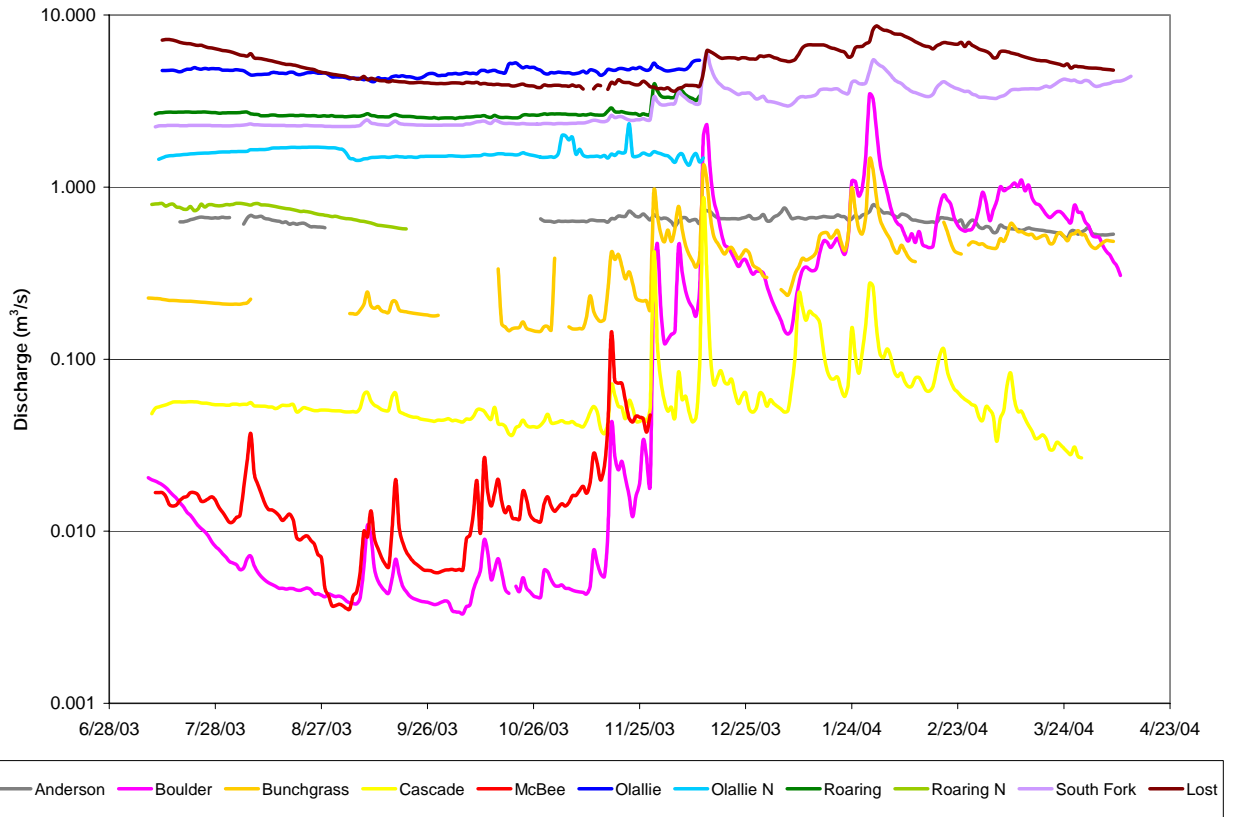


Figure 3. Daily average discharge of spring-fed and runoff-dominated streams between July 9, 2003 and April 12, 2004. Hydrographs are truncated at the last data download date or where there is missing data or low confidence in extrapolated discharge values.

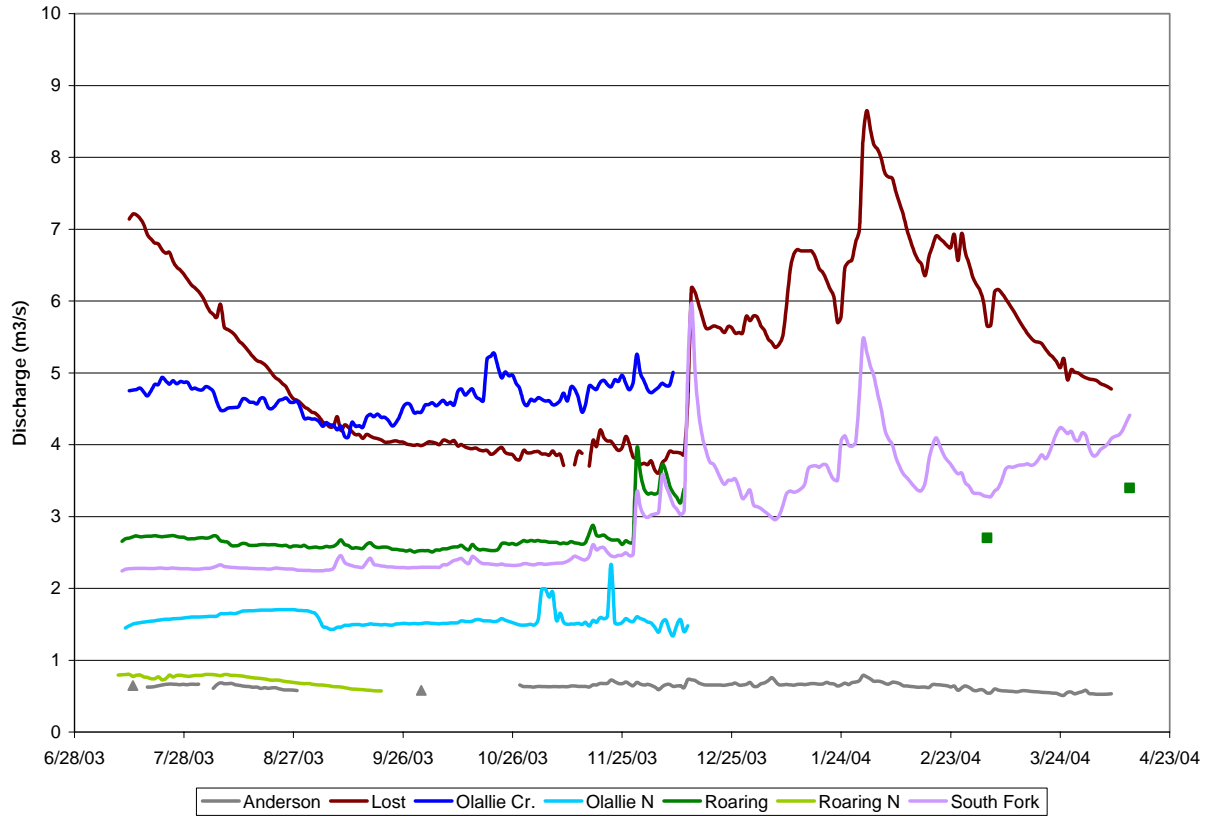


Figure 4. Daily hydrographs of spring-fed streams in the McKenzie River basin. Lines represent daily average flow estimated from stage-discharge relationships, while points represent single discharge measurements.

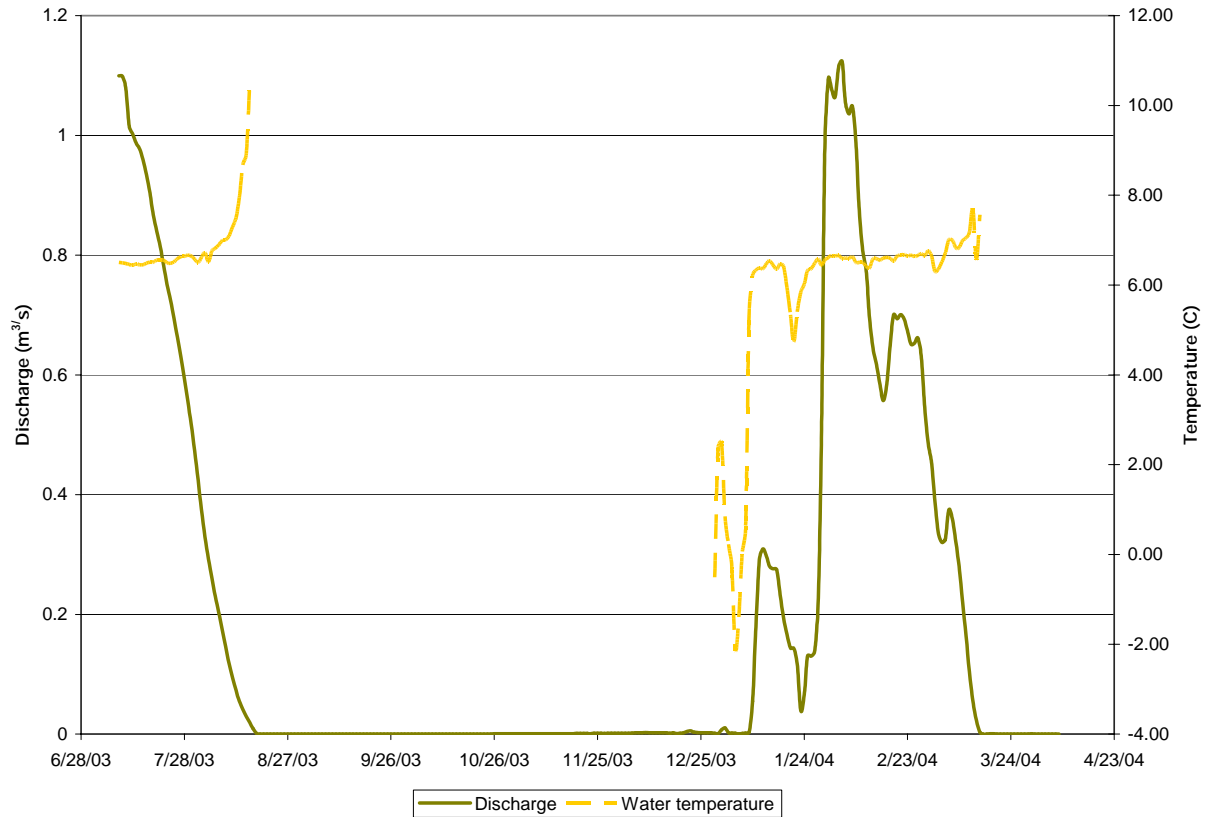


Figure 5. Discharge and water temperature of White Branch Creek near Highway 242. White Branch had no water in its channel from August 19 to October 25, 2003 and from March 16, 2004 until the end of the grant period.

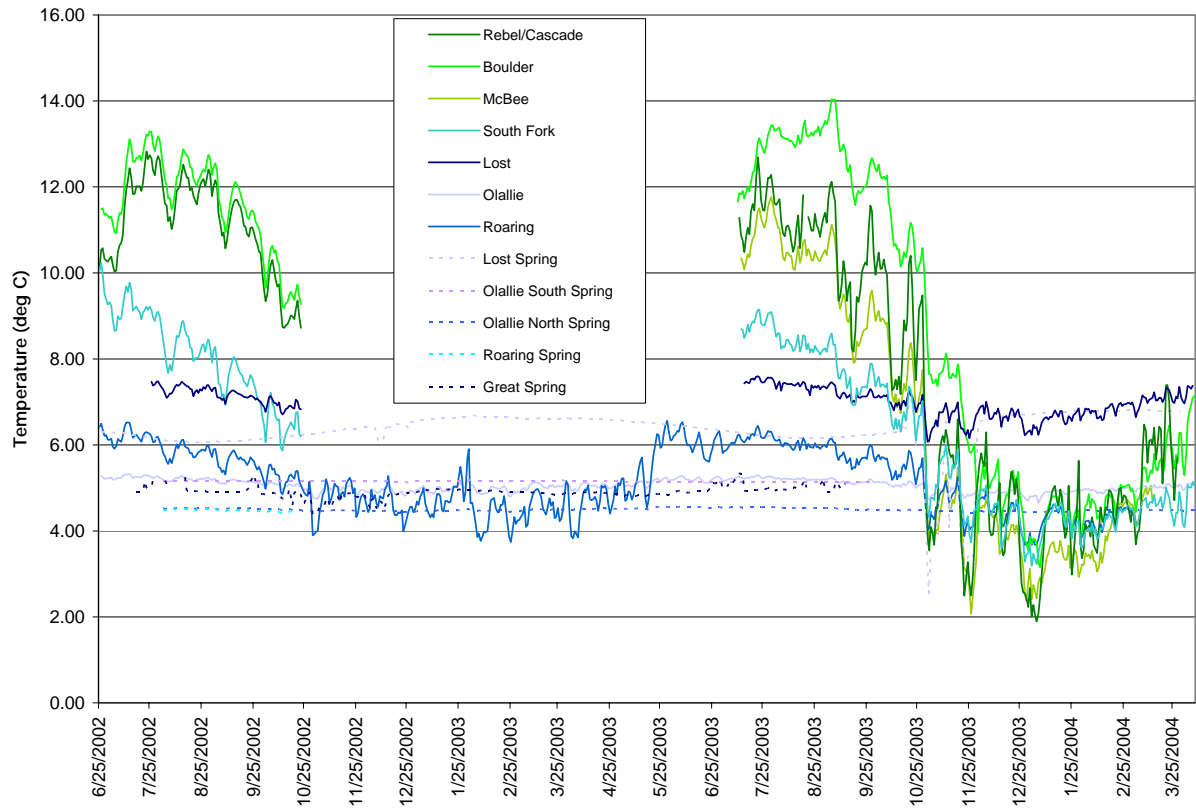


Figure 6. Water temperature histories of springs (dashed lines), spring-fed streams (blue colors), and runoff-dominated streams (green colors). Water temperature at springs measured by Hobo Water Temp Pro sensors, and in streams, temperature was measured using Hobo or Trutrack sensors.



# McKenzie River flow: August 5-7, 2003

**Discharge at Vida = 51 m<sup>3</sup>/s**  
**Gauged sources = 49 m<sup>3</sup>/s**  
**Spring-fed streams = 42 m<sup>3</sup>/s**

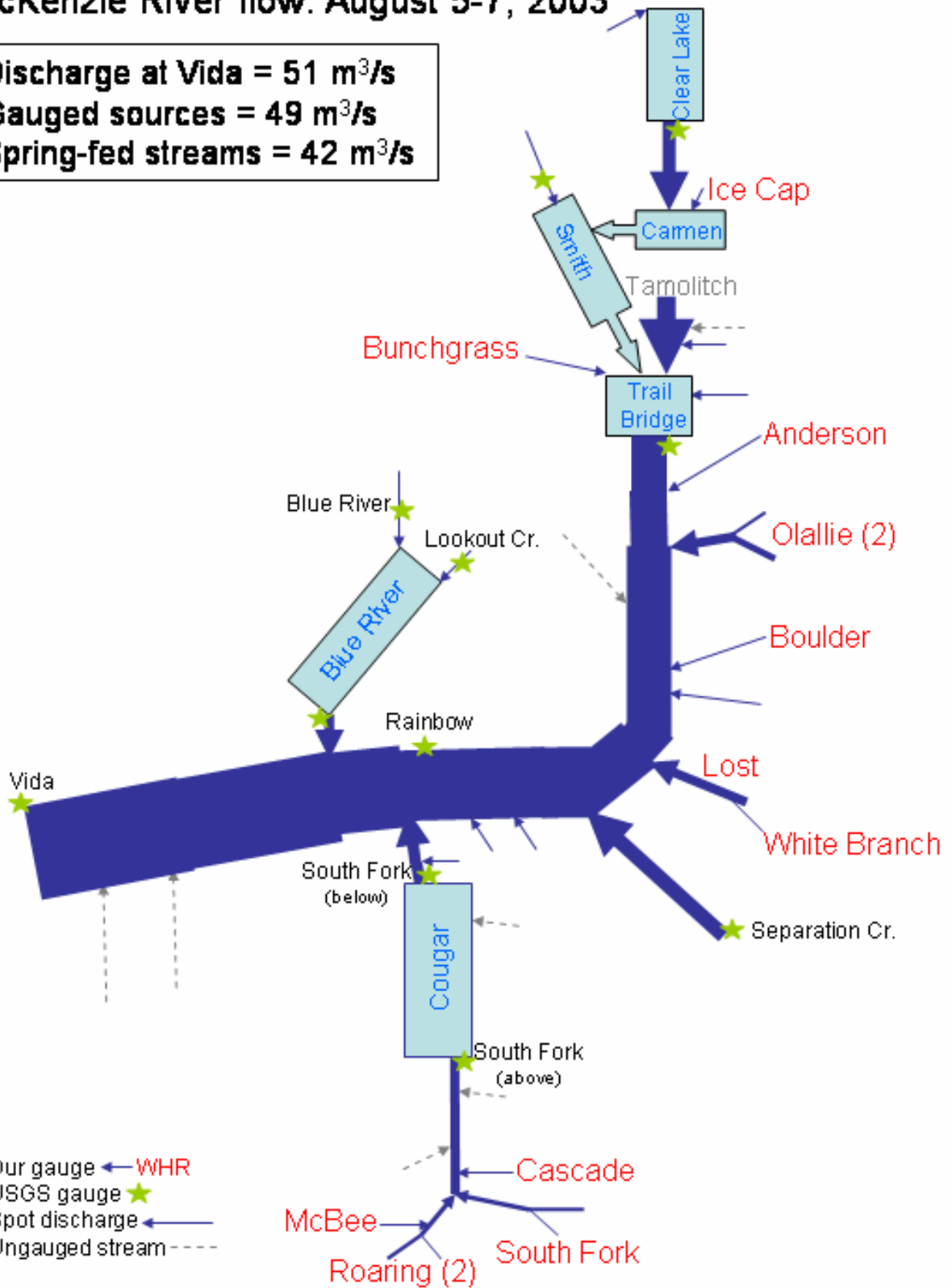


Figure 7. Sources of water to the McKenzie River during low flow (measured August 5-7, 2003).

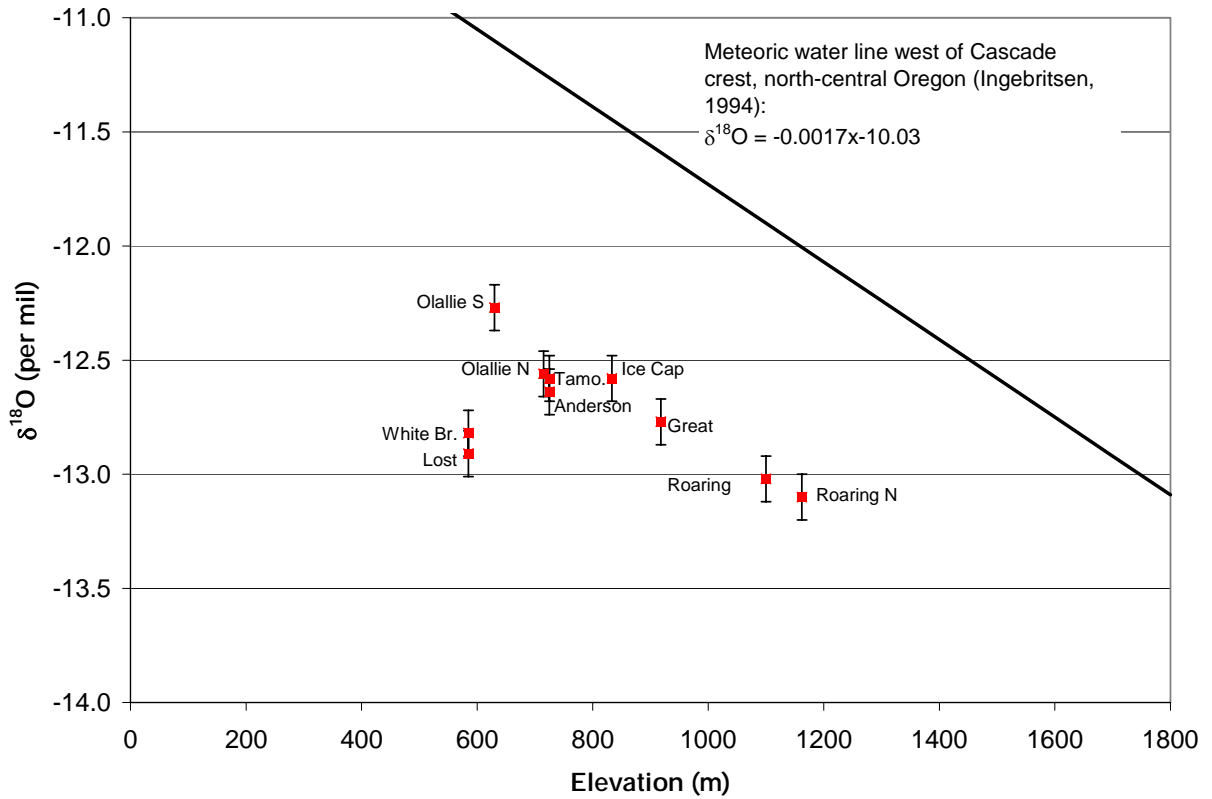


Figure 8. Average isotopic composition of spring water compared to spring elevation. Mean recharge elevation can be determined by projecting isotopic composition onto the meteoric water line.

Table 1. Tritium values for spring water samples collected November 15-17, 2003. One tritium unit (TU) is equal to 3.149 picocuries/L or 0.11815 Becquerels/L.

Spring	TU
Great	2.9±0.5
Lost	4.5±0.6
Olallie North	4.3±0.6
Olallie South	4.5±0.6
Roaring	6.1±0.7

# Temperature Effects of Streambed Heating

## Basic Information

<b>Title:</b>	Temperature Effects of Streambed Heating
<b>Project Number:</b>	2002OR2B
<b>Start Date:</b>	2/15/2002
<b>End Date:</b>	9/30/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 1st
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Models, Sediments, Water Quality
<b>Descriptors:</b>	TMDLs, water quality modeling, Bull Run River, temperature modeling
<b>Principal Investigators:</b>	Scott A. Wells, Robert L. Annear

## Publication

## Problem and Research Objectives:

The goal of this research is to examine the influence of streambed heating on stream water temperatures and incorporate a dynamic streambed heating algorithm in the CE-QUAL-W2 water quality model.

The objectives of this research are:

- Monitor streambed temperatures in the Lower Bull Run River to characterize vertical, longitudinal and lateral temperature gradients in different substrates.
- Monitor environmental factors influencing the river heat budget such as meteorological conditions, vegetation characteristics, light attenuation, and substrate geologic characteristics.
- Collect bathymetric cross section data to support model development.
- Conduct experimental work in a controlled environment to reduce the influence of wind, variable flow, and uncertainties with the substrate material.
- Develop a three-dimensional streambed heating algorithm for incorporation in the water quality model, CE-QUAL-W2 model.
- Implement the modified W2 model and calibrate it for the time period when field data were collected.

## Methods, Procedures, and Facilities:

There research work involved two components: A field component which was conducted during the summer of 2002 and an experimental lab component conducted during the fall of 2002.

### **Field Work**

#### **Bathymetric Data**

Bathymetric cross-sections were collected at nine locations in the field study reach on July 25<sup>th</sup> and July 26<sup>th</sup> 2002. Cross-section elevations were tied to a benchmark located on the Rt. 14 Bridge in the middle of the field study reach. The river channel cross-sections were combined with the stream bank topography from a U.S. Geological Survey (U.S.G.S.) Digital Elevation Model (DEM) to generate a contour plot of the river bathymetry. The contour plot was then sliced into 10 pieces to develop the CE-QUAL-W2 model segments.

#### **Stream Temperature Data**

Stream temperature data were collected at two locations upstream of the Rt.14 Bridge using OnSite StowAway temperature logger, recording at 10-minute intervals. The U.S.G.S. monitored one location downstream of the bridge at 15-minute intervals using a thermocouple. The two upstream monitoring sites upstream included replicate thermistors. The data collected at the sites were used for the model upstream boundary condition and for calibrating the model.

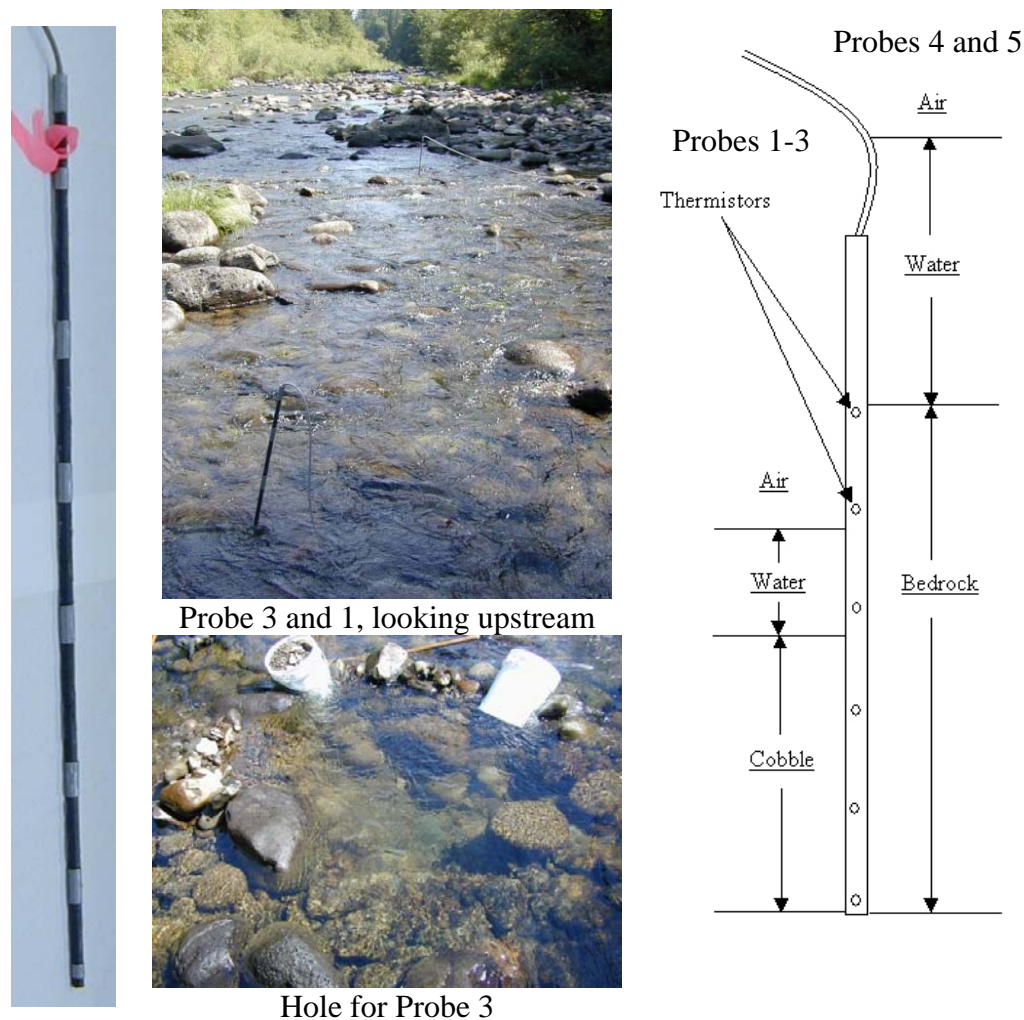
#### **Streambed Temperature Data**

Streambed temperatures were monitored at five locations in the study reach. Three locations were monitored above the Rt. 14 Bridge in cobble substrate (Probes 1 to 3) and two locations were monitored below the bridge were in bedrock substrate (Probes 4 and 5). The temperature probes were constructed using 6.35 mm diameter PVC pipe with a length of 1.25 m with 6 glass bead thermistors, spaced 20 cm a part. The probe was filled with silicone for waterproofing. Figure 1 shows one of the completed

probes. Two probes were placed in the field and after a week or more they were moved to a new location.

The probes placed in the cobble reach were placed at a maximum depth of 0.50 m due to the compact nature of the substrate and the inability of equipment to effectively penetrate deeper. The probe was placed in the hole, and the substrate replaced in the reverse order that it was removed. Figure 1 shows two probes placed in the streambed after the holes were filled. The substrate then settled around the probes, which was confirmed when the probes were removed a few weeks later. Only the bottom three thermistors were buried in the substrate.

Two probes, Probes 4 and 5, were placed in bedrock using holes drilled by the City of Portland, Water Bureau. The holes were drilled to depths of 1.05 and 1.0 m with diameters between 25 and 32 mm (1.0 to 1.25 in). The probes were placed in the holes so the top thermistor was just below the substrate – water interface as shown in Figure 1. The probe was pressed against the side of the drilled hole with a long narrow piece of wood, and then sand was used to fill in the backside of the hole.



**Figure 1. Streambed temperature probes, probes in the cobble went to a depth of 0.5 m below the sediment-water interface, probes in the bedrock were placed to a depth of 1 m.**

Probes 1 and 2 were placed for two weeks to examine lateral variability on streambed temperatures. Probe 2 was then removed from the substrate and was placed downstream of Probe 1 to investigate

longitudinal variability in streambed temperature (re-designated as Probe 3). After 2 weeks the two probes were removed and placed at the two bedrock sites Probes 4 and 5.

### **Streambed Substrate and Geology**

The streambed in the reach transitioned from cobble and boulder at the upstream end to primarily bedrock at the downstream end. The streambed substrate in the study area can be characterized by three reaches. Reach 1 is characterized primarily by boulders and large cobble and represents the toe end of a plane-bed reach with riffle to run unit characteristics in low flow. Reach 2 substrate is characterized primarily by boulders and bedrock with a very uneven bottom surface capturing some cobble. The reach is a turbulent cascade with a slope of 2.4%. Reach 3 is characterized as a mid-channel pool reach with the deepest parts of the pool closer to head of the reach. The substrate is primarily bedrock with boulders and large cobbles predominately on the sides and banks. The toe of the reach slopes upward and is dominated by large cobble and boulders overlying the bedrock.

- Bedrock substrate

The underlying river channel geology has been discussed by the U.S.G.S. (1996), Baldwin (1981) and Beeson and Moran (1979). The U.S. Forest Service mapped the river channel geology in 1997 as Columbia River Basalts. The bedrock substrate in the Reaches 1 and 2 (and elsewhere in the basin) are where the Columbia River Basalts have been exposed and remain resistant to fluvial erosion (U.S.F.S., 1997). In Reach 3 the holes were drilled in the bedrock to place two temperature probes. Samples of the bedrock substrate were collected during drilling. The bedrock particles are dark gray and appear to be fine grained indicating the substrate is likely part of the Columbia River Basalt Formation.

- Boulder/Cobble substrate

Three temperature probes were placed in Reach 1 for the first few weeks of the field study. Boulders and large cobble substrate dominated this reach and are believed to be lying over the Columbia River Basalt seen in Reaches 2 and 3. On August 18, 2002 Ground Penetrating Radar was used on two cobble substrate sites to determine the depth of the cobble overlying the bedrock. When digging the holes to place the temperature probes the particle size was observed to decrease with depth.

### **Meteorological Data**

Meteorological data were collected at two locations in the lower river: the U.S.G.S. gage station (14140000) and on the Rt. 14 Bridge. The monitoring site on the bridge measured solar radiation at 10-minute intervals. The monitoring site at the U.S.G.S. gage station was maintained by the City of Portland, Water Bureau and measured air temperature, relative humidity, wind speed and wind direction at 15-minute intervals.

### **Light Attenuation Data**

Light attenuation data was collected on July 25<sup>th</sup> and September 20<sup>th</sup>, 2002 at 21 monitoring sites. Data collected on July 25<sup>th</sup> used a spherical photosynthetic active radiation (PAR) sensor and measurements were taken above the water surface and at the bottom of the water column. Data collected on September 20<sup>th</sup> used an incident PAR sensor and measurements were taken just below the water surface and at several depths below the surface. The incident sensor was also inverted to measure radiation reflecting off the substrate.

## **Flow and Dye Study Data**

The large cobbles and boulders characterizing Reach 1 indicate there is the possibility of hyporheic flow. If hyporheic flow exists then the water would emerge at the end of Reach 1 where the cobble and boulder layer overlying the bedrock ends in Reach 2. A dye study was conducted on September 5<sup>th</sup> and surface water and groundwater levels were measured to investigate this issue.

- Dye study

A dye injection probe was placed in the streambed by digging a hole similar to the holes used for the streambed temperature probes. The probe consisted of a 1.27 cm diameter PVC with a hole drilled one cm from the bottom where a small tube with inner diameter of 3 mm was inserted and run on the inside of the PVC pipe to the top. The probe was placed in the streambed on August 30<sup>th</sup> and air was injected to ensure the tube was not blocked at the buried end. The dye study was conducted on September 5<sup>th</sup> to allow the substrate surrounding the probe to settle. The injection tube was a depth of 0.47 m below the surface of the substrate, similar to the deepest thermistors buried in the streambed. 48 ml of Rhodamine WT dye was injected in the tube at 8:15 am and then flushed with 20 ml of water. Based on visual observations in the tube there was no red dye present after flushing. Water samples were then taken downstream of the injection point at the three locations. Site "A" was located 7.6 meters downstream of the injection point. Site "B" was located 33 m downstream of the injection point, where the cobbles overlying the bedrock end. If the dye was to be transported downstream in the substrate then it would emerge near this monitoring site. Site "C" was located 0.3 m downstream of the injection point to monitor if the dye immediately surfaced.

- Water Level Measurements

The dye injection probe was also used to measure the water levels in the substrate and the river water level to determine if there was a gradient. The dye injection PVC pipe had a large enough diameter to place a rod in the pipe and measure the water level relative the top of the pipe. The river water level on the outside of the pipe was also measured relative to the top of the pipe.

## **Vegetative and Topographic Shade Data**

- Vegetation data

The vegetation data collected consisted of vegetation (tree) heights and the distance from the river centerline to the vegetation. A field person walked along the middle of the stream channel and used a laser range finder to measure both tree heights and the vegetation offset distances. The vegetation heights were converted to vegetation top elevations by adding the bank elevation to the tree height. The distance from the river centerline to the vegetation for each bank was used directly in developing the model file.

## **Lab work**

Several lab experiments were conducted to demonstrate streambed heating processes in a more controlled environment to reduce the influence of topographic and vegetative stream shading, cloud cover, atmospheric dust and moisture attenuation, wind, and variable flow. The results of the

experiments will be used with the streambed heating algorithm to test the algorithm's ability to handle a more simplified streambed heating case and to demonstrate the basic streambed heating processes.

### Experimental Design

The experiment was designed to monitor the temperature of substrate material in 2 buckets (5 gallons each) with overlying water exposed to constant radiation during the day and none at night. Each bucket had 4 temperature probes embedded in the substrate and 1 in the water above the substrate. The buckets were placed in a larger tub, which was filled with sand to provide a heat sink. The outside of the buckets and the air were also monitored with thermistors to better understand the buckets' boundary conditions. All thermistors recorded temperature at 5-minute intervals. The radiation was supplied by a narrow spot beam stage light, which produced approximately  $1010 \text{ W/m}^2$  at 2.3 m above the experiment. Radiation was measured at 10-minute intervals with a pyranometer placed between the two buckets. The lamp was turned on for 8.5 hours a day using a timer. Figure 2 shows a drawing of the experimental design with thermistor locations identified by numbers and letters.

Each bucket was filled with substrate material to a depth of 20 cm and then filled with water to a depth of 6 cm. Evaporated water from the buckets was replaced with water at room temperature. The first experiment used one bucket filled with sand and the other with gravel. The second experiment used one bucket with sand and gravel and the other with sand. The third experiment had both buckets filled with concrete, one painted white and the other painted black.

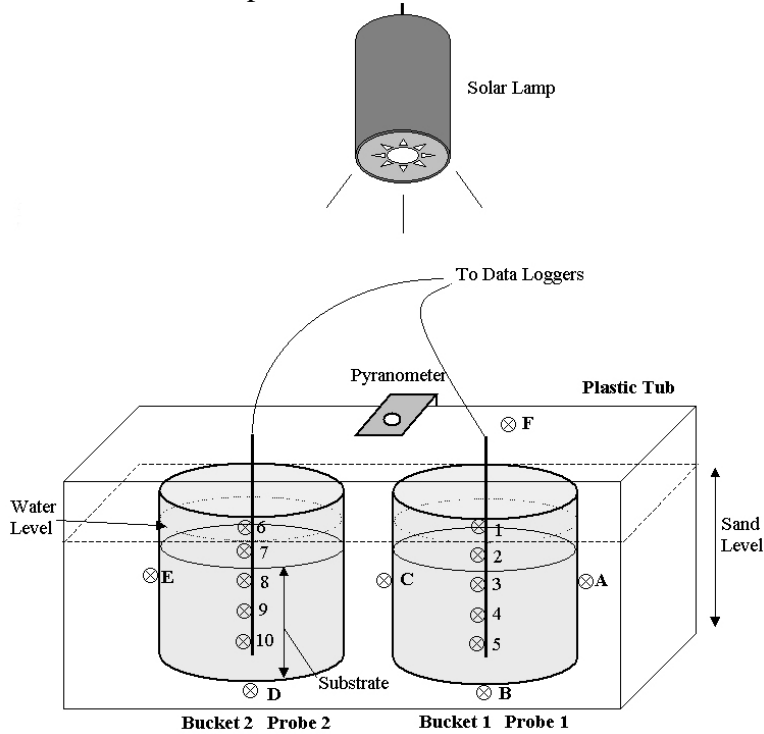


Figure 2. Experimental lab design

### Principal Findings and Significance:

The research work is currently still in progress with completion anticipated by the end of 2003. The field and lab work have been completed but the modeling work is still in progress. The fieldwork results show there is a vertical temperature gradient in both the cobble and boulder streambed and the bedrock



streambed. Figure 3 shows an 8-day period for one of the probes placed in the cobble and boulder streambed. The figure shows cooler temperature further down in the streambed material. Figure 4 shows a similar plot for the bedrock material. Temperature measurements near the sediment-water interface are similar to the water temperature measurements but deeper in the streambed the diurnal fluctuations are minimized and several degrees cooler. The lab experiments conducted also showed decreasing temperatures with depth. Figure 5 shows temperature measurements recorded in the sand and gravel media experiment conducted in the lab. The plot shows diurnal fluctuations in temperatures but the results indicate there are slightly different processes influencing the temperature measurements at larger depths. Because the lab experiment is based on a small amount of “substrate” material the sand surround the bucket may be influencing the temperatures recorded in the bucket. The data collected in the field and in the lab will be used to test the streambed heating algorithm.

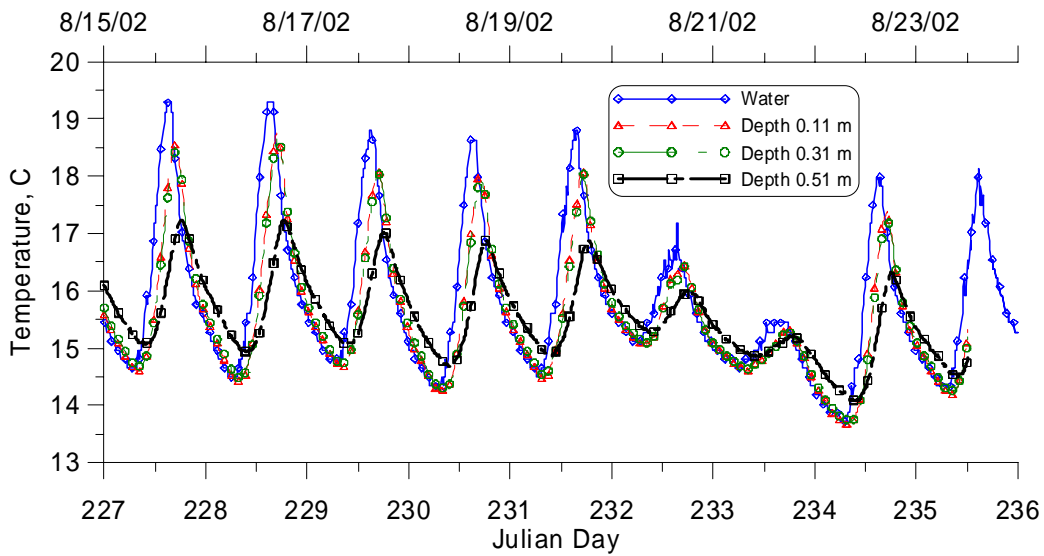


Figure 3. Streambed temperature Probe 1, cobble substrate

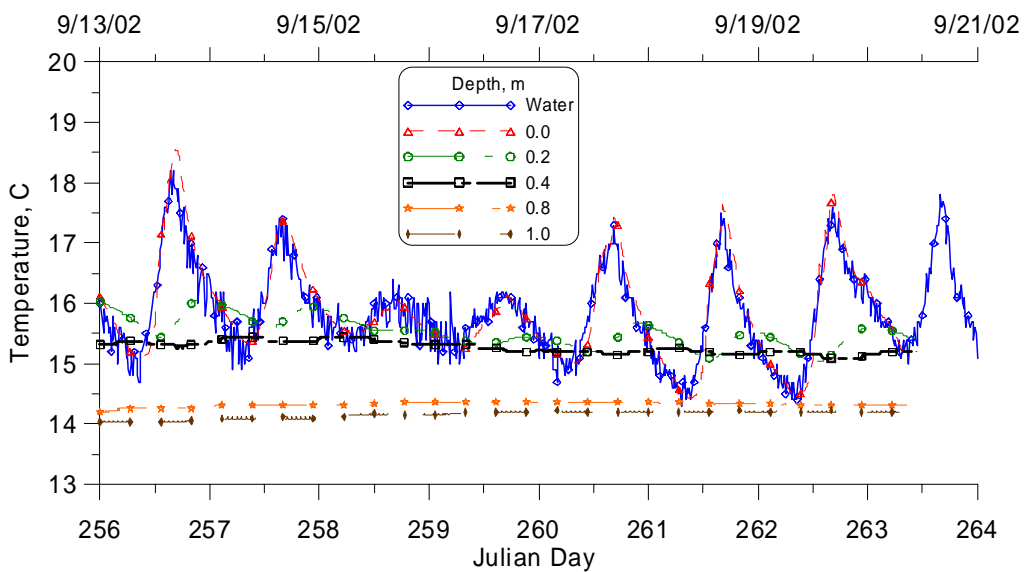
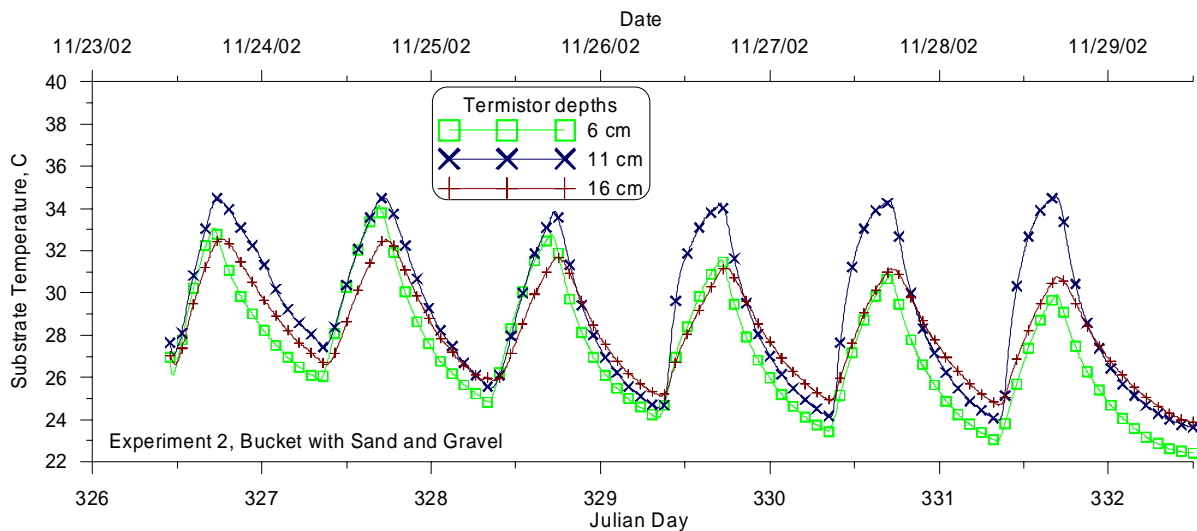


Figure 4. Streambed temperature Probe 5, bedrock substrate



**Figure 5. Experiment 2, measured temperatures in Sand and Gravel media bucket.**

### Training and publications:

Two abstracts for the research work have been submitted to conferences in the fall of 2003. The first abstract was submitted to the Pacific Northwest Clean Water Association Annual Conference in September and was recently accepted. The second abstract was submitted to the American Institute of Hydrology Conference in October.

When the work is completed papers will be submitted to various journals such as *Environmental Modeling and Software* and the *International Journal of River Basin Management*. In addition, a longer report will be submitted to the Center for Water and Environmental Sustainability.

### References

- Baldwin, E. M. (1981). *Geology of Oregon, Third Edition*, Kendall/Hunt Publishing, Dubuque, IA, 170 pp.
- Beeson, M. H., and Moran, M. R. (1979). "Columbia River Basalt Group stratigraphy in western Oregon." *Oregon Geology*, 41(1), 11-14.
- U.S. Forest Service (1997). *Bull Run Watershed Analysis*, Mt Hood National Forest, Pacific Northwest Region, U.S. Forest Service, Portland, OR, 521 pp.
- U.S. Geological Survey (1996). "Hydrogeological Setting and Preliminary Estimates of Hydrologic Components for the Bull Run Lake and the Bull Run Lake Drainage Basin, Multnomah and Clackamas Counties, Oregon." *Water Resources Investigations Report 96-4064*, Prepared in Cooperation with City of Portland, Bureau of Water Works, Portland, OR. 47 pp.

## **Information Transfer Program**

CWESSt continued its interest in supporting efforts to make water resources data sets accessible to potential users. Projects were selected that included: data set(s) for web use, techniques or methods for making data more accessible and/or useful to other users, direct connection to needs of user communities.

# Development of a relationship between water quality data and land use in the Oak Creek Watershed

## Basic Information

<b>Title:</b>	Development of a relationship between water quality data and land use in the Oak Creek Watershed
<b>Project Number:</b>	2003OR30B
<b>Start Date:</b>	2/15/2003
<b>End Date:</b>	2/14/2004
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 5th
<b>Research Category:</b>	None
<b>Focus Category:</b>	Nutrients, Management and Planning, Non Point Pollution
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Peter Nelson

## Publication

1. Poor, C., K.Vache, D.Godwin, J. Bennett, C. Blatchford, M. Cox, M. Dewey, F. Kizito, J. Melick, R. Mitchell, J. Mutti, J. Nicholas, L. Parker, J. Pennington, J. Schmalenberg, Spelts, J. McDonnell, Improvement of Process Description in Conceptual Runoff Models in the Ungauged Basins: A Case Study of Landuse Effects on Water Quality, EOS Trans. AGU, 85(17), Jt. Assem. Suppl., Abstract H53B-04.
2. Poor, C., J. McDonnell, P. Nelson, The Effects of Land Use on Nitrate and DOC Dynamics in a Mesoscale Watershed (in progress).

Problem and Research Objectives: The Oak Creek Watershed is 33 km<sup>2</sup>, and is located in Corvallis, Oregon. Oregon State University (OSU) manages approximately 40% of the watershed, with multiple uses including forestry, agricultural animal production, stadiums, and urban campus activities. It was determined in 1999 that these multiple uses are not managed in a coordinated manner. To minimize non-point source pollution and properly use public resources, coordination of management objectives and operations is essential. An Oak Creek Action Team was appointed in 1999 to determine key issues and recommend alternatives for Oregon State University.

The Oak Creek Action Team issued a report in June 2000 recommending additional monitoring and management actions to improve the health of Oak Creek and benefit the research and teaching activities in the watershed. This project will provide additional water quality data for the watershed and recommend management improvements, which will carry forward the Action Team's plan. The overall result of this project will be improved management (and thus water quality) and further development of the watershed as a research and teaching tool for OSU.

The objectives of this project are to establish baseline water quality data, to relate land use with water quality, and to recommend land use management improvements for the Oak Creek Watershed. Specific objectives include:

1. Process synoptic water quality samples taken in October 2002 to determine water quality parameters.
2. Analyze water quality data from November 2001 and October 2002 synoptic sampling to determine the seasonal baseline water quality conditions (spatially/longitudinally) in the watershed.
3. Develop a detailed temporal relationship between land use and water quality using baseline water quality and storm events.

Methods, Procedures, and Facilities: Methods for completing the project are summarized below:

1. Process synoptic water quality sampling conducted at 35 sites across the Oak Creek Watershed (Figure 1) in October, 2002 using the Environmental Engineering laboratory on the OSU campus. Specific constituents that will be determined are:
  - a. Nutrients (nitrate, ammonia, organic nitrogen, phosphate, organic phosphorous)
  - b. Electrical conductivity (EC), base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and major anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ).
  - c. Oxygen isotopes (for water source determination). (Note: Oxygen isotopic analyses will be conducted in collaboration with USGS Water Quality Laboratory, Menlo Park, California.)
2. Compare the water quality data from the November 2001 and October 2002 synoptic sampling events. The November sampling was conducted when antecedent conditions were relatively wet after the first fall rains, but nevertheless during baseline runoff conditions not influenced by any recent storm events. The October sampling was conducted during baseline runoff flow when antecedent conditions were still relatively dry. Figure 1 shows the speciation and distribution of nitrogen in the watershed from the November 2001 sampling. A similar analysis will be conducted for the October 2002 sampling. We anticipate there will be differences between the water quality constituents from these two sampling dates. Areas that were hydrologically isolated during dry conditions may be connected to the stream when conditions become wet, creating new sources of water quality constituents. We hypothesize that concentrations of water quality constituents such as nitrate will be higher after the first few fall storms (November 2001 sampling) than during dry conditions (October 2002 sampling).
3. Collect water quality samples in four subcatchments of varying land uses (forested, agricultural, residential and suburban) during a fall, winter, and spring storm event to determine how nitrate and DOC concentrations vary during storm events. Sampling sites are shown in Figure 3.

4. Use all water quality data to determine how land use affects water quality in the Oak Creek Watershed. Determine sources and sinks of nutrients.
5. The information derived from this analysis will be tabulated and put on the existing Oak Creek website (<http://cwest.orst.edu/oakcreek/index.htm>) for use by managers and the general public.

Existing equipment in the Environmental Engineering laboratories at Oregon State University that will be used in support of the proposed research include a Dionex Model DX 500 Ion Chromatograph, Dohrmann DC-190 Total Organic Carbon Analyzer, Hewlett-Packard Model 8453 Scanning UV-Visible Spectrophotometer, and Varian Liberty 150 ICP Atomic Emission Spectrophotometer. Other instrumentation to be used includes specific ion meters, automatic titrimeters, and laminar flow hood. Fieldwork will be supported by portable instruments including a pH meter, conductivity meter, and turbidimeter. Supporting facilities on the O.S.U. campus with a wide range of analytical capabilities are available on a cooperative basis, including the Radiation Center (isotope preparation and counting), Soil Science Laboratory (soil chemical and physical characterization), Agricultural Chemistry Laboratory (pesticide and organic compound analyses), Forest Sciences Laboratory (trace nutrients), and Oceanography Laboratory (ICP-MS for trace metals).

**Principal Findings and Significance:** Table 1 shows the average concentrations from the synoptic sampling in 2001 and 2002. In general, nitrate and sulfate concentrations are higher during the November 2001 sampling event (wet antecedent conditions). This may be due to the rising water table flushing these nutrients out of the soil during the wetting up sequence in the fall. The October 2002 sampling event occurred after the summer dry period, and thus most of the stream water is likely from groundwater. Magnesium, silica, DOC, and chloride concentrations were similar for both events. Excluding DOC, these ions are considered conservative, and therefore are not expected to change significantly. Calcium concentrations are lower during the November 2001 event, indicating there may be a dilution effect for this cation. Calcium concentrations in the groundwater may be higher, with soil water decreasing stream water concentrations when wet conditions occur.

**Table 1. Average Values of Water Quality Concentrations**

Date	calcium (mg/L)	magnesium (mg/L)	silica (mg/L)	DOC (mg/L as C)	chloride (mg/L)	nitrate-N (mg/L)	sulfate (mg/L)
October 2002	13.07362169	9.571983601	12.2592558	4.137051624	9.280862974	0.07148621	2.544722558
November 2001	10.29419934	8.772846957	12.1406596	3.721383705	8.967357209	0.516998524	7.762547234

To further investigate water quality in the Oak Creek Watershed, three storm events were sampled in subcatchments with four different land uses. For all storms, chloride concentrations were constant except for the suburban catchment. Figure 4 shows the general trend of chloride concentrations for the suburban catchment, which was seen for the three storm events. Constant chloride concentrations indicate that the sources of chloride in the catchment have similar concentrations. In the suburban catchment, chloride concentrations initially decrease on the rising limb of the hydrograph and then increase. This “dip” in chloride concentrations may be due to the altered nature of this catchment; storm water is routed to storm pipes that empty into Oak Creek. Thus there is a disconnect between the soil and storm water. The decrease in chloride concentrations could be due to the direct runoff of storm water, with the soil eventually wetting up and contributing to runoff. Nitrate concentrations showed a similar trend in the suburban catchment.

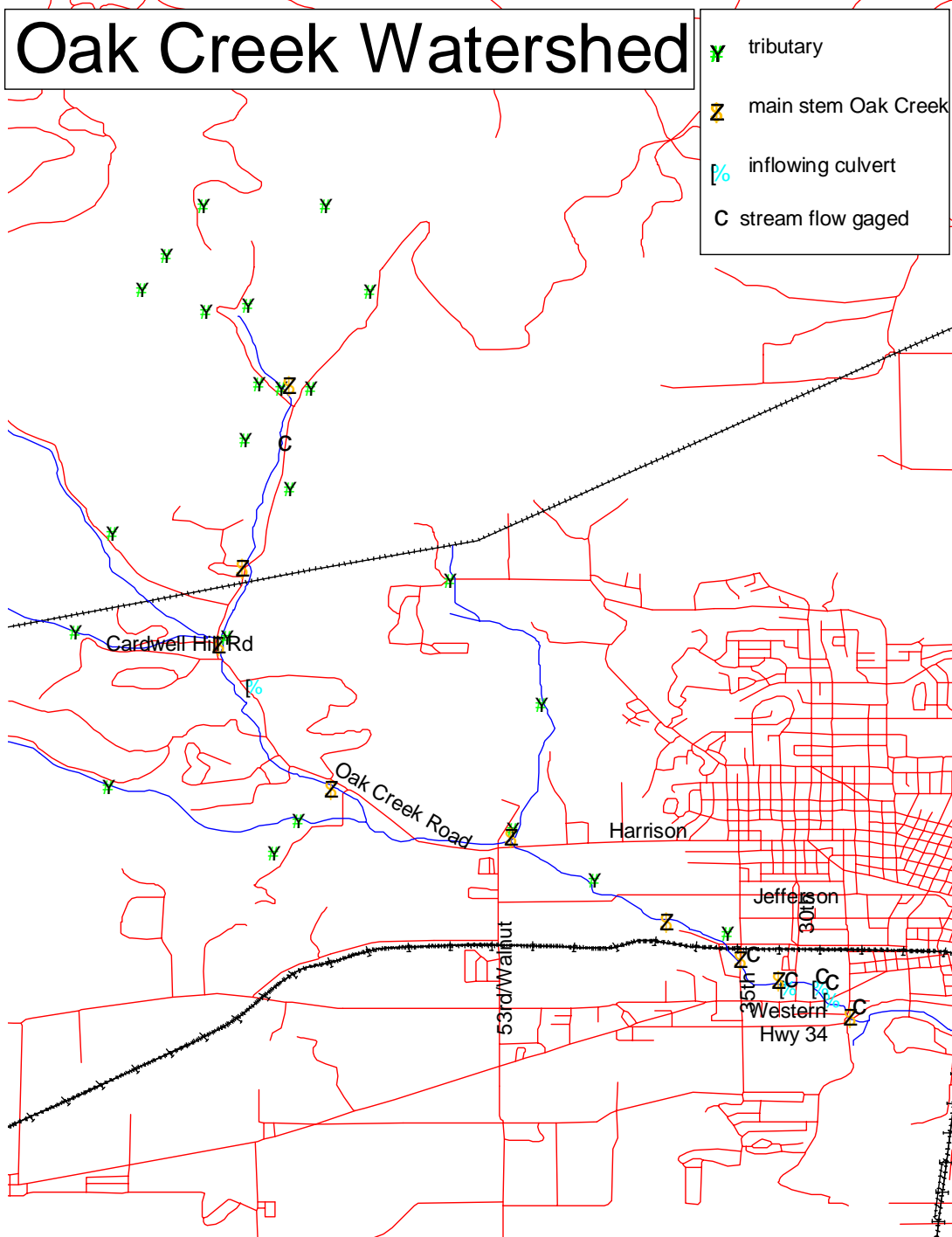
Both the forested and residential nitrate concentrations increased with the increase in flow for each storm. This indicates there is an unlimited source of nitrate that is not being diluted with rain water. Nitrate concentrations are shown in Figure 5 for the forested catchment. In the agricultural catchment, nitrate concentrations decreased with increasing flow for the fall (Figure 6) and winter storms, but increased with increasing flow for the spring storm (Figure 7). This may be due to an additional source during the spring; this storm event was right after the lambing period and a high density of sheep were grazing within the watershed. There were also cows grazing within the watershed that were not present during the fall and winter storms.

In general, the suburban catchment had the highest nitrate levels (~1.5 mg/L as N), followed by the residential and agricultural catchments (both ~0.2 mg/L as N), and the forested catchment (~0.04 mg/L as

N). This follows the general assumption that nitrate concentrations will increase with increasing development. Chloride concentrations also generally increased with increasing development, with the residential catchment having the highest chloride concentrations (~14 mg/L). DOC concentrations were similar for the forested, agricultural, residential, and suburban catchments. This is due to the abundant source of organic carbon (natural or landscape) in each catchment.

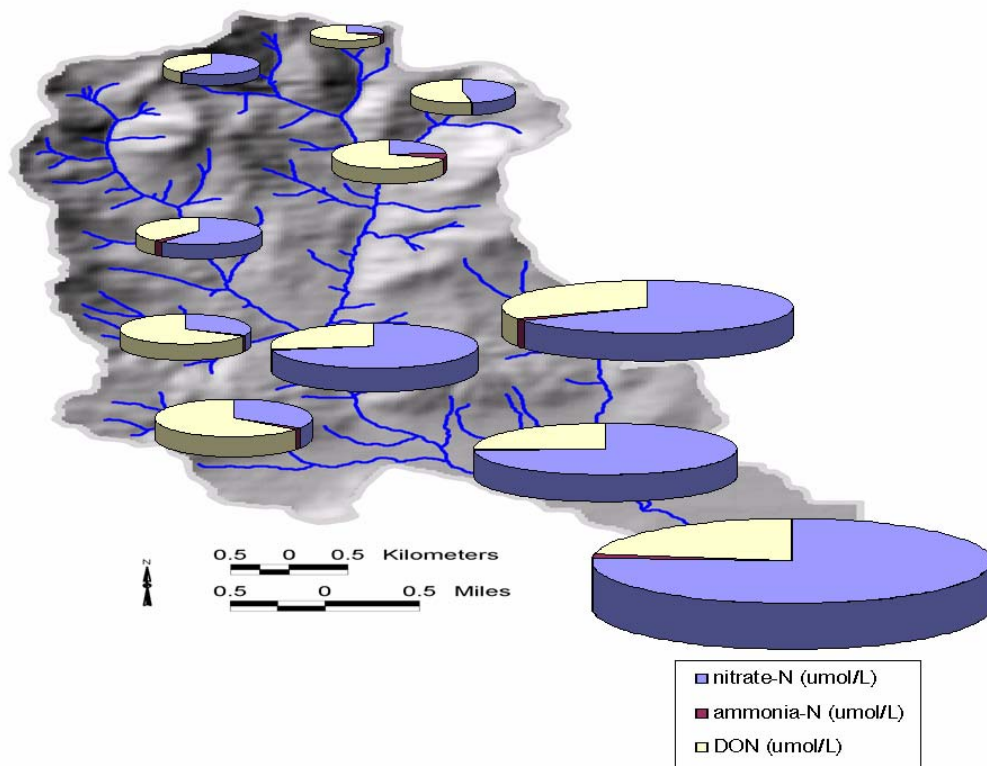
From this data, it appears that nitrate is strongly controlled by the hydrology of the catchment. Depending on the availability of sources, nitrate will either increase with increasing flow or be diluted by rain water. More work is needed to determine sources and timing of inputs. It is also apparent that land use affects nitrate concentrations. As development increases and the stream flow paths become increasingly disconnected with the soil, removal mechanisms such as denitrification are no longer occurring. Large riparian zones may help eliminate nitrate contamination to streams; if water flows through a riparian zone before it reaches the stream, nitrate concentrations will decrease. Since the natural stream no longer exists and a pipe drains the catchment, treatment of the storm water draining from the suburban catchment may be needed for this to occur.

Student Support (# and degree level): One PhD student (Cara Poor) was funded with this support.

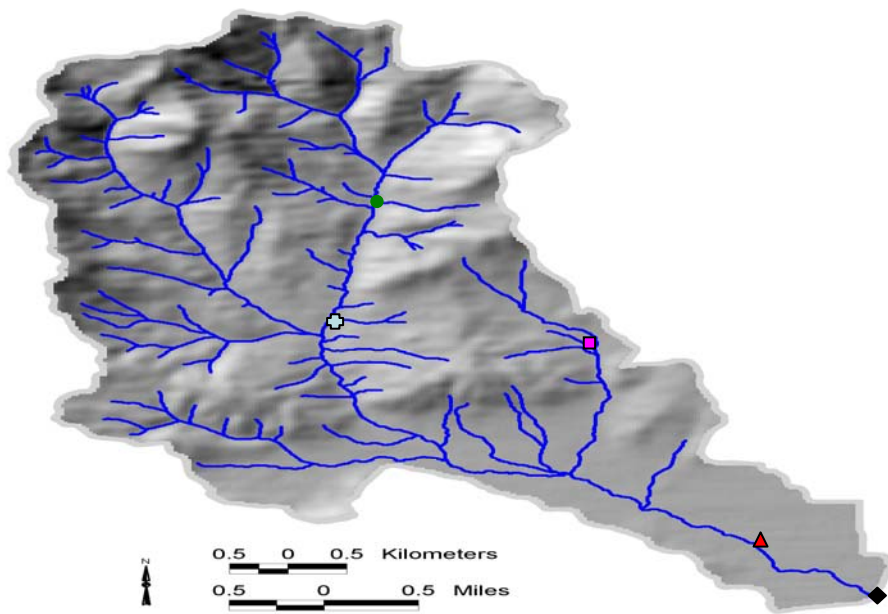


**Figure 1.** Locations of synoptic water quality samples, taken in November 2001 and October 2002.

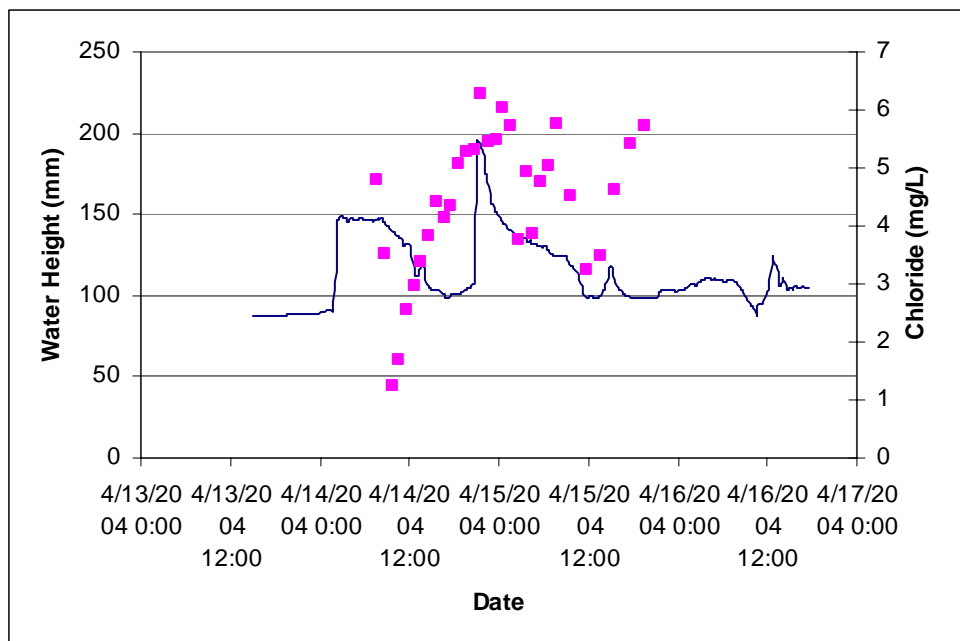




**Figure 2.** Results from November 2001 synoptic sampling. Pie charts are scaled to total nitrogen concentrations.



**Figure 3.** Storm Sampling Sites within the Oak Creek Watershed.



**Figure 4.** Chloride Concentrations in Suburban Catchment during the Spring Storm Event.

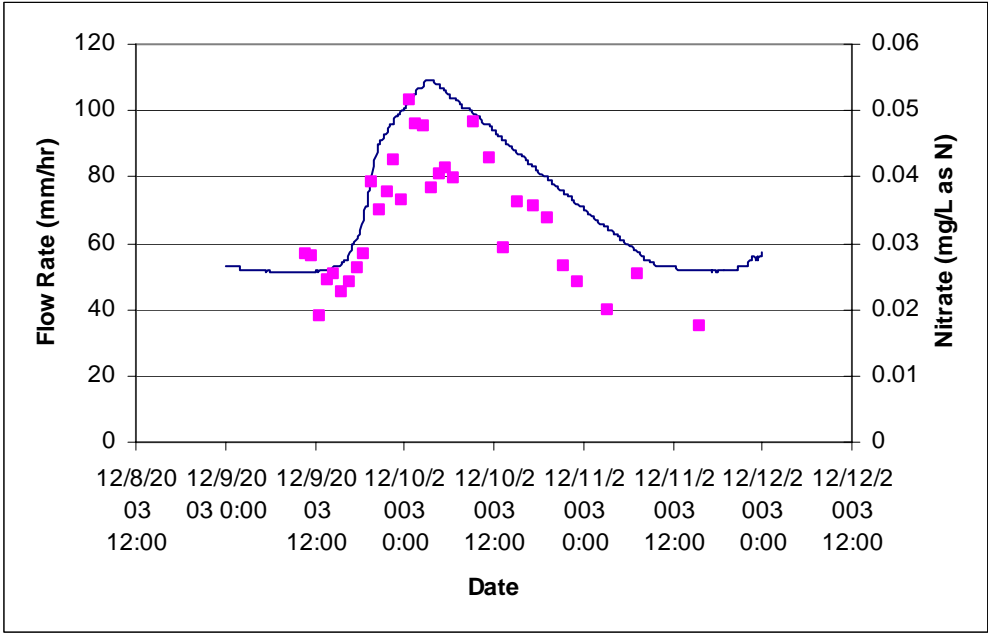


Figure 5. Nitrate Concentrations in the Forested Catchment during the Fall Storm Event.

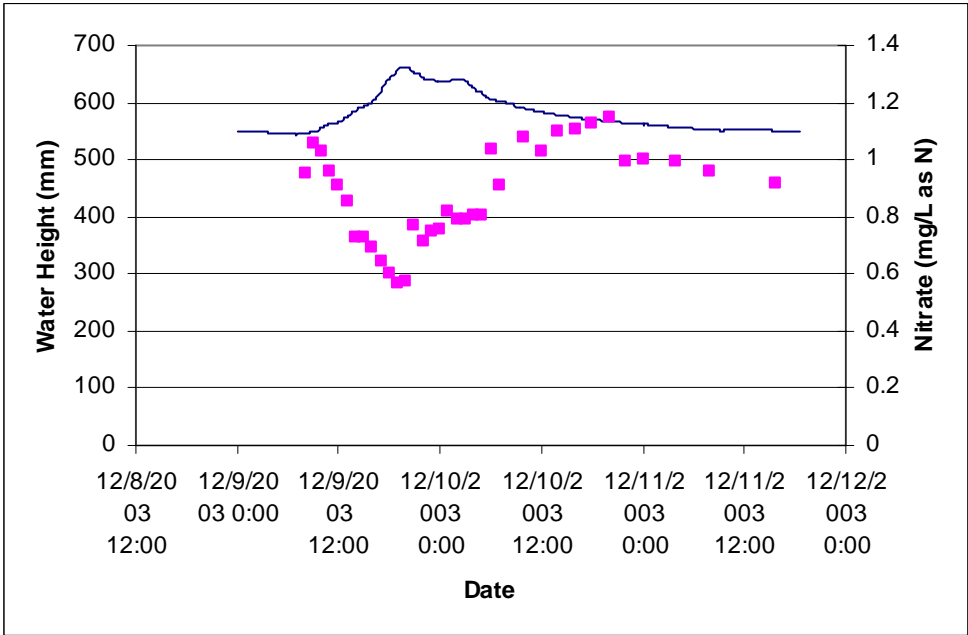
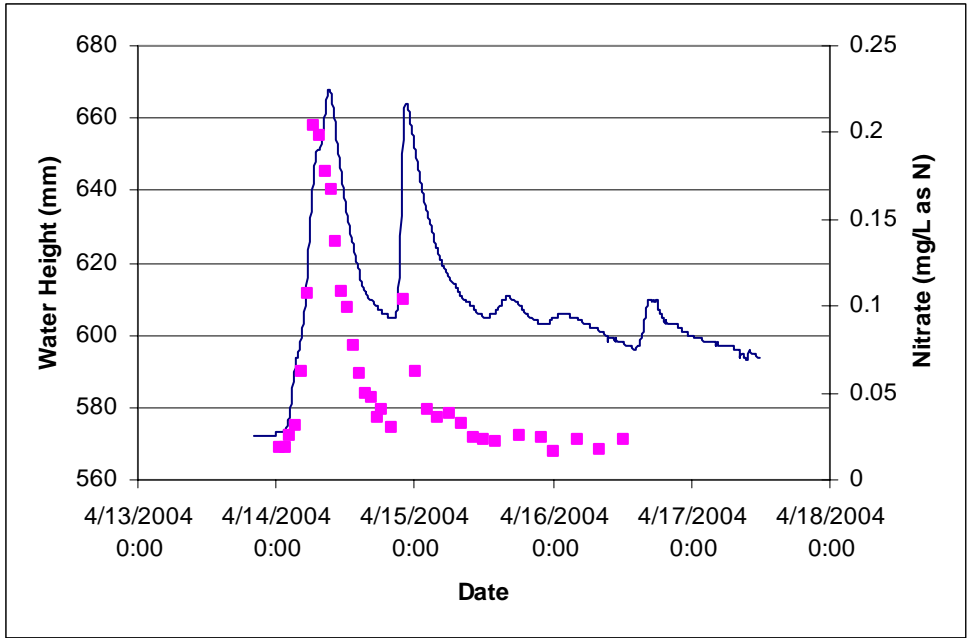


Figure 6. Nitrate Concentrations in the Agricultural Catchment during the Fall Storm Event.



**Figure 7.** Nitrate Concentrations in the Agricultural Catchment during the Spring Storm Event.

# Environmental Analysis of Wastewater Effluents and Biosolids-derived Endocrine Disrupting Chemicals in the Willamette River

## Basic Information

<b>Title:</b>	Environmental Analysis of Wastewater Effluents and Biosolids-derived Endocrine Disrupting Chemicals in the Willamette River
<b>Project Number:</b>	2003OR31B
<b>Start Date:</b>	4/15/2003
<b>End Date:</b>	4/14/2004
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 5th
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Toxic Substances, Management and Planning, Surface Water
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Tarek A. Kassim

## Publication

1. Kassim TA, 2004, Forensic analysis, mass balance and fate modeling of endocrine disrupting chemicals in wastewater treatment plants. 4th SETAC World Congress, Society of Environmental Toxicology and Chemistry, SESSION: A05 Endocrine-Disrupting Chemicals in Wastewater Treatment Effluents, 14-18 November, 2004, Portland, Oregon
2. Kassim, T.A., 2004, Multicomponent joint toxic effect modeling of organic contaminants from complex mixtures. 4th SETAC World Congress, Society of Environmental Toxicology and Chemistry, SESSION: B34 Toxicity of Complex Mixtures, 14-18 November, 2004, Portland, Oregon
3. Kassim, T.A., 2004, Forensic Analysis of Wastewater Effluents- and Biosolids-Derived Endocrine Disrupting Chemicals in the Willamette River. Gordon Research Conference, Environmental Sciences: Water, June 27 - July 2, 2004, Holderness School, Plymouth, NH
4. Kassim, T.A., 2002, Environmental Analysis and impact assessment of endocrine disrupters in the Willamette River Project approach. The 5th International Conference of the Balkan Environmental Association on Transboundary Pollution, 7-10 Nov. 2002, Belgrade, Yugoslavia
5. Kassim, T.A., 2004, Sorption/Dissipation Behavior of Veterinary and Human Antibiotics in Solid-Phase Environments. Gordon Research Conference, Environmental Sciences: Water, June 27 -

July 2, 2004, Holderness School, Plymouth, NH

## **Problem and Research Objectives:**

### **Background Information:**

An environmental endocrine disrupter is defined as an external compound that interferes with or mimics natural hormones in the body that are responsible for the maintenance, reproduction, development, and/or behavior of an organism (Folmar, 1993; Fry and Toone, 1981; Goodbred et al., 1996; Jobling et al., 1996; Schmitt et al., 1990; Smith et al., 1997; U.S. Environmental Protection Agency, 1997). Hypotheses about which chemicals may be endocrine disrupters, about the mechanisms through which they operate, and about which animals may be affected have been discussed in numerous publications (Kassim and Simoneit, 2001; Bevans et al., 1996; Colborn and Clement, 1992; Henny et al., 1996; Facemire et al., 1995; Guillette et al., 1994; Davis and Bortone, 1992; EPA, 1997); however, few regional or national studies related to assessment and water quality have been conducted to test these hypotheses.

The U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) program recently found evidence of endocrine disruption in common carp (*Cyprinus carpio*) and largemouth bass (*Micropterus salmoides*) collected from waterways that contain synthetic organic compounds. Various synthetic chemicals from several chemical groups have been identified as potentially having endocrine disrupting effects (Kassim and Simoneit, 2001). Some of these chemicals have the potential to cause reproductive impairment in aquatic organisms (Colborn and Clement, 1992; Henny et al., 1996; Facemire et al., 1995). Alteration in blood concentrations of sex steroid hormones and vitellogenin may be associated with reproductive impairment and other critical reproductive factors (Guillette et al., 1994; Davis and Bortone, 1992; EPA, 1997). Evidence indicates concentrations of sex steroid hormones (estrogen and testosterone) and vitellogenin (egg protein produced by females) were different in fish from contaminated and reference sites.

The generation and disposal of biosolids (used as soil amendments) and wastewater effluents produced at municipal wastewater treatment plants (WWTPs) are considered to be the main sources of EDCs' in the aquatic environment (Horwitz et al., 1996; Kendall et al., 1998; Snyder et al., 2000; USEPA, 1997). For example, approximately 900 kg of biosolids on a dry basis are produced from the treatment of 1 million gallons of wastewater (Ahlborg et al., 1995; Carlsen et al., 1995). These solids are typically dewatered on site and disposed of at landfills, incinerators or on agricultural fields. Disposal of sewage sludge on agricultural fields recycles the nutrients captured from municipal wastewater into agricultural soils. However, biosolids applied as soil amendments can contain significant quantities of EDCs derived from the municipal wastewater or organic metabolites produced during WWTPs. These organics have the potential to adversely impact soil receiving the biosolids, surface and groundwater in the vicinity of application, on crops grown on sludge-amended soils, and on animals and humans that may consume the crops grown on the soils.

### **Local State Problem Area:**

The Willamette River (Figure 1) is the 10<sup>th</sup> largest river in the United States and the heart of Oregon. In the 1930s, the Willamette was so polluted that fish were dying and the water was no longer safe for human use. Decades of local effort resulted in significant improvements to water quality and, by the 1970s, the Willamette became a model for what concerned citizens can accomplish in environmental restoration. Recently, another critical milestone in the history of the Willamette River has approached. A study performed in 1997 by the US-EPA and the Oregon-DEQ found that the aquatic environment of the river is contaminated with organic pollutants that causes several fish species to die or have deformation.

A recent investigation by the USGS National Water Quality Assessment (NAWQA) program has found that several fish species are dying or have deformations, as well as evidence of endocrine disruption in common carp and largemouth bass collected from the river. In addition, another study performed in 2001, carried out by the Principal Investigator and funded by the USGS, has indicated the presence of several EDCs in the river (Kassim, 2002).

### **Research Objectives and Approach:**

The current effort to investigate the occurrence and characterization of a comprehensive list of EDCs in both effluents and biosolids disposed from and/or generated in three major wastewater treatment plants (WWTPs) will help complement the understanding of EDCs' chemodynamics and their control in the Willamette River. This investigation was accomplished through the successful completion of the following tasks:

TASK 1 “COMPILATION OF RELEVANT RESEARCH”: A literature search was conducted to identify the most common OWCs present in US streams and rivers and their concentration ranges. The search did also aid in compiling relevant data regarding chemical, physical and toxicological characteristics for these OWCs.

TASK 2 “AN ENVIRONMENTAL FORENSIC/MOLECULAR MARKER APPROACH”: This provided the first comprehensive statewide investigation of the occurrence, characterization and source confirmation of a broad suite of organic wastewater contaminants (OWCs) of emerging environmental concern in two major sources (e.g., effluents and biosolids) in the Willamette River. These OWCs included antibiotics, other prescription and nonprescription drugs, steroids, reproductive hormones, personal care products, products of oil use and combustion, and other extensively used chemicals. The target OWCs were selected (see Table 1) because they are:

- Expected to enter the Willamette River environment through common wastewater effluent or biosolids (as soil amendments) pathways,
- Used in significant quantities in Oregon,
- Have human or environmental health implications,
- Are potential indicators of certain classes of compounds or sources, and/or
- Can be accurately measured using available technologies.

Although OWCs are just a small subset of the compounds being used by society, they represent a starting point for this synergistic investigation that examines their occurrence in the Willamette River.

TASK 3 “STATISTICAL ANALYSIS OF DATA”: Data collected were statistically examined in order to determine any significant interaction of the variables. The test results were analyzed using quantitative methods to summarize the information hidden in the multivariate data sets. This reduced the complex data matrix into a simpler form without distorting its information content and thus, the conclusions became more readily inferable. Analysis tools included multivariate analysis of variance, correlation analysis between variables, multiple regression analysis, linear programming and principal component analysis.

TASK 4 “FINAL RESEARCH REPORT”: Summary of test results and analyses performed were provided electronically for review and feedback.

#### Methods, Procedures, and Facilities:

The present project used the state of knowledge and information in the fields of environmental organic chemistry, environmental engineering, and computer science/programming. This required the use of state of the art instruments and latest modeling techniques.

**Sampling:** Both biosolids and wastewater effluents were collected from three major wastewater treatment plants (WWTPs) located on the Willamette River (Figure 1) . These WWTPs locations include Corvallis, Albany, and Salem.

**Characterization and Identification of OWCs:** The following sections summarize the approach used to characterize and identify the molecular compositions of OWCs in both effluents samples and biosolids, as follows:

#### Extraction and separation

An extraction protocol originally developed and revised by Kassim (1994; 1998) and Kassim and Simoneit (1995b) were further modified and verified for the qualitative and quantitative analyses of different organic classes found in both effluent and biosolids samples (Kassim and Simoneit, 2001). In brief, effluent samples were liquid/liquid extracted with methylene chloride-methanol (2:1). Biosolids were extracted in a Soxhlet apparatus with methylene chloride-methanol (2:1). All the extracts (EOM) were concentrated to 2 ml and hydrolyzed overnight with 35 ml of 6% KOH/methanol. The corresponding neutral and acidic fractions were successively recovered with *n*-hexane (4x30 ml), the latter after acidification (pH 2) with 6*N* HCl. The acidic fractions, previously reduced to 0.5 ml, will be esterified overnight with 15 ml of 10% BF<sub>3</sub>/methanol. The BF<sub>3</sub>/methanol complex were destroyed with 15 ml of water, and the methyl esters were recovered by extraction with 4x30 ml of *n*-hexane. The neutrals were fractionated by long column chromatography. The following fractions were collected:

- (I) 45 ml of *n*-hexane (aliphatic hydrocarbons, F1),
- (II) 25 ml of 10% methylene chloride in *n*-hexane (monoaromatic hydrocarbons "MAHs", F2),



- (III) 40 ml of 20% methylene chloride in *n*-hexane (polycyclic aromatic hydrocarbons "PAHs", F3),
- (IV) 25 ml of 50% methylene chloride in *n*-hexane (esters and ketones, F4),
- (V) 25 ml of methylene chloride (ketones and aldehydes, F5), and
- (VI) 50 ml of 10% methanol in methylene chloride (alcohols, F6).

The last fraction and an aliquot of the total extract were derivitized prior to gas chromatographic-mass spectrometric (GC-MS) analysis for further qualitative molecular examination by silylation with bis(trimethylsilyl)trifluoroacetamide. A recovery experiment for the long column chromatography were carried out using several deuterated standards.

#### Instrumental analyses

All samples were analyzed by gas chromatography (GC), GC-ECD, GC-MS. The GC-MS analyses of the samples were performed using a Hewlett-Packard 5973 MSD quadrupole mass spectrometer operated in the electron impact mode at 70eV and coupled to an HP Model 6890 gas chromatograph. The GC was equipped with a 30 m x 0.25 mm i.d capillary column coated with DB-5 (J & W Scientific, film thickness 0.25 µm) and operated using helium as carrier gas.

#### Identification and quantification

Compound identification was based on comparison with the GC retention times and/or mass fragmentation patterns of standard reference materials and with the help of the Library Molecular marker identification tabulated as follows: (a) *Positive*, when the sample mass spectrum, authentic standard compound mass spectrum, and their retention times agrees well; (b) *Probable*, same as above except no standards are available, but the sample mass spectrum agrees very well with the standard library; (c) *Possible*, same as above except that the sample spectrum contains information from other compounds but with minor overlap; and (d) *Tentative*, when spectrum contains additional information from possibly several compounds with overlap. Identification and response factors of several EDCs were determined using a suite of standard compounds. Quantification was based on the application of per-deuterated compounds for each respective EDC fraction as internal standards.

#### Organic carbon analysis:

Organic carbon analyses were carried out for all effluent and biosolids samples using a Carlo Erba NA-1500 CNS analyzer. The concentrations of all EDCs were calculated relative to the total organic carbon (TOC) content of the samples.

#### Characterization and Genetic-Source Partitioning

EDCs data and other chemical indices of the compositions of both effluents and biosolids were examined statistically in order to determine any significant environmental variations, and to construct a source-partitioning model specific for the Willamette. All statistical analyses and modeling approaches were performed using extended Q-mode factor analysis, linear programming and artificial intelligence-neural network programs and verified using Monte Carlo Simulation.

**Facilities:** The analyses were conducted in the Environmental Engineering Laboratory at Oregon State University. Adequate chemical laboratory space and the following instrument facilities for organic chemical identification and characterization are present under the direction of or accessible to the principal investigator. This includes: (a) a temperature programmable gas chromatograph coupled to a Chemstation data system (Hewlett-Packard 5890) for high molecular weight compound analyses, (b) one Hewlett-Packard 5973 MSD quadrupole GC-mass spectrometer coupled to a Chemstation data system, (c) elemental (CHN) analysis, (d) temperature controlled environmental chambers, (e) sample collection and coring equipment, and (f) multimedia modeling software.

#### Principal Findings and Significance:

The current pollution in the Willamette River is the result of anthropogenic activities. The present investigation indicated the presence of several chemicals of complex organic mixtures (COMs) or possible organic wastewater contaminants (OWCs) (see Tables 1 and 2).

The preliminary investigation indicated the occurrence of various toxic and endocrine disruptive complex organic mixtures (COMs) or organic wastewater contaminants (OWCs) in the Willamette River's surface water, and various WWTP-effluents and -biosolids for Willamette River treatment facilities. In general, WWTP-treated effluents and surface water samples from the Willamette River showed high concentrations of a large number of COMs/OWCs. This includes the following: 78 µg/L of total aliphatic hydrocarbons (e.g., *n*-alkanes, isoprenoids, UCMs, terpanes, diasteranes, and steranes); 230 ng/L of total polycyclic aromatic hydrocarbons (e.g., neutral and alkyl-substituted

compounds); 92 ng/L of veterinary and human antibiotics; 47 ng/L of non-prescription drugs (e.g., codeine and caffeine); 63 ng/L total phthalate esters; 74 ng/L bisphenol A; 180 ng /L nonylphenol; 125 ng/L sex steroid hormones and their metabolites (e.g., 17 $\beta$ -estradiol, 17 $\alpha$ -ethinylestradiol, mestranol, estrone, estriol, cholesterol, coprostanol and epi-coprostanol).

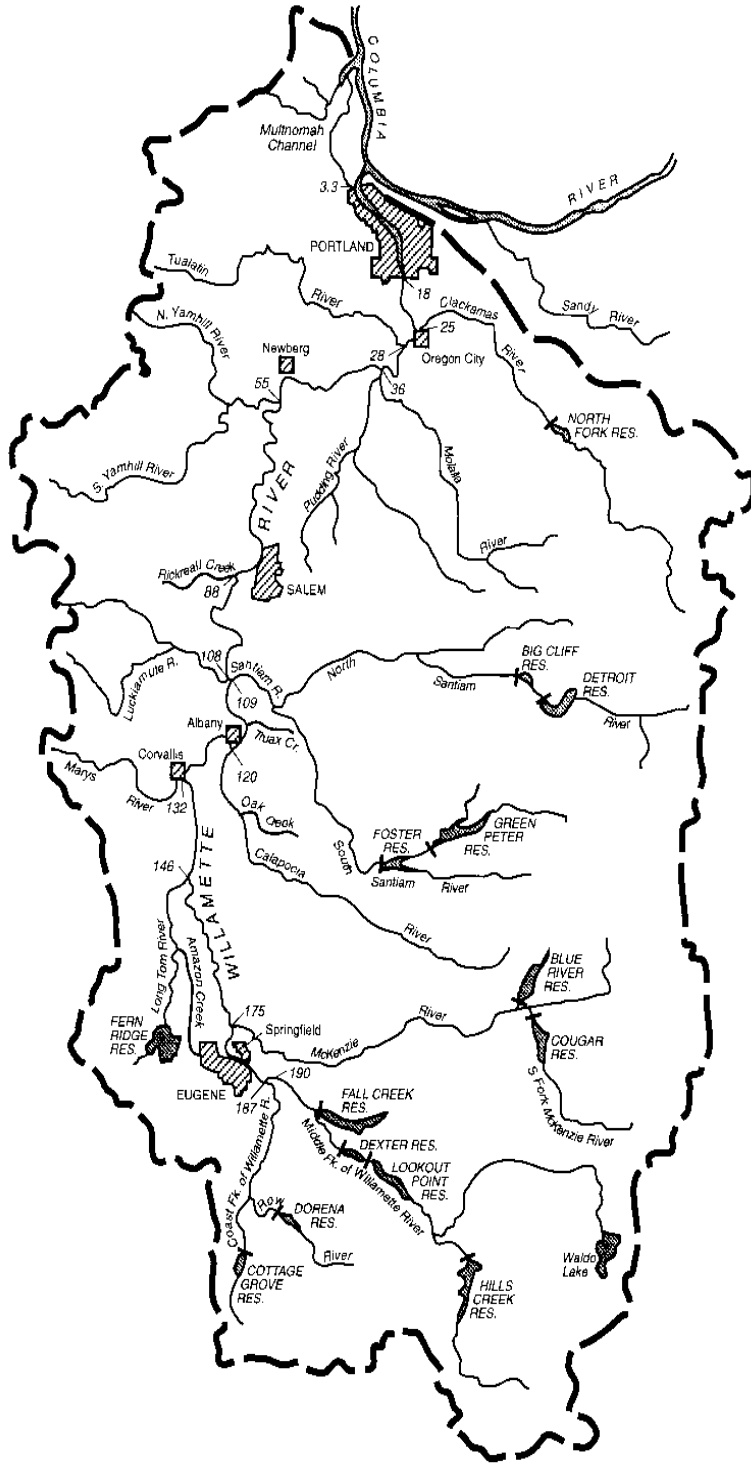


Figure 1. The Willamette River, Oregon

**Table 1. Contaminant Name, Chemical Composition and Molecular Weight representing the Willamette River Environment.**

COMPOUND		CHEMICAL COMPOSITION	MW	COMPOUND		CHEMICAL COMPOSITION	MW
#	NAME			#	NAME		
<b>(I) ALIPHATIC HYDROCARBONS</b>				<b>(II) POLYCYCLIC AROMATIC HYDROCARBONS</b>			
<i>n</i> -Alkanes				Neutral PAHs			
1	<i>n</i> -hexadecane	C <sub>16</sub> H <sub>34</sub>	226	69	Quinoline “benzo[b]pyridine”	C <sub>9</sub> H <sub>7</sub> N	129
2	<i>n</i> -heptadecane	C <sub>17</sub> H <sub>36</sub>	240	70	2,3-Dimethyl quinoline	C <sub>11</sub> H <sub>11</sub> N	157
3	<i>n</i> -octadecane	C <sub>18</sub> H <sub>38</sub>	254	71	Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178
4	<i>n</i> -nonadecane	C <sub>19</sub> H <sub>40</sub>	268	72	Anthracene	C <sub>14</sub> H <sub>10</sub>	178
5	<i>n</i> -eicosane	C <sub>20</sub> H <sub>42</sub>	282	73	Fluoranthene	C <sub>16</sub> H <sub>10</sub>	202
6	<i>n</i> -heneicosane	C <sub>21</sub> H <sub>44</sub>	296	74	Pyrene	C <sub>16</sub> H <sub>10</sub>	202
7	<i>n</i> -docosane	C <sub>22</sub> H <sub>46</sub>	310	75	11 H-Benzo[a]fluorene	C <sub>17</sub> H <sub>12</sub>	216
8	<i>n</i> -tricosane	C <sub>23</sub> H <sub>48</sub>	324	76	Benz[a]anthracene	C <sub>18</sub> H <sub>12</sub>	228
9	<i>n</i> -tetracosane	C <sub>24</sub> H <sub>50</sub>	338	77	Chrysene/triphenylene	C <sub>18</sub> H <sub>12</sub>	228
10	<i>n</i> -pentacosane	C <sub>25</sub> H <sub>52</sub>	352	78	Benzo[b+k]fluoranthenes	C <sub>20</sub> H <sub>12</sub>	252
11	<i>n</i> -hexacosane	C <sub>26</sub> H <sub>54</sub>	366	79	Benzo[e]pyrene	C <sub>20</sub> H <sub>12</sub>	252
12	<i>n</i> -heptacosane	C <sub>27</sub> H <sub>56</sub>	380	80	Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	252
13	<i>n</i> -octacosane	C <sub>28</sub> H <sub>58</sub>	394	81	Perylene	C <sub>20</sub> H <sub>12</sub>	252
14	<i>n</i> -nonacosane	C <sub>29</sub> H <sub>60</sub>	408	82	Indeno[1,2,3-cd]pyrene	C <sub>22</sub> H <sub>12</sub>	276
15	<i>n</i> -triacontane	C <sub>30</sub> H <sub>62</sub>	422	83	Dibenz[ah]anthracene	C <sub>22</sub> H <sub>14</sub>	278
16	<i>n</i> -hentriacontane	C <sub>31</sub> H <sub>64</sub>	436	84	Benzo[ghi]perylene	C <sub>22</sub> H <sub>12</sub>	276
17	<i>n</i> -dotriacontane	C <sub>32</sub> H <sub>66</sub>	450	85	Anthanthrene	C <sub>22</sub> H <sub>12</sub>	276
18	<i>n</i> -tritriacontane	C <sub>33</sub> H <sub>68</sub>	464	86	Coronene	C <sub>24</sub> H <sub>12</sub>	300
19	<i>n</i> -tetratriacontane	C <sub>34</sub> H <sub>70</sub>	478	87	Dibenzo[ae]pyrene	C <sub>24</sub> H <sub>14</sub>	302
20	<i>n</i> -pentatriacontane	C <sub>35</sub> H <sub>72</sub>	492	<b>Alkyl-Substituted PAHs</b>			
21	<i>n</i> -hexatriacontane	C <sub>36</sub> H <sub>74</sub>	506	<i>(Alkyl phenanthrene series)</i>			
22	<i>n</i> -heptatriacontane	C <sub>37</sub> H <sub>76</sub>	520	88	3-Methylphenanthrene (3MP)	C <sub>15</sub> H <sub>12</sub>	192
23	<i>n</i> -octatriacontane	C <sub>38</sub> H <sub>78</sub>	534	90	2-Methylphenanthrene (2MP)	C <sub>15</sub> H <sub>12</sub>	192
24	2,6,10-trimethylpentadecane (norpristane)	C <sub>18</sub> H <sub>38</sub>	254	91	9-Methylphenanthrene (9MP)	C <sub>15</sub> H <sub>12</sub>	192
25	2,6,10,14-tetramethylpentadecane (pristane)	C <sub>19</sub> H <sub>40</sub>	268	92	1-Methylphenanthrene (1MP)	C <sub>15</sub> H <sub>12</sub>	192
26	2,6,10,14-tetramethylhexadecane (phytane)	C <sub>20</sub> H <sub>42</sub>	282	93	Dimethylphenanthrenes	C <sub>16</sub> H <sub>14</sub>	206
27	Unresolved Complex Mixture (UCM)			94	Trimethylphenanthrenes	C <sub>17</sub> H <sub>16</sub>	220
<b>Tricyclic terpanes</b>				95	Tetramethylphenanthrenes	C <sub>18</sub> H <sub>18</sub>	234

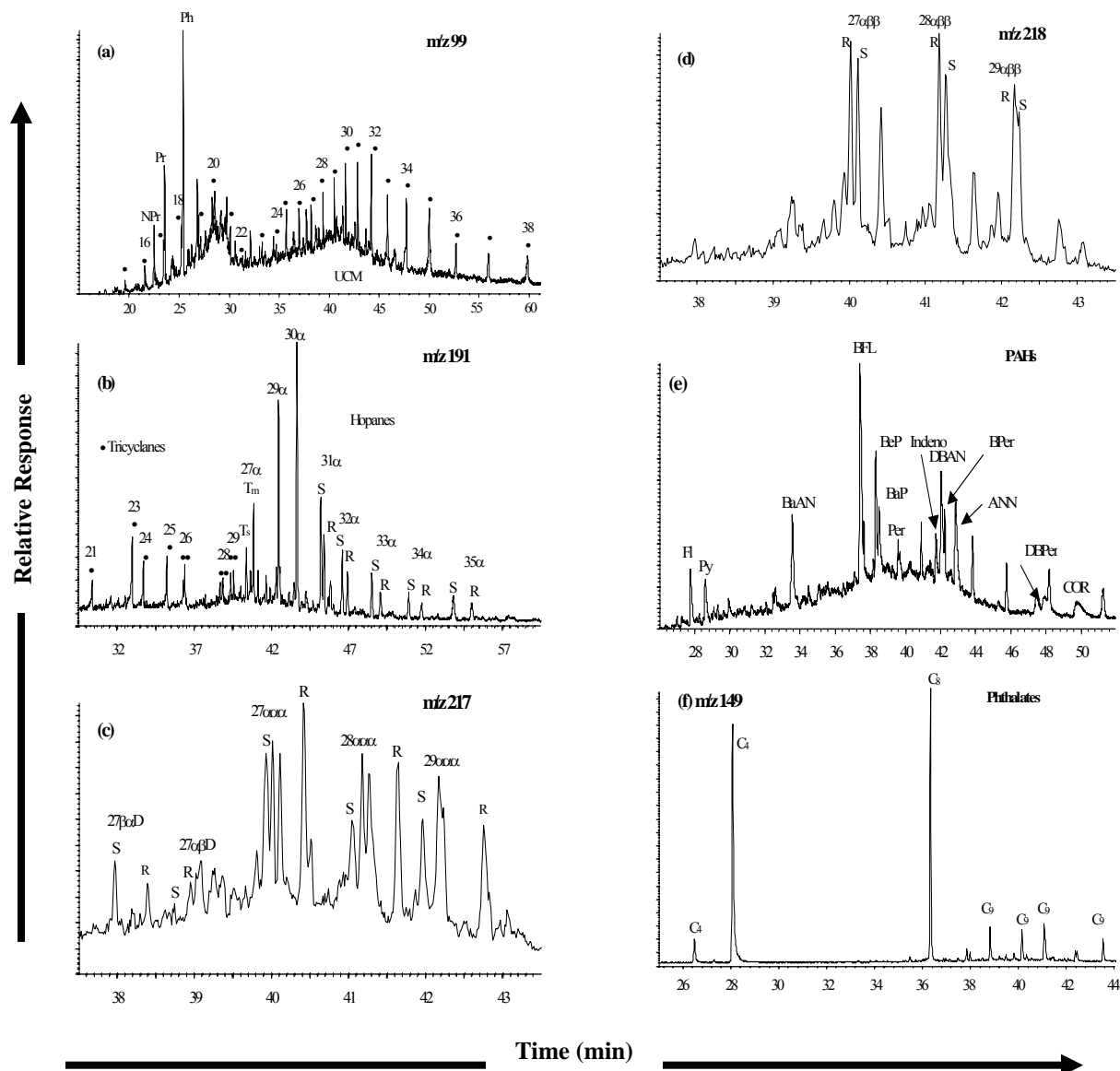
COMPOUND		CHEMICAL COMPOSITION	MW	COMPOUND		CHEMICAL COMPOSITION	MW
#	NAME			#	NAME		
<b>28</b>	C <sub>19</sub> -tricyclic	C <sub>19</sub> H <sub>34</sub>	262	<i>(Alkyl pyrene/fluoranthene series)</i>			
<b>29</b>	C <sub>20</sub> -tricyclic	C <sub>20</sub> H <sub>36</sub>	276	<b>96</b>	Methylpyrenes/fluoranthenes	C <sub>17</sub> H <sub>12</sub>	216
<b>30</b>	C <sub>21</sub> -tricyclic	C <sub>21</sub> H <sub>38</sub>	290	<b>97</b>	Dimethylpyrenes/fluoranthenes	C <sub>18</sub> H <sub>14</sub>	230
<b>31</b>	C <sub>23</sub> -tricyclic	C <sub>23</sub> H <sub>42</sub>	318	<b>98</b>	Trimethylpyrenes/fluoranthenes	C <sub>20</sub> H <sub>16</sub>	244
<b>32</b>	C <sub>24</sub> -tricyclic	C <sub>24</sub> H <sub>44</sub>	332	<i>(Alkyl 228 series)</i>			
<b>33</b>	C <sub>25</sub> -tricyclic	C <sub>25</sub> H <sub>46</sub>	346	<b>99</b>	Methyl-228	C <sub>19</sub> H <sub>14</sub>	242
<b>34</b>	C <sub>26</sub> -tricyclic (S)	C <sub>26</sub> H <sub>48</sub>	360	<b>100</b>	Dimethyl-228	C <sub>20</sub> H <sub>16</sub>	256
<b>35</b>	C <sub>26</sub> -tricyclic (R)	C <sub>26</sub> H <sub>48</sub>	360	<i>(Alkyl 252 series)</i>			
<b>36</b>	C <sub>28</sub> -tricyclic	C <sub>28</sub> H <sub>50</sub>	388	<b>101</b>	Methyl-252	C <sub>21</sub> H <sub>14</sub>	266
<b>37</b>	C <sub>29</sub> -tricyclic	C <sub>29</sub> H <sub>52</sub>	402	<b>102</b>	Dimethyl-252	C <sub>22</sub> H <sub>16</sub>	280
<b>Tetracyclic terpanes</b>				<b>103</b>	Trimethyl-252	C <sub>23</sub> H <sub>18</sub>	294
<b>38</b>	C <sub>24</sub> -tetracyclic (17,21-seco-hopane)	C <sub>24</sub> H <sub>42</sub>	330	<b>104</b>	Tetramethyl-252	C <sub>24</sub> H <sub>20</sub>	308
<b>39</b>	C <sub>28</sub> -tetracyclic (18,14-seco-hopane)	C <sub>28</sub> H <sub>50</sub>	386	<b>(III) NON-HYDROCARBONS</b>			
<b>40</b>	C <sub>29</sub> -tetracyclic (18,14-seco-hopane)	C <sub>29</sub> H <sub>52</sub>	400	<b>Phthalates</b>			
<b>Pentacyclic triterpanes</b>				<b>105</b>	Phthalic anhydride	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	148
<b>41</b>	18α(H)-22,29,30-trisnorneohopane (Ts)	C <sub>27</sub> H <sub>46</sub>	370	<b>106</b>	Dimethyl phthalate	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	194
<b>42</b>	17α(H)-22,29,30-trisnorhopane (Tm)	C <sub>27</sub> H <sub>46</sub>	370	<b>107</b>	Diethyl phthalate	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	222
<b>43</b>	17α(H),21β(H)-29-norhopane	C <sub>29</sub> H <sub>50</sub>	398	<b>108</b>	Bis(2-ethylhexyl) phthalate	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	390
<b>44</b>	17α(H),21β(H)-hopane	C <sub>30</sub> H <sub>52</sub>	412	<b>Phenols and Substituted Phenols</b>			
<b>45</b>	17α(H),21β(H)-homohopane (22S)	C <sub>31</sub> H <sub>54</sub>	426	<b>109</b>	Phenol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	94
<b>46</b>	17α(H),21β(H)-homohopane (22R)	C <sub>31</sub> H <sub>54</sub>	426	<b>110</b>	2,3,4,5,6-Pentachlorophenol	C <sub>6</sub> Cl <sub>5</sub> OH	266
<b>47</b>	17α(H),21β(H)-bishomohopane (22S)	C <sub>32</sub> H <sub>56</sub>	440	<b>Amines</b>			
<b>48</b>	17α(H),21β(H)-bishomohopane (22R)	C <sub>32</sub> H <sub>56</sub>	440	<b>111</b>	N,4-Dimethylbenzenamine	C <sub>8</sub> H <sub>11</sub> N	121
<b>49</b>	17α(H),21β(H)-trishomohopane (22S)	C <sub>33</sub> H <sub>58</sub>	454	<b>112</b>	N,N, 3-Trimethylbezenamine	C <sub>9</sub> H <sub>13</sub> N	134
<b>50</b>	17α(H),21β(H)-trishomohopane (22R)	C <sub>33</sub> H <sub>58</sub>	454	<b>Amides</b>			
<b>51</b>	17α(H),21β(H)-tetrakishomohopane (22S)	C <sub>34</sub> H <sub>60</sub>	468	<b>113</b>	N-(2, 4-Dmethylphenyl)formamide	C <sub>9</sub> H <sub>11</sub> NO	149
<b>52</b>	17α(H),21β(H)-tetrakishomohopane (22R)	C <sub>34</sub> H <sub>60</sub>	468	<b>Various Alcohols</b>			
<b>53</b>	17α(H),21β(H)-pentakishomohopane (22S)	C <sub>35</sub> H <sub>62</sub>	482	<b>114</b>	Dicyclopentadieneol	C <sub>10</sub> H <sub>13</sub> O	149
<b>54</b>	17α(H),21β(H)-pentakishomohopane (22R)	C <sub>35</sub> H <sub>62</sub>	482	<b>115</b>	[1,1' - Biphenyl]-2-ol	C <sub>12</sub> H <sub>10</sub> O	170
<b>Diasteranes</b>				<b>Acids</b>			
<b>55</b>	13α,17β-diacholestane (20S)	C <sub>27</sub> H <sub>48</sub>	372	<b>116</b>	Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122

COMPOUND		CHEMICAL COMPOSITION	MW	COMPOUND		CHEMICAL COMPOSITION	MW
#	NAME			#	NAME		
<b>56</b>	13 $\alpha$ ,17 $\beta$ -diacholestane (20R)	C <sub>27</sub> H <sub>48</sub>	372	<b>117</b>	Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	158
<b>Steranes</b>				<b>118</b>	Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	172
<b>57</b>	5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -cholestane (20S)	C <sub>27</sub> H <sub>48</sub>	372	<b>119</b>	Dodecanoic Acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	200
<b>58</b>	5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -cholestane (20R)	C <sub>27</sub> H <sub>48</sub>	372	<b>120</b>	Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	228
<b>59</b>	5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -cholestane (20S)	C <sub>27</sub> H <sub>48</sub>	372	<b>121</b>	Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256
<b>60</b>	5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -cholestane (20R)	C <sub>27</sub> H <sub>48</sub>	372				
<b>61</b>	5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -ergostane (20S)	C <sub>28</sub> H <sub>50</sub>	386				
<b>62</b>	5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -ergostane (20R)	C <sub>28</sub> H <sub>50</sub>	386				
<b>63</b>	5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -ergostane (20S)	C <sub>28</sub> H <sub>50</sub>	386				
<b>64</b>	5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -ergostane (20R)	C <sub>28</sub> H <sub>50</sub>	386				
<b>65</b>	5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -sitostane (20S)	C <sub>29</sub> H <sub>52</sub>	400				
<b>66</b>	5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -sitostane (20R)	C <sub>29</sub> H <sub>52</sub>	400				
<b>67</b>	5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -sitostane (20S)	C <sub>29</sub> H <sub>52</sub>	400				
<b>68</b>	5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -sitostane (20R)	C <sub>29</sub> H <sub>52</sub>	400				

**Table 1: List of Organic Wastewater Contaminants (OWCs) detected and characterized in the present project.**

<b>Organic Wastewater Contaminants of Complex Mixtures</b>			
<b>Veterinary and Human Antibiotics</b>	<p><b><u>Tetracyclines</u></b> Chlortetracycline Doxycycline Oxytetracycline Tetracycline</p> <p><b><u>Fluoroquinolones</u></b> Ciprofloxacin Enrofloxacin Norfloxacin Sarafloxacin</p>	<p><b><u>Macrolides</u></b> Erythromycin-H<sub>2</sub>O (<i>metabolite</i>) Tylosin Roxithromycin</p> <p><b><u>Sulfonamides</u></b> Sulfachlorpyridazine Sulfamerazine Sulfamethazine Sulfathiazole</p>	<p>Sulfadimethoxine Sulfamethiazole Sulfamethoxazole</p> <p><b><u>Others</u></b> Lincomycin Trimethoprim Carbadox Virginiamycin</p>
<b>Human Drugs</b>	<p><b><u>Prescription</u></b> Antacid Cimetidine Ranitidine antidepressant Fluoxetine Paroxetine Antihypertensive Enalaprilat Diltiazem</p>	<p>Metformin (<i>antidiabetic agent</i>)</p> <p>Digoxin Warfarin (<i>anticoagulant</i>) Salbutamol (<i>antiasthmatic</i>) Gemfibrozil (<i>antihyperlipidemic</i>) Dehydronifedipine (<i>antianginal metabolite</i>) Digoxigenin (<i>digoxin metabolite</i>)</p>	<p><b><u>Non-Prescription</u></b> Acetaminophen (<i>analgesic</i>) Ibuprofen (<i>anti-inflammatory, analgesic</i>) Codeine (<i>analgesic</i>) Caffeine (<i>stimulant</i>) 1,7-Dimethylxanthine (<i>caffeine metabolite</i>) Cotinine (<i>nicotine metabolite</i>)</p>
<b>Industrial and Household Wastewater Products</b>	<p><b><u>Insecticides</u></b> Diazinon Carbaryl Chlorpyrifos <i>cis</i>-Chlordane N,N-diethyltoluamide Lindane Methyl parathion Dieldrin</p> <p><b><u>Plasticizers</u></b> <i>bis</i>(2-Ethylhexyl)adipate Ethanol-2-butoxy-phosphate <i>bis</i>(2-Ethylhexyl)phthalate Diethylphthalate Triphenyl phosphate</p> <p><b><u>Detergent metabolites</u></b> <i>p</i>-Nonylphenol</p>	<p>Nonylphenol monoethoxylate Nonylphenol diethoxylate Octylphenol monoethoxylate Octylphenol diethoxylate</p> <p><b>Fire retardants</b></p> <p>Tri(2-chloroethyl)phosphate Tri(dichlorisopropyl)phosphate</p> <p><b><u>PAHs (fuel combustion)</u></b> Naphthalene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(<i>a</i>)pyrene Benzo(<i>e</i>)pyrene Benz(<i>a</i>)anthracene</p>	<p><b><u>Antioxidants</u></b> 2,6-di-<i>tert</i>-Butylphenol 5-Methyl-1H-benzotriazole Butylatedhydroxyanisole (BHA) Butylatedhydroxytoluene (BHT) 2,6-di-<i>tert</i>-Butyl-<i>p</i>-benzoquinone</p> <p><b><u>Others</u></b> Tetrachloroethylene (<i>solvent</i>) Phenol (<i>disinfectant</i>) 1,4-Dichlorobenzene (<i>fumigant</i>) Acetophenone (<i>fragrance</i>) <i>p</i>-Cresol (<i>wood preservative</i>) Phthalic anhydride (<i>used in plastics</i>) Bisphenol A (<i>used in polymers</i>) Triclosan (<i>antimicrobial disinfectant</i>) Petroleum Products: <i>n</i>-alkanes Hopanes and Steranes UCM</p>
<b>Sex &amp; Steroidal Hormones</b>	<p><b><u>Biogenics</u></b> 17<math>\beta</math>-Estradiol 17<math>\alpha</math>-Estradiol Estrone Estril Testosterone Progesterone</p>	<p><i>cis</i>-Androsterone</p> <p><b><u>Pharmaceuticals</u></b> Ovulation inhibitors: 17<math>\alpha</math>-Ethinylestradiol Mestranol 19-Norethisterone</p>	<p>Hormone replacement therapy: Equilenin Equilin</p> <p><b><u>Sterols</u></b> Cholesterol (<i>fecal indicator</i>) Coprostanol (<i>fecal indicator</i>) Stigmastanol (<i>plant sterol</i>)</p>

Typical characteristic examples of gas chromatography-mass spectrometry (GC-MS) fingerprinting of some of these compounds are shown in Figure 2. Complete information about the contaminant chemical name, Composition and molecular weight are shown in Tables 2 and 3. Chemical structures of both aliphatic and aromatic hydrocarbons are shown in Figures 3 and 4, respectively.



**Figure 2.** Typical GC-MS fingerprints for: (a) *n*-alkanes, *m/z* 99 (Pr = pristane, Ph = phytane, Npr = norpristane, UCM = unresolved complex mixture, numbers over peaks indicate carbon numbers); (b) hopane series, *m/z* 191; (c)  $\alpha\alpha\alpha$  sterane series, *m/z* 217; (d)  $\alpha\beta\beta$  sterane series, *m/z* 218; (e) PAH composition (Fl = fluoranthene, Py = pyrene, BaAN = benz[a]anthracene, BFL = benzo[b,k]fluoranthene, BeP = benzo[e]pyrene, BaP = benzo[a]pyrene, Per = perylene, Indeno = indeno[1,2,3-cd]pyrene, DBAN = dibenz[a,h]anthracene, BPer = benzo[ghi]perylene, ANN = anthanthrene, DBPer = dibenzo[ghi]perylene, Cor = coronene); and (f) C<sub>i</sub>-phthalate esters, *m/z* 149 (*i* = carbon number of ester groups).



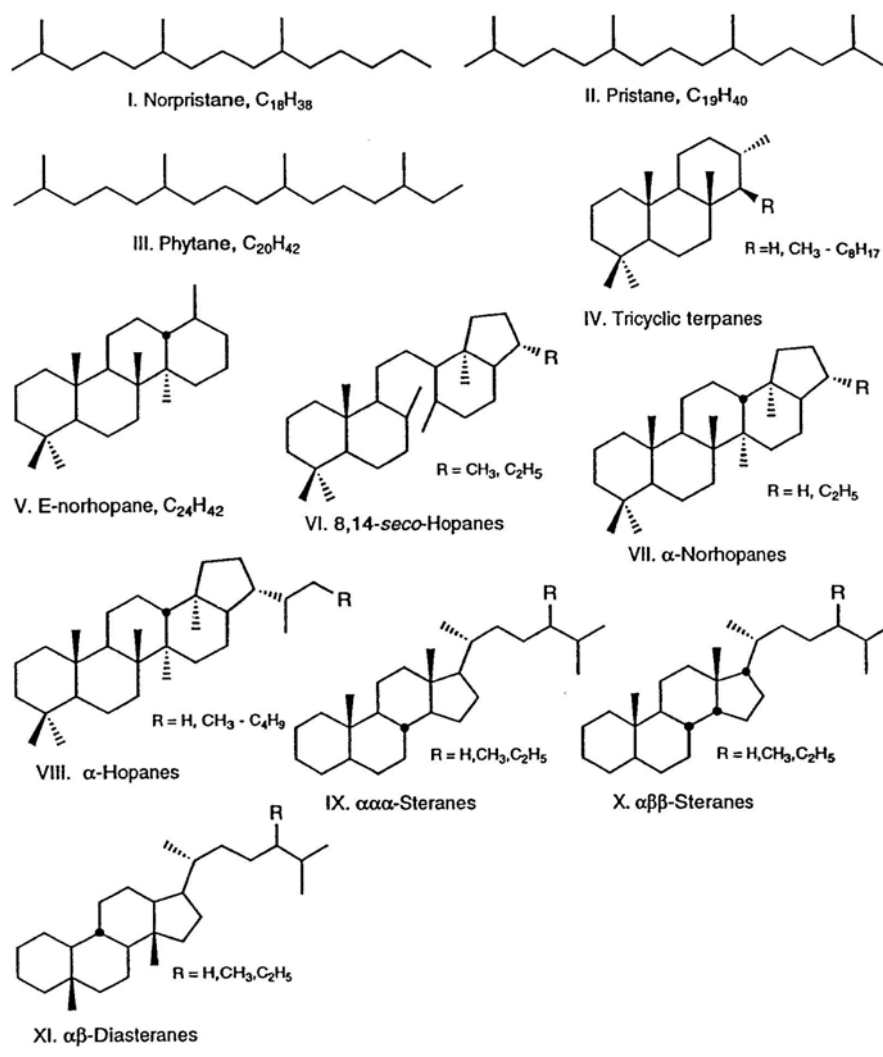


Figure 3. Chemical Structures of Some Aliphatic Hydrocarbons

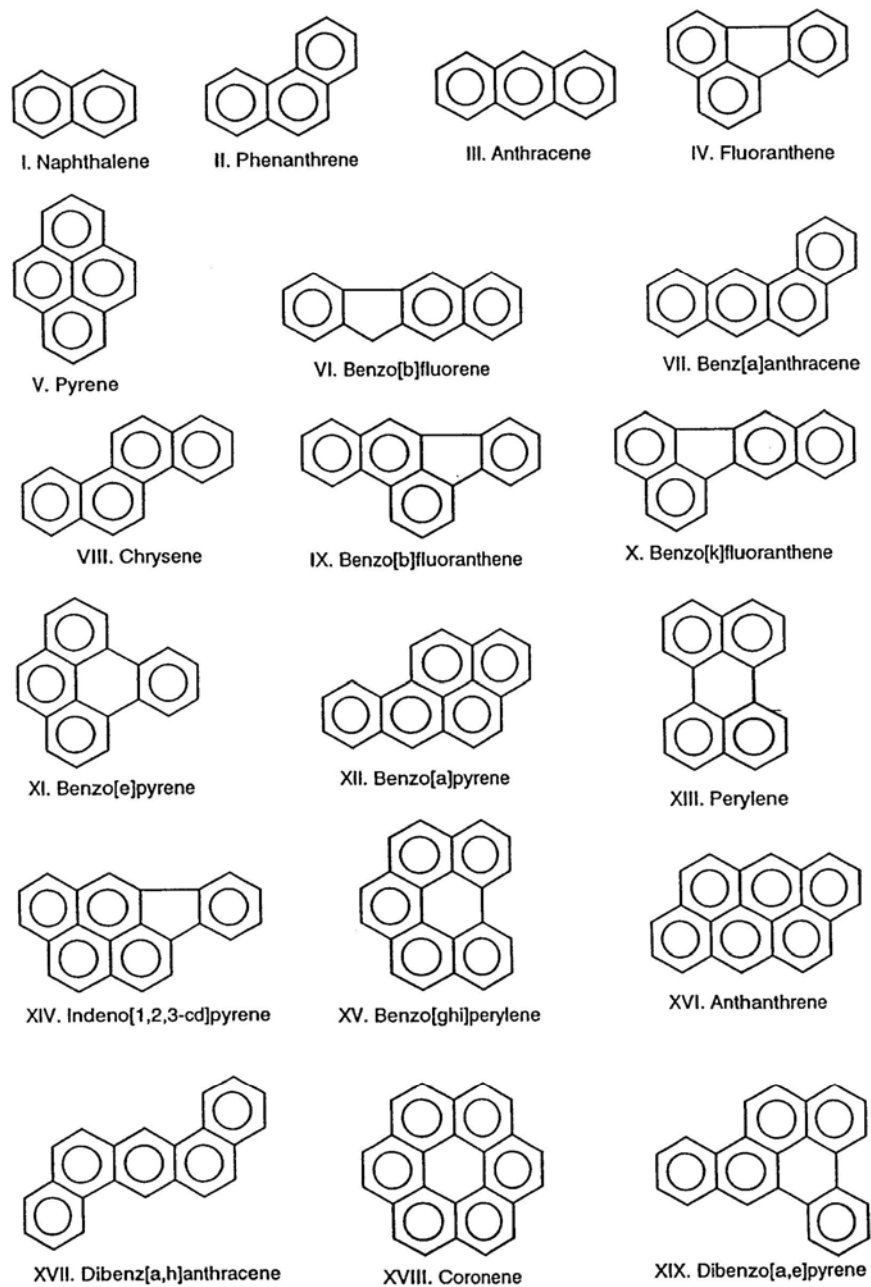


Figure 4. Chemical Structures of Some Polycyclic Aromatic Hydrocarbons

Based on the principal findings of the current investigation:

- Comprehensive research project was submitted to the United States Geologic Survey in March 2004. The project is entitled: "OCCURRENCE AND JOINT MULTICOMPONENT TOXIC/GENOTOXIC INTERACTION MODELING OF PHARMACEUTICALS, HORMONES AND OTHER ENDOCRINE DISRUPTING CHEMICALS IN THE WILLAMETTE RIVER", with Kenneth J. Williamson, and Bernd R.T. Simoneit (Co-Investigators), \$399,537 for two years
- Collaboration or an interaction with the Port of Portland and City of Portland research teams has been established.

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#### **Student Support (# and degree level):**

The present study was partially a part of the Masters' thesis for one graduate student in the Department of Civil, Construction and Environmental engineering at Oregon State University. The student has received some training about endocrine disrupting chemicals in the aquatic environment during the project.

# Development of a monitoring network and web-based database for effective watershed management in the Oak Creek Basin

## Basic Information

<b>Title:</b>	Development of a monitoring network and web-based database for effective watershed management in the Oak Creek Basin
<b>Project Number:</b>	2002OR1B
<b>Start Date:</b>	3/1/2002
<b>End Date:</b>	2/28/2004
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 5th
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Hydrology, Management and Planning, Surface Water
<b>Descriptors:</b>	Oak Creek, land use and water quality
<b>Principal Investigators:</b>	Jeffrey J. McDonnell

## Publication

1. McGlynn, B., J.J. McDonnell, M. Stewart, J. Seibert, 2003, On the relationships between catchment scale and streamwater mean residence time. *Hydrological Processes*, 17: 175-181.

### Problem and Research Objectives:

This project focused on Oak Creek, the home watershed for OSU. The University manages about 40% of the basin for multiple uses – forestry, agricultural, urban campus setting, large parking lots. As in many watersheds around Oregon, the Corvallis community has become increasingly concerned about whether OSU is an effective steward of the watershed and stream system. In 1999, OSU convened an Action Team who evaluated the conditions in the basin. The task force suggested specific management actions that should be taken. This work has not yet begun. Before this can happen effectively, this project will establish a monitoring network and web-based database for effective watershed management of the Oak Creek Basin. While some physical, chemical and biological data now exists for the watershed, it has not yet been synthesized and made available in a form useful for watershed management. This small project will provide an output that will be a useful template for future work in the watershed—available on the web for easy access by faculty, students and researchers.

Oregon has set watershed stewardship and stream health as a statewide priority. In many ways the State concerns are well represented within the Oak Creek watershed. Oregonians embrace salmon as a symbol of their Northwestern identity and they recognize that healthy salmon populations require healthy streams. At the same time, the federal Endangered Species Act and Clean Water Act increasingly focus attention on reduction of non-point source pollution and regulation of stream water quality. As the state's land grant college and primary agricultural and natural resources University, Oregon State has a responsibility to be a leader on watershed stewardship issues. Researchers at OSU are developing new understandings of ecological functions, nutrient cycling, agricultural technologies, but these are not implemented in our watershed. The proposed project will provide a basis to harness these energies within the Oak Creek watershed—for teaching, research and management.

This project set out to build upon the preliminary work by the Oak Creek Action Team for better management of the Basin. We:

1. Convened an Oak Creek Advisory Board that will engage appropriate people in the community
2. Determined the background water quality conditions (spatially/longitudinally) in the watershed
  - We built upon the 5 points sampled by the Oak Creek Task Force
  - We determined what the rain gauge network needs will be to adequately quantify precipitation inputs to the system
  - We will determined what stream gauging structures will be needed to adequately monitor flow within the system and allow for isolation of different land uses within the watershed.
3. Integrated existing GIS layers and data that exists across campus in a new Web site was launched in the last quarter of the project.

## Objectives of the Project

The objectives of this project were to set up an organization and monitoring infrastructure to support coordinated management of the Oak Creek basin. Specific objectives included:

- Organize an Oak Creek Advisory Board as recommended by the Oak Creek Action Team. The board will include representatives from several OSU colleges and from local community organizations.
- Hold a community meeting as a forum for community concerns and to describe current University management plans and activities. Disseminate this information to stakeholders in the watershed.
- Create an on-line database of available data for the watershed – this database will include biological, water quality, and GIS data sets that have been collected by OSU classes, government agencies, and citizen groups.
- Develop a comprehensive monitoring plan to determine spatial variation in water quality in the basin, prioritizing management actions, and measure baseline conditions that will enable future assessment of management effectiveness.

## Methods, Procedures, and Facilities:

Methods that we used to complete the project are summarized below:

1. We convened a new Oak Creek Advisory Board under the auspices of Rich Holdren. The Board included representatives from departments recommended by the former task force. The Board included members from the City of Corvallis, the Mary's River Watershed Council and an Oak Creek resident representative. Mark Taratoot, City of Corvallis, agreed to contribute \$500-\$2000 towards the city's involvement in the Board and its interactions with the group.
2. We performed a synoptic stream sampling survey at 35 sites across (see attached map) the Oak Creek watershed under low flow conditions. The aim was to examine how water quality measures scale (from headwaters to basin outlet) and vary across the discrete landuse changes within the watershed (forestry, agriculture, suburban, urban). Specific constituents were analyzed (using CCAL analytical facilities on the OSU campus):
  - a. Nutrients (N—NO<sub>3</sub>, NH<sub>4</sub>, DON--and P)
  - b. Flow
  - c. EC, base cations/anions
  - d. Oxygen isotopes (for water source determination)
  - e. Tritium (for water age dating)

Stream gauging with a current meter (and salt dilution under low flow conditions) accompanied the water sampling program. The gauging enabled us to gather low flow data at potential sites that we will consider for permanent gauging structures. One specific scientific output associated with the work was an analysis of the variance collapse of water quality measures with increasing catchment scale—this was presented as a poster at Fall AGU.

3. We gathered data layers for a watershed GIS database including:
  - a. Soils
  - b. Topography
  - c. Airborne imagery (visible, IR)—that we will fly within this project
  - d. Zoning
  - e. Landuse/landcover
  - f. Road network
  - g. Stream network
  - h. 1:24K DRG
  - i. COAS rainfall distribution models/historical records

Data layers existed for the McDonald Dunn forest as part of the Peavy Arboretum (Dave Lisne Director). We used the LIDAR data in the forested headwater zone for detailed DEM analysis. Specific scientific outputs associated with the GIS analysis were (1) a quantification of the topographic indices and other measures of water flow paths, (2) sub-basin size determination and contributing area mapping, (3) riparian location and extent.

4. Web development

We built upon the web page that was started under the auspices of the Oak Creek task force to make (1) the data sets available for web use, (2) the datasets accessible to the management community, scientific community and various stakeholders in the watershed. This new site was launched in Jan 2003 at:

**<http://oregonstate.edu/dept/oakcreek/index.html>**

5. Proposal writing

The PI led a proposal writing and submission effort as another capstone to this USGS funded work. This was directed to the USDA Cooperative State Research, Education and Extension Service. This proposal was not funded. As a post script to this project, NSF and the newly formed Consortium of Universities for the Advancement of Hydrological Sciences (CUAHSI) have developed a partnership to advance understanding of critical hydrologic processes. Based on CUAHSI efforts, the NSF will establish in 2005 a set of Long-Term Hydrologic Observatories funded at the level of \$10 million per site in capitol investment and \$3 million per year in operations. The NSF will release an rfp for proposals for Hydrological Observatories in January of 2005 with full proposals due April 1, 2005. Observatories will be selected on the basis of their regional representation and their viability as laboratories to study particular subsets of hydrologic problems nationally. The OSU Water and Watersheds group will aggressively pursue funding for the Willamette River Basin to be one of the selected CUAHSI observatories. The Oak Creek watershed and findings from this USGS project will feature prominently in that proposal. Largely due to the Oak Creek efforts, we have recently been successful in having the Willamette River Basin included in UNESCO Hydrology, Environment, Life and Policy (HELP) program. Selection by UNESCO as one of the 7-new HELP basins out of the 70 proposals submitted has encouraged us that the Willamette is a credible watershed and long term observatory for sustainability research. We see the HELP status



as a first step in achieving national and international prominence for our campus-wide activities within the basin.

#### Principal Findings and Significance:

The Principal Findings and Significance of the project can best be described by the detailed web site information <http://oregonstate.edu/dept/oakcreek/index.html>. This page chronicles the main contributions of the team, led by Maria Wright. This page has already contributed to local and regional benefits. On the local level, this web page will support coordinated management of the Oak Creek basin. Both community sentiment and federal legislation underlie this effort. It will create an organizational and data infrastructure which will help OSU manage lands more effectively and be more responsive to state and federal endangered species and clean water regulations. On a regional level, this web site will help OSU develop Oak Creek into a demonstration watershed where monitoring approaches and the effectiveness of Best Management Practices can be evaluated. This information would benefit state-wide efforts to improve watershed health for salmon and people. The web site will also help position OSU to apply for national grants studying watershed-scale nutrient processes and the effectiveness of Best Management Practices

#### Training and publications:

While the USGS project did not facilitate all of these papers, the ones highlighted were linked on some level to the topic of the grant:

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McGlynn, B., J.J. McDonnell, Stewart, M., Seibert, J. (2003). On the relationships between catchment scale and streamwater mean residence time. *Hydrological Processes*, 17: 175-181.

Ulenbrook, S., J.J. McDonnell and C. Leibundgut (2003). Preface: Runoff generation implications for river basin modelling. *Hydrological Processes*, Special Issue, 17: 197-198.

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McGlynn, B. and J.J. McDonnell (2003). The role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resources Research*, 39(4): 3-1 - 3-18.

Seibert, J, K. Bishop, A. Rodhe and J. McDonnell (2003). Groundwater dynamics along a hillslope: A test of the steady-state hypothesis. *Water Resources Research*, 39(1): 2-1 - 2-9.

McDonnell, J.J. (2003) Where does water go when it rains? Moving beyond the variable source area concept of rainfall-runoff response. *Hydrological Processes*, *Hydrological Processes*, 17: 1869-1875.

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# Remote Collaborations: Lateral Learning in Transboundary Water Conflicts

## Basic Information

<b>Title:</b>	Remote Collaborations: Lateral Learning in Transboundary Water Conflicts
<b>Project Number:</b>	2002OR7B
<b>Start Date:</b>	3/1/2002
<b>End Date:</b>	12/1/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 5th
<b>Research Category:</b>	Social Sciences
<b>Focus Category:</b>	Law, Institutions, and Policy, Management and Planning, Water Quantity
<b>Descriptors:</b>	transboundary water conflict, water law
<b>Principal Investigators:</b>	Aaron T. Wolf

## Publication

1. Wolf, Aaron T.; Kerstin Stahl; Marcia F. Macomber 2003. Conflict and Cooperation within International River Basins: The Importance of Institutional Capacity. *Water Resources Impact*, in press. (also available on the Universities Partnership for Transboundary Waters Website: <http://waterpartners.geo.orst.edu>)

## **Problem and Research Objectives:**

One critical hindrance to sustainability in long-term water management is the fact that, as water use intensifies so too does the potential for conflict between users. Conflicts over shared, or transboundary water resources occur at multiple scales, from sets of individual irrigators, to urban versus rural uses, to nations that straddle international waterways. Transboundary waters share certain characteristics that make their management especially complicated, most notable of which is that these basins require a more-complete understanding of the political, cultural, and social aspects of water, and that management is dependent on extremely intricate awareness of the decision-making process. The transboundary nature of water and its high potential for conflict are often overlooked aspects in training and education programs for water resource management practitioners.

The objective of this project was to promote dialogue among local and international scholars regarding the transboundary nature of water, and to design an international education and research program as a means for universities around the world to collectively contribute to building capacity to address and manage conflict within the institutions which govern water both within Oregon and abroad.

## **Methods, Procedures, and Facilities:**

This project utilized two forums for dialog to draw linkages between local and international settings of transboundary water dispute. The first forum, a one-day seminar entitled: *Water Resources in Transboundary Settings: Lessons from Around the World*, offered opportunities for lateral learning among Oregonian and international experts. The second was a two-day planning workshop for an international consortium of transboundary waters expertise, the Universities Partnership for Transboundary Waters. The workshop facilitated the creation of three programs, designed to provide specific information, education, and training needs for transboundary water management practitioners, students, and scholars around the world and in Oregon.

### Activity 1: SEMINAR: Water Resources in Transboundary Settings: Lessons from Around the World

The seminar was held on May 15, 2002, at Oregon State University. The morning session, entitled *Communicating Science: Lessons from the Klamath Basin*, featured presentations on local level transboundary water management issues, and was hosted by the Geological Society of America. The afternoon session, entitled *Conflict, Cooperation, and Dispute Resolution in International River Basins*, featured presentations on international transboundary water management issues, and was hosted by the College of Science and the Center for Water and Environmental Sustainability.

The seminar was open to the OSU community and featured the following presenters:

Douglas F. Markle, Fisheries & Wildlife, Oregon State University  
Michael Milstein, The Oregonian Newspaper  
Denise Lach, Center for Water and Environmental Sustainability, Oregon State University  
William S. Braunworth, Agricultural Administration, Oregon State University,  
Peter J. Ashton, University of Pretoria  
Michael E. Campana, University of New Mexico  
Ashim Das Gupta, Asian Institute of Technology, Thailand  
Alexander López Ramírez, National University of Costa Rica  
Anthony Turton, University of Pretoria, South Africa  
Patricia Wouters, University of Dundee, United Kingdom  
Aaron Wolf, Oregon State University

Activity 2: WORKSHOP: Planning Workshop for the Universities Partnership for Transboundary Waters  
Participants at the workshop:

- Identified gaps in water conflict information in four focus areas:
  - 1) information resources and outreach;
  - 2) coordinated research; and
  - 3) graduate and professional transboundary waters curricula.
- Defined the mission and scope of the Universities Partnership for Transboundary Waters
- Established activities, priorities and next steps for three programs – Education & Training, Outreach & Information Resources, and Coordinated Applied Research
- Established curricular areas for professional and graduate training and education

Participants included: Dr. Peter Ashton and Dr. Anthony Turton, University of Pretoria, South Africa; Dr. Ashim Das Gupta, Asian Institute of Technology, Thailand; Dr. Jan Lundqvist, Linköping University, Sweden; Dr. Patricia Wouters, University of Dundee, United Kingdom; Dr. Alexander López Ramírez, National University of Costa Rica, Costa Rica; Dr. Michael Campana, University of New Mexico, United States; Dr. Aaron Wolf, Dr. Mary Santelmann, Dr. Steve Lawton, Dr. Cherri Pancake, Ms. Marcia Macomber, and Ms. Lisa Gaines, Oregon State University, United States.

**Principal Findings and Significance:**

The principal findings drawn from the *Remote Collaborations: Lateral Learning in Transboundary Water Conflicts* project build on the recognition that the water crisis emerging around the world is essentially a governance crisis, how to ensure water is equitably and sustainably used. Water governance occurs at multiple levels, addresses how decisions are made, and who participates in the decision making process. Effective transboundary waters governance requires institutions, which provide a forum to bring stakeholders together to find joint solutions to meet water needs for humans, the economy, and the environment. These solutions must be both technically feasible and politically palatable to avoid conflict. Transboundary waters institutions can thus act as a mechanism to identify crises and resolve potential disputes; before they erupt and become intractable. Supporting and nurturing the development of both existing and future international river basin institutions will be a key ingredient to meeting the goals of human security and sustainable development around the world.

The *Remote Collaborations* participants identified the following capacity needs for transboundary waters institutions:

1. A cadre of transboundary waters champions

As the quality and quantity of water resources diminishes relative to demand, a specialized professional sector has emerged, comprising individuals who have been embroiled in, or tasked with steering past water conflict. These stakeholders include technical specialists and social and political actors, from staff within state agencies for health, water, and the environment, to members of diplomatic corps, to non-profit organizations; to researchers, to state legislators. Together, they constitute a team of “transboundary waters champions”, uniquely tasked with integrating the multiple aspects of water resource management, and harmonizing them across multiple local and national jurisdictions. These professionals have unique needs, not available within the framework of current training programs and universities. These needs center on the knowledge of skills and strategies to construct water management decisions that result in actions that are both technically and politically viable; and the ability to dialogue

with and learn from other stakeholders and their peers, in order to benefit from the successes and failures that have come before them.

## 2. Specialized interdisciplinary training

To address the transboundary nature of water, capacity building initiatives need to go well beyond the traditional physical approach to management and encourage the incorporation of multiple disciplines, from economics to law to sociology to public health and, especially, to conflict resolution. The traditional structure of most universities and management institutions are simply not organized along these lines. Fragmentation of interdependent water sectors into different colleges and agencies creates communication barriers between managers despite their common mission. What results are water professionals ill-equipped to address real-world water management needs – in particular - the ability to develop collaborative strategies with other sectors and/or nations to distribute limited water supplies among them in an equitable and sustainable manner.

## 3. Dissemination of lessons learned

Institutional arrangements, such as laws, treaties and river basin councils constitute a developing body of collective knowledge that is shaping the framework of emerging norms for the management of shared waters. Each existing institution represents the lessons learned from its formation and implementation within its own unique geographical and historical contexts. This collection of knowledge has the potential to inform the future and improve upon the past. Few resources exist to disseminate this information to transboundary water stakeholders in a medium which covers the global experience of conflict and cooperation regarding water resources. Such information can help predict and prevent potential conflict over water resources in a number of settings, or to resolve such disputes when they do occur.

## 4. Visualization tools

Information technology has great potential to provide tools which can assist in the visualization of complex water management problems, in a format which allows multiple issues and interests to be simultaneously represented, queried, and negotiated. The use of Geographic Information Systems, which combine multiple spatial databases containing biophysical as well as socioeconomic characteristics of a watershed, can be applied to facilitate collaborative decisions that affect availability and quality of water within international watersheds. These tools must be shaped in conjunction with transboundary waters decision makers they are targeted toward, to ensure their applicability to real world needs.

## Universities Partnership for Transboundary Waters – Oregonian Capacity and Expertise

The two day planning workshop for the Universities Partnership for Transboundary Waters resulted in the development of three programs listed below:

**Education & Training** – Specially designed courses and curriculum to educate and train a new generation of “transboundary waters champions” building capacity within water-related management institutions;

**Outreach & Information Resources** – Development and dissemination of information to assist decision makers in determining policies and investments best suited to regional cooperation and sustainable water use; and

**Coordinated Applied Research** – Multidisciplinary collaborative studies on cutting edge-issues, conducted by international research teams to promote north-south and east-west dialogue and build a common understanding of the global challenge of transboundary waters governance.

Oregon State University expertise will be represented in all three programs, with an initial focus on the following activities:

### 1. Development of an internet portal for transboundary waters information resources

Each university in the Partnership has developed specialized transboundary waters information resources and databases, and has the capacity to use information technology. OSU collaborators in the Partnership will spearhead an initiative to consolidate regional and sub-national scale databases into a web-based format that is searchable. Examples of searchable web-based information resources useful to transboundary waters stakeholders include:

- freshwater treaties, agreements, and laws
- digital atlas of transboundary river basins
- water conflict dispute resolution negotiating notes
- water conflict & cooperation event database
- indigenous/traditional methods of water dispute resolution
- reports, study abstracts, case studies
- annotated bibliographies of state-of-the art water conflict resolution

### 2. Hydrodiplomacy Geographic Information System and Decision Support Tools

Geographic Information Systems (GIS) provide an efficient framework to model and evaluate the multiple components of transboundary waters management simultaneously, using spatially referenced biophysical and socioeconomic data accurately depicted with maps. GIS technology can thus serve as an invaluable resource for education and capacity building for transboundary waters stakeholders, and can also act as a platform for negotiation and conflict management, helping groups with disparate world views (culturally or professionally) to collectively visualize common water resource issues, and to identify collaborative strategies to address them. Oregon State University will pool expertise from multiple colleges to develop a data rich web-accessible GIS, while simultaneously training students and practitioners with information technology skills necessary for its operation. The GIS itself is strengthened through its close association with the Partnership's Education & Training program. Applications can be iteratively tested and refined through interaction with students participating in the training and certificate programs to trouble shoot accessibility issues and maximize the GIS's relevance and utility to various user audiences.

### 3. Transboundary Waters Curriculum Series

The Transboundary Waters curriculum series focuses attention on the linkages between the way water is used and the way it is governed in different transboundary settings. A variety of curricula are offered, ranging in length from one hour to nine weeks, and constructed from four integrated course **modules**: Water & Ecosystems; Water & Economics; Water & Society; and Water & Governance. The first three modules form the basis of the series, and provide an in-depth look at transboundary water issues in three distinct and overlapping utilitarian contexts. The fourth module, Water & Governance, ties the series together by addressing the way shared waters have been, are, and might be managed to achieve or offset balance across political, economic, and ecological divides.

Courses for each curriculum are developed drawing from cross-cutting **themes** within each of the four modules. Example themes include Hydrodiplomacy; Law & Public Policy; Conflict Resolution; and Finance & Administration. To promote identification and understanding of distinctive *transboundary* issues, course material includes consideration of water issues in local, regional, and international basins. Students are thus able to survey different geographical settings, and to identify common drivers of conflict and cooperation across multiple spatial scales.



Oregon State University faculty will contribute to courses team taught with faculty from around the world, offering Oregon and United States perspectives on water governance, and pooling expertise from multiple colleges including; Geosciences, Sociology, Bioengineering; Agricultural Resource Economics; Anthropology; Political Science and Speech Communication.

**Training and Publications:**

Ten graduate students received training in transboundary water conflict through their attendance at the Water Resources in Transboundary Settings: Lessons from Around the World seminar and through direct interaction with participants and through volunteering with workshop logistics.

# Environmental Analysis and Impact Assessment of Endocrine Disrupters in the Willamette River: A Web-Based Information System

## Basic Information

<b>Title:</b>	Environmental Analysis and Impact Assessment of Endocrine Disrupters in the Willamette River: A Web-Based Information System
<b>Project Number:</b>	2002OR10B
<b>Start Date:</b>	2/15/2002
<b>End Date:</b>	2/14/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Oregon 5th
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Surface Water, Water Quality, Management and Planning
<b>Descriptors:</b>	Internet, databases, hydrology, watersheds, water quality, public education
<b>Principal Investigators:</b>	Tarek A. Kassim

## Publication

1. Kassim, Tarek A, 2002, Environmental analysis and impact assessment of endocrine disrupters in the Willamette River - Project Approach, 5th International Conference of the Balkan Environmental Association on Transboundary Pollution, 7-10 November 2002, Belgrade, Yugoslavia.
2. Kassim, T.A., 2004, FORENSIC ANALYSIS, MASS BALANCE AND FATE MODELING OF ENDOCRINE DISRUPTING CHEMICALS IN WASTEWATER TREATMENT PLANTS. 4th SETAC World Congress, Society of Environmental Toxicology and Chemistry, SESSION: A05 Endocrine-Disrupting Chemicals in Wastewater Treatment Effluents, 14-18 November, 2004, Portland, Oregon
3. Kassim, T.A., 2004, FORENSIC ANALYSIS OF WASTEWATER EFFLUENTS- AND BIOSOLIDS-DERIVED ENDOCRINE DISRUPTING CHEMICALS IN THE WILLAMETTE RIVER. Gordon Research Conference, Environmental Sciences: Water, June 27 - July 2, 2004, Holderness School, Plymouth, NH
4. Kassim, T.A., 2003, FORENSIC ANALYSIS, CHEMODYNAMICS AND ENVIRONMENTAL IMPACT ASSESSMENT OF COMPLEX ORGANIC MIXTURES. LECTURE, the Department of Environmental Engineering at Texas A&M University-Kingsville, Texas, January 24, 2003.

### **Problem and Research Objectives:**

The Willamette River of Oregon (Figure 1) is the 10<sup>th</sup> largest river in the United States. In the 1930s, the Willamette was so polluted that fish were dying and the water was no longer safe for human use. Decades of local effort resulted in significant improvements to water quality and, by the 1970s, the Willamette became a model for what concerned citizens can accomplish in environmental restoration. Recently, another critical milestone in the history of the Willamette River has approached. A study performed in 1997 by the US-EPA and the Oregon-DEQ found that the aquatic environment of the river is contaminated with organic pollutants that causes several fish species to die or have deformation. It is believed that, as in past successful efforts to improve the Willamette, the best approach would be an organized research plan with full synergistic involvement and participation by all interested private sectors, academic institutions and state parties. It is believed that the Department of Civil, Construction and Environmental Engineering at Oregon State University is currently playing a major role in the current state problem by developing a web-based information system of EDCs characteristic to the Willamette River.

The Willamette aquatic environment is contaminated with organic pollutants. According to the current state's water pollution, there is a real need to achieve an efficient and cost-effective investigation that will be helpful to the State of Oregon, DEQ and EPA for their assessment and management programs and feasibility study. The present project aims at building a web-based information system (WBIS) to investigate EDCs in the Willamette river aquatic environment and their potential effects on fish, and to provide background information on contaminant levels at different locations of the study sites. The main objectives of the present proposal are to help:

- Characterize the potential impact of organic contaminants based on the organic chemical composition of both water and sediment samples;
- Estimate the potential ecological effect of organic contaminants present in the Willamette river environment;
- Assign the potential impact to a certain fraction(s) or a group of individual contaminants; and Model the ultimate fate and transport of the characterized endocrine disrupting contaminant(s) in the study area.

The proposed WBIS consists mainly of three fundamental approaches (i.e., modules): Characterization and Source Partitioning (CSP), CHEModynamics (CHEM) and Environmental Impact Assessment (EIA) modules. These modules can be explained as follows:

- The "CSP" module is based on characterization and identification of the EDCs of both water and sediments from the Willamette River. The main pollution sources and transport of these EDCs can be further assessed based on some known pollutant locations in the river, hot spots, chemical indices, and linear programming, artificial intelligence and Monte Carlo Simulation models.
- The "CHEM" module is based on both physical and chemical properties of the characterized EDCs, partitioning data, and multimedia modeling software. This allows determining the fate and transport of these EDCs.
- The "EIA" module is based on information that will be collected from the literature about the relationship between chemical species and endocrine disrupters.

The proposed WBIS aids the elucidation of the impact, fate, and transport of EDCs present in the aquatic environment of the Willamette River.

### **Methods, Procedures, and Facilities:**

The present WBIS project uses the state of knowledge and information in the fields of environmental organic chemistry, toxicology, computer science/programming and environmental engineering. This requires the use of state of the art instruments and latest modeling techniques. The following is a summary:

#### Sampling

Water samples were collected by Niskin bottles from various locations in the Willamette River (Figure 1), which include Portland, Salem, Albany, Corvallis and Eugene stations.

#### Characterization and Identification of EDCs

The following sections summarize the approach used to characterize and identify the molecular compositions of EDCs in the aquatic environment of the Willamette River, as follows:

##### Extraction and separation

An extraction protocol originally developed and revised by Aboul-Kassim (1994; 1998) and Aboul-Kassim and Simoneit (2001) was modified and verified for the qualitative and quantitative analyses of different organic classes found in the aquatic environment of the Willamette River. In brief, water samples were liquid/liquid extracted with methylene chloride-methanol (2:1). All the extracts (EOM) was concentrated to 2 ml and hydrolyzed overnight with 35 ml of 6% KOH/methanol. The corresponding neutral and acidic fractions were successively recovered with *n*-hexane (4x30 ml), the latter after acidification (pH 2) with 6*N* HCl. The acidic fractions, previously reduced to 0.5 ml, were esterified overnight with 15 ml of 10% BF<sub>3</sub>/methanol. The BF<sub>3</sub>/methanol complex was destroyed with 15 ml of water, and the methyl esters were recovered by extraction with 4x30 ml of *n*-hexane. The neutrals were fractionated by long column chromatography. The following fractions were collected:

- a) 45 ml of *n*-hexane (aliphatic hydrocarbons, F1),
- b) 25 ml of 10% methylene chloride in *n*-hexane (monoaromatic hydrocarbons "MAHs", F2),
- c) 40 ml of 20% methylene chloride in *n*-hexane (polycyclic aromatic hydrocarbons "PAHs", F3),
- d) 25 ml of 50% methylene chloride in *n*-hexane (esters and ketones, F4),
- e) 25 ml of methylene chloride (ketones and aldehydes, F5), and
- f) 50 ml of 10% methanol in methylene chloride (alcohols, F6).

The last fraction and an aliquot of the total extract were derivitized prior to gas chromatographic-mass spectrometric (GC-MS) analysis for further qualitative molecular examination by silylation with bis(trimethylsilyl)trifluoroacetamide. A recovery experiment for the long column chromatography was carried out using several deuterated standards.

Various PCB congeners and pesticide fractions were also be analyzed according to the methods described by Aboul-Kassim and Simoneit (2001). Measurement of the PCB congeners and pesticides required a clean up of the lipid matrix, liquid-liquid partitioning procedure followed by isolation of the PCBs and pesticides using a normal-phase LC procedures. The normal-phase LC procedures separated the analytes into two fractions, one containing the PCBs and the lower polarity chlorinated pesticides (HCB, 2,4'-DDE, and 4,4'-DDE) and the second fraction containing the more polar chlorinated pesticides. The separation of PCBs and pesticides reduced the possible co-elution of many of the pesticides with PCB congeners of interest. These two fractions were analyzed by gas chromatography-electron capture detector (GC-ECD). Other trace organic pollutants (e.g., phthalate esters) were determined and characterized according to Aboul-Kassim and Simoneit (2001).

##### Instrumental analyses

All samples were analyzed by gas chromatography (GC), GC-ECD, GC-MS. The GC-MS analyses of the samples were performed using a Hewlett-Packard 5973 MSD quadrupole mass spectrometer operated in the electron impact mode at 70eV and coupled to an HP Model 6890 gas chromatograph. The GC is equipped with a 30 m x 0.25 mm i.d capillary column coated with DB-5 (J & W Scientific, film thickness 0.25 μm) and operated using helium as carrier gas.

##### Identification and quantification

Compound identification was based on comparison with the GC retention times and/or mass fragmentation patterns of standard reference materials and with the help of the Library Molecular marker identification was tabulated as follows:

- (a) *Positive*, when the sample mass spectrum, authentic standard compound mass spectrum, and their retention times agreed well;

- (b) *Probable*, same as above except no standards were available, but the sample mass spectrum agreed very well with the standard library;
- (c) *Possible*, same as above except that the sample spectrum contained information from other compounds but with minor overlap; and
- (d) *Tentative*, when spectrum contained additional information from possibly several compounds with overlap.

Identification and response factors of several EDCs were determined using a suite of standard compounds. Quantification was based on the application of per-deuterated compounds for each respective EDC fraction as internal standards.

#### Organic carbon analysis

Organic carbon analyses will be carried out for all the Willamette river samples using a Carlo Erba NA-1500 CNS analyzer. The concentrations of all EDCs will be calculated relative to the total organic carbon (TOC) content of the samples.

#### Characterization and Source Partitioning (CSP) Module

EDCs data and other chemical indices of the compositions of the aquatic environment of the Willamette river samples were examined statistically in order to determine any significant environmental variations, and to construct a source-partitioning model specific for the Willamette. All statistical analyses and modeling approaches were performed using extended Q-mode factor analysis, linear programming and artificial intelligence-neural network programs and verified using Monte Carlo Simulation.

#### CHEModynamics (CHEM) Module

Fate and transport of various organic pollutants have been studied in different environmental media (Aboul-Kassim, 1998; Aboul-Kassim and Simoneit 2001). Chemodynamic behavior of EDCs characteristic to the Willamette was investigated based on both physical and chemical properties of the characterized EDCs, partitioning data, and multimedia modeling software. This allowed determining the fate and transport of these EDCs.

#### Environmental Impact Assessment (EIA) Module

The "EIA" module is based on information that was gathered from the literature about the relationship between chemical species and endocrine disruption. Various databases have been searched and summarized which helped build the proposed WBIS.

#### **Principal Findings and Significance:**

The current pollution in the Willamette River is the result of anthropogenic activities. The present investigation indicated the presence of several chemicals of complex organic mixtures (COMs) or possible organic wastewater contaminants (OWCs). Regardless of sampling locations, the group of COMs/OWCs of anthropogenic origin includes aliphatic hydrocarbons (*n*-alkanes, hopanes, steranes, UCM), polycyclic aromatic hydrocarbons (PAHs) and phthalates.

Results of this study will be shared with environmental, assessment and management teams from the: (a) City of Portland - Bureau of Environmental Services; (b) Port of Portland - Environmental Program; (c) Oregon-Department of Environmental Quality; (d) USGS – Portland Office; (e) EPA – Region X - Portland Office; and (f) concerned local citizens in the Willamette area who live and share the river will be also informed.

Based on the principal findings of the current investigation:

- Comprehensive research project was submitted to the United States Geologic Survey in March 2004. The project is entitled: "OCCURRENCE AND JOINT MULTICOMPONENT TOXIC/GENOTOXIC INTERACTION MODELING OF PHARMACEUTICALS, HORMONES AND OTHER ENDOCRINE DISRUPTING CHEMICALS IN THE WILLAMETTE RIVER", with Kenneth J. Williamson, and Bernd R.T. Simoneit (Co-Investigators), \$399,537 for two years

- Collaboration or an interaction with the Port of Portland and City of Portland research teams has been established.

**Student Support (# and degree level):**

The present study was partially a part of the Masters' thesis for one graduate student in the Department of Civil, Construction and Environmental engineering at Oregon State University. The student has received some training about endocrine disrupting chemicals in the aquatic environment during the project.

## Student Support

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 RCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	1	0	0	0	1
<b>Masters</b>	15	0	0	0	15
<b>Ph.D.</b>	3	0	0	0	3
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	19	0	0	0	19

## Notable Awards and Achievements

## Publications from Prior Projects