Pullman Stormwater Pilot Study for Pesticides, PCBs, and Fecal Coliform Bacteria, 2005-2006



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Pullman Stormwater Pilot Study for Pesticides, PCBs, and Fecal Coliform Bacteria, 2005-2006

by

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October 2006

Waterbody Number: WA-34-1020 (South Fork Palouse River) This page is purposely left blank for duplex printing

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Glossary and Acronyms

Glossary

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State periodically to prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards, and are not expected to improve within the next two years.

Catchment: The area draining to that storm drain.

Clean Water Act: Federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the Total Maximum Daily Load (TMDL) program.

Fecal coliform: That portion of the coliform group of bacteria which is present in intestinal tracts and feces of warm-blooded animals as detected by the product of acid or gas from lactose in a suitable culture medium within 24 hours at 44.5 plus or minus 0.2 degrees Celsius. Fecal coliform are "indicator" organisms that suggest the possible presence of disease-causing organisms. Concentrations are measured in colony forming units per 100 milliliters of water (cfu/100 mL).

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the nth root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface water runoff from agricultural lands, urban areas, forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the National Pollutant Discharge Elimination System (NPDES) program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Phase II stormwater permit: The second phase of stormwater regulation required under the federal Clean Water Act. The permit is issued to smaller municipal separate storm sewer systems (MS4s) and construction sites over one acre.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than five acres of land.

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state, including change in temperature, taste, color, turbidity, or odor of the waters, or such discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state as will or is likely to create a nuisance or render such waters harmful, detrimental, or injurious to the public health, safety, or welfare, or to domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or to livestock, wild animals, birds, fish, or other aquatic life.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands, and all other surface waters and water courses within the jurisdiction of Washington State.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from exceeding (not meeting) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms

Ecology:	Washington State Department of Ecology
EPA:	U.S. Environmental Protection Agency
NSQD:	National Stormwater Quality Database
QA:	Quality assurance
QC:	Quality control
RM:	River mile
RPD:	Relative percent difference
USGS:	U.S. Geological Survey
WAC:	Washington Administrative Code
WSU:	Washington State University

Abstract

Stormwater discharges from Phase II jurisdictions will soon be regulated by the Washington State Department of Ecology under the National Pollutant Discharge Elimination System (NPDES) program. Municipal stormwater loads of 303(d) listed toxic pollutants from Phase II stormwater systems have not been previously studied by Ecology.

A pilot study was undertaken to determine the concentrations of the 303(d) listed pollutants in municipal stormwater samples. The results may be used in developing Total Maximum Daily Loads for toxic compounds and fecal coliform bacteria in the South Fork Palouse River subwatershed. The city of Pullman and Washington State University are the only proposed Phase II entities in this watershed.

From December 2005 to April 2006, three storm drain outfalls were sampled for chlorinated pesticides, PCBs, fecal coliform bacteria, and conventional pollutants. 4,4'-DDE (a historical pesticide), PCBs, and fecal coliform bacteria were detected in all samples from the Pullman storm pipe outfalls. The pesticides dieldrin and heptachlor epoxide were detected in all but one sample.

Many of the toxic pollutant detections were near the reporting limits, and all detections are qualified as estimates due to the interfering "dirtiness" of the stormwater sample matrix. The conventional pollutant concentrations, including fecal coliform bacteria, were comparable to those found in the National Stormwater Quality Database, an ongoing study by Pitt and Maestre (2005).

The annual mass load of the toxic 303(d) listed pesticides, PCBs, and fecal coliforms were estimated from the measured concentrations using the Simple Method (Schueler, 1987). These stormwater concentrations may be used to (1) plan further studies to more accurately characterize stormwater sources, and (2) initiate actions to prevent stormwater sources of these chemicals in the storm drain systems.

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Introduction

The Washington State Department of Ecology (Ecology) has listed segments of the Palouse River under Section 303(d) of the Clean Water Act. These listings are for non-attainment of water quality standards and human health criteria promulgated on Washington State in the U.S. Environmental Protection Agency (EPA) National Toxics Rule. EPA requires that states set priorities for cleaning up 303(d) listed waters and establish a Total Maximum Daily Load (TMDL) for each impaired waterbody. A TMDL is a cleanup plan that entails an analysis of how much of a pollutant load a waterbody can assimilate without violating water quality standards.

By EPA mandate in November 2002, a TMDL must address the pollutant loads in stormwater from a permitted stormwater discharge. Stormwater runoff can accumulate and transport pollutants such as pesticides, fertilizers, fecal matter, oil and grease, trash, and sediment via the stormwater conveyance system to receiving waters and thus degrade water quality. Ecology has issued a draft version of the Phase II Municipal Stormwater Permit for Eastern Washington for public comment, and the final permit is anticipated in the fall of 2006.

Pullman, Washington, will likely be the only Phase II municipality that Ecology will regulate for stormwater in the Palouse River watershed; therefore, the study area was limited to the South Fork Palouse River. Pullman and Moscow, Idaho, are the two largest population centers in the Palouse River watershed according to the 2000 census, with populations of 24,675 and 21,207, respectively. Since Pullman's population exceeds 10,000, the city will qualify for Phase II stormwater permit coverage and will be regulated as a small municipal separate storm sewer system (MS4). EPA has not yet made a final determination on Phase II permitting for Moscow which is also located within the watershed (Misha Vakock, EPA Region 10, 5/19/05 telecommunication).

A 2005-06 pilot study was undertaken to determine the concentrations of the 303(d) listed constituents in Pullman stormwater. This source of pollutants has only recently been monitored for inclusion in toxics TMDLs by Ecology. In addition, this effort will aid future study designs by providing an understanding of pollutant variability among three storm drains and storm events samplings. A relative sense of the load of the pollutants to the receiving waters was calculated using simple and common assessment procedures.

Currently permitted discharges in the South Fork of the Palouse River watershed include industrial discharges, municipal wastewater treatment plants, and construction stormwater general permit holders. Stormwater pollutant concentrations from the industrial discharges, municipal wastewater treatment plant, and construction stormwater general permit holders are not a part of this study.

South Fork Water Quality

The South Fork Palouse River watershed drains approximately 130 square miles of predominantly dry land agriculture as well as urban, commercial, and industrial developments from Pullman, Washington, and Moscow, Idaho (Pelletier, 1993). The South Fork Palouse River is approximately 45 stream miles long with the initial 13.4 stream miles in the state of Idaho. From the Washington-Idaho border, the South Fork flows through downtown Pullman and meets the mainstem Palouse River at the town of Colfax, Washington. The mainstem Palouse River then empties into the Snake River. Figure 1 illustrates the location of the Palouse River watershed and the South Fork of the Palouse River.

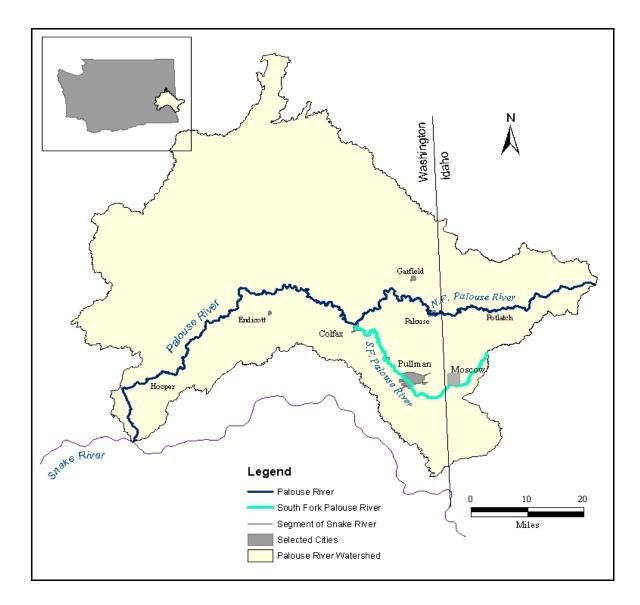


Figure 1: The Palouse River Watershed and the South Fork Palouse River Basin

Both the mainstem Palouse River and South Fork are listed on the Washington State 303(d) list for water quality impairments. On the mainstem, there are six listings for toxic pollutants that are at Category 5 status, which requires a TMDL. Category 5 bacterial listings include one on the mainstem and 11 listings on the South Fork. See Appendix A for the complete list of impaired waterbodies.

Several TMDL studies are underway in the Palouse River watershed to address these impairments. Quality assurance (QA) project plans for temperature and fecal coliform TMDLs have been published, and the field studies are underway (Bilhimer et al., 2006, and Mathieu and Carroll, 2006, respectively). Additional QA project plans, for dissolved oxygen and pH TMDLs, were recently published (Carroll and Mathieu, 2006).

303(d) Toxicity Re-evaluation Study

Impaired reaches of the lower mainstem (below Colfax) Palouse River are listed for nonattainment of the EPA human health criteria for the toxic compounds 4,4'-DDE, dieldrin, heptachlor epoxide, alpha-BHC, and PCB-1260 in edible fish tissue. These historical chlorinated pesticides and polychlorinated biphenyls (PCBs) were banned in the United States due to ecological concerns in the 1970s and 1980s and are now classified by EPA as probable human carcinogens. Appendix B provides background information on these toxic 303(d) listed pollutants.

A field study to re-assess the toxic compound concentrations of pesticides and PCBs in edible fish tissue began in 2005 (Johnson et al., 2005). A TMDL is being developed for PCBs and dieldrin based on the fish sampling in 2005 which indicated that most of the South Fork was impaired by these two contaminants (Johnson et al., in progress).

Given the Phase II requirements to quantify stormwater pollutant streams in upcoming TMDLs and the results of the fish tissue re-evaluation results, this study was undertaken as a pilot project to ascertain toxins and fecal coliform concentrations in stormwater.

Goals and Objectives

The objectives of this study were to determine the concentrations of 303(d) listed pollutants in Pullman stormwater and to estimate loading from the Phase II jurisdictional limits. Study results acquired by the project will be used to accomplish the following goals outlined in the QA project plan (Lubliner, 2005).

- 1. Develop a stormwater loading analysis which will quantify the stormwater load of chlorinated pesticides, PCBs, and fecal coliform bacteria from the city of Pullman, including Washington State University (WSU), into the South Fork Palouse River.
- 2. Identify critical input data to incorporate into future stormwater sampling plans for use in TMDLs.
- 3. Develop a factor to relate land use to stormwater pollutant loading.
- 4. Evaluate models, if applicable, used to estimate stormwater loads.

Study Design

Sampling took place during the winter, wet season of 2005-06, defined as November 1 through April 30. The criterion for stormwater discharge sampling was the occurrence of 0.2 inches of rainfall in a 24-hour period as measured at the Spokane Regional Airport via real time gages, following a dry period (no measurable rain) of at least 24 hours. Online weather predictions and the WSU rain gage were monitored, as Pullman can have a differing weather pattern from Spokane (airdata.ce.wsu.edu/weather.htm).

Stormwater samples were collected and analyzed from three storm events, on October 31, 2005, January 30, 2006, and April 5, 2006. Storm duration and intensity are likely the greatest factors in pollutant generation; however, logistical restrictions effectively reduced the sampling efforts to grab and manual compositing grab sampling at any given period of the storm event. On the day of sampling, the three storm discharge pipes were visited a total of three times each in approximately a two hour rotation. Discharge velocity was measured using a portable Swoffer meter.

Pesticide and PCB samples were collected as manual composites spanning the three rotations. The manual composite technique involved adding one-third of a gallon to the sample container on each rotation. Composites were kept on ice at all times. Once collected and mixed, they were poured into appropriate containers for pesticide and PCB congener analysis. Sample containers were cleaned to EPA QA/QC specifications.

Fecal coliform bacteria and other stormwater characterization parameters – total suspended solids, turbidity, alkalinity, chloride, total persulfate nitrogen, nutrients, and total organic carbon/ dissolved organic carbon – were taken as single grab samples into appropriate containers in duplicate on the first rotation and sampled again on the third rotation. Detailed methodology can be reviewed in the QA project plan (Lubliner, 2005).

Samples were transported to Ecology's Manchester Environmental Laboratory in coolers at 4°C, and processed within the specified holding time for all samples, with one exception. The coolers from the first sampling event missed the plane in Spokane and arrived at Manchester Laboratory after the holding period (24 hours) for fecal coliform samples. Therefore, the fecal coliform results were estimates and qualified with a "J". Chain-of-custody procedures were followed during all collections.

Site Selection

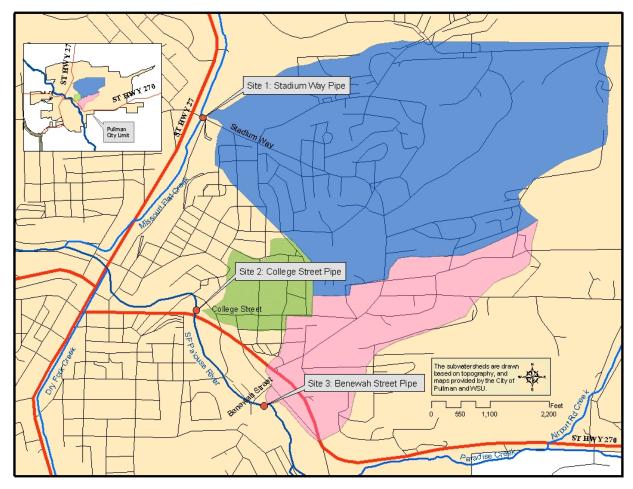
The City of Pullman stormwater runoff drains into four area creeks – Airport, Paradise, Missouri Flat, and Dry Fork– which empty into the South Fork Palouse River within the Pullman city limits.

Three storm drain outfalls were selected for sampling within the Pullman city limits; these outfalls presented typical urban land uses, ease of access, and safety during winter weather.

- 1. The first storm drain outfall, Stadium Way, is located near the Jack in the Box restaurant, at the intersection of Grand Avenue and Stadium Way. This site has the largest catchment, approximately 552.7 acres as drawn. This storm drain empties into Missouri Flat Creek which flows approximately 0.7 miles to the South Fork Palouse River near Whitman Street. Mixed land uses include light commercial, residential, and portions of the WSU campus.
- 2. The second site, College Street, drains the southwestern side of WSU and has the smallest area in the study, with only a 54.5 acre catchment. This drain includes both the old and new buildings as well as some light industrial areas on the campus.
- 3. The third site, Benewah Street, includes an area along Highway 270, Latah Street, and the southern end of the WSU campus. The land uses are institutional, commercial, and industrial. This storm drain empties into the South Fork Palouse River near Benewah Street. This catchment drains approximately 168.5 acres, as drawn.

Figure 2 shows the approximate storm drain locations and associated catchments (the area draining to that storm drain). The catchments are drawn based from a combination of topography and street layout from the City of Pullman, a surface water drainage map from WSU, and USGS 1:24K quad maps. Figure 2 may be inaccurate due to outdated source materials; however, it represents the current understanding of surface water drainage to the pipes sampled.

Photographs of the storm pipe outfalls are available in Appendix F.



* This map illustrates the catchments draining to the sampled storm drains; however, it may be inaccurate. These catchments are drawn from engineering specifications provided by the City of Pullman, WSU, and USGS topographic maps.

Figure 2: Pullman Storm Drain Catchments and Sampling Sites for the 2005-06 Pilot Study

Quality Assurance / Quality Control

Manchester Laboratory performed the chlorinated pesticide analyses as well as the conventional pollutant analyses. The PCB congener analysis was performed by a contracted laboratory, Pacific Rim Laboratories, using an isotopic dilution method where each sample is spiked with labeled PCB congeners. Listed in Table 1 are the constituents measured in stormwater from the City of Pullman storm drains.

Toxics ¹	Conventionals ²	Conventionals ³
4,4'-DDE*	Fecal coliform	Temperature
Dieldrin*	Ammonia	pН
Heptachlor epoxide*	Nitrate	Dissolved oxygen
alpha-BHC*	Total persulfate nitrogen	Conductivity
PCBs	Orthophosphate	
	Total suspended solids	
	Turbidity	
	Chloride	
	Total dissolved carbon	
	Total organic carbon	

Table 1: Stormwater Elements Analyzed

¹Measured at Manchester Laboratory, except PCB congeners which were measured by contract at Pacific Rim Laboratory.

²Measured at Manchester Laboratory using standard protocols.

³Measured in the field with calibrated meters.

*The chlorinated pesticide list analyzed by Manchester Laboratory includes more constituents than listed above. See Appendix C for a complete list of analytes.

Quality Control

Sample collection, sample delivery, instrument calibration, and analysis for the conventional pollutants and PCBs were achieved without problems, with one exception: The first set of stormwater samples missed the intended flight in Spokane and arrived after the holding time for bacteria had been exceeded; therefore, results are qualified as estimates. Instrument calibration and overall pesticides analysis had some problems due to suspected matrix interferences. See discussion below.

Field Duplicates and Laboratory Replicates

Field duplicates are samples taken side-by-side in the field, whereas *laboratory replicate* means the sample is run through analysis twice by the laboratory. The variability in field duplicates is calculated as the relative percent difference (RPD) between a sample and its duplicate as a percent of the mean. Table 2 shows the number of duplicates and RPDs for the 303(d) listed pollutants. Conventional pollutant data are presented in Appendix D.

A complete list of detected pesticides and the calculated relative percent difference of duplicates is in Appendix E.

202(d) Dollutonta	Number of Duplicates	Relative Percent Difference			
303(d) Pollutants		Stadium	Benewah	College	
4,4'-DDE	1^a	15	6	21	
Alpha-BHC	1^a	17	6	0	
Dieldrin	1^a	8	4	80 ^b	
Heptachlor epoxide	1^a	13	4	45	
PCBs	1	NA	NA	46	
Fecal coliforms	3°	15	19	82 ^d	

Table 2: Field Duplicate Relative Percent Differences of 303(d) Listed Pollutants.

NA – No duplicate taken

^a - One duplicate per storm drain for the entire study

^b - These may be due to interferences in the matrix

^c - Highest RPD of three duplicates. One each storm, per storm drain.

^d - Samples exceeded holding time for fecal coliform bacteria from first storm event.

The QA project plan specified a 20% RPD for the 303(d) pesticides; this RPD was met for 4,4'-DDE and Alpha-BHC. The College Street duplicate exceeded 20% for dieldrin and heptachlor epoxide. The dieldrin RPD of 80% was limited to only the one sample bottle with the other two storm drain RPDs at less than 8%. The high dieldrin RPD may be due to interferences in the matrix. Differences in very small numbers can lead to misleadingly high RPDs, such as heptachlor epoxide where sample and duplicate values were 0.19 and 0.12 ng/L, respectively.

The fecal coliform bacteria counts were fairly close, with RPDs less than 20% with the exception of one duplicate sample from the first storm event of 82% RPD. The holding time was exceeded for the first storm events fecal coliform samples.

Quantitation Limits

Overall, the conventional constituents and PCBs easily met the detection limit specifications set forth in the QA project plan. The expected range of results, the lowest concentrations of interest (lowest concentrations practically attainable within the constraints of this project), and the associated reporting limits are presented in Table 3 for conventional constituents and in Table 4 for pesticides and PCBs.

All laboratory quality control measures for the conventional pollutant samples (calibration, replicates, blanks, spikes and control) met quality assurance targets.

The reporting limit represents the lowest number where the analyte was definitely quantified, below which it is considered an estimate. The reporting limit will be affected by the analyte concentration and matrix interferences.

The final detection limit for pesticides was between 0.11 - 5.1 ng/L, and the reporting limit was found to be 0.064 - 3.2 ng/L. These limits are the lowest currently achievable with the selected methods.

Analyte	Expected Range of Results	Actual Detected Range of Results	Reporting Limit	
Fecal coliform	$1-10^4$ cfu/mL	39 - 4900 cfu/mL	1 cfu/100 mL	
Total suspended solids	1-500 mg/L	4 -273 mg/L	1 mg/L	
Turbidity	1-1000 NTU	8 - 330 NTU	1 NTU	
Alkalinity	50-100 mg/L	14 - 163 mg/L	5 mg/L	
Nitrate+nitrite-N	0.01 - 10.0 mg/L	0.24 - 2.4 mg/L	0.01 mg/L	
Ammonia	0.01 - 0.5 mg/L	0 - 0.3 mg/L	0.01 mg/L	
Total persulfate nitrogen	0.025 - 10.0 mg/L	0.47 - 2.8 mg/L	0.025 mg/L	
Total phosphorus	0.01 - 1.0 mg/L	0.18 - 0.67 mg/L	0.001 mg/L	
Orthophosphate	0.01 - 0.5 mg/L	0.005 - 0.21 mg/L	0.003 mg/L	
Chloride	1-10 mg/L	2.2 - 43.2 mg/L	0.1 mg/L	
Total organic carbon	1-10 mg/L	2.5 - 9.9 mg/L	1 mg/L	
Dissolved organic carbon	1-10 mg/L	2.1 - 8.8 mg/L	1 mg/L	

Analyte	Ranges in Detections (ng/L)	Reporting Limit for Non-Detects (ng/L)
PCB Congeners	1.48 - 11.3	0.002 - 2.62
Pesticide Analytes:		
alpha-BHC	0.039 - 0.52	
beta-BHC	0.12 - 0.25	0.3 - 3.2
gamma-BHC (lindane)	0.72 - 2.5	
delta-BHC	ND	0.062 - 3.1
aldrin	ND	0.062 - 3.2
dieldrin	0.38 - 5.1	0.064 - 0.31
endrin	0.11 - 0.78	0.3 - 3.2
heptachlor epoxide	0.12 - 0.38	0.32 - 3.2
endrin aldehyde	ND	0.19 - 3.2
endrin ketone	0.46 - 0.8	0.3 - 3.2
endosulfan I	0.48 - 0.5	0.064 - 3.2
endosulfan II	0.32 - 0.43	0.064 - 3.2
endosulfan sulfate	ND	0.3 - 3.2
methoxychlor	ND	1.6 - 3.2
4,4'-DDE	1.3 - 4.8	
4,4'-DDD	0.12 - 2.0	0.064 - 3.2
4,4' - DDT	1.3 - 4.9	2.3 - 3.2
trans-chlordane (gamma)	0.31 - 0.53	
cis-chlordane (alpha-chlordane)	0.35 - 0.55	

Table 4: Stormwater Sample Quantitation Limits for PCBs and Chlorinated Pesticides (ng/L; parts per trillion).

"--" the reporting limit is the same as the detected values ND – not detected

Analytical Problems with Pesticides

An increased effort was required to clean the stormwater sample extracts in order to achieve the desired reporting limits for chlorinated pesticides. The samples contained an unknown complex matrix that interfered with the analysis. To the eye, the samples were dark in color and contained settleable and suspended particulates. The samples remained oily and dark after extraction and contained precipitates. The large volume injection procedure used in the analysis concentrates the sample by 15 times and also concentrates the interferences. All pesticide results were qualified as estimates due to poor recovery of quality control samples and should be considered biased low. Procedural notes on the method of clean up used by Manchester Laboratory are detailed in Appendix C.

Instrument Calibration and Surrogate Recovery

Instrument calibration was acceptable for all analytes, with two exceptions for the pesticides analysis.

- 1. During each storm event, the continuing calibration verification procedure showed poor recoveries for some pesticides. A surrogate recovery during the initial calibration was slightly high for the samples of the third storm event. The suite of surrogate compounds used by Manchester Laboratory were poorly recovered (<50%) due to matrix interferences for each of the storm event samplings.
- 2. The laboratory spikes were poorly recovered during the first and second storm event.

Overall, all the sample results are qualified as estimates due to poor surrogate, matrix spike, and continuing calibration recoveries due to the complex matrix interferences. Therefore, all the samples are likely to be biased low.

Field Blanks for Pesticides

The only field blank for pesticides analysis was sent to Manchester Laboratory with the wrong water, and is therefore discredited as a true field transfer blank. Distilled water, rather than certified clean water, was poured into a clean container as a field transfer blank from the second storm event. Distilled water has not undergone a process to remove any organics in the sample and cannot be assumed to be free from contaminants. The Walla Walla Pesticide and PCB TMDL (Johnson, 2004) used field transfer blanks and did not find transfer contamination.

The dieldrin results for the stormwater samples collected on January 30, 2006 in this current study are considered to be valid measurements.

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Results

Rainfall

Rainfall data were obtained from online gages housed at WSU at the top of Dana Hall (<u>http://airdata.ce.wsu.edu/weather.htm</u>) and at the Spokane Airport (National Weather Service and NOAA website (<u>www.wrh.noaa.gov/otx/climate/lcd/lcd.php</u>). The Spokane Airport is approximately 80 miles north of Pullman. Figure 3 shows the rainfall for both locations.

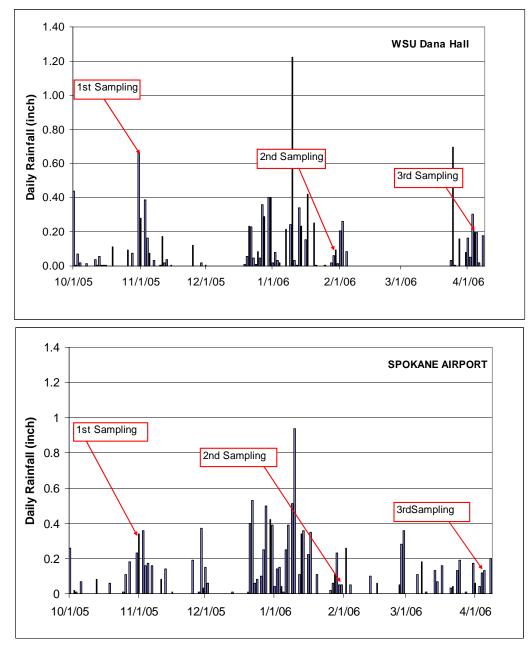


Figure 3: Rainfall Data for Pullman and Spokane, October 2005 - April 2006

Spokane appears to have more rainy days, probably due to small local storm cells. There were nine qualifying storms in Pullman over the course of this 2005-06 study. Due to availability of field personnel, timing, and weather anomalies, several ideal storms were missed. There were larger regional storms that appear to cover both locales, such as the January 10, 2006 event. Table 5 shows the rainfall for each day of the sampling as gaged by WSU and the Spokane Airport.

Location	Day	10/31/05	1/30/06	4/5/06
Pullman - WSU	Previous 24 hrs	0	0.06	0.2
Fullman - w SU	Day Sampled	0.66	0.09	0.2
Spokono Airport	Previous 24 hrs	Trace	0.42	0.12
Spokane Airport	Day Sampled	0.23	0.39	0.13

Table 5: Rainfall (inches) on Sampling Days and the Prior 24 Hours

Shaded = met criteria

- 1. The first storm event sampling October 31, 2005 met the study criteria as the first day of rain after 30 days of no rain above 0.1 inches. The field crew had good timing to catch the beginning of the storm, as only 0.35 inches of rain had fallen since midnight at the beginning of sampling around 9 a.m. on October 31, 2005.
- 2. The second storm event sampling on January 30, 2006 did not meet the 0.2 inches requirement. Predicting rainfall each day with correct timing is difficult, particularly from a distance. Rainfall at the Spokane Airport for the day before showed 0.42 inches; however, in Pullman very little rain fell (0.06 inches). The next day when Ecology's field crew set out, the Spokane Airport rain gage easily met the criteria with 0.39 inches of rain whereas in Pullman it only amounted to 0.09 inches. Clearly, the rainfall in Spokane was only a local storm event.
- 3. The third sampling took place on April 5, 2006. Sampling occurred after the peak rainfall day, approximately five days into the storm event. A total of 0.2 inches fell on April 5, 2006. Obviously, the criterion of no measurable rainfall the previous 24 hours was not met; however, the importance of another sampling day increased as the deadline for this study was April 30, 2006.

Velocity measurements were made during each rotation at each storm drain using a Swoffer velocity meter. It was not uncommon to experience a surge of water from each site's drain pipe. On several occasions the stormwater surge reached 1 foot depth in a pipe of approximately 3.8 feet in diameter.

The discharge rate was calculated from the area of the water in the pipe times the measured velocity at each rotation. The area of the water in the pipe was found from measured pipe radius and water width in the pipe. See equations below:

Calculation of Discharge at a Culvert:

$$Discharge\left(\frac{ft^{3}}{s}\right) = Area(ft^{2})*Velocity\left(\frac{ft}{s}\right)$$

$$Area of Water(ft^{2}) = Culvert Radius^{2}*\left[\frac{(\theta - Sin\theta)}{2}\right]$$

$$Sector Angle \ \theta (rad) = 2*ArcSin\left[\frac{(StreamWidth)}{2*Culvert Radius}\right]$$

$$Culvert Radius(ft) = Measured \ (diameter/2)$$

$$Stream Width(ft) = Measured \ as width \ of \ water \ in \ pipe$$

$$Velocity\left(\frac{ft}{s}\right) = Measured \ at \ mouth \ of \ pipe$$

The measured stormwater velocities and averaged discharge for that storm event are shown in Table 6.

Table 6: Velocity and	Calculated Discharge Measur	rements by Storm Drain
2	Ũ	2

Storm Drain	Date	Measured Velocity (ft/s)			2		Averaged Discharge
		Rotation 1	Rotation 2	Rotation 3	(cfs)		
College Street							
Large concrete pipe	10/31/2005	0.44	0.04	0.11	0.68		
	1/30/06	0.56	0.03	0.00	0.20		
	4/5/2006	0.04	0.71	0.21	0.99		
Benewah Street							
Large concrete pipe	10/31/2005	0.69	0.19	0.26	1.74		
	1/30/06	0.38	0.04	0.02	0.53		
	4/5/2006	0.66	0.86	0.45	2.49		
Stadium Way							
Small plastic pipe	10/31/2005	6.99	6.43	7.32	2.41		
	1/30/06	8.56	6.92	6.17	2.52		
	4/5/2006	9.19	8.53	6.89	2.86		
Large concrete pipe	10/31/2005	3.84	0.00	3.97	1.10		
	1/30/06	2.62	0.00	0.00	0.05		
	4/5/2006	4.92	4.76	2.10	2.38		

Field crew noted on occasion that there was some difficulty in measuring velocity from the storm pipes. The Stadium Way storm site has two pipes coming from the same catch basin junction box at different heights and sizes (see Appendix F). The small plastic pipe is slightly lower and tends to carry water more often than the larger pipe. At this site, on two occasions there was water spilling from the casement around the pipes that was impossible to measure. Also the bank was sloughing into the stream which made footing questionable. The average combined discharge is reported for the Stadium Way storm pipes. The Benewah storm pipe was not perfectly round, and therefore the discharge was calculated from the larger diameter which was found width-wise.

Stormwater Pollutant Concentrations and Aquatic Life Aquatic Life Criteria

Pesticides and PCBs

Washington State water quality criteria from sections (3) and (5) of Washington Administrative Code (WAC) 173-201A-040 apply to instream water concentrations of pesticides and PCBs. The underlying assumptions for the aquatic life criteria may not be appropriate for stormwater concentrations at the end-of-pipe. Fish and aquatic life cycles may not be occurring within the city of Pullman storm conveyance system. The criteria presented in Table 7 are presented for the purposes of a reference, and do not apply to end-of-pipe water concentrations.

Table 7: Instream Washington State Water Quality Criteria* for Chlorinated Pesticides and PCBs (ng/L; parts per trillion).

Chemical	Criteria for Protection of Aquatic Life			
Chemicai	Freshwater Chronic ¹	Freshwater Acute ²		
4,4'-DDE	—	—		
Dieldrin	1.9	2,500		
Heptachlor epoxide		—		
PCBs	14	2,000		

*WAC 173-201A-040

¹ 24-hour average not to be exceeded

² an instantaneous concentration not to be exceeded at any time

— no criteria

Table 8 presents the concentrations of the 303(d) listed compounds detected at the three stormwater outfall locations.

Table 8: Concentrations of 303(d) Listed Pesticides and PCBs in Pullman Stormwater Samples Collected in 2005-06 (ng/L, pptr).

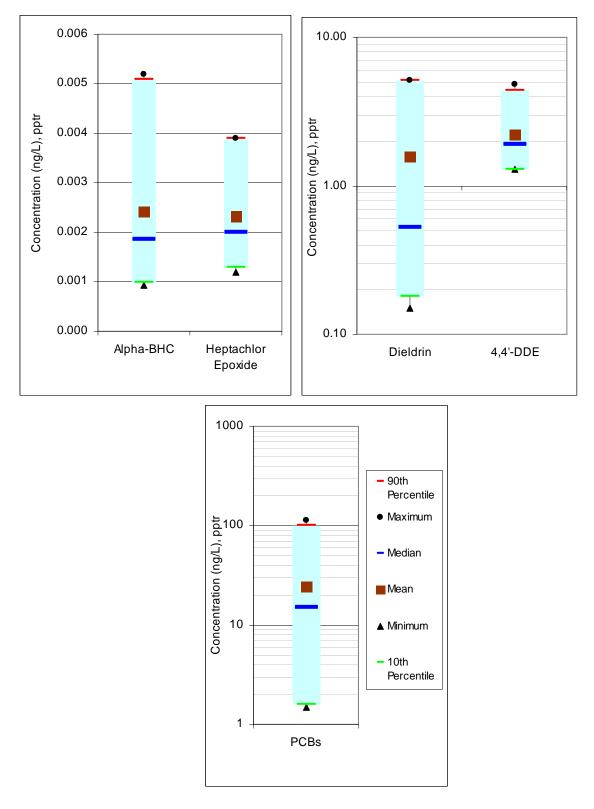
Storm Drain	Date	Alpha-BHC	Dieldrin	Heptachlor epoxide	4,4'-DDE	Total PCBs
G(1'	10/31/05	0.49 J	0.31 UJ	0.39 J	2.0 J	4.1
Way	1/30/06	0.10 J	0.50 J	0.16 J	2.0 J	1.5
	4/5/06	0.20 J	0.36 J	0.18 J	4.8 J	11.3
	10/31/05	0.46 J	0.37 J	0.38 J	1.3 J	8.3
College Street	1/30/06	0.21 J	0.53 J	0.33 J	1.7 J	18.2
	4/5/06	0.15 J	0.11 J	0.16 J	1.5 J	13
	10/31/05	0.52 J	1.3 J	0.32 UJ	2.0 J	17.1
Benewah Street	1/30/06	0.17 J	5.0 J	0.23 J	3.3 J	18.3
Succi	4/5/06	0.20 J	2.0 J	0.20 J	1.4 J	45.3

J = The analyte was positively identified. The associated numerical result is an estimate due to matrix interferences. UJ = The analyte was not detected at or above the reporting limit. Individual stormwater concentrations for dieldrin and PCBs were below aquatic life criteria. The highest dieldrin concentration, 5.0 ng/L, is 2000 times lower than the acute instream criteria. The highest measured PCB concentration, 45.3 ng/L, is roughly 23 times lower than the acute instream criteria. There is undoubtedly a cumulative load from many storm drains to the same waterbody that may affect the instream concentrations of these toxic compounds. However, the instream water concentrations were not measured in the South Fork Palouse River or Missouri Flat Creek as part of this stormwater pilot study. The Palouse River toxics TMDL study, which is in progress, will assess the risk to aquatic life and human health criteria from these pollutants. The chronic aquatic life criteria are not appropriate for stormwater samples without year-round sampling from the storm drains to assess the chronic exposure.

Dieldrin concentrations were highest during the second storm event and were an order of magnitude higher at Benewah Street than the two other drains for each of the three storm events. Interestingly, the second stormwater sampling event with only 0.09 inches of rainfall did not meet the QA project plan criteria. This might suggest that dieldrin concentrations are related to rainfall.

The first sampled storm event conditions were typical of a first-flush scenario, with the previous 24-hour dry period and a strong storm event with 0.6 inches of rainfall on the day of sampling. There did not appear to be a consistent pattern between the toxic pollutants and the stormwater discharge rates. With the exceptions of alpha-BHC and heptachlor epoxide, chemical concentrations were highest from the first storm event sampling on October 31, 2005.

The statistical measures of central tendency, relative standing, and dispersion for the 303(d) compounds found in the Pullman storm drains are illustrated by Figure 4.



The scales within the three graphs are different.

Figure 4: Standard Statistical Quantities of Measured Toxicants in Pullman Stormwater Samples, 2005-06.

Figure 4 only represents the detected values. The distributions were found to be lognormal using the MCTA*sta3.0* tool that can be found at Ecology's website <u>www.ecy.wa.gov/programs/tcp/tools/toolmain.html</u>. The tool uses a probability plot method and the Wilkes-Shapiro test.

Relatively little was found from the literature about the concentrations, ranges, and dispersion characteristics of toxic pollutants in stormwater samples. The concentration range was small for alpha-BHC and heptachlor epoxide, and slightly larger for 4,4'-DDE and dieldrin. PCB concentrations were the most variable. The concentrations of both 4,4'-DDE and PCBs were lowest for the first storm sampling at each of the three storm drains. The observed ranges for alpha-BHC and heptachlor epoxide appear to be related to environmental conditions such as rainfall and wash-off potential.

The highest rainfall and discharge measured during the course of the study was from the first storm event sampled, and the lowest was from the second sampling. PCB concentrations do not appear to be related to the amount of rainfall or discharge. The highest concentrations of PCBs from Benewah Street and Stadium Way were from the third storm event sampled. The third sampling event was characterized with the previous four days of rain and 0.2 inches of rainfall on the day of sampling. But increased days of rain did not show an increase at the College Street storm drain. College Street showed a fairly constant PCB concentration regardless of rainfall amount. The PCB concentrations for each drain across the three storm events are graphically represented by Figure 5.

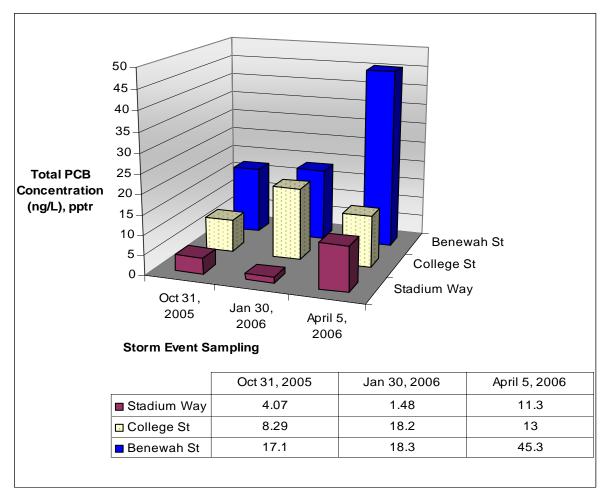


Figure 5: Total PCB Concentrations at the Three Field Locations for Each Storm Event, 2005-06

At this point in time, few Ecology studies have analyzed the concentrations of toxic pollutants in stormwater. The Spokane River PCB TMDL analyzed four grab samples from storm drains that empty into the Spokane River (Serdar et al., 2006). Although the contributing catchment area for each drain was usually larger, the range in PCB concentrations (5 - 83 ng/L, pptr) from the one sampling was comparable to those found in Pullman storm drains.

Storm drain sediments have more commonly been the target for screening studies for metals, pesticides, and hydrocarbons. A PCB contaminant tracing study done on Bellingham storm drains in 1993 measured the sediment concentrations of PCB 1254 (Cubbage, 1994). Two storm drain sediments had detectable concentrations of 69 and 72 μ g/kg dry weight (ppb), but none exceeded criteria for fresh or marine sediments. Cubbage also found 4,4'-DDT concentrations ranging from 7.5 – 9.7 ug/kg in Bellingham storm drain sediments.

Fecal Coliform Bacteria and Other Pollutants

Bacterial concentrations in stormwater may be a result of wet-weather washing of the watershed surfaces, re-suspension of bacteria in sediments, or transport of point sources to stormwater conveyance systems. In some stormwater sampling studies, a relationship can emerge with the highest bacterial concentrations at either the high or low end of the discharge range. If the higher concentrations occur at low streamflows, a point source might be suspected. This may be supported if in fact the higher flows had the lowest concentrations, resulting in a dilution effect. Some other studies might reveal that after the first plug of stormwater, the remaining samples had lower concentrations. This would indicate there is a "first-flush effect" where some surfaces are washed off following a build-up of bacteria.

The South Fork Palouse River and Missouri Flat Creek are designated as a Class A to maintain the beneficial uses including drinking water recharge, recreation, and stock watering. This limits the instream fecal coliform concentrations to a geometric mean value of 100 colonies/100 mL, and not more than 10 percent of all samples obtained for calculating the geometric mean value exceeding 200 colonies/100 mL. Stormwater concentrations at the end-of-pipe are not held to the receiving water instream criteria, unless specified as such by a TMDL. A TMDL investigation has already begun on the Palouse River watershed (Mathieu and Carroll, 2006).

Bacterial concentrations at the end-of-pipe were measured as part of this pilot project to ascertain the fluctuations that might be found in Pullman's stormwater.

Stormwater samples were collected at the first and third rotation for each of the three storm events. Individual concentrations and discharges for each rotation can be found in Table 9.

		First Ro	otation	Third Rotation		
Location	Date	Concentration	Discharge	Concentration	Discharge	
		(cfu/100 mL)	(cfs)	(cfu/100 mL)	(cfs)	
	10/31/05	1250	3.7	940	4.5	
Stadium Way	1/30/06	1900	3.1	190	2.2	
	4/5/06	1300	7.5	510	2.7	
	10/31/05	1065 ¹	1.7	2650	0.3	
College Street	1/30/06	400	0.6	38.5	*	
	4/5/06	2400 ²	0.1	325	0.6	
	10/31/05	2650	3.7	2100	0.9	
Benewah Street	1/30/06	315	1.4	380	0.1	
	4/5/06	2100	2.3	4900	1.4	

Table 9: Bacterial Concentrations and Discharge Measurements

¹ - Fecal duplicate RPD was 80%, exceeded holding time.

² - Fecal duplicate RPD was 50%.

* Discharge was not quantified.

There appears to be too few samples at each drain to discover a relationship between discharge and bacterial concentration.

A statistical summary by storm drain is presented in Figure 6. Complete general chemistry and fecal coliform data are presented in Appendix D.

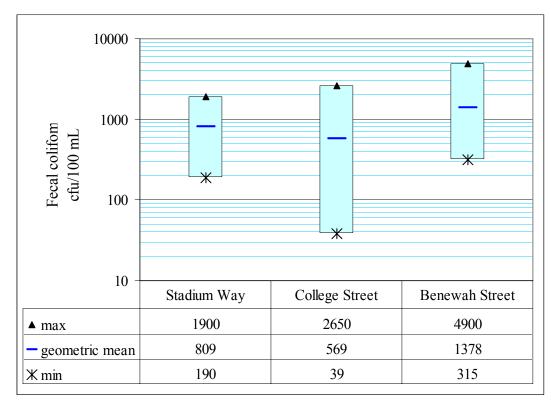


Figure 6: Standard Statistical Quantities of Measured Fecal Coliform Bacteria in Pullman Stormwater Samples, 2005-06 (cfu/100 mL).

The bacterial concentration results from the three Pullman storm drains are highly variable, which was anticipated. And as expected, the data follow a lognormal distribution, where the geometric mean is approximately equal to the median value.

A suite of common conventional pollutants was also measured at the three storm drains as part of this pilot project. Table 10 presents the median from the two rotations taken at each drain for each storm event sampled.

	Fecal Coliform (mpn/100 mL)	Ammonia (mg/L)	Nitrate+ Nitrite (mg/L)	Total Phosphorus (mg/L)	Total Suspended Solids (mg/L)
Pullman Storm Drains (27)					
Number of observations	27	27	27	27	27
% of samples above detection	100	100	100	100	100
Median	1300	0.15	0.52	0.26	60
Coefficient of variation	0.77	0.42	0.82	0.46	0.99
NSQD ¹					
Mixed Residential (611)					
Number of observations	336	282	531	552	582
% of samples above detection	94	59	98	96	98
Median	11210	0.39	0.57	0.28	66
Coefficient of variation	3.2	1.6	0.78	1.7	1.6
Mixed Commercial (324)					
Number of observations	116	173	284	290	297
% of samples above detection	95	67	97	99	100
Median	5400	0.60	0.58	0.26	55
Coefficient of variation	3	1	0.7	1.5	1.3

Table 10: Comparison of Conventional Pollutants from Pullman Storm Drains (2005-06) and the National Study NSQD Database Version 1.1 1970 - 2003.

¹-The National Stormwater Quality Database (version 1.1), Pitt et al., 2004.

The concentrations of conventional pollutants monitored from the Pullman storm drains compare favorably to stormwater concentrations seen throughout the nation for the mixed residential and commercial land uses. The comparison data come from a nationwide study by the University of Alabama and the Center for Watershed Protection (Pitt et al., 2003). They have compiled a National Stormwater Quality Database (NSQD, version 1.1) for a portion of the National Pollutant Discharge Elimination System (NPDES) municipal separate storm sewer system (MS4) stormwater permit holders. The data set covers over a ten-year period from more than 200 municipalities throughout the country (Pitt and Maestre, 2005).

A first-flush assessment is not possible in this pilot study given only three storm events, and the fact that only the first storm event sampled (10/31/05) had no rain in the 24 hours prior to sampling. The NSQD data for paired stormwater samples included more than 3700 event data sets from 66 municipalities in 17 states. Turbidity, pH, fecal coliform, fecal streptococcus, total nitrogen, dissolved phosphorus, and orthophosphorus did not show a statistically significant first flush in any land use category (Maestre et al., 2004).

Discussion

Simple Method Model

For this pilot study, the Simple Method (Schueler, 1987) was used to estimate the pollutant loads carried by Pullman stormwater from the measured concentrations. The Simple Method is a unit area load model that estimates loads of chemical constituents as a product of annual runoff volume and pollutant concentration, as:

$$L = 0.226 * R * C * A$$

Where: L = Annual load (lbs) R = Annual runoff (inches) C = Pollutant concentration (mg/L) A = Area (acres) 0.226 = Unit conversion factor

Variables used in the Simple Method calculation are shown in Table 11. The overall impervious fraction for Pullman is estimated to be 25% (see discussion below), and this value was used to calculate Rv in the Simple Method.

Table 11: Variables used in the Simple Method Pollutant Load Calculations

Variable		Value
A (acres)	=	5671.8
R (inches)	=	5.45
P (inches)	=	22
Pj	=	0.9
Rv	=	0.275

Pollutant loads to the receiving waters were calculated for each measured parameter based on an average concentration value from the three stormwater collection sites.

Annual Runoff

For the Simple Method, the instantaneous discharge of the storm drains is not used. Instead the annual runoff from a watershed is estimated by the model as the product of rainfall, fraction of events that yield runoff, and a runoff coefficient (Rv). Runoff volume is calculated as:

$$R = P * Pj * Rv$$

Where: R = Annual runoff (inches) P = Annual rainfall (inches) Pj = Fraction of annual rainfall events that produce runoff (usually 0.9) Rv = Runoff coefficient

Rv = 0.05 + (0.9*Impervious Fraction)

The value for Rv(0.9) refers to the fraction of events that produce runoff, which is assumed to be true for the Pullman area and South Fork Palouse River watershed. This may introduce an investigator bias into the Simple Method results.

The Stormwater Management Manual for Eastern Washington (Figure 4.3.1) shows that Pullman's annual average rainfall range is 22-24 inches. The University of Washington Climate website (<u>www.climate.washington.edu/index.html</u>) calculates an average annual rainfall from 1940-2004 at the Pullman NW station to be 21.3 inches. The average annual rainfall of 22 inches was used in the Simple Method.

Impervious Fraction

In a national effort to characterize land use, impervious area, and stormwater pollution, Maestre et al. (2004) found that, given comparable medium density residential areas, the runoff generated was more dependent on the impervious area than the size of the storm event. Rainfall from even the smallest storm events wash the surface of each impervious area and drain into the nearest storm drain. On average, there are more small events in a wet season, hence the importance of impervious areas becomes clear.

Pullman is a small town with a somewhat unique distribution of typical urban land uses. Washington State University dominates the city's economy, and students' needs dominate the layout of the city. The university campus has a mixture of large buildings, parking lots, and walkways that are impervious; however, there are several open areas and much landscaping with mature trees. Dense housing with scattered light commercial areas surrounds the university, as would be expected. The private housing sector and downtown area of Pullman largely serve students and faculty. The downtown is relatively small and is confined to only a few major streets in roughly a five-block radius.

The following land uses were grouped based on Pullman's demographics.

- 1. Near the outskirts of the city limits and beyond reside the area's farm families and the greatest amount of open space. Agriculture and open space are lumped together because without actual soil moisture absorption rates, both are expected to absorb rainwater at the same rates. Estimating imperviousness in a given landscape is difficult and prone to error, particularly if source maps are out of date.
- 2. Commercial, industrial, and institutional land uses were combined, largely a choice of convenience. Hill et al. (2003) note that total impervious area (TIA) is not equivalent to effective impervious area (EIA). For example, the paved walkways on the WSU campus drain into the adjacent lawns and do not contribute to runoff. The value of 50% for the commercial, industrial, and institutional was chosen because this category is dominated by WSU that is not as impervious as downtown.

Table 12 provides typical literature values of imperviousness to land-use designations.

Pilot Study.				
Land Use	Hill et al., 2003 ^a		NSQD ^b	Palouse Pilot Study
	TIA	EIA	TIA	TIA
Low density residential (1 unit per 2-5 acres)	10	4	-	15
Medium density residential (1 unit per acre)	20	10	-	25

35

60

90

24

48

86

42-45

83/70

4

35

40

50

15

Table 12: Comparative Imperviousness by Land Use and Assigned Values (%) Used in the

^a Hill et al. (2003), originally compiled by Dinicola (1989).

High density (multi-family or 8+units per acre)

"Suburban" density (4 units per acre)

Commercial / Industrial/ Institutional

^b National Stormwater Quality Database (Maestre et al. 2004).

TIA - total impervious area

Open Space

EIA - effective impervious area

Although the City of Pullman provided a zoning map, the land-use map (Figure 7) was based more on the provided city layout Computer Aided Design (CAD) files and physical characteristics of the built environment. The zoning map would have lead to far greater imperviousness, as it includes future development rather than current density and imperviousness.

The developed portions of the city centered around the university and close to the downtown area. However, large housing developments are expanding into the open areas; therefore, the imperviousness of Pullman is expected to rapidly change in the near future.

A weighting factor was developed by multiplying the literature-based impervious percentage by the percent of coverage in Pullman to find the percentage of area that has each degree of imperviousness (Table 13). This weighting factor column was then summed to find the imperviousness of the city as a whole.

The overall imperviousness of 25% seems relatively low for a town of Pullman's population. This may be a result of large agricultural or undeveloped areas within the city limit.

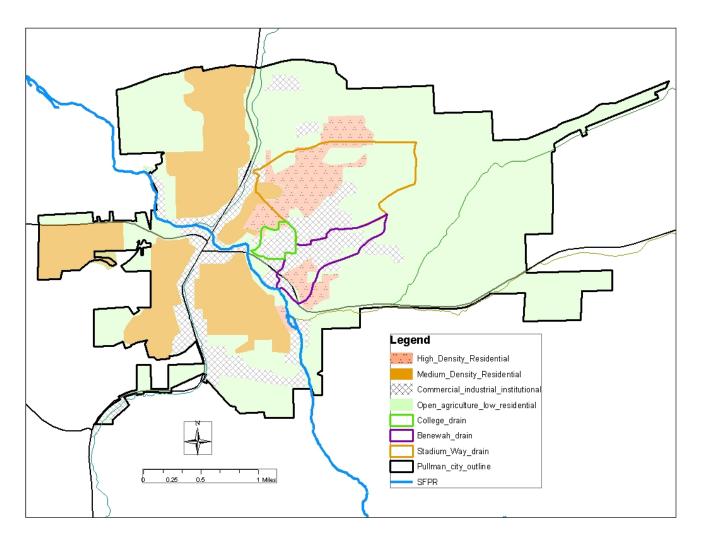


Figure 7: Land Uses in the City of Pullman

Land Use	Area (acres)	% Area of City Limit	Impervious Fraction ¹	Weighted Impervious Area ²
High Density Residential	363.7	6.4%	40%	3%
Medium Density Residential	1159.6	20.3%	35%	7%
Commercial, Industrial, Institutional	715.1	12.5%	50%	6%
Open Space, Agriculture, Low Density Residential	3473.1	61.8%	15%	9%
Totals	5711.5	100%	NA	25%

Table 13: Land Use within Pullman City Limits

¹ Based on literature values and field observations during pilot study. ² Equals (%Area)*(%Impervious)

Stormwater Loads

Pesticides and PCBs

DDT and dieldrin were commonly used in cities as insecticides in the 1950s and into the late 1960s. The source pathways for these legacy chemicals would be storm event washing from pesticide mixing centers, transfer centers, vehicle loading areas, waste disposal areas, and application areas.

Nonpoint PCB sources could include any historical transformer manufacturers, transformer storage areas, or transformer waste deposition throughout the watershed. In some areas throughout the country, PCBs were sometimes used as the binder for DDT when applied in urban areas. It is not known if this practice occurred in Pullman. In addition, atmospheric deposition has been regarded as an important source pathway for PCBs (Datta et al., 1998).

PCBs and several chlorinated pesticides were detected in the stormwater samples from the three Pullman storm drains. The three storm drain concentrations were fairly similar to each other for each of the chlorinated pesticides, with the exception of dieldrin which was higher at the Benewah Street field site. PCB concentrations were slightly higher at the Benewah site. There are no comparable Ecology studies that have assessed the load of these 303(d) toxic pollutants from stormwater.

The total annual load was calculated (Table 14) based on the mean concentration for each 303(d) listed pollutant and the annual runoff (R), calculated using the Simple Method. A non-detect was included in the mean as one-third of the reporting limit to avoid overestimation by just averaging the detected values.

303(d) Listed Pollutants	Mean Pollutant Concentration ¹ (ng/L)	Daily Load (mg/day)	Annual Load (lbs/yr)		
alpha-BHC	0.27	2.4	0.002		
heptachlor epoxide	0.23	2.0	0.002		
dieldrin	1.18	10.2	0.008		
4,4'-DDE	2.16	18.7	0.015		
total PCBs	15.23	132.1	0.106		

Table 14: Simple Method Load Estimations for 303(d) Listed Toxics in Pullman Stormwater.

¹Mean concentration from all stormwater samples taken during the pilot study, 2005-06.

Fecal Coliform Bacteria

Both Missouri Flat Creek and the South Fork Palouse River are Class A waters and 303(d)-listed for fecal coliform bacteria. Fecal coliform bacteria are found in the wastes from warm-blooded animals including humans. Common environmental sources for fecal coliform bacteria in the watershed include wildlife, livestock, pets, septic systems, improper disposal of human feces at recreation sites, and improperly connected sewers, which are all subject to stormwater transport. The most likely controllable sources of human feces in an urban watershed are sanitary can management, septic system up-keep, and detection of improperly connected sewers.

Generally, stormwater concentrations at the end-of-pipe are not held to the receiving water standards unless specified as such by a TMDL. Bacterial concentrations were monitored as part of this pilot project to ascertain the fluctuations that might be found in Pullman's stormwater. The daily bacterial concentration is the average of the concentrations from the two rotations for each sampling day. The discharge is averaged from the three measurements made each sampling day. The calculated fecal coliform load for the day sampled for each storm drain is presented in Table 15.

Storm		First Ro	tation	Third Ro	Average Daily	
Drain	Date	Concentration (cfu/100 mL)	Discharge (cfs)	Concentration (cfu/100 mL)	U	
Stadium	10/31/05	1250	3.7	940	4.5	1.4E+06
Way	1/30/06	1900	3.1	190	2.2	9.7E+05
vv ay	4/5/06	1300	7.5	510	2.7	1.7E+06
Callaga	10/31/05	1065 ¹	1.7	2650	0.3	3.9E+05
College Street	1/30/06	400	0.6	38.5	0	3.4E+04
Succi	4/5/06	2400 ²	0.1	325	0.6	6.2E+04
Donouroh	10/31/05	2650	3.7	2100	0.9	1.8E+06
Benewah Street	1/30/06	315	1.4	380	0.1	7.1E+04
Street	4/5/06	2100	2.3	4900	1.4	1.8E+06

Table 15: Average Daily Fecal Coliform Bacteria Counts and Loads

¹ - Fecal duplicate relative percent difference was 80%, exceeded holding time.

² - Fecal duplicate relative percent difference was 50%.

High variability in fecal coliform bacteria counts from nonpoint stormwater sources was expected, given that only three storm events were sampled. There does not appear to be a clear cause-and-effect relationship between discharge and bacterial concentration. More samples are needed to gain statistical confidence in the mean value. Too few data points were collected to estimate the annual load using the Simple Method Model for calculating fecal coliform bacteria. The bacterial load to the South Fork Palouse River will be further investigated in future TMDL studies.

Conclusions

The Pullman stormwater pilot study accomplished the goals set in the QA project plan. The following data were collected to develop a stormwater loading analysis: rainfall amounts, land-use information, and pollutant concentrations. Based on these data, the imperious areas and pollutant loads were calculated.

The amount of rainfall did not appear to correlate with the concentrations of dieldrin, 4,4'-DDE, or PCBs. Dieldrin concentrations appeared to be diluted somewhat by heavier rainfalls, whereas 4,4'-DDE concentrations appeared to increase with increased rainfall. The observed ranges for dieldrin, 4,4'-DDE, and PCBs are likely to be associated with different land uses in the three catchments. The Benewah Street and College Street storm drain catchments were relatively higher in 4,4'-DDE and PCB concentrations which may be related to the industrial and commercial land uses in these catchments.

Using the Simple Method, a loading rate was developed for the pesticides and PCBs found in stormwater from Pullman storm drains. The Simple Method provides a reasonable estimate of the stormwater pollutants loads. Observed ranges in fecal coliform bacteria counts and daily loads are presented to aid future Total Maximum Daily Load (TMDL) and pollutant management efforts. A bacterial loading rate will be developed in the upcoming Palouse River TMDL study.

The results from this pilot project indicate that, cumulatively, stormwater is a source of the 303(d) listed toxic and bacteria pollutants to the South Fork Palouse River.

Recommendations

There are several practical constraints that influenced the design of the Pullman stormwater pilot study: sufficient seasonal rainfall, logistics of catching the front end of the storm, and availability of field personnel.

As a result of this study, the following recommendations are made:

- Remain flexible in the storm sampling effort. Monitoring real-time rainfall at a different location from the sampling site can lead to false starts and wasted efforts. The mid-January storms coincided with decreased personnel availability or were weekend storm events. Automatically triggered stormwater samplers may have captured samples from the weekend or holiday storms. However, automated sampling equipment can be as time-consuming as a field crew visit due to setup, calibration, and holding-time limitations. Dedicated field crews and sampling availability, on standby seven days a week, are necessary if the goal is to catch criteria storms.
- In light of the presence of dieldrin and PCBs in Pullman stormwater and the potential for cumulative adverse water quality impacts, Ecology, the City of Pullman, and Washington State University (WSU) should work cooperatively to identify and clean up sources of these chemicals to the storm drain system. The Eastern Washington Stormwater Manual outlines several basic source control and treatment best management practices to prevent sediment and particulates from entering the stormwater conveyance systems.
- The Benewah Street storm drain appeared to have higher dieldrin, PCB, and fecal coliform bacteria concentrations in comparison to the other two drains. If the City of Pullman or WSU intends to conduct their own sampling, this storm drain catchment would be a good candidate for investigation.
- Methods to clean up interfering matrices from stormwater pesticide samples should be investigated. Stormwater samples may be more common in the future and will present many challenges for laboratory analysis.
- Given the variability in fecal coliform concentrations, Pullman's stormwater should be examined over the course of a calendar year to provide data from non-storm-related time periods and streamflows.
- The timing of the highest toxic concentrations in the samples was mixed; therefore, future studies should characterize the whole storm as well as the whole season.

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Appendices

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Appendix A – 303(d) Listings for the South Fork Palouse River

Washington State has produced a list that divides all waterbodies into one of five categories. This information can also be found at www.ecy.wa.gov/programs/wq/303d/wq_assessment_cats.html.

Category 1: **Meets Tested Standards.** Placement in this category does not necessarily mean that a waterbody is free of all pollutants. Most water quality monitoring is designed to detect a specific array of pollutants, so placement in this category means that the waterbody met standards for all pollutants for which it was tested. Specific information about the monitoring results may be found in the individual listings.

Category 2: **Waters of Concern.** Waters where there is some evidence of a water quality problem, but not enough to require production of a Total Maximum Daily Load (TMDL) at this time. There are several reasons why a waterbody would be placed in this category. A waterbody might have pollution levels that are not quite high enough to violate the water quality standards, or there may not have been enough violations to categorize it as impaired according to Ecology's listing policy. There might be data showing water quality violations, but the data were not collected using proper scientific methods. In all of these situations, these are waters that we will want to continue to test.

Category 3: **No Data.** A category that will be largely empty. Waterbodies that have not been tested will not be individually listed, but if they do not appear in one of the other categories, they are assumed to belong here.

Category 4: **Polluted Waters that Do Not Require a TMDL.** Waters that have pollution problems that are being solved in one of three ways.

Category 4a has a TMDL and is for waterbodies that have an approved TMDL in place and are actively being implemented.

Category 4b has a pollution control plan and is for waterbodies that have a plan in place that is expected to solve the pollution problems. While pollution control plans are not TMDLs, they must have many of the same features and there must be some legal or financial guarantee that they will be implemented.

Category 4c is impaired by a non-pollutant and is for waterbodies impaired by causes that cannot be addressed through a TMDL. These impairments include low water flow, stream channelization, and dams. These problems require complex solutions to help restore streams to more natural conditions.

Category 5: **Polluted Waters that Require a TMDL.** The 303(d) list is the traditional list of impaired waterbodies. Placement in this category means that Ecology has data showing that the water quality standards have been violated for one or more pollutants, and there is no TMDL or pollution control plan. TMDLs are required for waterbodies in this category.

Polluted Waters Listings (Category 5) for the South Fork Palouse River

The following water quality parameters are included on the 303(d) list as of 1996. The listing basis is available at <u>http://apps.ecy.wa.gov/wats/WATSQBEHome.asp</u>

Dissolved Oxygen

- (8142) 3 excursions beyond the criterion at USGS station 13346990 (at Pullman) in 1992 and 1994. 1 excursion beyond the criterion at USGS station 13348000 (at Pullman) on 8/4/94.
- (8105) 3 excursions beyond the criterion at USGS station 13346000 (near Colfax) in 1994 and 1995. 2 excursions beyond the criterion at USGS station 13349200 (at Colfax) on 8/2/94 and 8/3/94.

During the assessment of data, it was determined that WQ Policy 1-11 (updated 9/03) was overly restrictive for the number of years of data excursions needed to list for dissolved oxygen impairments. Based on a review of monitoring studies for dissolved oxygen statewide, it was determined that multiple (3 or more) excursions for at least two years of monitoring should be used as an alternative indicator that a waterbody continues to be impaired. (Susan Braley, Ecology/Water Quality Program, 2003)

Fecal Coliform

(6709) Joy, 1987, 2 excursions beyond the upper criterion at river mile (RM) 19.5 on 9/16/87 and 9/17/87.

(6712) Joy, 1987, 2 excursions beyond the upper criterion at RM 23.5 on 9/16/87 and 9/17/87.

Pelletier, 1993. station SF1 (S.F. Palouse Sampling Site #1) shows a geometric mean of 238 cfu/100 mL with 67% exceeding the percentile criterion out of 6 samples collected during 1991.

(6711) Joy, 1987, 2 excursions beyond the upper criterion at RM 22.9, 22.5, and 22.4 on 9/16/87 and 9/17/87.
 Pelletier, 1993. station MFC3 (Missouri Flat Creek Sampling Site) shows a geometric mean of 1011 cfu/100mL with 100% exceeding the percentile criterion out of 5 samples collected during 1991.

(6707) Joy, 1987, 1 excursion beyond the upper criterion at RM 21.2 on 9/16/87, RM 20.9 and 20.6 on 9/16/87 and 9/17/87.

Pelletier, 1993, station SF2 (S.F. Palouse Sampling Site #2) shows a geometric mean of 811 cfu/100mL with 100% exceeding the percentile criterion out of 6 samples collected during 1991.

Pelletier, 1993, station SF3 (S.F. Palouse Sampling Site #3) shows a geometric mean of 934 cfu/100mL with 100% exceeding the percentile criterion out of 5 samples collected during 1991.

(6708) Joy, 1987, 2 excursions beyond the upper criterion at RM 18.7 on 9/16/87 and 9/17/87.

Pelletier, 1993, station SF5 (S.F. Palouse Sampling Site #5) shows a geometric mean of 117 cfu/100mL with 80% exceeding the percentile criterion out of 5 samples collected during 1991.

(6710) Hallock, 2004, Ecology ambient station 34B110 shows a geometric mean of 150.2 exceeded the criterion in year 2002 and a geometric mean of 140.3 exceeded the criterion in year 2003; 7 of 12 samples (58.3%) in year 2002 exceeded the percentile criteria.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 114 exceeds the criterion and that 38% of the samples exceeds the percentile criterion from 8 samples collected during 2001.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 91 does not exceed the criterion and that 33% of the samples exceeds the percentile criterion from 12 samples collected during 2000.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 253 exceeds the criterion and that 58% of the samples exceeds the percentile criterion from 12 samples collected during 1999.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 224 exceeds the criterion and that 42% of the samples exceeds the percentile criterion from 12 samples collected during 1998.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 183 exceeds the criterion and that 45% of the samples exceeds the percentile criterion from 11 samples collected during 1997.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 516 exceeds the criterion and that 100% of the samples exceeds the percentile criterion from 6 samples collected during 1996.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 565 exceeds the criterion and that 73% of the samples exceeds the percentile criterion from 11 samples collected during 1995.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (Palouse R. S.F. at Pullman) shows a geometric mean of 295 exceeds the criterion and that 67% of the samples exceeds the percentile criterion from 3 samples collected during 1994.

Joy, 1987, 2 excursions beyond the upper criterion at RM 21.4 on 9/16/87 and 9/17/87.

- (10448) Pelletier, 1993, station SF4 (S.F. Palouse Sampling Site #4) shows a geometric mean of 501 cfu/100mL with 100% exceeding the percentile criterion out of 6 samples collected during 1991.
- (10450) Pelletier, 1993, station SF6 (S.F. Palouse Sampling Site #6) shows a geometric mean of 125 cfu/100mL with 60% exceeding the percentile criterion out of 5 samples collected during 1991.

Pelletier, 1993, station SF7 (S.F. Palouse Sampling Site #7) shows a geometric mean of 168 cfu/100mL with 60% exceeding the percentile criterion out of 5 samples collected during 1991.

(10452) Pelletier, 1993, station SF8 (S.F. Palouse Sampling Site #8) shows a geometric mean of 111 cfu/100mL with 60% exceeding the percentile criterion out of 5 samples collected during 1991.

Data are only available in printed format. The water segment is listed as Category 5 based on the 1998 assessment.

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(6729) U.S. Geological Survey data from NWIS database station 13346000 (near Colfax) shows 21 excursions beyond the criterion out of 51 samples collected between 1992 and 1995.

U.S. Geological Survey data from NWIS database station 13349200 (at Colfax) shows 33 excursions beyond the criterion out of 95 samples collected between 1992 and 1995.

Temperature

(8130) 14 excursions beyond the criterion at USGS station 13349200 (at Colfax) between 1993, 1994 and 1995.

The following water quality parameters are included on the new 303(d) list of 2002/2004:

Dissolved Oxygen

(11137) Hallock, 2003, Ecology ambient station 34B110 shows a total of 3 samples in year 2003 exceeded the criterion.

Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (SF Palouse River at Pullman) shows 9 excursions beyond the criterion out of 41 samples collected between 1993 - 2001 measured on these dates: 94/10/10, 95/06/05, 95/07/10, 95/08/07, 95/09/05, 95/11/06, 96/07/08, 96/08/05, 96/09/03,

Fecal Coliform

(6712) Joy, 1987, 2 excursions beyond the upper criterion at RM 23.5 on 9/16/87 and 9/17/87.

Pelletier, 1993, station SF1 (S.F. Palouse Sampling Site #1) shows a geometric mean of 238 cfu/100 mL with 67% exceeding the percentile criterion out of 6 samples collected during 1991.

(10450) Pelletier, 1993, station SF6 (S.F. Palouse Sampling Site #6) shows a geometric mean of 125 cfu/100 mL with 60% exceeding the percentile criterion out of 5 samples collected during 1991.

Pelletier, 1993, station SF7 (S.F. Palouse Sampling Site #7) shows a geometric mean of 168 cfu/100 mL with 60% exceeding the percentile criterion out of 5 samples collected during 1991.

Temperature

(3724) Ecology unpublished data from core ambient monitoring station 34B110 (Palouse R. S.F. at Pullman) shows a 7-day mean of daily maximum values of 22.2 for mid-week 13 July 2001.
Hallock, 2001, Ecology Ambient Monitoring Station 34B110 (SF Palouse River at Pullman) shows 3 excursions beyond the criterion out of 40 samples collected between 1993 - 2001.

Polluted Waters Listings (Category 4a) for the South Fork Palouse River

Ammonia-Nitrogen

(8827) Joy, 1987, 3 excursions just downstream of the Pullman Wastewater Treatment Plant in 9/86. Palouse River, S.F. TMDL approved by EPA on 9/9/94.

Polluted Waters Listings (Category 5) for the Mainstem Palouse River

The following water quality parameters are included on the 303(d) list as of 1996. The listing basis is available at <u>http://apps.ecy.wa.gov/wats/WATSQBEHome.asp</u>

4,4'-DDE

(8819) Davis and Serdar, 1996. Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.(14190) Hopkins et al. 1985. Excursions beyond the National Toxic Rule criterion in a multiple fish composite of edible tissue of largenose sucker and northern squawfish samples collected in 1984.

Dieldrin

(8818) Davis and Serdar, 1996. Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.

Heptachlor Epoxide

(8822) Davis and Serdar, 1996. Excursions beyond the criterion in edible squawfish tissue in 1994.

Total PCBs

(8820) Davis and Serdar, 1996. Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.

ALPHA-BHC

(14191) Hopkins et al. 1985. Excursions beyond the National Toxic Rule criterion in a multiple fish composite of edible tissue of largenose sucker and northern squawfish samples collected in 1984.

Dissolved Oxygen

(11133) Hallock, 2003, Ecology ambient station 34A170 shows a total of 1 sample in year 2003 exceeded the criterion.

Hallock, 2001, Ecology Ambient Monitoring Station 34A170 (Palouse River at Palouse) shows 10 excursions beyond the criterion out of 58 samples collected between 1993 - 2001.

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(16922) U.S. Army Corps of Engineers unpublished data at station Palouse 6 show 6 excursions beyond the criterion out of 8 Hydrolab measurements collected in 1997.

(6732) Hallock, 2004, Ecology ambient station 34A070 shows that 9 of 32 samples exceed the criterion.
 Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse River at Hooper) shows 22 excursions beyond the criterion out of 59 samples collected between 1993 - 2001.

U.S. Geological Survey data from NWIS database station 13351000 (at Hooper) shows 55 excursions beyond the criterion out of 250 samples collected between 1992 and 2001.

(42553) Hallock, 2004, Ecology ambient station 34A120 shows that 4 of 14 samples exceed the criterion.

Temperature

(3723) Ecology unpublished data from core ambient monitoring station 34A170 (Palouse R. at Palouse) show a 7-day mean of daily maximum values of 26.9 for mid-week 13 August 2001.

Hallock, 2001, Ecology Ambient Monitoring Station 34A170 (Palouse River at Palouse) shows 6 excursions beyond the criterion out of 54 samples collected between 1993 – 2001.

- (11130) Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse River at Hooper) shows 10 excursions beyond the criterion out of 57 samples collected between 1993 2001.
- (8115) Excursions beyond the criterion at USGS station 133460000 (near Colfax) during 1992, 1993, 1994 and 1995.

Fecal Coliform

(16791) Hallock, 2004, Ecology ambient station 34A070 shows 1 of 12 samples (8.3%) in year 2002 exceeded the percentile criterion and 1 of 12 samples (8.3%) in year 2003 exceeded the percentile criterion.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 15 does not exceed the criterion and that 0% of the samples does not exceed the percentile criterion from 8 samples collected during 2001.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 25 does not exceed the criterion and that 0% of the samples does not exceed the percentile criterion from 13 samples collected during 2000.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 23 does not exceed the criterion and that 0% of the samples does not exceed the percentile criterion from 13 samples collected during 1999.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 50 does not exceed the criterion and that 0% of the samples does not exceed the percentile criterion from 13 samples collected during 1998.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 77 does not exceed the criterion and that 8% of the samples does not exceed the percentile criterion from 12 samples collected during 1997.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 18 does not exceed the criterion and that 0% of the samples does not exceed the percentile criterion from 4 samples collected during 1996.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 42 does not exceed the criterion and that 0% of the samples does not exceed the percentile criterion from 11 samples collected during 1995.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 67 does not exceed the criterion and that 20% of the samples exceeds the percentile criterion from 10 samples collected during 1994.

Hallock, 2001, Ecology Ambient Monitoring Station 34A070 (Palouse R. at Hooper) shows a geometric mean of 38 does not exceed the criterion and that 9% of the samples does not exceed the percentile criterion from 11 samples collected during 1993.

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Appendix B – Background Information on the South Fork Palouse River 303(d) Pesticides and PCBs¹

Alpha-BHC – Prior to 1977, alpha-BHC was a component of lindane, an insecticide used to control pests including flies, aphids, and grain weevils. Alpha-BHC is no longer produced in the United States.

DDT – Insecticide used on a variety of crops and for control of insect-borne diseases. DDT was banned in 1972. DDE and DDD are toxic breakdown products of DDT. DDD also had some use as the insecticide Rothane. Total DDT measurements include DDT+DDE+DDD.

Dieldrin – Broad spectrum insecticide primarily used on termites, on other soil-dwelling insects, and on corn, cotton, and citrus. Production and most major uses of dieldrin were banned in 1974. All uses were voluntarily canceled by industry in 1987. Aldrin and dieldrin have similar chemical structures and commercial uses. Aldrin rapidly breaks down to dieldrin in plants and animals and when exposed to sunlight or bacteria.

Heptachlor epoxide – A breakdown product of heptachlor and a contaminant in heptachlor and chlordane formulations. Heptachlor was used to control soil insects and as a seed protectant and household insecticide. Major uses of heptachlor were suspended in 1978.

PCBs – Widely used in industrial applications as insulating fluids, plasticizers, in inks and carbonless paper, and as heat transfer and hydraulic fluids, but also had a variety of other uses. EPA restricted manufacture of PCBs to sealed systems in 1977. In 1979, EPA banned PCB manufacture, processing, and distribution but allowed continued use in closed electrical systems. EPA phased out the use of electrical equipment containing PCBs through regulations in 1982 and 1985.

Detailed profiles of the above chemicals – including use, regulations, environmental occurrence, and health effects – have been prepared by the Agency for Toxic Substances and Disease Registry and are available at <u>www.atsdr.cdc.gov/atsdrhome.html</u>.

¹ Summarized from information in EPA (1992a, 2000) and the Agency for Toxics Substances and Disease Registry (ATSDR) Website <u>www.atsdr.cdc.gov/toxpro2.html</u>.

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Appendix C – Pesticides Measured at Manchester Environmental Laboratory

Pesticides

The following pesticides were analyzed by Ecology's Manchester Environmental Laboratory for this pilot study:

alpha-BHC beta-BHC gamma-BHC (lindane) delta-BHC heptachlor aldrin heptachlor epoxide trans-chlordane (gamma) cis-Chlordane (alpha) endosulfan I (alpha-endosulfan) dieldrin endrin endrin ketone endosulfan II (beta-endosulfan) endrin aldehvde endosulfan sulfate 4.4'-DDE 4,4'-DDD 4.4'-DDT methoxychlor toxaphene chlordane (technical)

Problems with Large Volume Injection and "Dirty" Stormwater Samples

Overall, the conventional constituents and PCBs easily met the quality assurance specifications in the QA project plan. Additional changes/steps were required for chlorinated pesticides to clean the samples and remove the interfering matrix.

Each water sample was extracted with methylene chloride following EPA SW-846 Method 3510, then solvent exchanged into iso-octane. The sample extracts were dark and contained a black precipitate which indicated an interfering matrix.

The first set of stormwater samples were run using two techniques. The large volume injection (LVI) technique is a highly sensitive method that concentrates the sample 15 times and is used to achieve a lower detection limits. Alpha-BHC, heptachlor epoxide, dieldrin, and 4,4'-DDE were analyzed from the first storm event (10/31/05) using the LVI technique, and the remaining

chlorinated pesticides were run using the standard GC-ECD. The standard pesticide GC-ECD analysis did not yield a low enough reporting limit (3.2 ng/L) and was discontinued.

The LVI technique was to detect chlorinated pesticides for the rest of the project, but not without incident. Lessons were learned from the first set of stormwater samples because they fouled the GC columns and suppressed the analyte recoveries. All samples results are qualified as estimates due to the poor surrogate, matrix spike, and continuing calibration verification recoveries.

The goal with the second and third storm event samples (1/31/06 and 4/5/06) was to use the LVI technique for each analyte. A reduction of the complex interfering matrix in the stormwater samples was attempted. This procedure involved solvent exchange into iso-octane; the extract was eluted through a 100 mg micro Florisil® column with a 50% v/v hexane/preserved diethyl ether solution to remove interference. The extracts were solvent exchanged and reduced to 1 mL in volume. Then one portion of the extract was treated with concentrated sulfuric acid, and the other portion was analyzed without acid treatment. These methods are adaptations of EPA SW-846 methods 3510, 3620, 3665, and 8081.

The results from the second and third stormwater results had improved reporting limits. Alpha-BHC, heptachlor epoxide, dieldrin, and 4,4'-DDE are reported to approximately 0.06 ng/L whereas all other analytes are reported to approximately 0.3 ng/L. The micro Florisil® treatment improved the recovery of the analytes, and the acid treatment reduced some of the interferences. However, the interfering matrix still had a severe effect and was likely co-concentrated with the sample. This caused fouling of the GC columns which suppressed surrogate recoveries, precision of the continuing calibration, and signal clarity. The matrix and all the results for the stormwater samples are qualified as estimates. When the analyte signal could not be clearly ascertained, the estimated reporting limit "UJ" is reported.

Overall, the analytes that could not be detected due to interference at levels greater than the reporting limit are reported at reporting limits raised to the level of that interference and qualified as not detected at an estimated reporting limit, "UJ". All samples are qualified as estimates due to poor recoveries of known standards and should be considered to be biased low.

Appendix D – Conventional Parameter Results

Parameter		Sta	adium Way		Co	ollege Street	t	Benewah Street		
i uluinetei		10/31/05	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06
Alkalinity	Initial	47.1	103.0	36.3	14.1	26.0	104.0	22.2	48.4	39.0
Alkalinity	Final	39.0	136.0	89.0	35.5	152.0	51.1	52.6	163.0	61.7
Ammonia	Initial	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.1	0.3
7 minionia	Final	0.2	0.2	0.1	0.1	0.0	0.1	0.2	0.0	0.1
Chloride	Initial	4.9	25.2	6.4	1.8	11.7	37.7	2.2	15.8	19.1
Cilloride	Final	3.8	30.2	14.3	4.2	43.2	10.6	6.4	35.8	13.9
Dissolved	Initial	6.8	4.5	3.1	5.6	2.4	5.7	4.9	2.1	6.0
Organic Carbon	Final	7.9	4.9	5.0	8.8	2.3	3.2	8.7	2.4	4.1
Fecal Coliforms ¹	Initial	1250	1900	1300	1065 ³	400	2400 ⁴	2650	315	2100
recai Comornis	Final	940	190	510	2650	39	325	2100	380	4900
Nitrate-Nitrite	Initial	0.5	1.4	0.4	0.2	0.3	0.5	0.2	0.5	0.5
minale-minite	Final	0.4	1.7	0.7	0.5	2.4	0.7	0.5	0.3	0.7
Orthophosphorus	Initial	0.1	0.2	0.1	0.1	0.0	0.1	0.1	0.1	0.1
Ormophosphorus	Final	0.1	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.1
Phosphorus	Initial	0.2	0.4	0.5	0.2	0.5	0.7	0.2	0.3	0.4
rilospilorus	Final	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Total Organic	Initial	8.7	4.7	4.6	6.7	2.7	7.6	6.0	2.4	6.8
Carbon	Final	9.9	5.0	5.2	8.9	2.5	3.9	9.4	2.4	5.5
Total Persulfate	Initial	1.0	1.8	0.7	0.5	0.4	1.9	0.5	0.7	1.1
Nitrogen	Final	0.8	2.0	1.1	0.8	2.8	0.7	0.9	1.7	0.9
Total Suspended	Initial	27.5	78.5	272.5	20.0	157.5	142.0	18.5	63.7	104.0
Solids	Final	46.0	15.0	67.0	8.0	4.0	23.0	23.5	5.0	85.0

Table D-1: General Chemistry and Fecal Coliform Concentrations in Pullman Stormwater Samples Collected in 2005-06.

Parameter		Stadium Way		College Street			Benewah Street			
		10/31/05	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06
Turbidity ²	Initial	28.3	185	330	17.5	155	133.3	16	140	110
Turblatty	Final	35	40	180	15	8.3	34	26	38	95

Units are mg/L unless otherwise indicated. All analytes were positively identified by Manchester Laboratory. ¹ - Fecal coliforms are measured in #/100 mL ² - Turbidity is measured as NTU ³ - Fecal duplicate relative percent difference was 80%, likely due to exceeded holding time. ⁴ - Fecal duplicate relative percent difference was 50%.

Appendix E – PCB and Pesticide Results

RPD =	difference of 2 results	×100
KI D =	mean	~100

Table E-1: Concentrations of 303(d) Listed PCBs in Pullman Stormwater Samples Collected in 2005-06 (ng/L).

DCD	Way Storn	n Drain	College Street Storm Drain					Benewah Street Storm Drain			
PCB	10/31/05	1/30/06	4/5/06	10/31/05	Replicate 10/31/05	RPD^1	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06
Monochlorobiphenyls	53	210	22.1	25	29.9		144	20	24.5	147	20
Dichlorobiphenyls	107	35	699	87.6	132		42.8	346	123	38.4	487
Trichlorobiphenyls	101	50	298	116	171		364	383	601	400	1746
Tetrachlorobiphenyls	708	198	1545	802	1056		2360	1170	3388	2270	7095
Pentachlorobiphenyls	1653	561	4657	2560	4037		8260	3636	7661	8130	19012
Hexachlorobiphenyls	945	385	3112	1735	2779		5040	3923	4119	5790	12758
Heptachlorobiphenyls	211	126	668	600	1228		1820	1652	819	1210	3102
Octachlorobiphenyls	61	35	187	211	412		78.8	1026	187	188	925
Nonachlorobiphenyls	20	20	57.4	79.1	149		93.6	731	25.7	91.2	170
Decachlorobiphenyl	222	10	19.8	165	181		10	88.4	155	44.5	21.4
Total PCB	4070	1480	11300	6380	10200	46.1*	18200	13000	17100	18300	45300

 RPD^{1} = relative percent difference calculated as the difference between the original and duplicate, divided by the average. *QA project plan specified a replicate RPD of 50% or less.

A 1 /	St	tadium Way		College Street			Benewah Street		
Analyte	10/31/05	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06	10/31/05	1/30/06	4/5/06
alpha-BHC	0.49	0.10	0.2	0.46	0.21	0.15	0.52	0.17	0.20
beta-BHC	3.1	0.31	0.18	3.1	0.31	0.15	3.2	0.22	0.18
gamma-BHC (lindane)	3.1	0.93	1.4	3.1	0.72	1.25	3.2	0.87	2.50
heptachlor	14	0.31	0.06	3.1	0.29	0.06	3.2	0.14	0.06
heptachlor epoxide	0.39	0.16	0.18	0.38	0.33	0.16	0.32	0.23	0.20
aldrin	3.1	0.31	0.06	3.1	0.31	0.06	3.2	0.31	0.06
dieldrin	3.1	0.50	0.36	0.37	0.53	0.11	1.3	5	2
endosulfan I	3.1	0.31	0.5	3.1	0.31	0.49	3.2	0.66	0.06
endosulfan II	3.1	0.31	0.32	3.1	0.31	0.25	3.2	0.87	0.06
endosulfan sulfate	3.1	0.31	0.83	3.1	0.82	0.94	3.2	0.97	0.96
endrin	3.1	0.55	0.41	3.1	0.82	0.19	3.2	0.85	0.57
endrin ketone	3.1	0.38	0.5	3.1	1.7	0.54	3.2	0.58	0.80
endrin aldehyde	3.1	0.46	0.06	3.1	0.72	0.25	3.2	0.92	0.38
4,4'-DDE	2.0	1.95	4.8	1.3	1.7	1.45	2.0	3.3	1.4
4,4'-DDD	3.1	0.26	0.35	3.1	0.12	0.08	3.2	0.61	0.24
4,4'-DDT	3.1	1.65	3.2	3.1	2.3	1.50	3.2	4.65	1.9
methoxychlor	3.1	1.36	1.6	3.1	2.7	1.66	3.2	1.13	1.80
trans-chlordane (gamma)	3.1		0.53	3.1		0.37	3.2		0.39
cis-chlordane (alpha-chlordane)	16	—	0.55	15	—	0.39	16	_	0.32
toxaphene	310		_	310	_		320	_	

Table E-2: Pesticide Analysis Results (ng/L) of Pullman Stormwater Samples Collected in 2005-06.

BOLD = (J) The analyte was positively identified. The associated numerical result is an estimate. Not bold = (UJ) The analyte was not detected at or above the reported estimated result.

Analyte	Stadium RPD	Benewah RPD	College RPD
alpha-BHC	16.7	6.1	0.0
beta-BHC	3.3	27.3	40.0
gamma-BHC (lindane)	4.3	11.5	8.0
Heptachlor	3.3	7.4	3.2
Heptachlor epoxide	12.5	4.4	45.2
Dieldrin	8.0	4.0	80.4
Endrin	89.9	16.5	81.1
endosulfan I	3.3	105.3	2.1
endosulfan II	3.3	10.4	148.2
4,4'-DDD	3.9	11.6	43.9
4,4'-DDE	15.4	6.1	20.7
4,4'-DDT	18.2	10.8	26.7
delta-BHC	3.3	0.0	3.2
Aldrin	3.3	0.0	3.2
endrin ketone	42.1	48.3	29.6
endrin aldehyde	24.2	17.4	48.0
endosulfan sulfate	3.3	48.7	4.3
methoxychlor	138.2	171.7	125.3
trans-chlordane (gamma)			30.1
cis-chlordane (alpha-chlordane)			18.2

Table E-3: The RPD in Chlorinated Pesticides between Duplicate Stormwater Samples for Sites in Pullman, 2005-06.

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Appendix F – Photographs from Storm Event on April 5, 2006



Large pipe diameter is 3 feet.

Small pipe diameter is 0.7 feet.

Width of water in large pipe was 2.3 feet and discharge was 4.3 cfs.

Small pipe was full and fast. Discharge in small pipe was 3.2 cfs.

Figure F-1: Stadium Way Stormwater Discharge Pipe at 1st Rotation (13:44 pm)



Pipe diameter is 3.63 feet.

Width of water in pipe was 3.2 feet; discharge was 0.09 cfs.

Figure F-2: College Street Stormwater Discharge Pipe at 1st Rotation (12:15 pm)



Pipe diameter is 3.63 feet.

Width of water in pipe was 3.46 feet; discharge was 0.49 cfs.

Figure F-3: College Street Stormwater Discharge Pipe at 2nd Rotation (14:15 pm)



Pipe height and width are 3.8 and 4.25 feet, respectively.

Width of water in pipe was 3.9 feet; discharge was 2.29 cfs.

Figure F-4: Benewah Street Stormwater Discharge Pipe 1st Rotation (13:10 pm)