

AN ABSTRACT OF THE THESIS OF

Jay Frentress for the degree of Master of Science in Water Resources Science and Botany and Plant Pathology on June 8, 2010.

Title: Stream DOC, Nitrate, Chloride and SUVA Response to Land Use during Winter Baseflow Conditions in Sub-basins of the Willamette River Basin, OR

Abstract approved:

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To better understand the impact of land use on stream nutrient export, a synoptic sampling of 57 sub-basins within the Willamette River basin was conducted during winter baseflow conditions (February 2009). I assessed whether stream dissolved organic carbon (DOC),  $\text{NO}_3^-$  and  $\text{Cl}^-$  and specific ultra-violet absorbance (SUVA) values were correlated with individual watershed land use variables: percent urban, agriculture, and forest. Simple linear regression analysis indicated that stream DOC,  $\text{NO}_3^-$  and  $\text{Cl}^-$  increased significantly with increasing percent agriculture and urban area in sampled watersheds, and decreased significantly with increasing percent forest. Stream order and watershed area were not significantly related to any stream chemistry variables. Simple linear regression analysis indicated that SUVA, a measure of the aromaticity of DOC, decreased

significantly with increasing percent urban area in catchments, but was not significantly related to percent agriculture or urban. Ordination of streams on the basis of their chemistry supported simple linear regression analyses, clustering of streams with low SUVA values and higher DOC,  $\text{NO}_3^-$ , and Cl concentrations, which were also largely associated with increasing percent urban, and slightly less associated with increasing percent agriculture. Results indicate that stream nutrient concentrations are strongly influenced by associated land use within the watershed. SUVA results suggest a combination of land use and variable hydrologic flowpaths affects the composition of stream DOC under winter baseflow conditions.

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Stream DOC, Nitrate, Chloride and SUVA Response to Land Use during Winter

Baseflow Conditions in Sub-basins of the Willamette River Basin, OR

by

Jay Frentress

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I understand my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Jay Frentress, Author

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# **Stream DOC, Nitrate, Chloride and SUVA Response to Land Use during Winter Baseflow Conditions in Sub-basins of the Willamette River Basin, OR**

## **1 Introduction**

Stream dissolved organic material (DOM) is of fundamental importance because of its regulatory role in the ecology of streams, ability to modulate stream pH and attenuate UV light, as well as its ability to sorb and transport heavy metals like mercury (Battin et al., 2008; Kitis et al., 2001; Morris et al., 1995; Ravichandran et al., 1998; Wetzel et al., 1995; Wigington Jr et al., 1996). DOM is also a precursor to the production of trihalomethanes in water treatment facilities during the chlorination process (Fram et al., 1999). Watershed export of stream DOM represents a significant nutrient loss from nutrient-limited watersheds (Perakis and Hedin, 2002; Qualls and Haines, 1992) and recent work has highlighted the importance of stream DOM export as a significant loss of terrestrial carbon globally (Battin et al., 2008).

Land use has been linked to stream chemistry and nutrient export from watersheds (Howarth et al., 2002). Understanding the influence of land use on nitrogen and carbon cycling in streams is important to for predicting the potential impact of future land development. For example, production and application of synthetic nitrogen fertilizers has greatly increased global agricultural productivity, though much of this reactive nitrogen is lost to the aquatic system (Eickhout et al., 2006; Gruber and Galloway, 2008). Increasing

agricultural land use in catchments has been repeatedly linked with increased nitrogen in streams (Accoe et al., 2002; Dalzell et al., 2007; Donner et al., 2004; Evans, 2007; Poor and McDonnell, 2007; Royer and David, 2005; Wilson and Xenopoulos, 2008b).

While a strong link between agriculture and increased nitrogen in streams has been established, the effects of agriculture on the concentration and composition of dissolved organic carbon (DOC) are less understood (Vidon et al., 2008; Wilson and Xenopoulos, 2008b). In some catchments, agriculture land use was not related to DOC concentrations (Wilson and Xenopoulos, 2008a), in others agricultural catchments enhanced DOC export as well as in-stream DOC production during algal blooms (Royer and David, 2005).

Much work has focused on the movement of terrestrial-derived organic material into the stream network (Aitkenhead-Peterson et al., 2003). DOC is also produced within the stream network. In-stream production of DOC has been linked with algal productivity (Kaplan and Bott, 1982). Given the established connection between increased agricultural land use and increased nitrogen loads, agricultural land use is expected to increase algal productivity and in-stream DOC. However, few studies have focused on the influence of agricultural land use on in-stream DOC production. The chemical composition of DOC is often used to characterize DOC into refractory and labile portions. Specific ultraviolet absorbance (SUVA) is a common metric for characterizing DOC; high SUVA values are associated with refractory, aromatic DOC content (Weishaar et al., 2003).

Warrner et al. found that tile drains from agricultural areas carried high concentration, low-SUVA (labile) DOC, though stream water had higher SUVA; they concluded that the timing of low-SUVA DOC inputs coincident with inorganic N loading could result in the rapid uptake of low-SUVA DOC (2009).

Landscape features, such as wetlands, have also been linked to DOC production and delivery to aquatic systems (Frost et al., 2006). At regional scales, the proportion of wetlands and peatlands in watersheds appear the strongest predictor of high riverine DOC export (Mulholland, 2003). Streams from watersheds dominated by forested wetlands in Maine were found to have DOC concentrations 50% higher than agriculturally-dominated watersheds (Cronan et al., 1999). In addition to linking wetland cover with increased stream and lake DOC concentrations, the proximity of wetlands to stream systems has also been associated with increased DOC concentrations in aquatic systems (Xenopoulos et al., 2003). This linkage emphasizes the importance of hydrologic transport mechanisms in connecting terrestrial DOC sources to aquatic systems.

The connectedness of landscape sources of DOC and the stream network is fundamentally important to understanding processes that transfer nutrients from terrestrial areas to aquatic systems. Hydrologic connections during precipitation and snowmelt events play a strong role in DOC export (Boyer et al., 1997). Furthermore, hydrologic connectivity during storms appears to elicit strong stream DOC response in catchments dominated by agricultural land use (Dalzell et al., 2007; Vidon et al., 2008). The study site for this work, the

Willamette River basin, may express similar DOC dynamics during winter baseflow periods, when the soils are saturated, highly connected to the stream, and highly responsive to small increases in precipitation.

It appears that although the connection of agricultural land use to export of nitrogen is well-established, the dynamics of stream DOC concentration and composition and their relationships to agricultural and urban land use are poorly understood. This study was initiated to better understand how land use affects the type and concentration of stream DOC exported from a range of watersheds with differing land uses.

I hypothesized that nitrogen and carbon from agricultural and urban land uses within catchments strongly influence stream nitrate and DOC concentrations during winter baseflow periods in the Willamette River basin. DOC concentrations in sampled sub-basins of the Willamette River basin were expected to respond to increases in proportions of urban and agricultural land use due to in-stream production of DOC from elevated nitrate levels (hypothesis 1). Furthermore, in-stream production of DOC was expected impart a distinct signature on stream DOC composition and be detected by changes in SUVA (hypothesis 2).

I tested these hypotheses by comparing  $\text{NO}_3^-$ , DOC, and SUVA values amongst watersheds with differing proportions of agricultural, urban, and forested land use. I predicted that: <sup>(1)</sup> SUVA values would decrease with increasing nitrate concentrations; <sup>(2)</sup> Nitrate and DOC concentrations would

increase with increasing proportions of agriculture and urban area while decreasing with increasing proportion of forested area; and <sup>(3)</sup> SUVA would decrease with increasing proportions of agriculture and urban area and increase with increasing proportions of forest area.

## **2 Site Description**

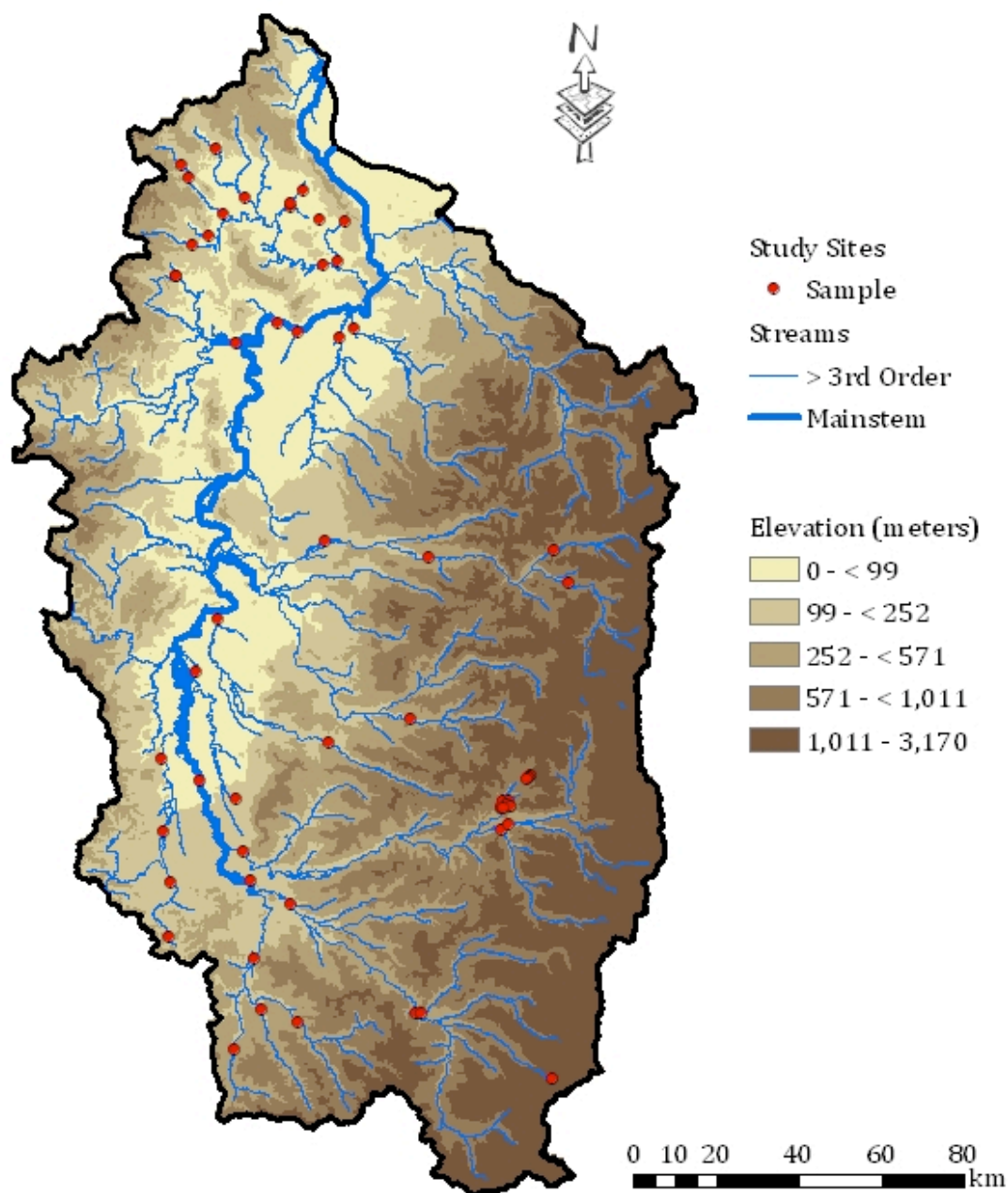
### **2.1 Willamette River Basin**

The Willamette River basin was chosen for this study because it exhibits a range of land use types and distinctive, seasonal hydrologic response. The Coast and Cascades Ranges surround the 29,728 km<sup>2</sup> watershed. A combination of geologic history, land development, and season variations in precipitation create a unique environment for hydrologic and nutrient studies.

The Willamette River basin ranges in elevation from 3 m at the mouth of the Willamette River to 3,199-m at the peak of Mt. Jefferson (Figure 1). The basin extends 288 km along its north-south axis and 160 km from west to east. Bordering the Willamette River basin's western edge, the Coast Range is formed largely from uplifted continental crust and marine sediment. The volcanic Cascades Range, which forms the eastern and southern boundaries of the watershed, forms the steep, quickly draining slopes and deep valleys typical of the western Cascades Range. The Coast Range consists of sandstones and siltstones and weathers easily, exporting fine sediments and exposing incised, landslide-prone slopes (Gannett and Caldwell, 1998).

**Figure 1 Willamette River basin Elevation and Sample Location**

Elevation (meters above sea level) in the Willamette River basin is depicted. Study sample sites are noted with red dots and occur along the mainstem Willamette River and multiple tributaries. For display purposes, only streams larger than 3<sup>rd</sup> order are shown.



The valley floor of the Willamette River basin has experienced episodic sedimentation, most notably between 13 and 15 thousand years ago when



multiple, large ice dams of the Missoula Valley broke and released vast quantities of water and sediment, which excavated the Columbia gorge and backfilled the Willamette Valley. These flood events covered the valley up to an elevation of 120 m above sea level and, as the flood receded, deposited the silts and clays that formed the poorly drained, clayey soils typically observed in the valley (Gannett and Caldwell, 1998; O Connor et al., 2001; Woodward et al., 1998). Significant, recurring flood events on the Willamette River deposited alluvium throughout the floodplain, resulting in areas that support abundant agricultural productivity.

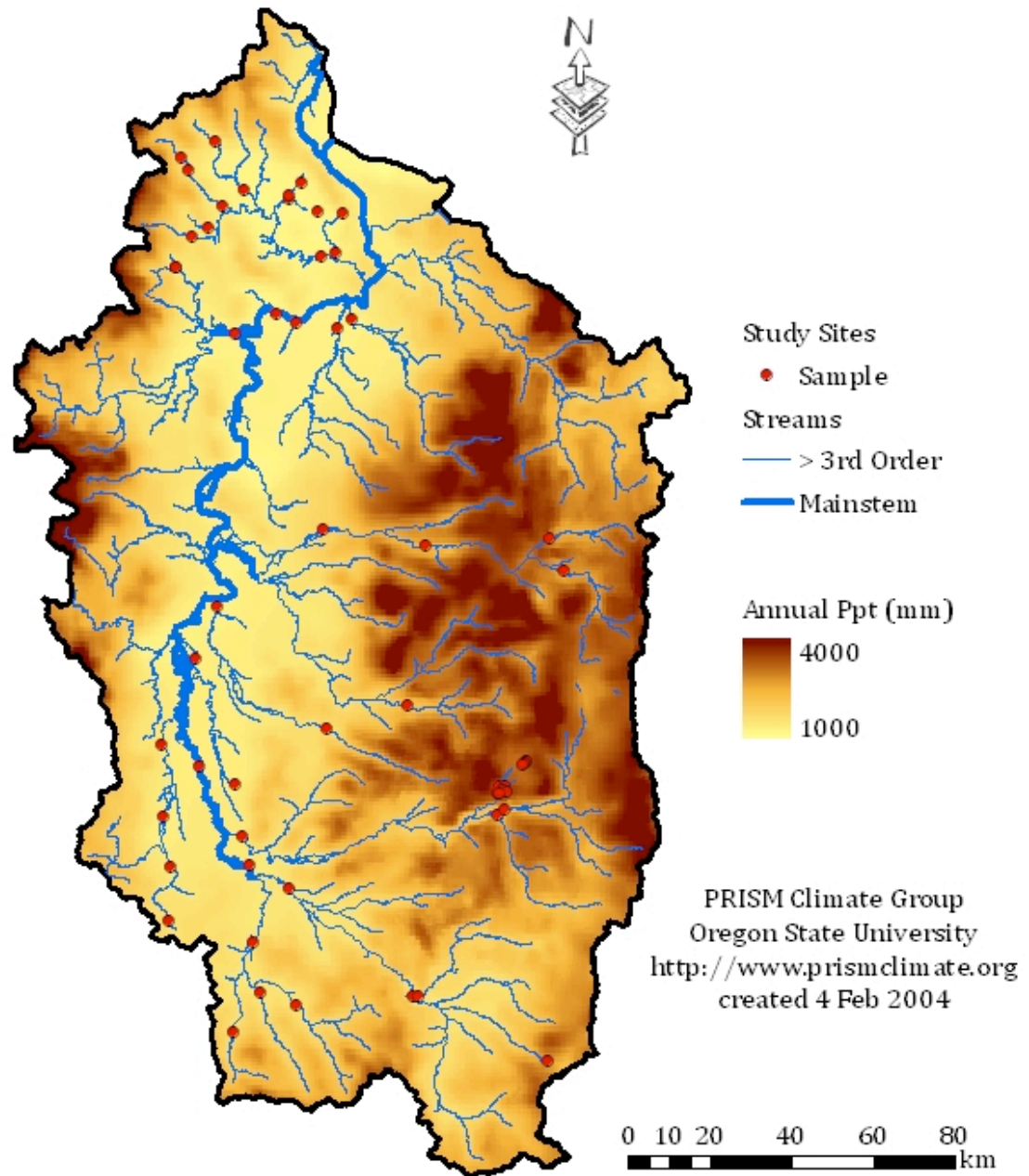
## **2.2 Climate**

The Willamette River basin's climate is strongly influenced by the Pacific Ocean. During winter, the wet and warm Pacific air meets cold and dry continental air, producing frequent storms and rainfall. Less than 5 percent of the annual rainfall in the Willamette River basin occurs during July and August with more than 75% occurring between October and March (Uhrich and Wentz, 1999). Mean annual precipitation ranges from less than 1000 to more than 4000 mm yr<sup>-1</sup> and varies according to topography with high elevation sites receiving the most; measured 1971-1990, (Figure 2, PRISM, 2004). Discharge from the Willamette River averages more than 900 m<sup>3</sup> s<sup>-1</sup> annually; measured 1973-1991 in Portland, Oregon (Woodward et al., 1998). Discharge from the Willamette River and selected sites across the Willamette River basin reflect seasonal precipitation

(Figure 3). Discharge for the same sites during 30 days prior and 14 days post-sampling indicate that samples were procured on the receding limb of the hydrograph.

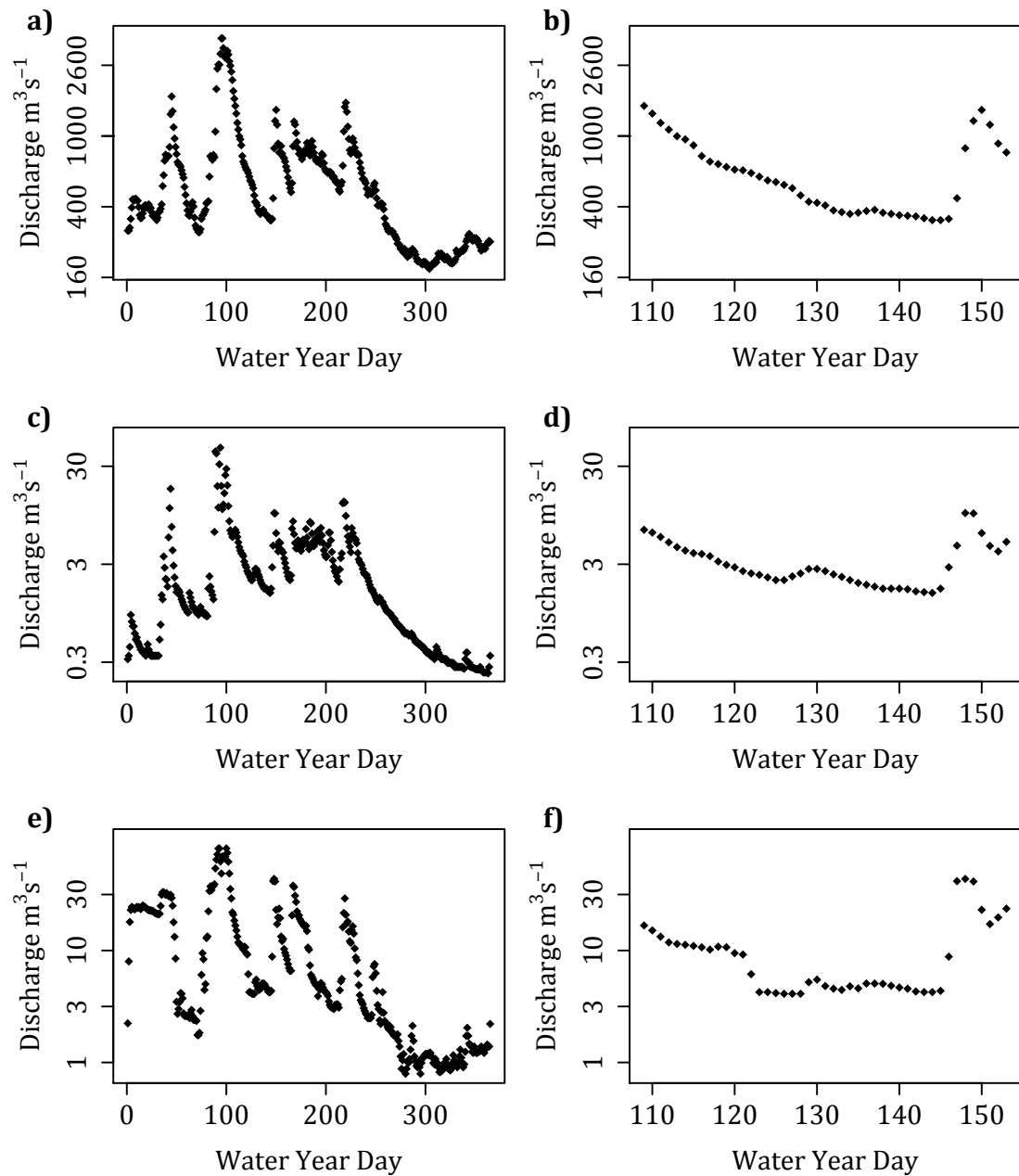
**Figure 2 Willamette River Basin Annual Precipitation**

Annual average precipitation throughout the Willamette River Basin (PRISM, 2004).



### Figure 3 Mean Daily Discharge in the Willamette River Basin

Mean daily discharge values ( $\text{m}^3 \text{s}^{-1}$ ) for the Willamette River at Newburg, OR (a, b), Lookout Creek at Blue River (c, d), and the Long Tom River at Monroe, OR (e, f) are shown below. Mean daily discharge values, plotted on log-scales, for the 2009 water year (October 1, 2008 – September 30, 2009) are depicted (a, c, e). Mean daily discharge values for 30 days prior and 14 days post sampling are also depicted (sample dates: 136-139; b, d, f).



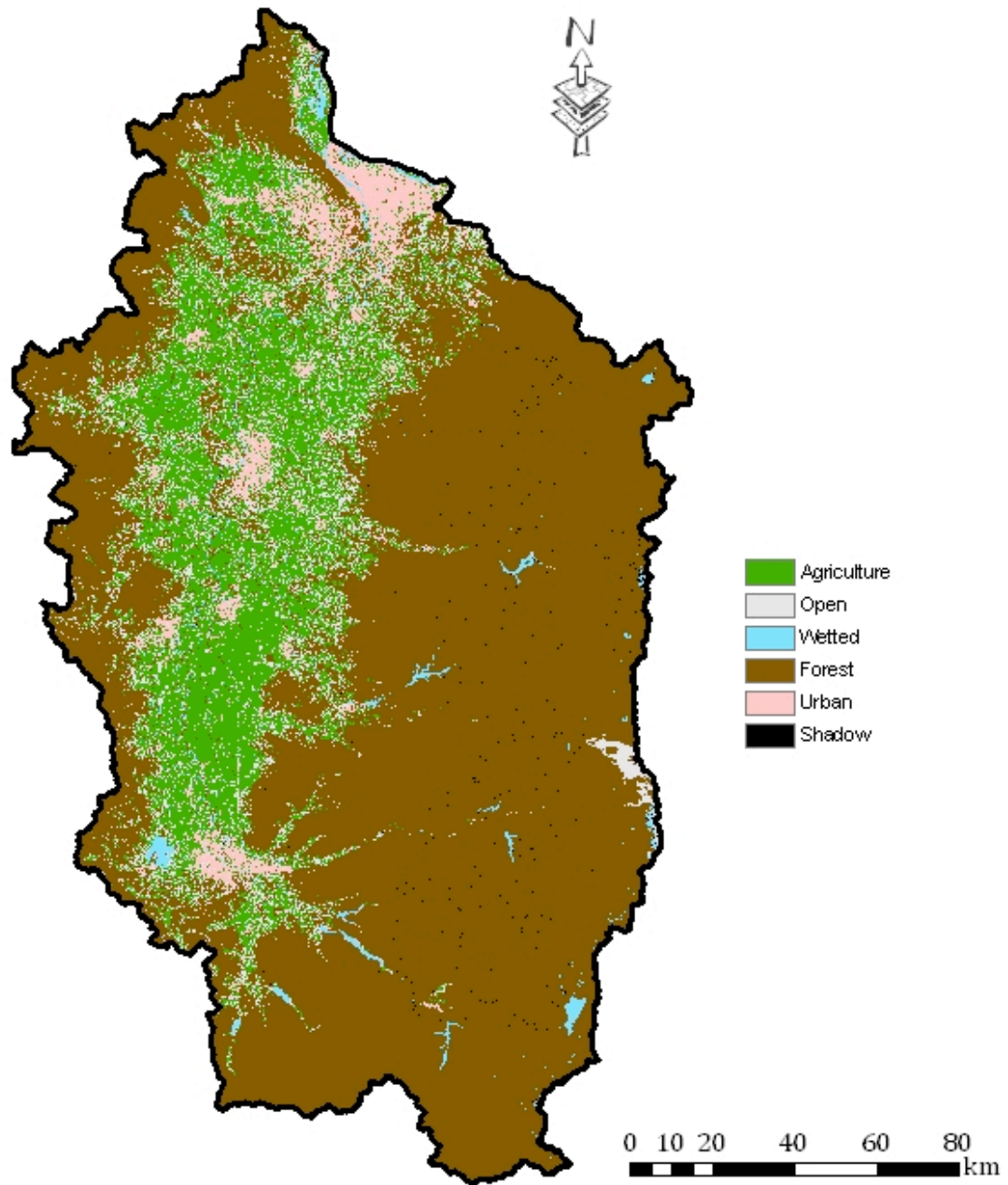
## **2.3 Population and Land Use**

The banks of the Willamette River have supported human populations for at least 10,000 years. The Willamette River basin makes up only 12 percent of the area of the state of Oregon, but it contains 68 percent of the state's population, with more than 2 million people mostly concentrated along the Willamette River in the Portland, Salem, and Eugene-Springfield areas. Populations in the Willamette River basin are largely concentrated in urban areas, with more than 80 percent of people living within urban growth boundaries. By 2050, the population is expected to be twice the 1990 census estimate, with potentially as many as 4 million living in the watershed (PNWERC, 2002).

There are three dominant land uses within the Willamette River basin. Forests cover 68 percent of the Willamette River basin and are concentrated in (Figure 4). Agriculture comprises 19 percent of the total basin land cover and while urban land use comprises 5 percent of the Willamette River basin, however urban areas cover the most agriculturally suitable soils - deep, fertile silty-clay soils concentrated within the floodplain of the Willamette River and its tributaries (PNWERC, 2002).

**Figure 4 Land Use in the Willamette River Basin.**

Land use classes were condensed to 5 categories – agriculture, open, wetted, forest and urban (PNWERC, 2002).



## **3 Methods**

### **3.1 Stream Selection Criteria and Sample Collection**

Sample locations distributed throughout the Willamette basin were determined according to accessibility and to reflect three dominant land uses: forest, agricultural, and urban. A typical Willamette River basin stream begins in the forested upland catchments of the Cascades or Coast Ranges, continues down-slope through the agriculturally developed valley and through the highly urbanized areas within the floodplain of the Willamette River. When possible, the same stream was sampled at multiple points to allow one stream profile to represent multiple land uses (Table 1, Figure 5). The furthest downstream site sampled on the mainstem of the Willamette was in Newburg, OR – upstream from the most urbanized area in the Willamette River basin. Sampling downstream from the Newburg location was not possible because of poor accessibility due to excessive bridge height and was also avoided because of tidal influence from the Columbia River.

**Table 1 Stream Sample Location and Elevation.**

Stream name, elevation (meters above sea level), stream order, tributary system, longitude and latitude of sample locations are listed below. Tributary systems refer to major tributaries to the Willamette River. All samples were collected February 13-16, 2009.

Name	Elev.	Order	Tributary	Longitude	Latitude
Calapooia River	57	4	Calapooia	123°7'41.13"	44°37'12.89"
Calapooia River	162	3	Calapooia	122°47'8.06"	44°21'1.45"
Coast Fork Willamette River	168	5	Coast Fork	123°0'46.96"	43°52'36.04"
Mosby Creek	213	3	Coast Fork	122°59'37.28"	43°45'57.97"
Coast Fork Willamette River	241	4	Coast Fork	123°4'26.13"	43°40'37.5"
Row River	256	5	Coast Fork	122°52'59.81"	43°44'15.23"
Long Tom River	86	5	Long Tom	123°17'44.99"	44°18'46.94"
Long Tom River	100	5	Long Tom	123°17'31.65"	44°9'15.28"
Coyote Creek	114	4	Long Tom	123°16'3.47"	44°2'29.69"
Coyote Creek	139	3	Long Tom	123°16'15.44"	43°55'29.79"
McKenzie River	122	5	McKenzie	123°2'50.95"	44°6'42.04"
Cougar Creek	352	4	McKenzie	122°15'41.85"	44°9'26.31"
McKenzie River	356	5	McKenzie	122°14'24.52"	44°10'6.64"
Lookout Creek	409	3	McKenzie	122°15'43.88"	44°12'19.24"
Blue River	416	3	McKenzie	122°15'44.52"	44°12'26.11"
HJA WS 9	425	1	McKenzie	122°15'28.13"	44°12'14.16"
HJA WS 10	430	1	McKenzie	122°15'35.88"	44°13'12.55"
HJA WS 1	457	1	McKenzie	122°14'8.93"	44°12'30.67"
HJA WS 3	460	1	McKenzie	122°14'31.02"	44°13'11.8"
HJA WS 2	548	1	McKenzie	122°14'38.31"	44°12'48.19"
HJA WS 6	863	1	McKenzie	122°11'0.64"	44°16'0.51"
HJA WS 7	908	1	McKenzie	122°10'45.15"	44°16'11.1"
HJA WS 8	955	1	McKenzie	122°10'23.89"	44°16'24.23"
Middle Fork Willamette River	159	5	Middle Fork Willamette	122°54'21.72"	43°59'52.44"
Middle Fork Willamette	315	5	Middle Fork	122°31'38.71"	43°45'19.42"



River			Willamette		
North Fork			Middle		
Middle Fork	317	4	Fork	122°30'41.63"	43°45'27.18"
Willamette			Willamette		
River			Middle		
Salt Creek	1265	2	Fork	122°7'7.76"	43°36'36.03"
			Willamette		
Molalla River	24	5	Molalla	122°42'23.31"	45°15'20.78"
Muddy Creek	66	4	Muddy	123°11'24.14"	44°30'10.22"
Muddy Creek	103	3	Muddy	123°4'10.03"	44°13'41.8"
North Santiam	132	5	N Santiam	122°47'39.82"	44°47'23.71"
River					
North Santiam	243	5	N Santiam	122°28'38.53"	44°45'19.8"
River					
Breitenbush	533	4	N Santiam	122°5'40.44"	44°46'3.33"
River					
North Santiam	544	4	N Santiam	122°2'59.51"	44°41'45.99"
River					
North Santiam	820	3	N Santiam	122°16'52.38"	4°29'23.14"
River					
Pudding River	24	5	Pudding	122°45'3.93"	45°13'59.79"
South Santiam	231	4	S Santiam	122°32'18.48"	44°23'56.92"
River					
Tualatin River	31	5	Tualatin	122°47'57.3"	45°23'43.75"
Fanno Creek	39	3	Tualatin	122°45'15.33"	45°24'10.26"
Beaverton Creek	43	3	Tualatin	122°53'59.8"	45°31'17.82"
Dairy Creek	48	4	Tualatin	123°2'29.95"	45°32'23.77"
Rock Creek	49	3	Tualatin	122°53'58.51"	45°31'46.47"
Gales Creek	50	3	Tualatin	123°6'31.86"	45°30'26.21"
Beaverton Creek	51	2	Tualatin	122°48'48.98"	45°29'37.04"
Bethany Creek	54	2	Tualatin	122°51'51.07"	45°33'26.69"
Scoggins Creek	56	3	Tualatin	123°9'18.39"	45°27'29.25"
Tualatin River	64	3	Tualatin	123°12'17.26"	45°26'9.93"
West Fork Dairy	67	3	Tualatin	123°8'3.08"	45°38'57.5"
Creek					
Fanno Creek	79	2	Tualatin	122°43'52.78"	45°29'15.52"
Iller Creek	94	2	Tualatin	123°13'1.61"	45°35'5"
Gales Creek	115	3	Tualatin	123°14'34.97"	45°36'41.77"
Willamette	15	7	Willamette	122°56'35.06"	45°15'56.79"
River					
Willamette	89	6	Willamette	123°10'41.12"	44°16'1.39"
River					

Willamette River	131	6	Willamette	123°1'30.46"	44°2'45.82"
Yamhill River	24	6	Yamhill	123°4'21.23"	45°13'20.44"
Turner Creek	61	3	Yamhill	123°15'33.6"	45°22'17.65"
North Yamhill	62	4	Yamhill	123°15'33.6"	45°22'17.65"

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Stream samples were collected February 13-16, 2009. Sample collection was scheduled to avoid large storm systems that move through the area during winter. Weather throughout sample collection was characteristically overcast with light rain. Stream samples were collected from near the surface of the stream thalweg, the fastest-flowing portion along the stream profile, using bridges where major roads crossed target streams. A handheld global positioning system (Garmin GPS 12) was used to record latitude and longitude coordinates for each sample location. A bridge sampler, consisting of three, one-Liter HDPE Nalgene™ bottles, two of which were used to weight the sampler, was lowered to the stream and rinsed three times with stream water before retrieving water for analysis. Samples were immediately filtered through pre-combusted 0.7-μm glass-fiber paper (Whatman™ GF/F), divided into acid-rinsed 60 mL HDPE Nalgene™ bottles, and stored in the dark at 4 °C until they could be frozen (within 12 hours) prior to analysis.

### 3.2 Chemical analyses

Stream samples were analyzed for concentrations of total nitrogen, ammonium, nitrate/nitrite, total organic carbon, and chloride. Ammonium ( $\text{NH}_4^+$ ), nitrate/nitrite ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ), and chloride ( $\text{Cl}^-$ ) concentrations were determined via flow injection analysis using a Lachat QuikChem 4200 Analyzer (Lachat, 1992). Total dissolved organic carbon (DOC) was determined using the high-temperature catalytic combustion method using a Shimadzu TOC-Vchs Analyzer (Shimadzu, 2001). Total nitrogen, including inorganic and organic forms of nitrogen, was determined using the catalytic thermal decomposition and chemiluminescence detection method using a Shimadzu TOC-V/TN analyzer (ENV, 1996; Jones and Daughton, 1985). Laboratory analyses were performed by the United States Department of Agriculture, and the Cooperative Chemical Analytical Laboratory (Corvallis, OR) using contemporary published methodology and safety protocols (APHA, 1992; US EPA, 1987).

Specific ultra-violet absorbance (SUVA) was determined after Weishaar et al, (2003) using a Shimadzu 1201 UV-VIS Spectrometer. Ultra-filtered Millipore Milli-Q™ water was used for calibration. Samples and sample blanks were placed in quartz-crystal, Whatman™ sample cuvetts and absorbance<sub>254nm</sub> determined. SUVA values are determined by normalizing absorbance<sub>254</sub> for sample DOC concentration and have the units  $\text{abs}_{254} \text{ L mg}^{-1} \text{ cm}^{-1}$ . SUVA is the direct measure of light a sample of carbon absorbs and correlates to the percent aromaticity and molecular weight of carbon (Chin et al., 1994; Weishaar et al., 2003). Samples

with high SUVA values have higher molecular weights and contain higher amounts of aromatic rings of carbon – reflecting a refractory carbon source, as aromaticity is negatively related to biodegradability (Kalbitz et al., 2003). Hence, low SUVA values indicate low molecular weight and percent aromaticity and are more labile.

### **3.3 GIS**

Land use data for the Willamette River Basin were downloaded from the Laboratory for Applications in Remote Sensing (LARSE) of the Pacific Northwest Environmental Research Consortium (<http://www.fsl.orst.edu/larse/wrb/wrb.html>). Physical watershed attributes including size, elevation, and stream length were determined using a digital elevation model (DEM, 30-m resolution) and river shapefile (<http://www.fsl.orst.edu/pnwerc/wrb/access.html>).

The Willamette River Basin Mapping Project Version 2 from the LARSE dataset was used to determine contributing proportions of land use to total watershed area. The term ‘land use’ refers to the built environment (roads, buildings etc.) while ‘land cover’ refers to features such as forests and streams (PNWERC, 2002). The difference between terms is largely dependent on the

extent of information available for each area and interpretation; throughout this document, the terms land use and land cover are used interchangeably.

The LARSE dataset contained 35 land use classes that were combined into representative categories of agricultural, forested, open, wet, and urban land use. The combined agricultural category was comprised of 15 agricultural crop types: berries & vineyards, double crops, hops, mint, radish seed, sugar beet seed, row crop, grass, burned grass, field crop, hayfield, late field crop, pasture, irrigated field crop, and orchard. The combined forest category was comprised of 8 forest types: Christmas trees, open forest, semi-closed forest, closed hardwood forest, closed mixed forest, closed conifer forest (1-80 yr), closed conifer forest (81-200 yr), closed conifer forest (>200 yr). The combined urban category was comprised of 3 urban land use types: built high density, built medium density, and built low density. The combined open category was comprised of 5 land use types: barren, park, bare/fallow, natural shrubland and natural grassland. The combined wet category was comprised of 3 land use types: snow/ice, water, and flooded/marsh. Land use types were defined by the PNWERC (2002).

ArcGIS 9.3 (ESRI 2008) with the ArcHydro Tools Extension was used to delineate watersheds from sampling locations. Watershed polygon shapefiles for each sampling point were created and converted to raster images consisting of many individual, spatially referenced cells. Raster images reflecting individual watershed size and shape were then converted to a binary format, overlaid on the Willamette River basin land use raster image and analyzed using Visual C++

v.6™. Total area for each land use was determined by summing the pixels within each land use. Dividing this sum by the total number of pixels in the watershed produced percent composition for each land use type within each watershed (Table 2, Figure 4).

Calculating total watershed area from raster images could potentially present a problem for small watersheds because pixel shape differs from the original watershed polygons. Large polygons with complex perimeters often contain many small, triangular polygons. If the triangles are drawn at the same scale of pixels (one pixel represents a square: 30 x 30 m) the edge of the triangle may not line up perfectly with the square pixel and a discrepancy in area can occur; across hundreds or thousands of polygons the discrepancy in area could potentially be large; this difference would likely be greatest in small watersheds with large perimeter to area ratios. However, net area differences between raster-based estimates and estimates derived from watershed polygons were calculated and found to be negligible: < 0.8 percent; except for one small (5.6 km<sup>2</sup>) watershed where there was a 1.7 percent in area estimates between methods.

Given the relatively low resolution of the DEM (30 m) and potential for error in estimating area of small watersheds with raster land use maps, land use for eight of nine sampled watersheds in the HJ Andrews Experimental Forest (HJA) were assumed equal in proportion values determined for the 63 km<sup>2</sup>

watershed of Lookout Creek, which drains all of the HJA. Elevation and watershed area for HJA sites was determined from published values (Vanderbilt et al., 2003).

### **3.4 Statistical analysis**

Pearson's correlation coefficients ( $r$ ) were calculated to test the hypothesis that DOC,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and SUVA values were correlated with watershed attributes – land use, elevation, and stream order. Correlation coefficients were calculated for transformed and untransformed variable combinations. Simple linear regression models were used to quantify the rate of change in response variables with changes in explanatory variables. To determine whether correlation amongst stream chemistry variables was associated with land use, elevation or watershed area, Principal Components Analysis (PCA) was used.

Correlation, linear regression and PCA assume that variables are linearly correlated. Additionally, correlation and linear regression assume that variables: <sup>1)</sup> are from a normally distributed population, <sup>2)</sup> have consistent standard deviation (homogeneity of variance), and <sup>3)</sup> samples are independent of one another (Ramsey and Schafer, 1997). PCA requires that response variables are linearly related and are not overly influenced by outliers. PCA is fairly robust to violation of the normality assumption (McCune et al., 2002). Multiple linear regression analysis was not used due to the interdependence of the explanatory variables. Multiple linear regression models assume independence among

explanatory variables; finite land area forces individual land use categories to be highly dependent on each other.

To satisfy linear regression model assumptions for linearity and normality,  $\log_{10}$  (stream chemistry variables), logit (percent land use variables),  $\log_{10}$  (elevation), and fourth root (watershed area) transformations were applied. Logit transformations are appropriate for proportion data and follow the form:  $\text{logit}(x) = \ln(x/[1-x])$  (Ramsey and Schafer, 1997). To satisfy assumptions of normality and linearity, regression models including nitrate omitted nitrate values with less than detectable levels ( $0.025 \text{ mg L}^{-1}$ ). For regression models including percent urban or agriculture land uses, only sites with > 0 percent agriculture or urban cover were included. Regression analyses were calculated using R (2.10.1 GUI 1.31 Leopard build 5537, 32-bit) according to accepted methodologies (Ramsey and Schafer, 1997).

Simple linear regression analysis was performed for each combination of stream chemistry dependent variables on land use explanatory variables, Table 2. A simple, linear model was fitted to the observed response and explanatory variables, estimating two terms, the slope intercept and regression coefficient (slope), by repeatedly minimizing least squares difference for calculated models (Ramsey and Schafer, 1997). The model describing the simple linear regression of DOC on percent agriculture:  $[\text{DOC}] = \text{intercept} + (\text{coefficient} * \text{percent Agriculture})$ .



**Table 2      Linear Regression Model Formulae**

Linear Regression Model
$\log_{10}(\text{DOC}) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Agriculture}/100)$ $\log_{10}(\text{DOC}) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Forest}/100)$ $\log_{10}(\text{DOC}) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Urban}/100)$ $\log_{10}(\text{DOC}) = \beta_0 + \beta_1 * \log_{10} (\text{Elevation})$
$\log_{10}(\text{NO}_3^-) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Agriculture}/100)$ $\log_{10}(\text{NO}_3^-) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Forest}/100)$ $\log_{10}(\text{NO}_3^-) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Urban}/100)$ $\log_{10}(\text{NO}_3^-) = \beta_0 + \beta_1 * \log_{10} (\text{Elevation})$
$\log_{10}(\text{Cl}^-) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Agriculture}/100)$ $\log_{10}(\text{Cl}^-) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Forest}/100)$ $\log_{10}(\text{Cl}^-) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Urban}/100)$ $\log_{10}(\text{Cl}^-) = \beta_0 + \beta_1 * \log_{10} (\text{Elevation})$
$\log_{10}(\text{SUVA}) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Agriculture}/100)$ $\log_{10}(\text{SUVA}) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Forest}/100)$ $\log_{10}(\text{SUVA}) = \beta_0 + \beta_1 * \text{logit } (\% \text{ Urban}/100)$ $\log_{10}(\text{SUVA}) = \beta_0 + \beta_1 * \log_{10} (\text{Elevation})$

Principal components analysis (PCA) was used to ordinate stream chemistry values in a two-dimensional space that accounted for the interrelatedness of chemistry variables. PCA is similar to simple regression models but thrives on interdependence among model parameters. PCA requires that variables are linearly related and normally distributed, though it is robust to departures from the assumption of normality (McCune et al., 2002). Ordination inputs for PCA included DOC,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and SUVA values for each sample site;  $\log_{10}$  transformations were applied to improve the statistical qualities of the data.

Principal components are vectors built from the input variables and are selected to maximize the variance along each component (axis). Multiple components are generated, each composed of differing combinations of coefficients for each variable; components are selected for their interpretability while the ordination technique mathematically arranges response variables across the ordination plane. Each variable is scaled to its unit length, which allows the distance between plotted points to be used as an approximation of relatedness between samples across multiple response variables (McCune et al., 2002). Without such scaling, variables with large units ( $\text{Cl}^-$  ranged from 0.5 to 16.6  $\text{mg Cl L}^{-1}$ ) out-weigh variables with smaller units ( $\text{NO}_3^-$  ranged from 0.025 to 2.8  $\text{mg NO}_3\text{-N L}^{-1}$ , Table 4).

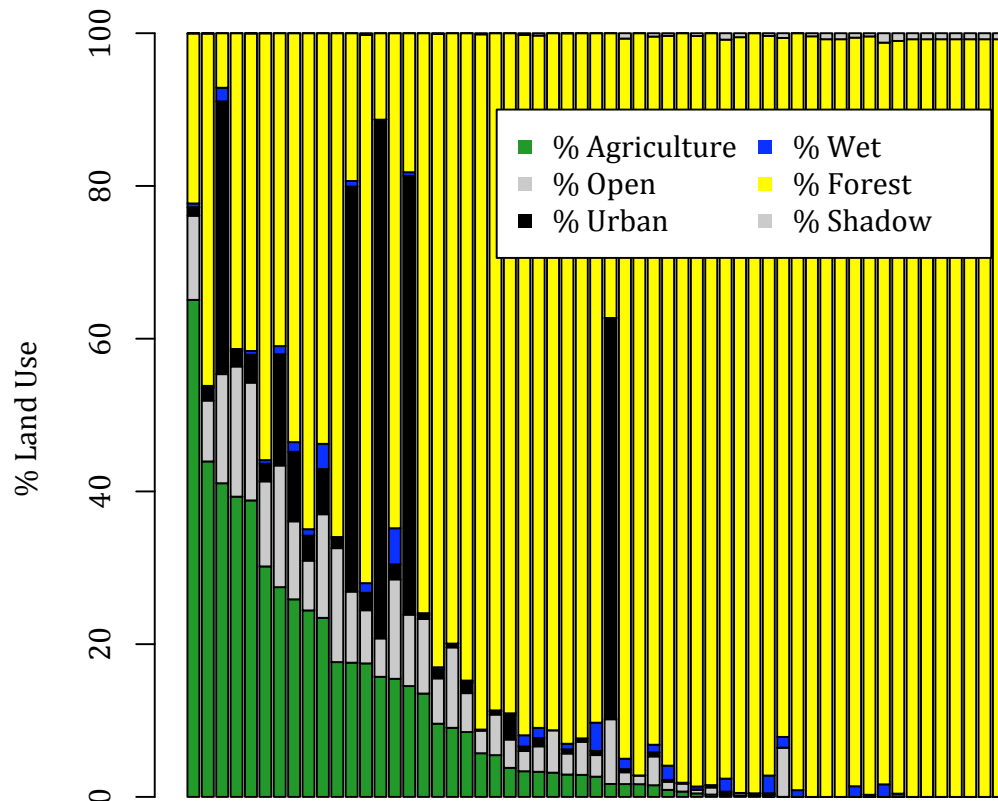
Once components for graphical interpretation have been selected, explanatory variables are overlain on the ordination plot to assess their relations to two ordination axes. While the ordination axes have no units of measure (entities are scaled in terms of standard deviations from centroids), each comprises a group of related variables and can be interpreted as such (*i.e.* the 'nutrient enrichment' axis). Explanatory variables that cluster in the ordination space are related to the response variables, while non-clustering points demonstrate a lack of relationship between combinations of response and explanatory variables (McCune et al., 2002).

## **4 Results**

Watershed land use for sampled streams ranged widely. Forested land use was the most common, ranging from 7 to 99.6 percent and averaging nearly 79 percent (Figure 5, Table 3, Appendix A). Agriculture was the second most common land use, averaging 9.5 percent and ranging from 0 to 65 percent. Urban land use averaged only 5.8 percent and ranged from 0 to 68 percent. Urban land use was heavily concentrated in 5 sites, which ranged in percent urban from 35 – 68. Open land use in sampled watersheds ranged from 0 to 17.5 percent and averaged 4.8 percent while wetted land use averaged only 0.7 percent and ranged from 0 to 4.7 percent. The site with the largest watershed area, Willamette River at Newburg, contained 72 percent forest, 17.5 percent agriculture, 7 percent open, 2.3 percent urban, and 1.3 percent wetted area.

**Figure 5 Willamette River Basin Land Use by Watershed**

Vertical bars represent watershed land use for each stream sample, samples arranged in order of decreasing percent agriculture. Percent agriculture, urban, forest, wet, and open are shown. The percent of watershed area covered by topographic shadow appears at the top of the plot (very small in most watersheds).



**Table 3 Stream Name, Watershed Area, and Percent Land Use**

Land use values for watersheds at the HJA were based on proportions from the Lookout Creek watershed.

Stream Name	Area (ha)	Ag (%)	Forest (%)	Urban (%)	Wet (%)	Open (%)
Beaverton Creek	9557	17.6	19.4	53	0.7	9.3
Beaverton Creek	1578	15.7	11.3	67.9	0	5
Bethany Creek	558	41.1	7.1	35.7	1.8	14.3
Blue River	12309	0	99.6	0	0	0
Breitenbush River	25661	0	98.6	0	0.4	0
Calapooia River	95789	43.9	46.1	1.7	0.3	8
Calapooia River	26743	5.7	91	0.1	0	3
Champoeg Creek	6432	78.1	5.3	3.3	0.8	12.6
Cougar Creek	55215	0	98	0	1.4	0
Coyote Creek	26820	17.7	66	1.3	0.2	14.9
Coyote Creek	8103	9	79.9	0.5	0	10.5
Dairy Creek	39174	24.4	64.9	3.3	0.8	6.5
Fanno Creek	8156	14.5	18.2	57.4	0.5	9.3
Fanno Creek	600	1.7	37.3	52.5	0	8.5
Gales Creek	19506	8.5	84.8	1.4	0.3	5.1
Gales Creek	9735	0.3	98.5	0.3	0	0.9
Iller Creek	1261	3.2	91.3	0	0	5.6
Long Tom River	103760	23.4	53.8	5.9	3.3	13.6
Long Tom River	68596	15.5	64.8	2	4.7	13
Lookout Creek	6345	0	99.2	0	0	0
McKenzie River	346450	1.5	92.7	0.5	1	3.8
McKenzie River	134202	0	91.5	0	1.4	6.4
Molalla River	89314	9.6	82.9	1.2	0.3	5.9
Mosby Creek	24235	0.7	98.1	0.1	0	1
Muddy Creek	36753	65.1	22.3	1.1	0.5	11
Muddy Creek	7864	39.3	41.3	2	0.3	17
North Santiam River	178091	1.7	94.3	0.4	1.4	1.5
North Santiam River	132978	0.3	96.8	0.1	1.7	0.3
North Santiam River	51202	0	97.1	0	1.6	0
North Santiam River	14359	0	99.3	0	0.3	0
North Yamhill River	12863	5.5	88.7	0.4	0.2	5.3

Pudding River	125320	38.8	41.6	3.7	0.5	15.4
Rock Creek	6592	27.5	41	14.6	1.1	15.9
Row River	55247	0.2	99.5	0	0	0.3
Salt Creek	9106	0	99.1	0	0.9	0
Scoggins Creek	11312	2.7	90.3	0.5	3.7	2.8
South Santiam River	47878	0.2	99	0	0	0.3
Tualatin River	168720	25.9	53.5	9.1	1.3	10.2
Tualatin River	11130	2.9	92.3	0.3	0.2	4.3
Turner Creek	3980	13.5	75.9	0.5	0.3	9.8
West Fork Dairy Creek	10812	3.8	89.1	3.2	0.2	3.7
Willamette River	2156655	17.5	71.8	2.3	1.3	7
Willamette River	889133	3.3	90.7	1.1	1.3	3.3
Willamette River	526725	3.4	91.7	0.6	1.5	2.6
Willamette River, Coast Fork	142157	2.9	93	0.5	0.7	2.8
Willamette River, Coast Fork	21045	1.7	97.2	0	0	1.1
Willamette River, Middle Fork	348179	0.9	95.6	0.3	1.9	1.1
Willamette River, Middle Fork	175831	0.1	96.9	0.2	2.3	0.2
Willamette River, North Fork Middle Fork	56360	0.5	98.3	0	0.4	0.5
Yamhill River	190581	30.2	55.9	2.3	0.5	11.1
HJA WS 1	96	0	100	0	0	0
HJA WS 2	60	0	100	0	0	0
HJA WS 3	100	0	100	0	0	0
HJA WS 6	13	0	100	0	0	0
HJA WS 7	15	0	100	0	0	0
HJA WS 8	21	0	100	0	0	0
HJA WS 9	9	0	100	0	0	0
HJA WS 10	10	0	100	0	0	0

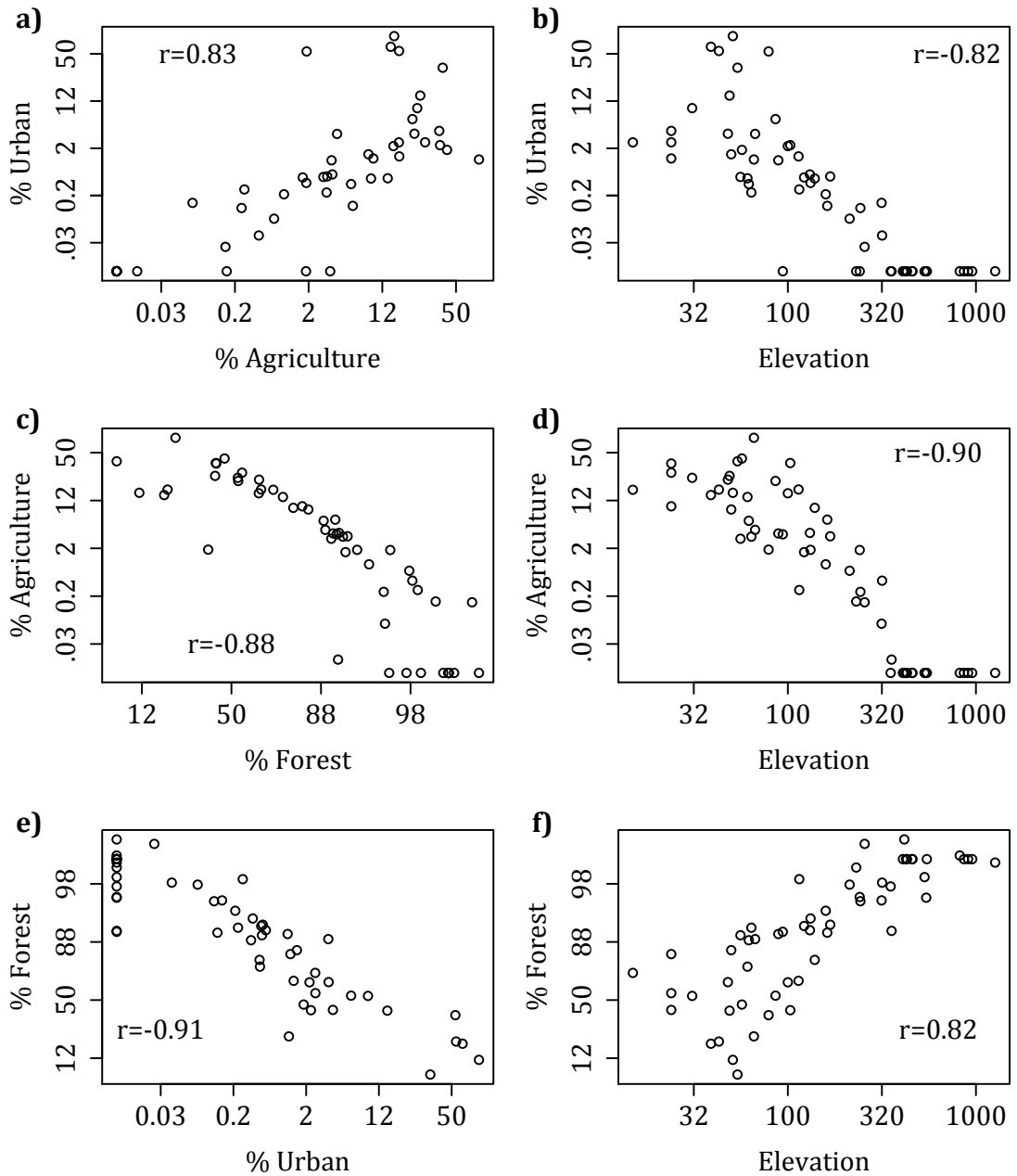
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#### **4.1 Correlation Amongst Land Use and Elevation**

The agricultural, urban and forested proportions of land use in sampled sub-basins of the Willamette River basin were strongly interrelated (Figure 6). Land use proportions also tended to be correlated with elevation. Urban and agricultural land uses tended to be more dominant at lower elevations, while forested land uses were dominant at higher elevations. Such correlation makes direct determination of causal effects of land use from statistical models difficult. Correlations for the proportions of wet and open area in sampled sub-basins were also constructed (Appendix B).

### Figure 6 Correlations Amongst % Land Use and Elevation

Percent urban and agriculture are positively correlated (a, b) while each is negatively correlated with percent forest (a, c, d). Percent urban and agriculture are positively correlated with elevation, while percent forest is negatively correlated (b, d, f). Axes are plotted on logit-transformed scales.





## 4.2 Stream Chemistry Variable Correlations

Stream chemistry variables (DOC, TN,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and SUVA) ranged over two orders of magnitude across sampled sites (Table 4). Stream dissolved organic carbon (DOC) ranged from  $0.32 \text{ mg C L}^{-1}$  to  $4.6 \text{ mg C L}^{-1}$ , averaging  $1.3 \text{ mg C L}^{-1}$  across all sites. Nitrate ( $\text{NO}_3^-$ ) values ranged from undetectable ( $< 0.05 \text{ mg N L}^{-1}$ ) to  $2.8 \text{ mg N L}^{-1}$ , and averaged  $0.4 \text{ mg N L}^{-1}$ . Nitrate made up most of the dissolved inorganic nitrogen (DIN); ammonium ( $\text{NH}_4^+$ ) contributed little to DIN in most streams, averaging  $0.05 \text{ mg N L}^{-1}$  and ranging from undetectable ( $< 0.05 \text{ mg N L}^{-1}$ ) to  $1.89 \text{ mg N L}^{-1}$ . Total nitrogen (TN), which includes organic nitrogen, averaged  $0.52 \text{ mg N L}^{-1}$  and ranged from undetectable ( $< 0.05 \text{ mg N L}^{-1}$ ) to  $3.6 \text{ mg N L}^{-1}$ . Samples below the nitrogen detection limit were presumed to contain some nitrogen and assigned a value of 0.025 (one-half the analytical detection limit) for TN,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . Specific ultra-violet absorbance (SUVA) ranged from 0.03 to  $0.08 \text{ abs}_{254} \text{ L mg}^{-1} \text{ cm}^{-1}$ , averaging  $0.05 \text{ abs}_{254} \text{ L mg}^{-1} \text{ cm}^{-1}$ . Chloride concentrations ranged from  $0.52 \text{ mg Cl L}^{-1}$  to  $16.6 \text{ mg Cl L}^{-1}$ , and averaged  $4.3 \text{ mg Cl L}^{-1}$ .

**Table 4 Stream Chemistry Summary Statistics**

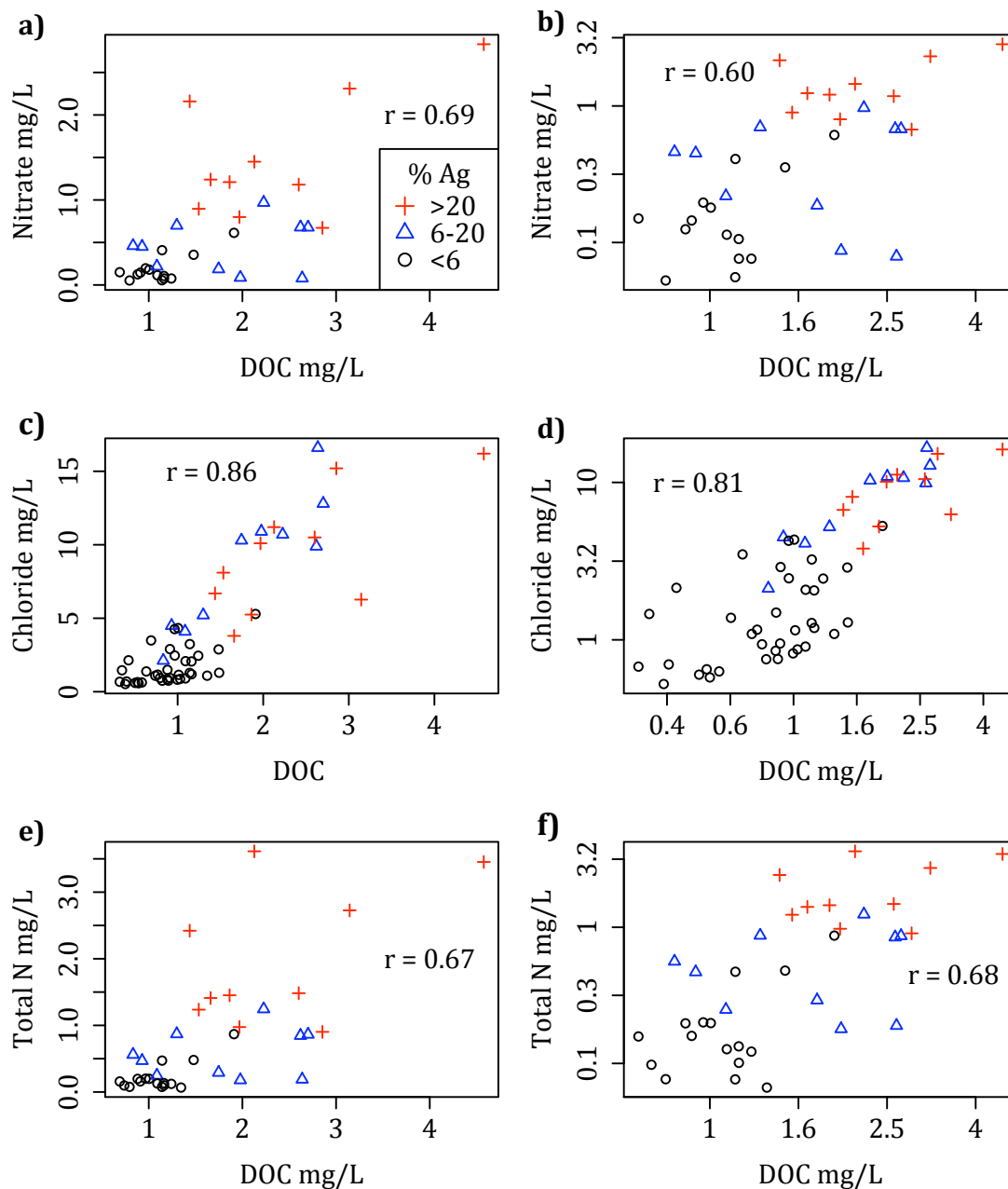
Mean, standard deviation, and coefficient of variation DOC,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , Total Nitrogen (TN), SUVA and  $\text{Cl}^-$  (n=57 sites).

	DOC (mg L <sup>-1</sup> )	$\text{NO}_3^-$ (mg L <sup>-1</sup> )	$\text{NH}_4^+$ (mg L <sup>-1</sup> )	TN (mg L <sup>-1</sup> )	$\text{Cl}^-$ (mg L <sup>-1</sup> )	SUVA (abs <sub>254</sub> L mg <sup>-1</sup> cm <sup>-1</sup> )
Mean	1.3	0.4	0.06	0.52	4.2	0.05
St. Dev.	0.82	0.62	0.24	0.83	4.4	0.01
Coeff. Var.	0.62	0.56	3.9	1.6	1.0	0.27
Range	0.32-4.6	0.025- 2.8	0.025- 1.9	0.025- 3.6	0.5-16.6	0.03-0.08

Stream DOC was positively correlated with stream nitrate, total nitrogen and chloride (Figure 7). Stream nitrate was positively correlated with chloride and total nitrogen (Figure 8). Given the high degree of correlation between nitrate and total nitrogen ( $r=0.96$ ), only nitrate was included in regression analyses. Stream nitrate was poorly correlated with SUVA though after log-transformation and exclusion of nitrate values less than the detectable limit, a negative correlation was evident ( $r= -0.46$ , Figure 8). SUVA was only weakly correlated with DOC and chloride (Figure 9).

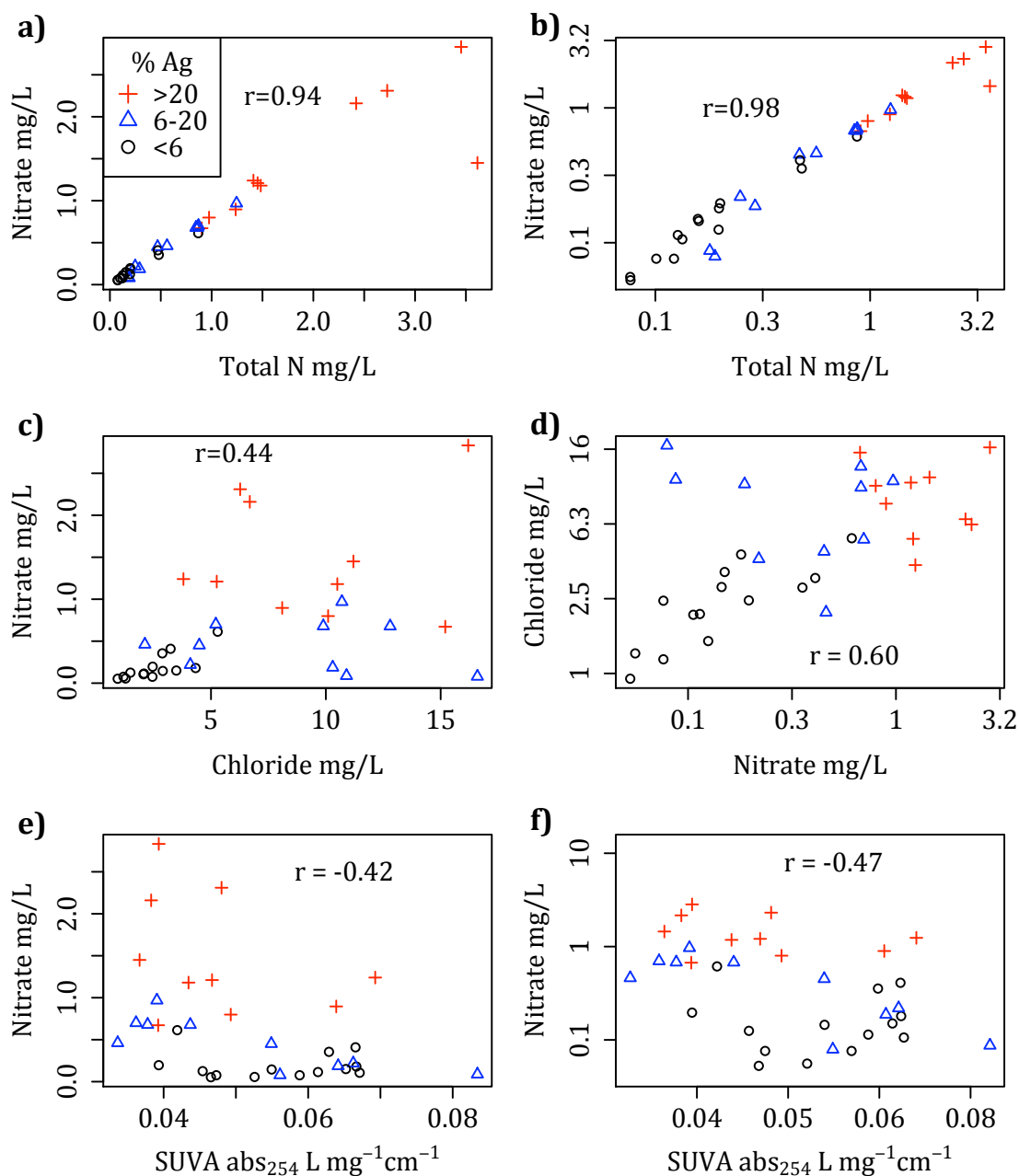
### Figure 7 Bivariate Correlations with DOC

DOC is positively correlated with nitrate, chloride and total nitrogen. Correlations are shown on log-log (b, d, f) and linear (a, c, e) scales. Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). For correlations with nitrate and total nitrogen variables, only values greater than the detection limit were included.



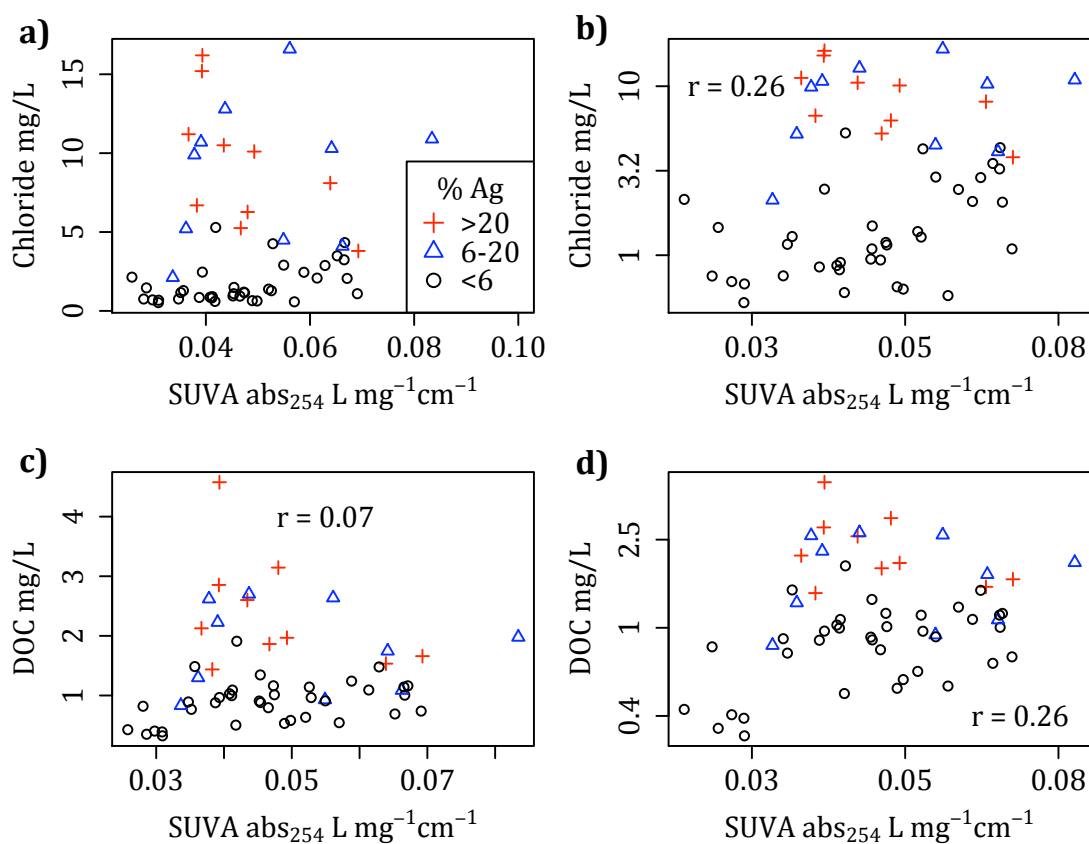
### Figure 8 Bivariate Correlations with Nitrate

Nitrate is positively correlated with total nitrogen and chloride but poorly correlated with SUVA. Correlations are shown on log-log (b, d, f) and linear (a, c, e) scales. Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). For correlations with nitrate and total nitrogen variables, only values greater than the detection limit were included.



### Figure 9 Bivariate Correlations with SUVA

Stream SUVA is poorly correlated with stream chloride and stream DOC concentrations. Log-transformed variable correlations are shown in b, d, and f while untransformed variable correlations are shown in a, c, and e. Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). Note that in c and d, SUVA is normalized by DOC concentration.



### 4.3 Stream Chemistry Relationship to Land Use, Elevation, Area, and Stream Order

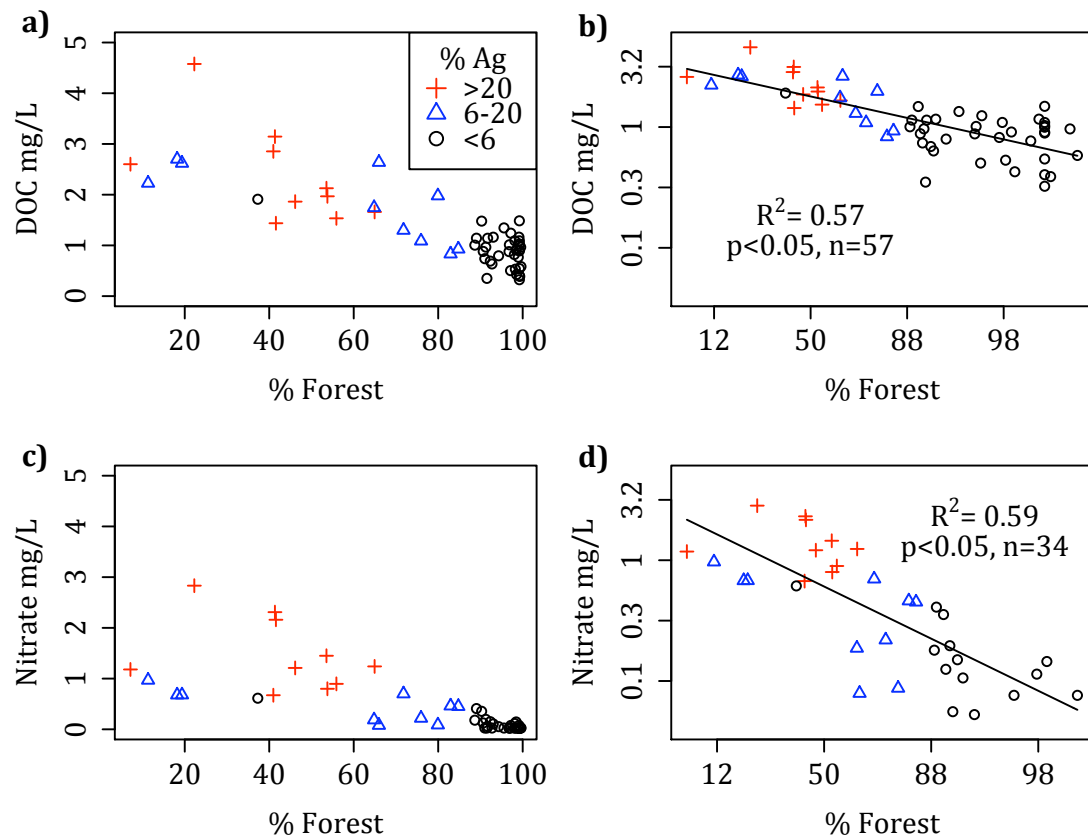
DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  were significantly ( $p < 0.05$ ) related to the proportion of basin area in forest, agriculture, and urban (all of which were correlated with one another, Figures 10 -15). SUVA values were significantly related to proportion of basin area in urban land use (Figure 15 c, d). DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  were also significantly ( $p < 0.05$ ) related to elevation (Appendix D). Watershed area and stream order were not correlated with stream chemistry variables and were omitted entirely from the regression analysis.

#### 4.3.1 Stream Chemistry Relationship to Forest

Stream DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  concentrations were significantly ( $p < 0.05$ ) negatively related to percent forested area in sampled sub-basin sites of the Willamette River basin (Figure 10, 11); SUVA values were not significantly related to percent forested area (Figure 11 c, d). DOC concentration was significantly negatively related to the percent of forest cover ( $r^2 = 0.56$ , Figure 10 b). As the proportion of forest area in a basin increased from 12 to 50 percent, mean DOC decreased from 2.7 to 1.8  $\text{mg C L}^{-1}$ . As forest area increased from 50 to 88 percent of the basin area, mean DOC concentration decreased by almost a third (34%) (from means of 1.8 to 1.2  $\text{mg C L}^{-1}$ ); an additional 10 percent increase in forest from 88 to 98 percent of the basin area resulted in an additional 34 percent decrease in mean DOC concentration (from means of 1.2 to 0.8  $\text{mg C L}^{-1}$ ).

**Figure 10 Relationship of DOC and Nitrate to the Proportion of Forest Area in Sampled Sub-basins of the Willamette River Basin, Oregon, February 12-15, 2009.**

DOC and nitrate are negatively related to percent forest (a, b, c, d). Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Watersheds with less than detectable levels of nitrate were omitted from the nitrate regression (d).



Nitrate concentration was significantly ( $p < 0.05$ ) negatively related to the percent of forest cover ( $r^2 = 0.58$ , Figure 10 c, d). As the proportion of forest area in a basin increased from 12 to 50 percent, mean nitrate concentration decreased from 1.6 to 0.6 mg N L<sup>-1</sup>. As forest area increased from 50 to 88 percent of the basin area, mean nitrate concentration decreased by almost two-thirds (63%) (from means of

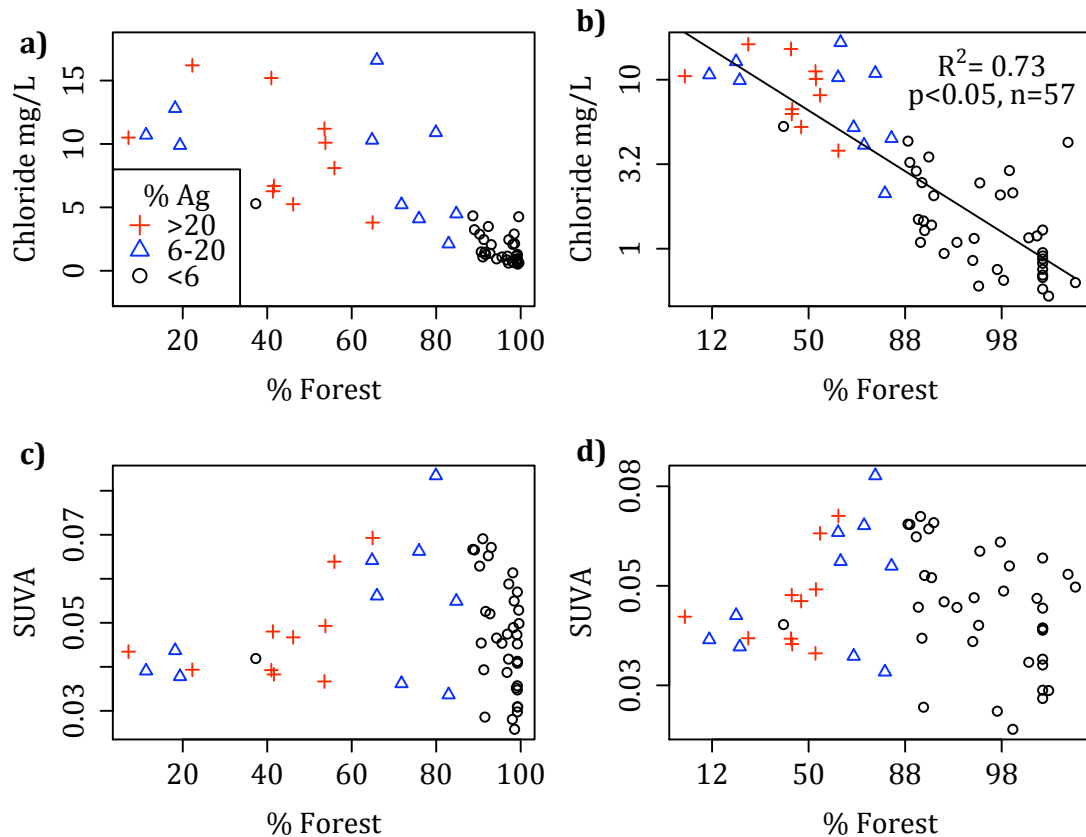
0.6 to 0.2 mg N L<sup>-1</sup>); an additional 10 percent increase in forest from 88 to 98 percent of the basin area resulted in an additional 63 percent decrease in mean nitrate concentration (from 0.2 to 0.08 mg N L<sup>-1</sup>).

Stream chloride concentrations were significantly ( $p < 0.05$ ) negatively related to percent forest in sampled sub-basin sites of the Willamette River basin (Figure 11 a, b). Chloride concentration was significantly negatively related to the percent of forested area ( $r^2 = 0.73$ , Figure 11 b). As the proportion of forest area in a basin increased from 12 to 50 percent, mean chloride concentration decreased from 15 to 6.6 mg Cl L<sup>-1</sup>. As forest area increased from 50 to 88 percent of the basin area, mean chloride concentration decreased by more than a half (56%) (from means of 6.6 to 2.9 mg Cl L<sup>-1</sup>); an additional 10 percent increase in forest from 88 to 98 percent of the basin area resulted in an additional 56 percent decrease in mean chloride concentration (from 2.9 to 1 mg Cl L<sup>-1</sup>).



**Figure 11 Relationship of Chloride and SUVA to the Proportion of Forest in Sampled Sub-basins of the Willamette River Basin, Oregon, February 12-15, 2009.**

Chloride is negatively related to percent forest (a, b). Linear scale plots (a, c) and log-logit scale plots with regression models when possible (b, d) are depicted. Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). SUVA ( $\text{abs}_{254} \text{ L}^{-1} \text{ mg}^{-1} \text{ cm}^{-1}$ ) was not linearly related to increasing percent forest (c, d).



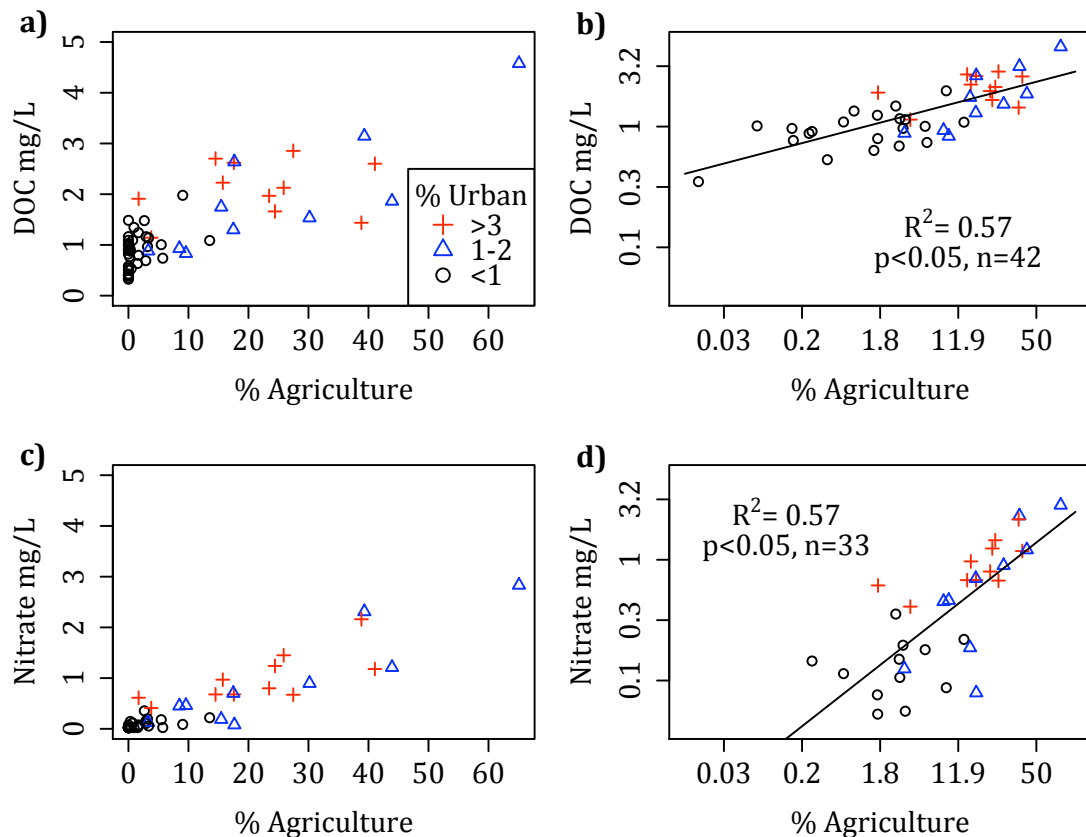
Stream SUVA values were not significantly related to percent forest in sampled sub-basin sites of the Willamette River basin (Figure 11 d). As the proportion of forest area in a basin increased, the variability of SUVA increased, making a specific trend between SUVA and increasing percent forest difficult to discern (Figure 11 c).

### 4.3.2 Stream Chemistry Response to Agriculture

Stream DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  concentrations were significantly ( $p < 0.05$ ) negatively related to percentages of agricultural land in sampled sub-basin sites of the Willamette River basin (Figures 12, 13); SUVA values were not significantly related to agriculture (Figure 13 c, d). DOC concentration was significantly positively related to the percent of agriculture cover ( $r^2 = 0.56$ , Figure 12 a, b). As the proportion of agriculture area in a basin increased from 0 to 2 percent, mean DOC concentration increased from 0.7 to 1.08  $\text{mg C L}^{-1}$ . As agriculture area increased from 2 to 12 percent of the basin area, mean DOC concentration increased by almost one-half (48%, from means of 1.08 to 1.6  $\text{mg C L}^{-1}$ ); an additional 38 percent increase in agriculture from 12 to 50 percent of the basin area resulted in an additional 48 percent increase in mean DOC concentration (from 1.6 to 2.4  $\text{mg C L}^{-1}$ ).

**Figure 12 Relationship of DOC and Nitrate to the Proportion of Agriculture in Sampled Sub-basins of the Willamette River Basin, Oregon, February 12-15, 2009.**

DOC and nitrate are positively related to percent agriculture, (a, b, c, d). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Plotted point colors and shapes indicate the proportion of urban land use in sampled watersheds – legend same for all plots (a). Watersheds with less than detectable nitrate or zero percent agriculture land cover were omitted from regression analyses (b, d).



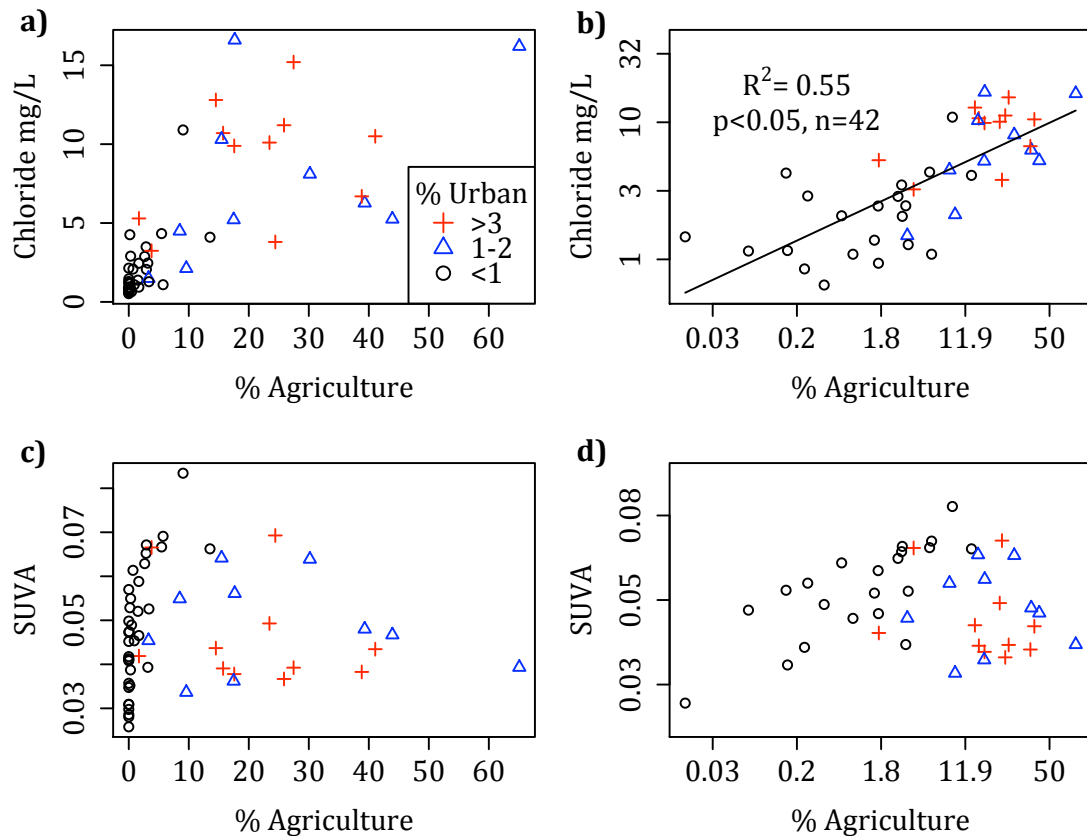
Stream nitrate concentrations were significantly positively related to percent agriculture in sampled sub-basin sites of the Willamette River basin ( $r^2 = 0.56$ ; Figure 12 c, d). As the proportion of agriculture area in a basin increased from 0 to 2 percent, mean nitrate concentration increased from 0.04 to 0.13 mg N L<sup>-1</sup>. As

agriculture area increased from 2 to 12 percent of the basin area, mean nitrate concentration increased by two orders of magnitude (211 percent, from means of 0.13 to 0.43 mg N L<sup>-1</sup>); an additional 38 percent increase in agriculture from 12 to 50 percent of the basin area resulted in an additional 211 percent increase in mean nitrate concentration (from 0.43 to 1.4 mg N L<sup>-1</sup>).

Stream chloride concentrations were significantly positively related to percent agriculture in sampled sub-basin sites of the Willamette River basin ( $R^2 = 0.54$ , Figure 13 a, b). As the proportion of agriculture area increased from 0 to 2 percent, mean chloride concentration increased from 1.4 to 2.7 mg Cl L<sup>-1</sup>. As agriculture area increased from 2 to 12 percent of the basin area, mean chloride concentrations increased by nearly one magnitude (93%, from means of 2.7 to 5.1 mg Cl L<sup>-1</sup>); an additional 38 percent increase in agriculture from 12 to 50 percent of the basin area resulted in an additional 93 percent increase in mean chloride concentration (from 5.1 to 9.9 mg Cl L<sup>-1</sup>).

**Figure 13 Relationship of Chloride and SUVA to the Proportion of Agriculture in Sampled Sub-basins of the Willamette River Basin, Oregon, February 12-15, 2009.**

Chloride is positively related to percent agriculture (a, b) while SUVA ( $\text{abs}_{254} \text{ L}^{-1} \text{ mg}^{-1} \text{ cm}^{-1}$ ) was not linearly related to percent agriculture (c, d). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Plotted point colors and shapes indicate the proportion of urban in sampled watersheds – legend same for all plots (a). Sites with zero percent agricultural land use were not included in regression analyses or log-logit scale plots.



Stream SUVA values were not significantly related to percent agriculture in sampled sub-basin sites of the Willamette River basin (Figure 13 d). SUVA values did appear to decrease with increasing percent agriculture though high variability made a trend difficult to discern (Figure 13 c).

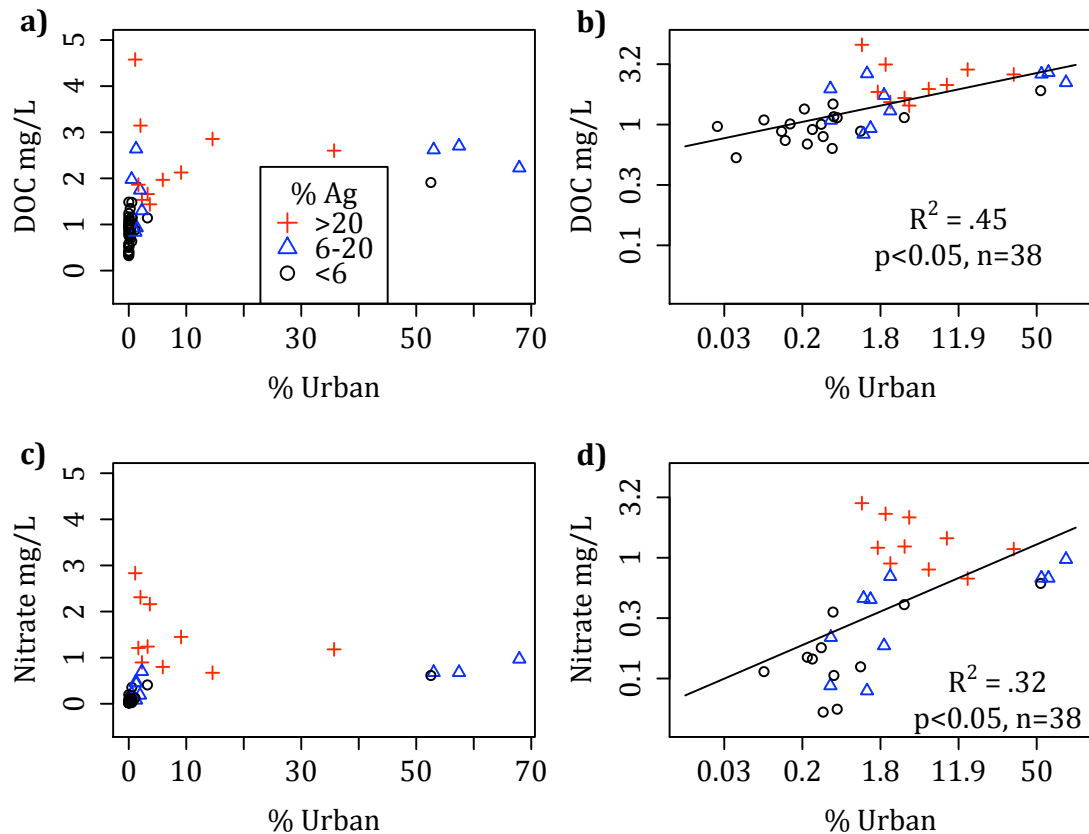
### 4.3.3 Stream Chemistry Relationships to Urban Land Use

Stream DOC,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and SUVA exhibit a non-linear response to percent urban, increasing rapidly with small changes in percent urban but not responding to additional increases in percent urban area (Figures 14 a, b and 15 a, b). After  $\log_{10}$  and logit transformation, stream DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  concentrations were significantly ( $p < 0.05$ ) positively related, while SUVA was significantly ( $p < 0.05$ ) negatively related, to percent urban area in sampled sub-basin sites of the Willamette River basin (Figures 14, 15).

DOC concentration was significantly positively related to the percent of urban cover ( $r^2 = 0.56$ , Figure 14 b). As the proportion of urban area in a basin increased from 0 to 2 percent, mean DOC concentration increased from 1.1 to 1.4  $\text{mg C L}^{-1}$ . As urban area increased from 2 to 12 percent of the basin area, mean DOC concentration increased by almost a third (36%, from means of 1.4 to 2.0  $\text{mg C L}^{-1}$ ); an additional 38 percent increase in urban area from 12 to 50 percent of the basin area resulted in an additional 36 percent increase in mean DOC concentration (from 2.0 to 2.7  $\text{mg C L}^{-1}$ ).

**Figure 14 Relationship of DOC and Nitrate to the Proportion of Urban Area in Sampled Sub-basins of the Willamette River Basin, Oregon, February 12-15, 2009.**

DOC and nitrate are positively related to percent urban area (a, b, c, d). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). Sites with zero percent urban area or less than detectable nitrate concentrations were not included in regressions (b, d).



Stream nitrate concentrations were significantly positively related to percent urban area in sampled sub-basin sites of the Willamette River basin ( $r^2 = 0.29$ ) (Figure 14 c, d). As the proportion of urban area in a basin increased from 0 to 2 percent, mean nitrate concentration increased from 0.2 to 0.4 mg N L<sup>-1</sup>. As urban area increased from 2 to 12 percent of the basin area, mean nitrate concentration

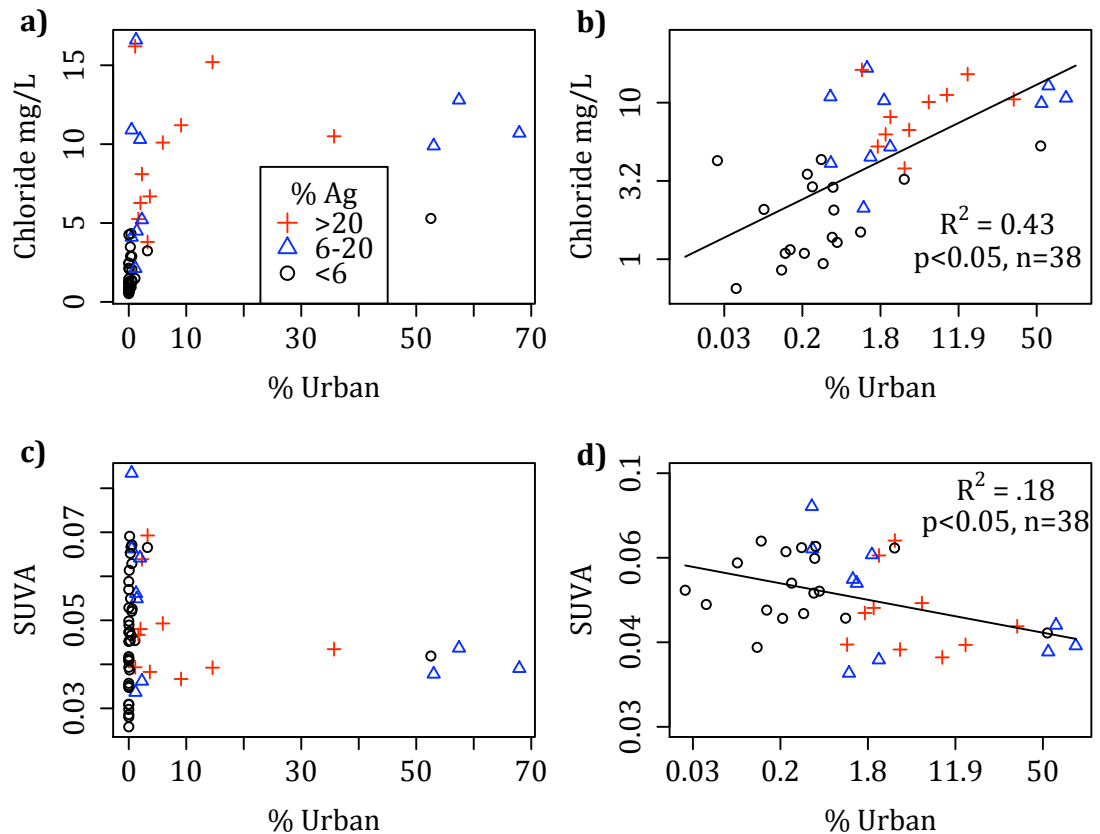
increased by almost one order of magnitude (90 percent) (from means of 0.4 to 0.7 mg N L<sup>-1</sup>); an additional 38 percent increase in urban area from 12 to 50 percent of the basin resulted in an additional 90 percent increase in mean nitrate concentration (from 0.7 to 1.3 mg N L<sup>-1</sup>).

Stream chloride concentrations were significantly positively related to percent urban area in sampled sub-basin sites of the Willamette River basin, ( $R^2 = 0.42$ , Figure 15 a, b). As the proportion of urban area increased from 0 to 2 percent, mean chloride concentration increased from 2.4 to 4.2 mg Cl L<sup>-1</sup>. As urban area increased from 2 to 12 percent of the basin area, mean chloride concentration increased 75 percent (from means of 4.2 to 7.4 mg Cl L<sup>-1</sup>); an additional 38 percent increase in urban from 12 to 50 percent of the basin area resulted in an additional 75 percent increase in mean chloride concentration (from 7.4 to 13.0 mg Cl L<sup>-1</sup>).



**Figure 15 Relationship of Chloride and SUVA to the Proportion of Urban Area in Sampled Sub-basins of the Willamette River Basin, Oregon, February 12-15, 2009.**

Chloride was significantly positively, while SUVA ( $\text{abs}_{254} \text{ L}^{-1} \text{ mg}^{-1} \text{ cm}^{-1}$ ) was significantly negatively, related to percent urban area (a, b, c, d). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Plotted point colors and shapes indicate the proportion of urban in sampled watersheds – legend same for all plots (a). Sites with zero percent urban area were omitted from regressions (c, d).



Stream SUVA values were significantly ( $p < 0.05$ ) negatively related to percent urban area in sampled sub-basin sites of the Willamette River basin though with large variability ( $R^2 = 0.18$ ; Figure 15 c, d). As the proportion of urban area increased from 0 to 2 percent, mean SUVA values decreased (from 0.055 to 0.050  $\text{abs}_{254} \text{ L mg}^{-1} \text{ cm}^{-1}$ ). As urban area increased from 2 to 12 percent of the basin

area, mean SUVA values decreased by 9 percent (from means of 0.050 to 0.046  $\text{abs}_{254} \text{ L mg}^{-1} \text{ cm}^{-1}$ ); an additional 38 percent increase in urban from 12 to 50 percent of the basin area resulted in an additional 9 percent decrease in mean SUVA values (from 0.046 to 0.042  $\text{abs}_{254} \text{ L mg}^{-1} \text{ cm}^{-1}$ ).

#### **4.4 Principal Components Analysis**

Two principal components explained nearly 90 percent of the variance in stream chemistry variables (Table 5). Each axis, or principal component, is comprised of a vector of coefficients and their log-transformed stream chemistry variables DOC,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and SUVA. Ordinations overlain with each site variable are contained in Appendix D. Summary results for each overlay are depicted (Table 6).

**Table 5**      **Variance Explained within Stream Chemistry Variables by PCA Axes**

Eigenvectors (coefficients) for two axes (principal components). Each stream chemistry variable (DOC, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and SUVA) is included in the principal component. Eigenvectors for three axes are listed, values greater than or less than 0.40 are italicized. The percent of variance explained by each axis as well as cumulative percent explained are also included.

	Axis 1	Axis 2
DOC	<i>0.5619</i>	-0.0695
NO3	<i>0.5504</i>	-0.2361
CL	<i>0.5799</i>	-0.0626
SUVA	0.2122	<i>0.9672</i>
% Variance	66.395	23.412
% Cumul. Variance	66.395	89.807

**Table 6**      **Correlation Matrix of Explanatory Variables with Axes 1 and 2**  
Correlations (Pearson's r and Kendall's tau) of site variables (transformed; see methods) with PCA axes.

	Axis 1			Axis 2		
	r	R <sup>2</sup>	tau	r	R <sup>2</sup>	tau
% Ag	0.879	0.772	0.716	0.093	0.009	0.028
% For	-0.877	0.768	-0.679	0.186	0.035	0.077
% Urb	0.831	0.69	0.684	-0.083	0.007	-0.018
% Wet	0.267	0.072	0.146	-0.108	0.012	-0.09
% Open	0.797	0.635	0.676	0.128	0.016	0.011
Elevation	-0.791	0.625	-0.6	-0.056	0.003	0.012
Area	0.084	0.007	0.025	0.037	0.001	0.038

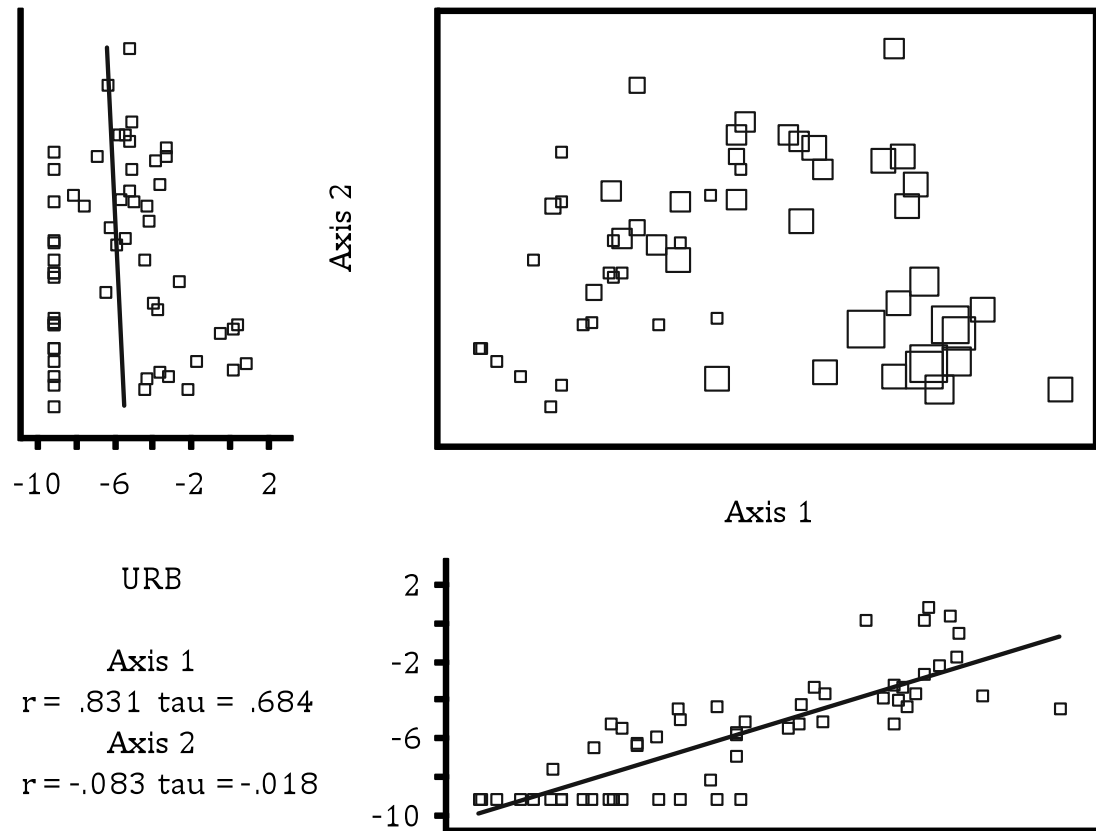
Subsequent to ordination of stream chemistry variables and selection of axes 1 and 2 as having the greatest ability to explain variability, percent agriculture, forest, urban, open and wet area, as well as watershed area and

elevation, were overlain on the two-dimensional plots. Generally speaking, Axis 1 was positively correlated with DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  concentrations, while Axis 2 was positively correlated with SUVA (Table 5).

While urban area is not correlated with Axis 2 ( $r = -0.083$ , small regression plot in upper left corner, Figure 16), there was a distinct clustering of high urban, low SUVA, high DOC, high  $\text{NO}_3^-$  and high  $\text{Cl}^-$  points in the lower right corner of the ordination plot. Urban area was correlated to Axis 1 ( $r = 0.831$ , small regression plot in lower right corner, Figure 16). When only sites with urban area are used in correlations with principal components, the proportion of urban area is more strongly correlated to axis 2 ( $r = -0.69$ ) though less so correlated with axis 1 ( $r = 0.70$ , Figure 17).

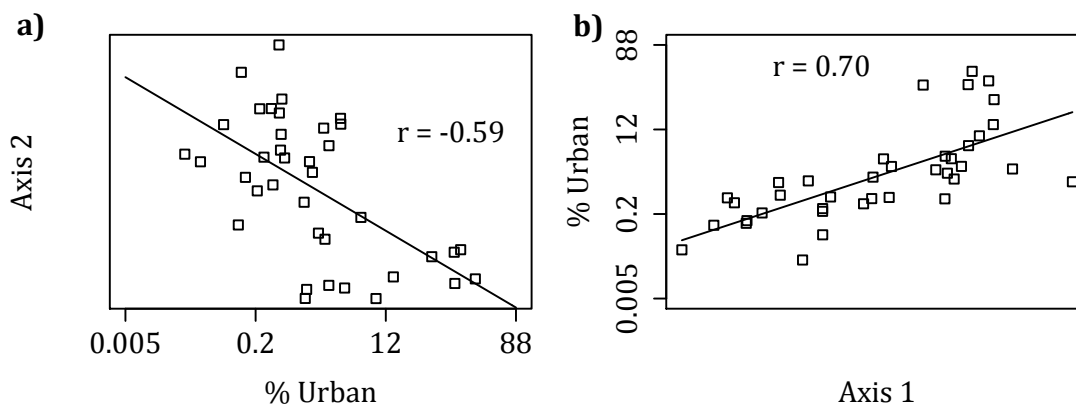
**Figure 16      Ordination of Stream Chemistry along Principal Components  
– Proportion Urban Overlain**

Ordination of stream chemistry along principal components, axes 1 and 2. Size of points within main plot, upper right, indicate proportion of logit-transformed urban area in each sampled watershed. Left-hand plot indicates variation of urban area along Axis 2; Lower right-hand plot indicates variation of urban area along Axis 1.



**Figure 17 Correlation of % Urban Area with Principal Components**

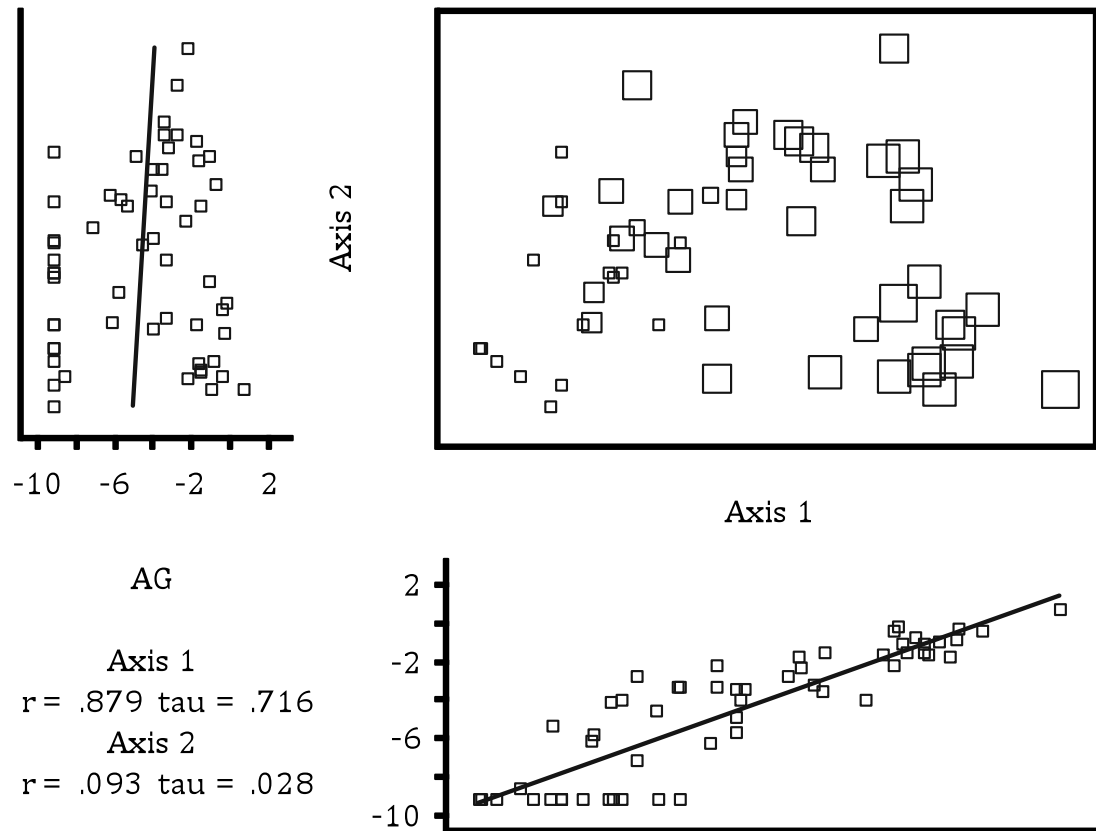
Axes 2 and 1 correlated with the proportion of urban area in sampled watersheds. Sites with no urban area have been omitted from correlations.



Agriculture area was not correlated with Axis 2 ( $r = 0.093$ , small regression plot in upper left corner Figure 18) and there was a tendency for sites with high agricultural area, high DOC, high  $\text{NO}_3^-$ , high  $\text{Cl}^-$ , but low SUVA to cluster toward the right side of the ordination. Agriculture area was correlated with Axis 1 ( $r = 0.879$ , small regression plot in lower right corner, Figure 18, Table 6). When only sites with agricultural area are used in correlations with principal components, the proportion of agricultural area remains poorly correlated to axis 2 (Pearson's  $r = -0.20$ ) and well correlated with axis 1 (Pearson's  $r = 0.70$ , Figure 19).

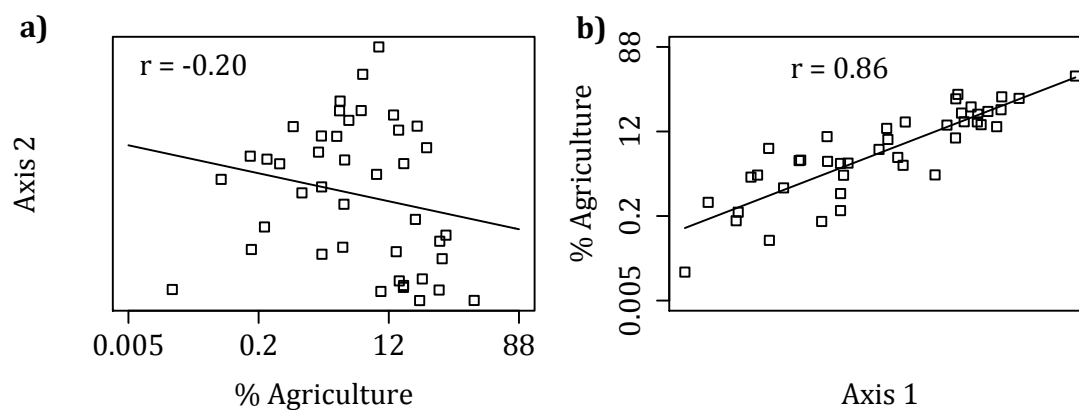
**Figure 18      Ordination of Stream Chemistry along Principal Components  
– Proportion Agriculture Overlain**

Ordination of stream chemistry along two principal components: Axes 1 and 2. Size of plotted points (squares) within main plot, upper right, indicates proportion of logit-transformed agricultural area in each sampled watershed. Left-hand plot indicates variation of agricultural area along Axis 2; Lower right-hand plot indicates variation of agricultural area along Axis 1.



**Figure 19 Correlation of % Agriculture Area with Principal Components**

Axes 2 and 1 correlated with the proportion of agriculture area in sampled watersheds. Sites with no agriculture area have been omitted from correlations.





## 5 Discussion

### 5.1.1 River Continuum Concept in the Willamette River Basin

Nitrate and DOC concentrations were expected to respond similarly to differences in land use among sites, presumably due to in-stream production of DOC stimulated by elevated nitrate levels (hypothesis 1). Furthermore, in-stream production of DOC was expected impart a distinct signature stream DOC, which could be detected by changes in SUVA (hypothesis 2). It was predicted that: <sup>(1)</sup> SUVA would decrease with increasing nitrate concentrations; <sup>(2)</sup> Nitrate and DOC concentrations would increase with increasing percent agriculture and urban area while decreasing with increasing percent forested area; <sup>(3)</sup> SUVA would decrease with increasing percent agriculture and urban area and increase with increasing percent forest area.

The above predictions are consistent with the dominant paradigm describing stream ecosystems, as outlined in the River Continuum Concept (RCC), that predicts the relative dominance of various in-stream controls on stream chemistry at increasing spatial scales. The RCC is borne out of the energy equilibrium theory of fluvial morphologists, where upstream kinetic energy is dissipated downstream in the shape and size of the channel leading to dynamic equilibrium between upstream and downstream morphology. The RCC incorporates biological response along a continuum, whereby energy released

from upstream areas is utilized efficiently downstream, and predicts that biotic communities respond to this dynamic interaction across the longitudinal stream gradient (Vannote et al., 1980).

In general the RCC views headwater systems as heterotrophic, with productivity/respiration (P/R) ratios of less than 1, and receiving particulate matter directly from adjacent terrestrial zones. These materials are processed by stream biota and provide an ecological energy base. As these materials are processed, some of the processed materials are lost to downstream flow, thus increasing the downstream concentration of available nutrients. Biotic communities in downstream reaches are adapted to utilize this nutrient availability. In this manner, downstream reaches dynamically respond to upstream cycling patterns (Vannote et al., 1980).

The RCC predicts that as the observer moves downstream and watershed size and stream order increase, the proportion of nutrients contributed directly by adjacent terrestrial zones is diminished because of the large amount of pre-existing stream nutrients from upstream sources. The proportion of exported materials from nearby terrestrial zones is overwhelmed by the disproportionately large amount of in-stream nutrients already present. In lower reaches, with higher stream orders and larger watershed areas (defined relative to headwater reaches), stream chemistry is dominated by in-stream processing of available nutrients and the system transitions to an autotrophic state,  $P/R > 1$  (Vannote et al., 1980). Objections to the RCC are numerous and generally focus on

whether it can be legitimately extrapolated to large river basin scales as well as its restriction of the river basin to just lentic (non-moving) and lotic (moving) environments while ephemeral and intermittently inundated areas of the basin are excluded (Junk et al., 1989; Sedell et al., 1989; Statzner and Higler; Thorp and Delong, 1994; Thorp et al., 2006; Ward and Stanford, 1983; Winterbourn et al., 1981).

In the Willamette River basin, headwater systems occur in higher elevation, forested areas with steep slopes, high precipitation and quickly draining soils that are less suited to agricultural and urban land uses. These higher elevation areas in the western Cascades of the Willamette River basin receive little atmospheric nitrogen and are typically nitrogen-limited (Sollins et al., 1980; Vanderbilt et al., 2003). A persisting appetite for nitrogen in these systems diminishes the amount of nitrogen available for hydrologic transport. Headwater streams are particularly suited for efficient retention of inorganic nitrogen species, in part due to a legacy of low-nitrogen availability, and also because of headwater stream morphology. Headwater streams have high surface area to volume ratios, maximizing available substrate area for microbial nutrient uptake (Peterson et al., 2001).

This ability of headwater streams to efficiently retain nitrogen species was demonstrated in the LINX studies (Lotic Intersite Nitrogen Experiment). The LINX I (ammonium) and LINX II (nitrate) addition experiments used labeled nitrogen species ( $^{15}\text{N-NO}_3^-$  and  $^{15}\text{N-NH}_4^+$ , respectively) to directly measure

nitrogen uptake and found that these nitrogen species were rapidly and efficiently cycled in headwater streams (Ashkenas et al., 2004; Mulholland et al., 2008; Peterson et al., 2001). Ammonium was rapidly consumed and most transformed into nitrate. There was also direct evidence that adjacent riparian vegetation removed ammonium from the stream channel directly, supporting the dominance of associated terrestrial areas on headwater stream systems as purported by the RCC. Nitrate was also utilized quickly, though with a slower uptake velocity than ammonium; meaning the average nitrate molecule travelled further downstream before being incorporated or transformed. Nitrate uptake efficiency decreased with increased nitrate concentration; stream biota increased nitrate uptake as concentration increased but not in direct proportion, leading to a decrease in the total proportion of nitrate removed from the stream column.

### 5.1.2 Stream Chemistry in the Willamette River Basin Reflects Land Use

Stream chemistry in the Willamette River basin during winter, baseflow conditions relates strongly to watershed land use characteristics. Stream DOC,  $\text{NO}_3^-$  and  $\text{Cl}^-$  are significantly related to the proportion of urban, agriculture and forest area as well as elevation. SUVA values are more variable, though significantly related to the proportion of urban area in basins.

Observed nitrate concentrations during winter baseflow conditions in the Willamette River basin are significantly negatively related to increasing percent forest, which is in agreement with previous studies reflecting the ability of

nitrogen-limited catchments to efficiently retain inorganic nitrogen species (Ashkenas et al., 2004; Peterson et al., 2001). All of the 23 sites with less than detectable levels of nitrate have more than 90 percent forest area. It should be noted however, that some nitrogen-limited catchments export a significant amount of nitrogen as organic materials (Perakis and Hedin, 2002) and that while multiple studies have focused on inorganic nitrogen cycling rates and measured losses from catchments, the loss of organic materials and in-stream cycling of organic materials is less understood.

In addition to biotic controls on stream nutrient concentrations, hydrology exerts strong influence on the type and quantity of exported solutes. Precipitation events are important contributors to the flux of dissolved nutrients from forested catchments (Hinton et al., 1997). Studies conducted during intense precipitation events (non-baseflow conditions) in small, forested catchments at the HJ Andrews in the Willamette River basin indicate that, during baseflow conditions, stream water is generally reflective of groundwater sources with low DOC concentrations and SUVA values (Hood et al., 2006; van Verseveld et al., 2008; van Verseveld et al., 2009).

Observed DOC concentrations and SUVA values from predominately forested catchments during winter baseflow conditions reflect low DOC concentrations and low SUVA values observed in groundwater in previous studies (Hood et al., 2006; van Verseveld et al., 2008; van Verseveld et al., 2009). Some of the lowest SUVA values occur in the most forested catchments, however,

SUVA is highly variable with increasing percent forested area. The high variability observed in this study could be reflective of multiple hydrologic flowpaths at larger catchment scales. While previous studies (Hood et al., 2006; van Verseveld et al., 2008; van Verseveld et al., 2009) relating low SUVA values to groundwater focused on small catchments (< 1000 ha), the large range in size of forested catchments of this study (the average size of the 34 catchments with more than 90 percent forest was 9,730 ha) likely contain sub-basins whose baseflow periods retain hydrologic connections with the surface soil horizons, which are known to impart high SUVA values during storm events (van Verseveld et al., 2008; van Verseveld et al., 2009) .

DOC and  $\text{NO}_3^-$  were significantly positively related to increasing agriculture and urban area in the sampled sub-basins of the Willamette River basin (Figures 13-16), suggesting in-stream production of DOC due to increased nitrate availability. It appears likely that direct application of fertilizer is contributing to elevated nitrate levels in agricultural catchments during winter baseflows in the Willamette River basin, which could explain the sharp increase in nitrate with small increases in proportion of the catchment used by agriculture. Atmospheric deposition in the western Cascades was found to be around  $1.6\text{-}2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  while a standard application rate for grass seed production (a predominant type of agricultural land use in the Willamette River basin) is  $169\text{-}199 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Vanderbilt et al., 2003; Youngberg, 1980).

The results of this work indicate a strong stream chemistry signal from the valley floor of the Willamette River basin. Given the high rate of nitrogen addition in agricultural areas, adjacent land use appears to account for more of the observed trends in stream chemistry than did differences in catchment size or stream order. While at large scales the proportion of catchment land use remains mostly forest (~72% for the largest sub-basin – 21,553 km<sup>2</sup>), as streams enter the valley they appear to be increasingly influenced by the adjacent terrestrial land use within the valley, more than would be predicted by the RCC.

The increased availability of stream nitrate is predicted to decrease SUVA values as in-stream production increased. SUVA values, however, show great variability across land use and elevation and are not related to percent forest or percent agriculture. SUVA values are negatively related to increasing percentages of urban area in sampled sub-basins, however, only 16% of the variability in SUVA is explained by the proportion of urban area in sampled watersheds. SUVA values were negatively correlated with nitrate concentrations, which increase significantly with the percentages of agriculture and urban land use (and decreased with percentages of forested land use). The positive relationship of nitrate and DOC concentrations to percentages of urban land use, taken with the negative relationship of SUVA values to percentages of urban area, suggest that in-stream carbon production may be a strong control of DOC in urban catchments.

Given the positive relationships of nitrate and DOC with percentages of agricultural land use, it follows that SUVA values should reflect predominantly in-stream production of DOC with increasing proportions of agriculture. However, SUVA values are not related to proportions of agriculture area in catchments, indicating that in-stream production was not the only source of DOC in catchments with large proportions of agriculture area. High SUVA values in catchments with large proportions of agriculture area may indicate that refractory sources of carbon have direct hydrologic connections to the stream.

### 5.1.3 The Flood Pulse Concept in the Willamette River basin

In contrast to the RCC, the Flood Pulse Concept (FPC) seeks to incorporate the river's floodplain into the over-arching paradigm used to understand basin behavior and predict basin response to change (Junk et al., 1989). The FPC maintains that, at large scales, basin response becomes discontinuous and compartmentalized according to the specific physical and biological forces of near-stream areas (lateral influence), while still reflecting the inputs and integrated in-stream processing from upstream compartments (longitudinal influence). Rather than describing the stream as a physical continuum, increasing in discharge and decreasing in connectivity to the system it flows through, the FPC includes the interconnectivity of the stream to its floodplain environment as an integral component explaining large river basin behavior and productivity (Junk et al., 1989).



The FPC was developed primarily for large river basins that experience natural flows (non-dammed) but is also applicable to river basins whose floodplains experience periods of frequent inundation – whether from bank overflow, elevated groundwater tables, or precipitation-induced overland flow. These frequent but temporary hydrologic events can facilitate the rapid exchange of organic and inorganic materials between the floodplain and stream channel (Junk et al., 1989).

The valley floor of the Willamette River basin has the potential to rapidly develop surface connectivity during intense precipitation. A combination of seasonal precipitation, near-surface groundwater tables and slow soil drainage characteristics contribute to the valley floor hydrologic response during the wet season (October – April). The Willamette River basin experiences a Mediterranean climate, with little or no rainfall through the summer followed by a wet winter. As dry soils in the valley wetten with the onset of fall rains, the groundwater table is elevated and soils become saturated. After this wetting-up period, small increases in precipitation can overcome the ability of the soil to transmit water, both because of intersecting groundwater tables with the soil surface and surface saturation. Saturation results in flooding low-lying areas and the development of intermittent and ephemeral stream channels that rapidly connect to the main stream channel. Stream networks, the total length of stream channels in a given area ( $\text{km km}^{-2}$ ), expand during the winter during and after frequent, intense rainfall events, leading to an overall two-order increase in

magnitude of stream networks (Wigington Jr et al., 2003; Wigington et al., 2005). The development of saturated areas that directly route water from adjacent terrestrial land uses to the stream is important for understanding sources of water and water solutes in the stream channel.

This study targeted sampling to coincide with the wet season when valley and hillslope soils are closest to saturation and terrestrial areas have maximum hydrologic connectivity to the stream. Once rains cease in spring, valley soils slowly drain and groundwater tables fall, contracting stream networks to the perennial channels. It is likely that, had a basin-wide synoptic sampling event occurred during summertime, distinctly less terrestrial influence in downstream sites would be evident and downstream reaches would more closely reflect upstream inputs, as predicted by the RCC. The relative dominance of upstream inputs on stream chemistry in downstream catchments would most likely be contributable the lack of hydrologic connectivity between agricultural soils and stream channels - the valley floor generates little streamflow after it loses saturation and the groundwater tables recede.

The Willamette River basin appears to express strong landscape controls on stream chemistry during the winter baseflow period, which corroborates results from other studies linking DOC export to land use during precipitation events (Vidon et al., 2008). Results contradict results of others who find a strong association between forested catchments and increased DOC export, though the low proportion of wetlands in the Willamette River basin makes direct

comparison difficult (Dalzell et al., 2007). The high variability of SUVA values in agricultural catchments is probably explained by a direct hydrologic connections between agricultural soils and the stream channel; this inference and supported by other studies in the Willamette River basin that documented expansion of stream networks during winter storm events (Wigington et al., 2005).

## 6 Conclusion

Stream DOC,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  concentrations are significantly related to land use during winter baseflow conditions in sub-basins of the Willamette River basin. Stream DOC, nitrate, and chloride concentrations are positively correlated with one another and increase with proportions agriculture and urban area, and decrease with proportions of forest area in sampled sub-basins. SUVA values decrease with proportions of urban area in sampled sub-basins and are negatively correlated with nitrate concentrations but are not significantly related to DOC,  $\text{Cl}^-$ , or other land uses.

In general, the River Continuum Concept, (Vannote et al., 1980), explains much of the variability in stream chemistry across sampled sub-basins in the Willamette River basin. A typical Willamette River basin stream begins in the forested upland catchments of the Cascades and Coast Ranges, continues down-slope through the agriculturally developed valley, and then travels through the highly urbanized areas within the floodplain of the Willamette River. Sampled streams in forested watersheds have low nitrate and DOC concentrations, indicative of low-nutrient environments with efficient retention mechanisms.

As streams travel through agricultural and urban areas, high nitrate and DOC concentrations indicate strong terrestrial N loading and in-stream production. The decreasing SUVA values with increasing percent urban land use probably suggest the strong role of in-stream carbon production in urban streams. Despite higher nitrate and DOC concentrations in sampled streams with

high percent agriculture, SUVA values are highly variable and indicate multiple sources of stream DOC, potentially from in-stream production (low SUVA) and from hydrologically connected surface runoff (high SUVA) from nearby agricultural soils.

The Flood Pulse Concept, (Junk et al., 1989), however, appears better able than the RCC to explain observed stream chemistry during winter baseflow conditions in the Willamette River basin. While some in-stream production is evident, as the RCC predicts, the high variability of SUVA indicates strong inputs from nearby agricultural areas and is best explained by the FPC. The FPC incorporates the lateral influence of the floodplain, which builds up organic materials that are quickly transported to the stream network at moments when the floodplain is in direct hydrologic connection to stream channels. Agricultural areas of the Willamette River basin are concentrated in the valley floor, the historic floodplain of the Willamette River. The FPC emphasizes the importance of near-stream areas in exporting material to the stream and can account for the high variability of SUVA values observed in catchments with relatively large proportions of agricultural area.

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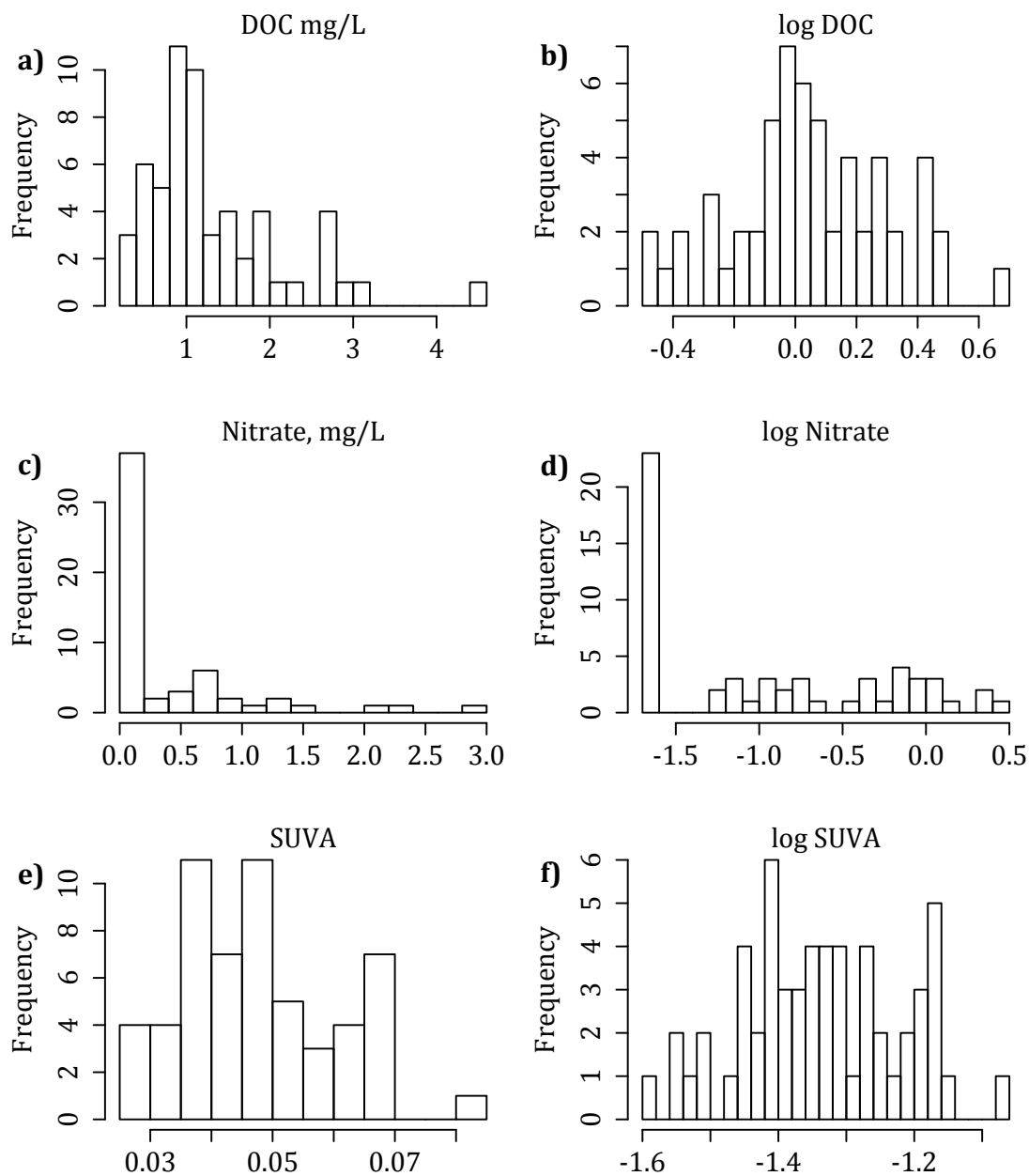
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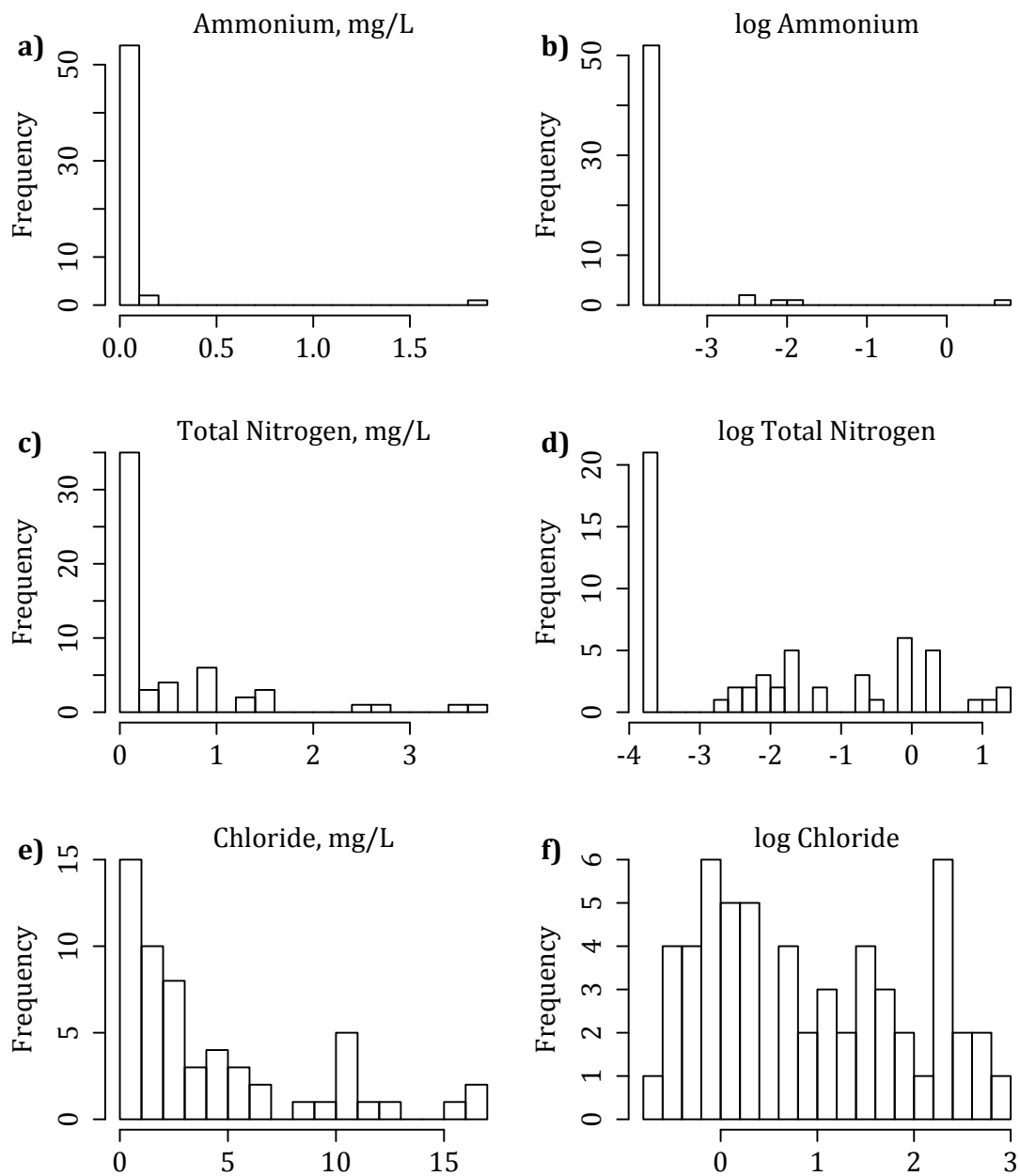
## **APPENDICES**

## Appendix A Histograms of Untransformed and Transformed Variables

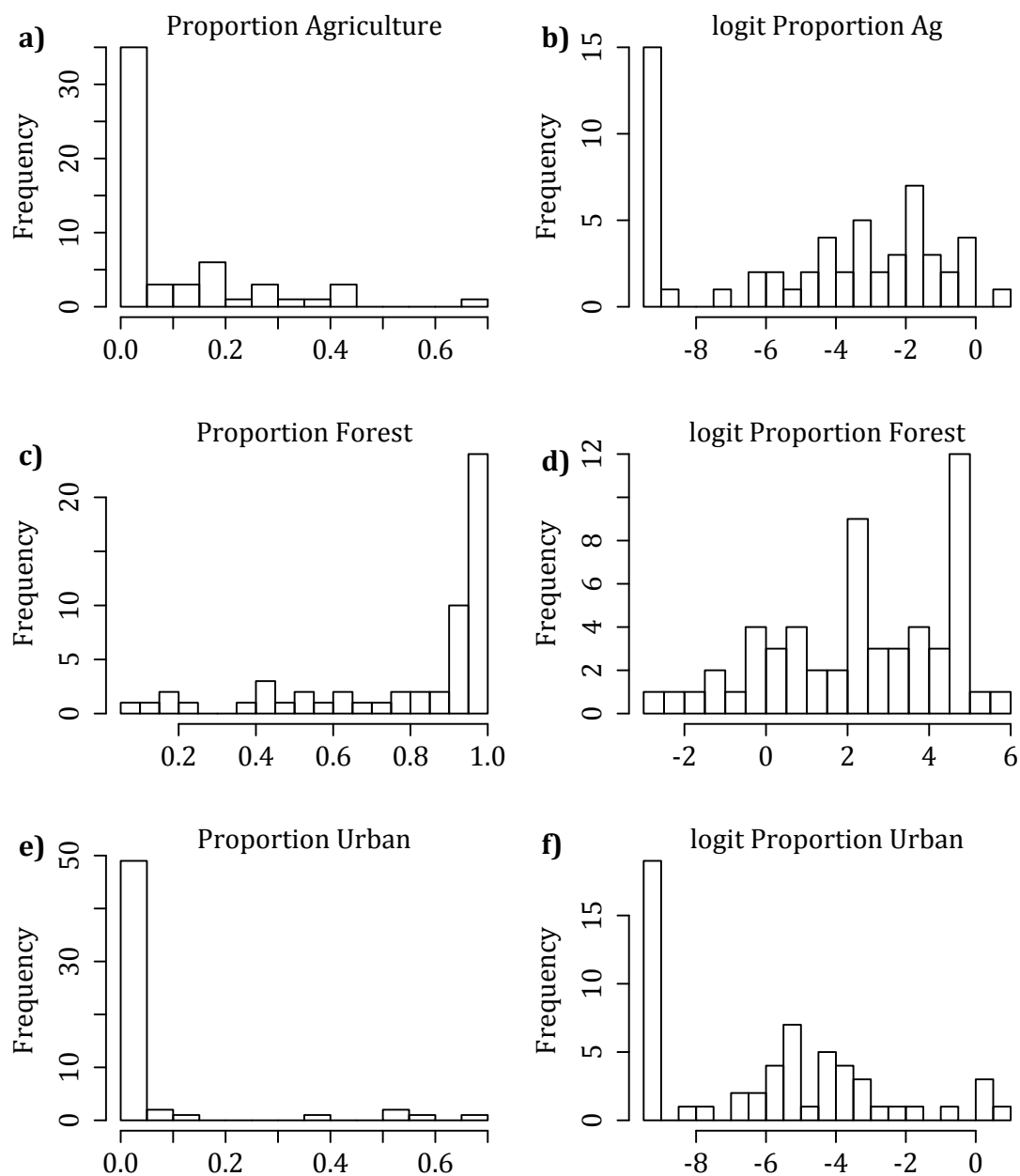
Appendix A1. Histograms of Untransformed and Transformed DOC and Nitrate Concentrations and SUVA values



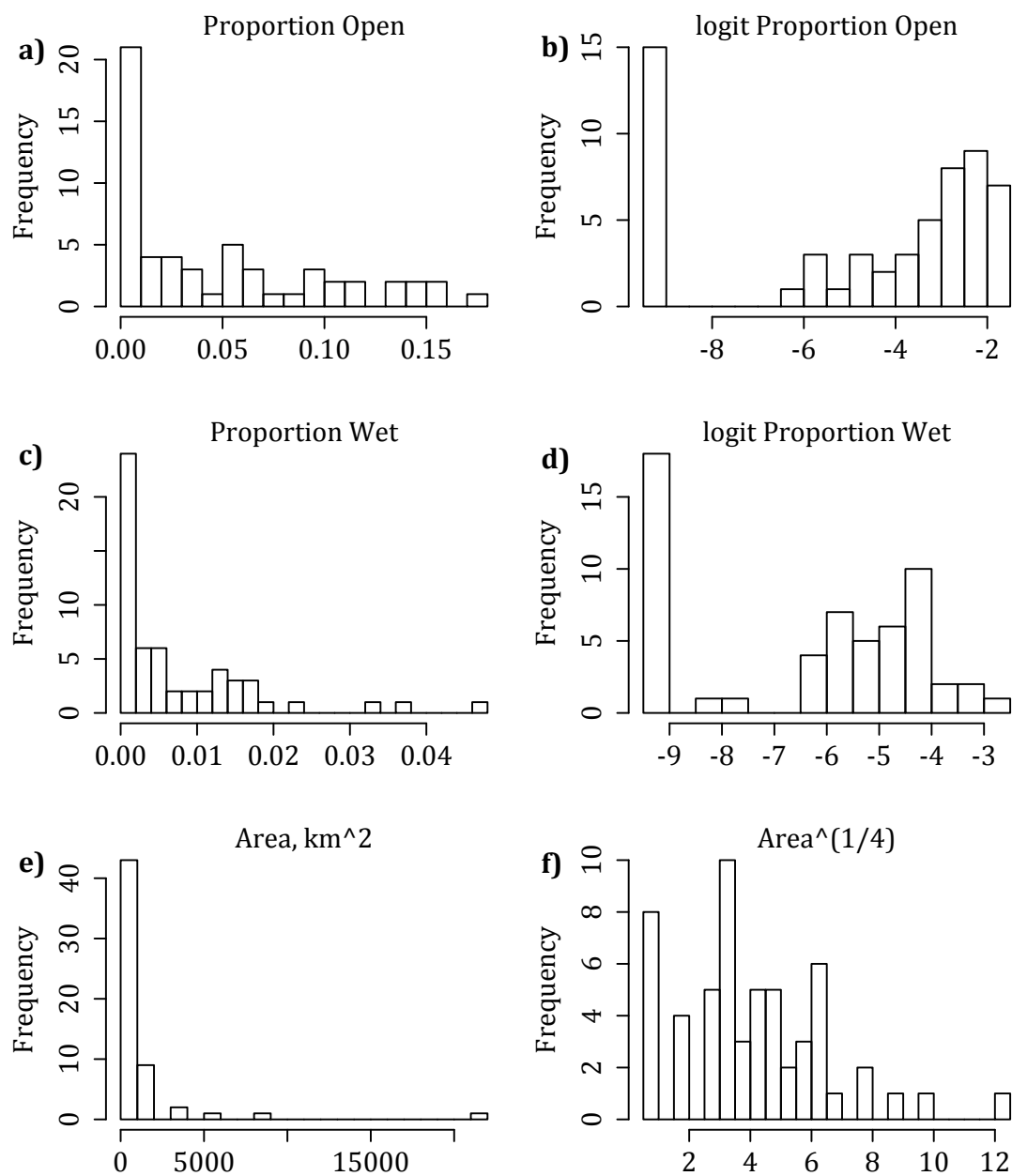
Appendix A2. Histograms of Untransformed and Transformed Ammonium, Total Nitrogen and Chloride Concentrations.



Appendix A3. Histograms of Untransformed and Transformed Proportion of Agriculture, Forest, and Urban Land Use.

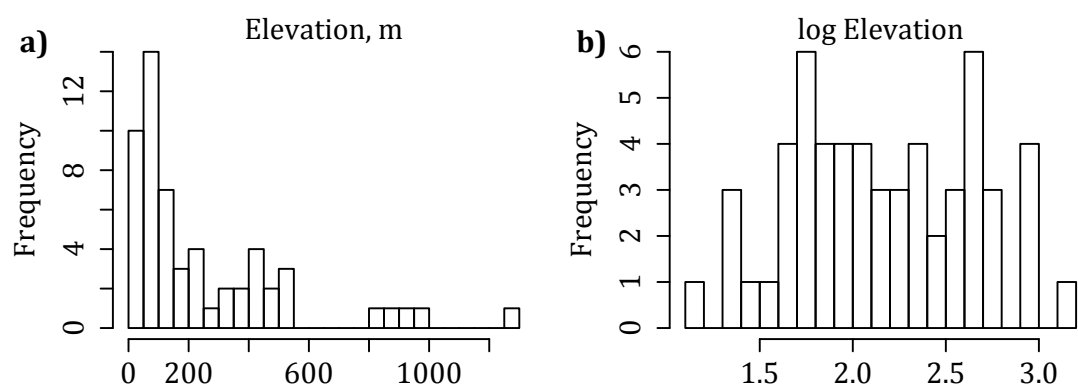


Appendix A4. Histograms of Untransformed and Transformed Proportion of Open and Wet Land Use and Watershed Area.



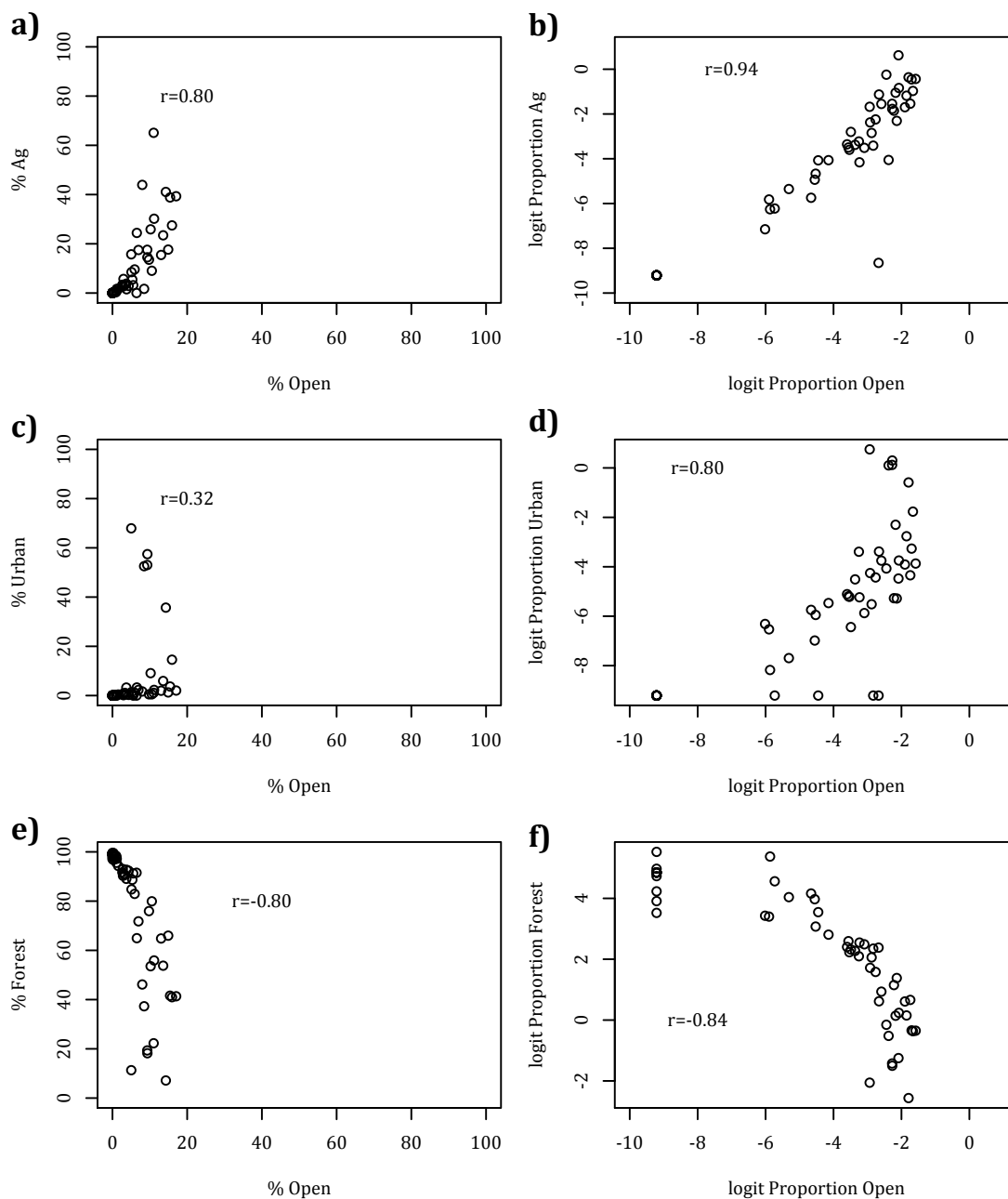


## Appendix A5. Histograms of Untransformed and Transformed Elevation.

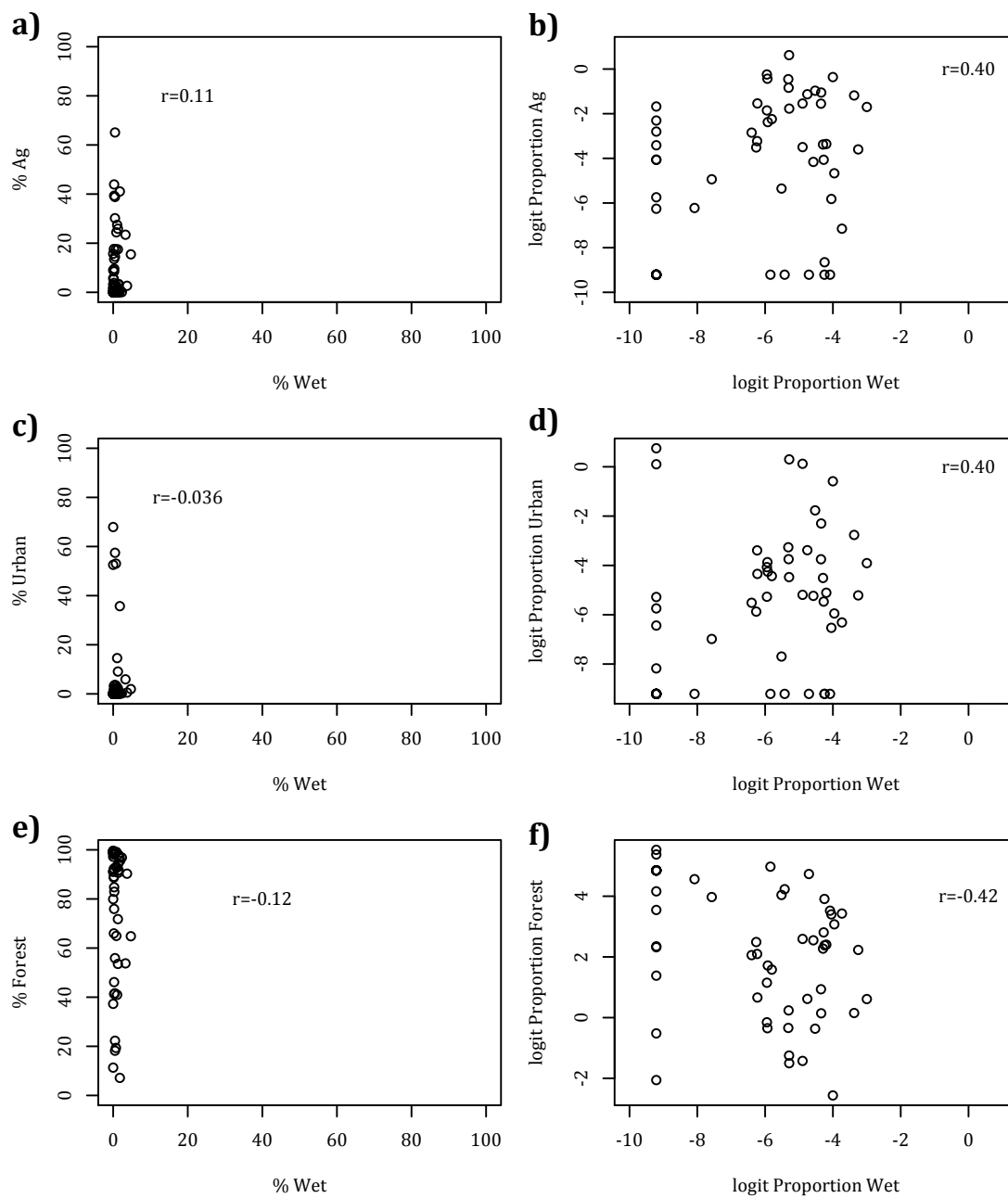


## Appendix B: Correlation of Proportion of Wet and Open Area with other Watershed Characteristics

Appendix B1. Correlations of Proportion Open Area with Proportion Agriculture, Urban and Forest

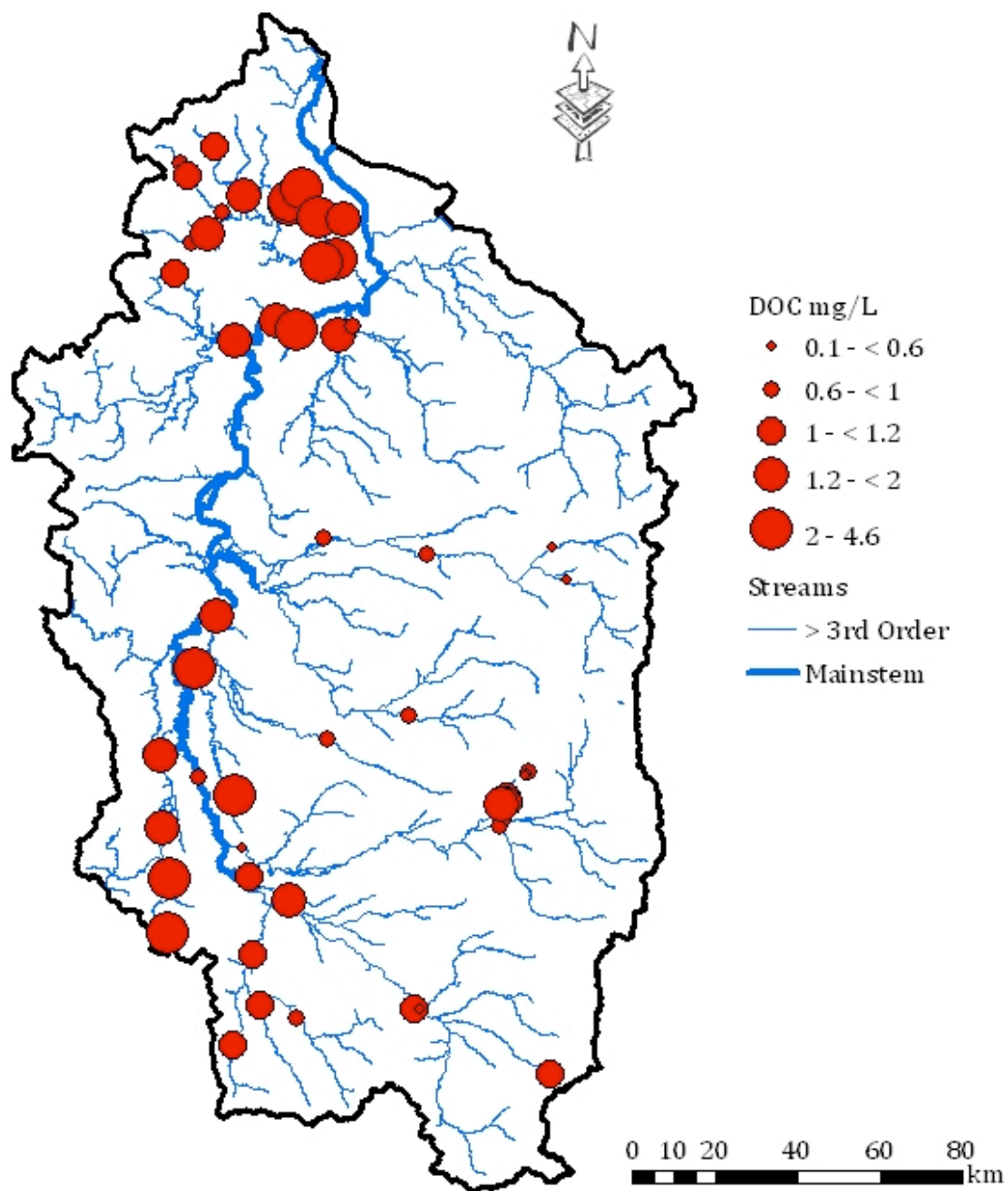


## Appendix B2 Correlations of Proportion Wet Area with Proportion Agriculture, Urban and Forest

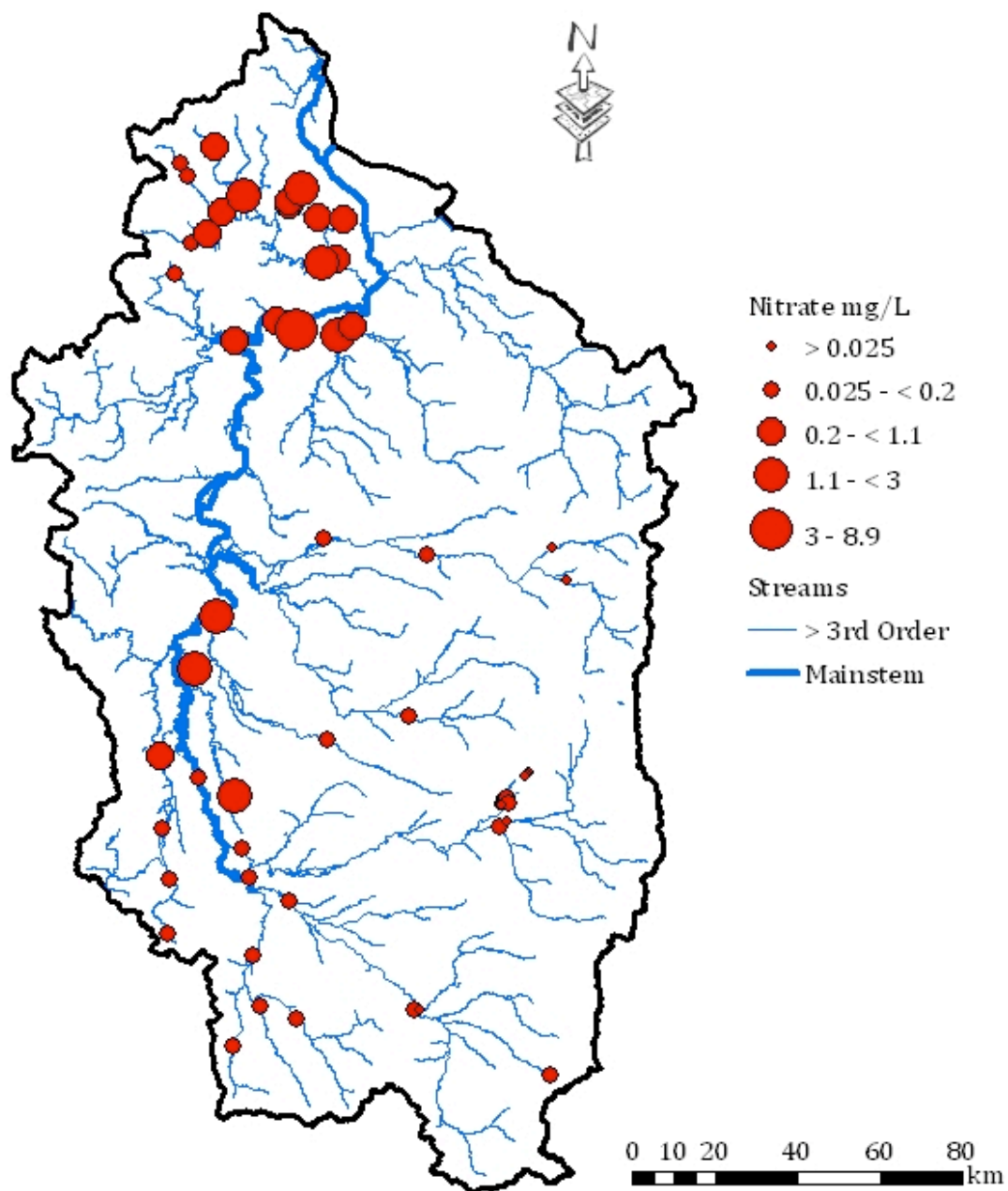


## Appendix C: Stream Chemistry Maps

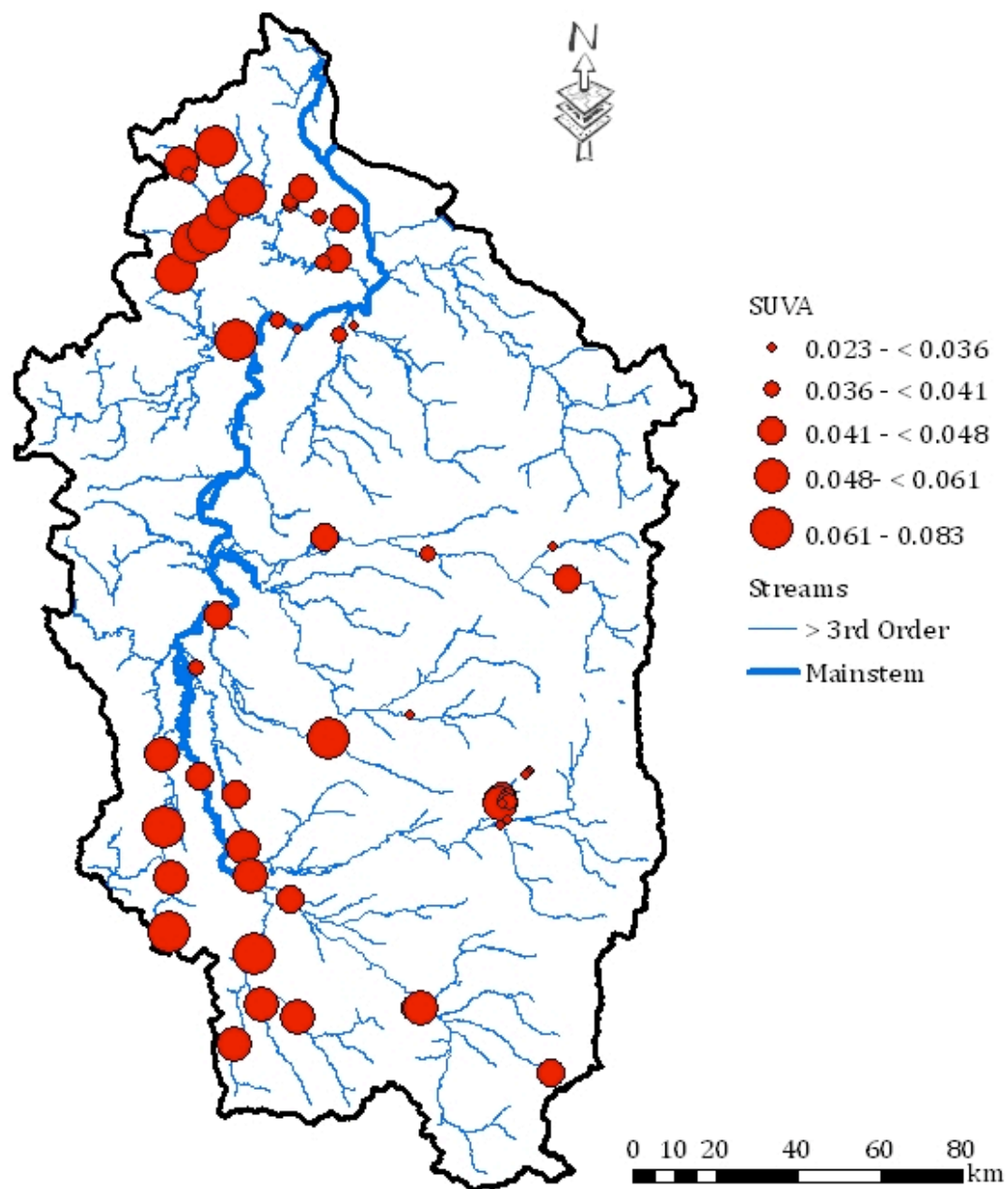
Appendix C1. Map of DOC Concentrations from Sub-basins in the Willamette River Basin during February 13-16, 2009



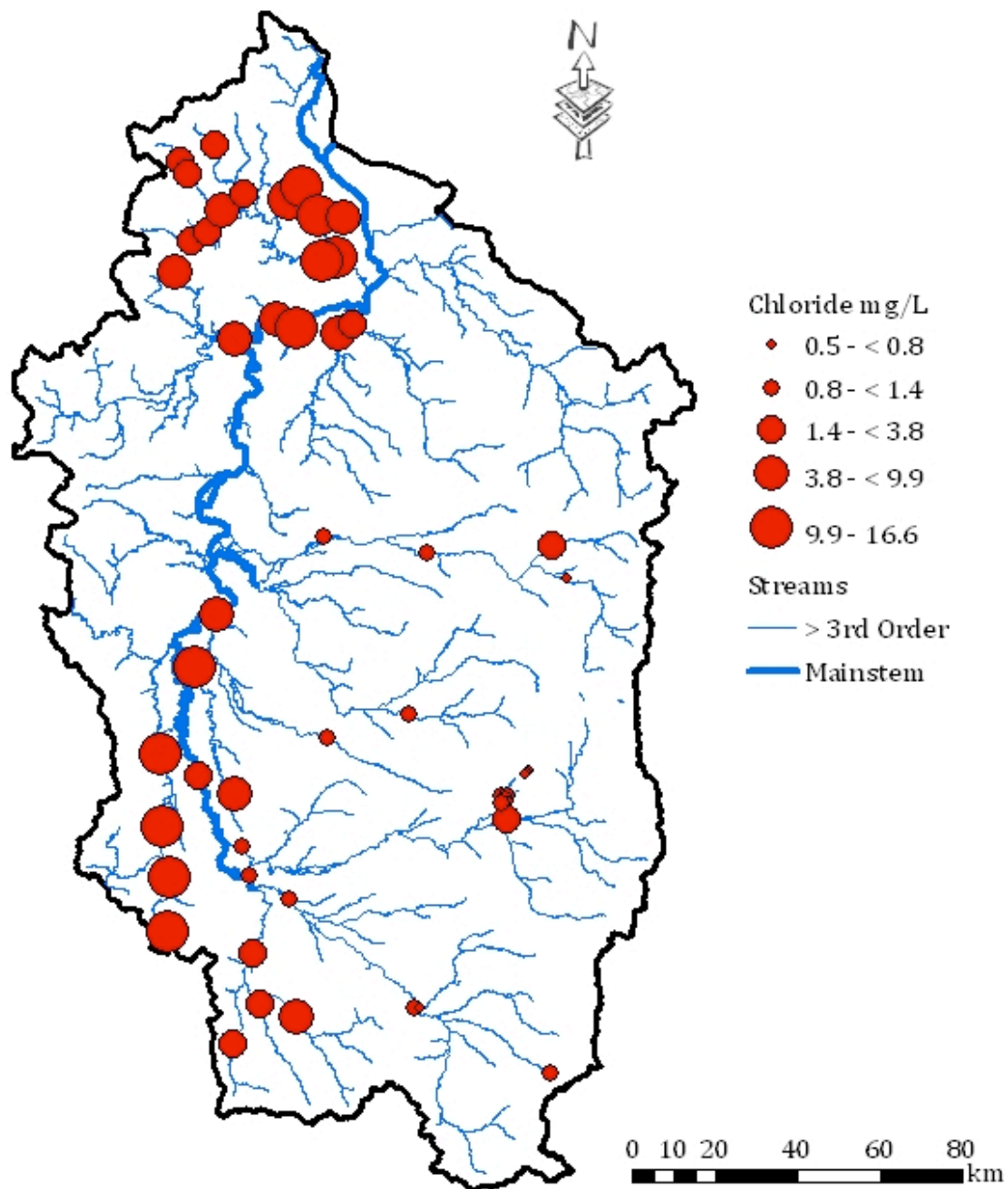
Appendix C2. Map of Nitrate Concentrations from Sub-basins in the Willamette River Basin during February 13-16, 2009



Appendix C3. Map of SUVA Values from Sub-basins in the Willamette River Basin during February 13-16, 2009



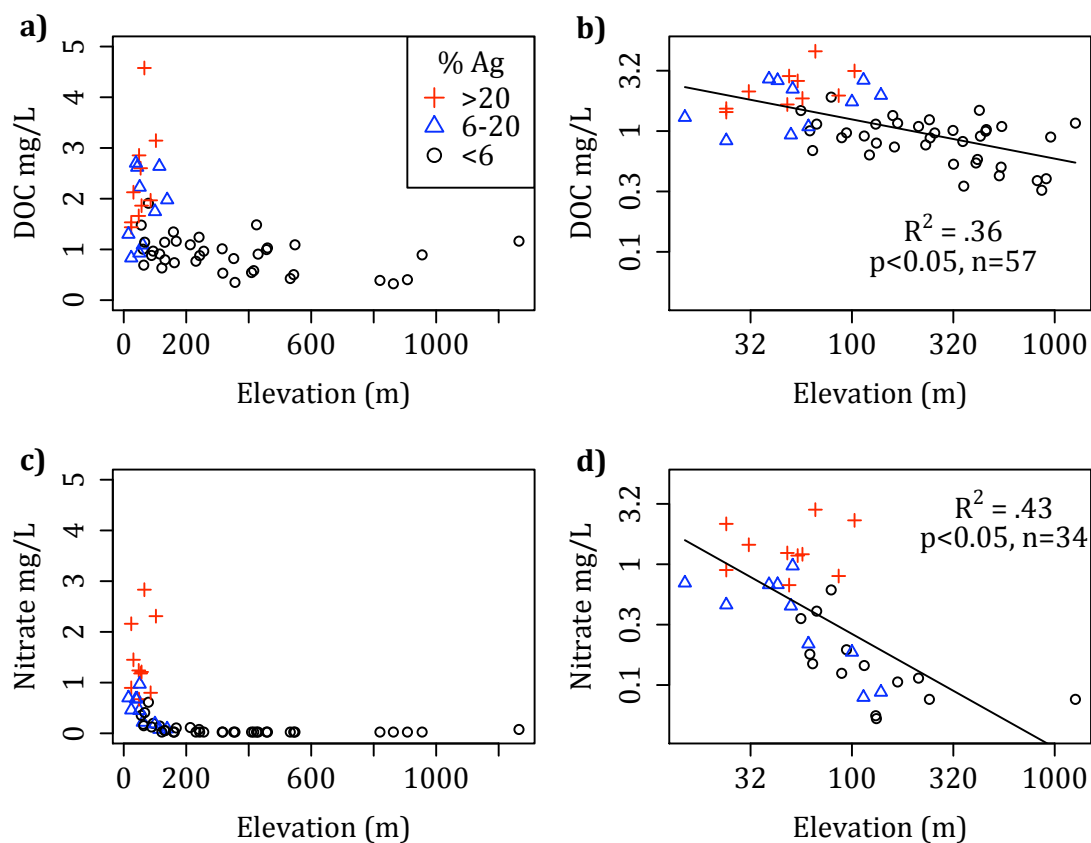
Appendix C4. Map of Chloride Values from Sub-basins in the Willamette River Basin during February 13-16, 2009



## Appendix D: Relationship of Stream Chemistry to Elevation

### Appendix D1. DOC and Nitrate Relationships with Elevation

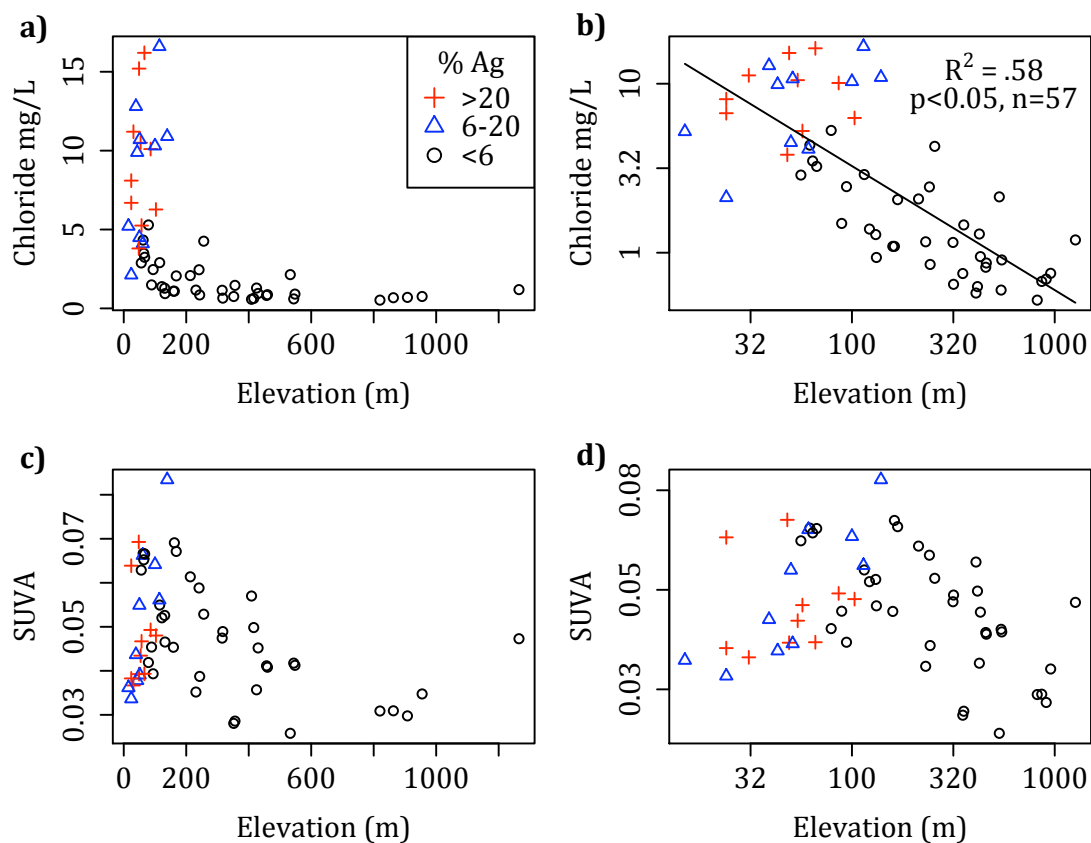
DOC and nitrate were negatively related to elevation (a, b, c, d). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Plotted point colors and shapes indicate the proportion of agriculture in sampled watersheds – legend same for all plots (a). Sites with zero less than detectable levels of nitrate were omitted from regression analysis (d).





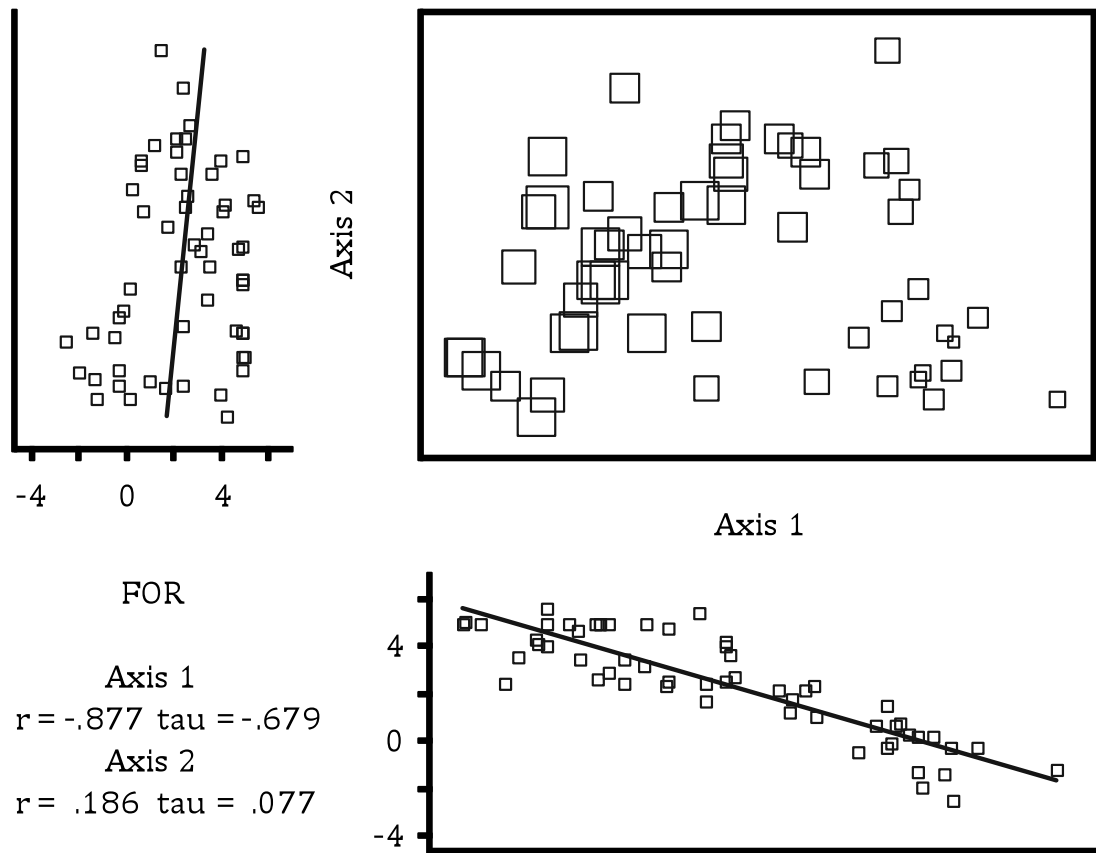
## Appendix D2. Chloride and SUVA relationships with Elevation.

Chloride was negatively related to elevation, while SUVA ( $\text{abs}_{254} \text{ L}^{-1} \text{ mg}^{-1} \text{ cm}^{-1}$ ) was not related to elevation (a, b, c, d). Linear scale plots (a, c) and log-logit scale plots with regression models (b, d) are depicted. Plotted point colors and shapes indicate the proportion of urban in sampled watersheds – legend same for all plots (a).

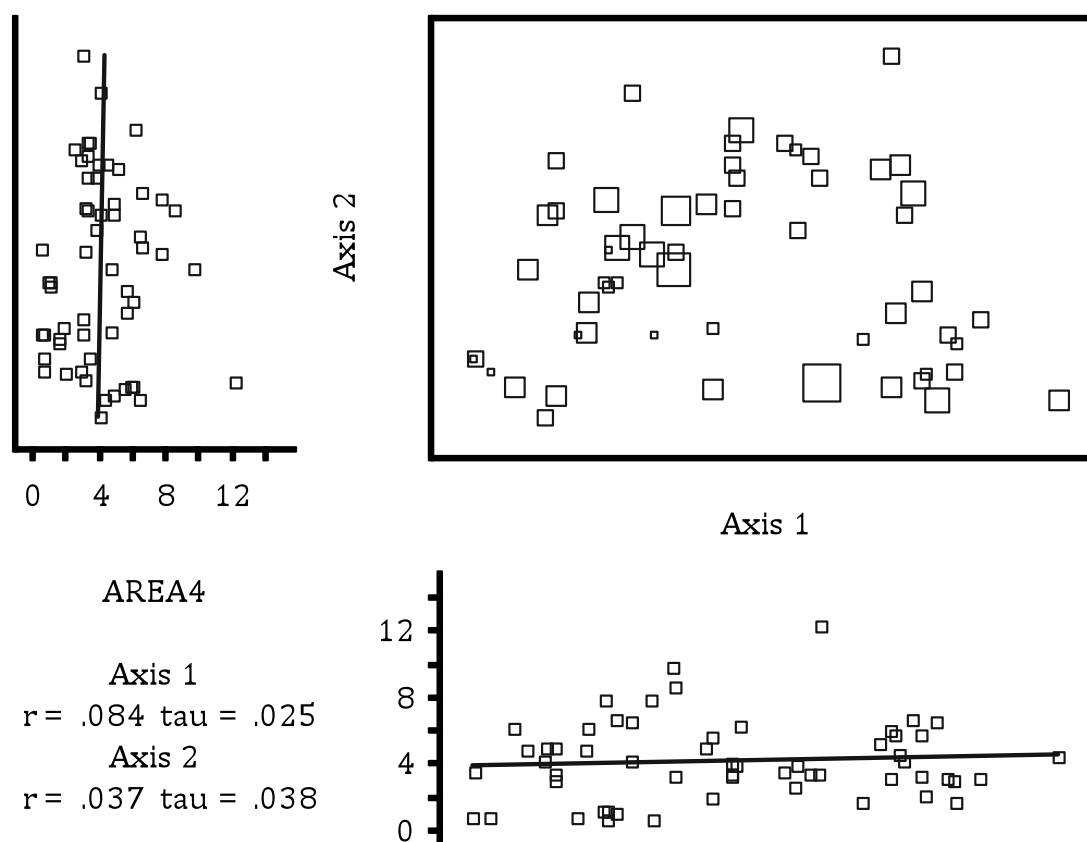


## Appendix E: Principal Components Analysis

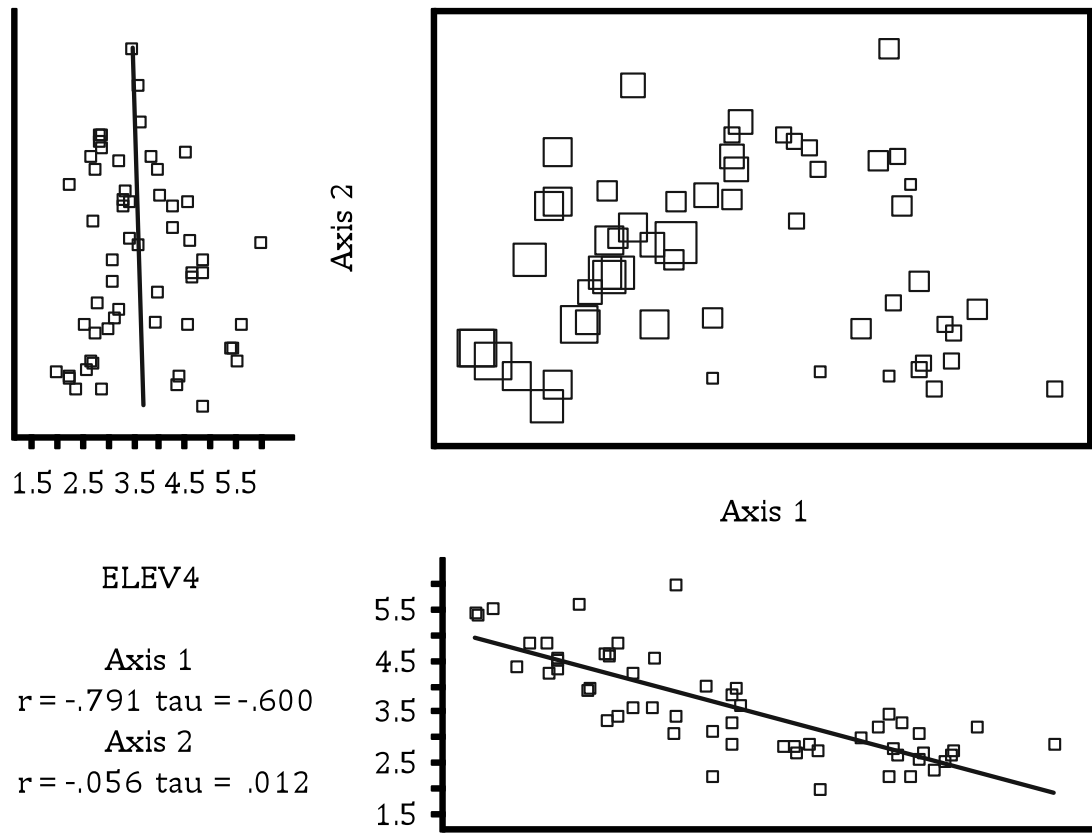
### Appendix E1. Principal Components Analysis with Percent Forest Overlain



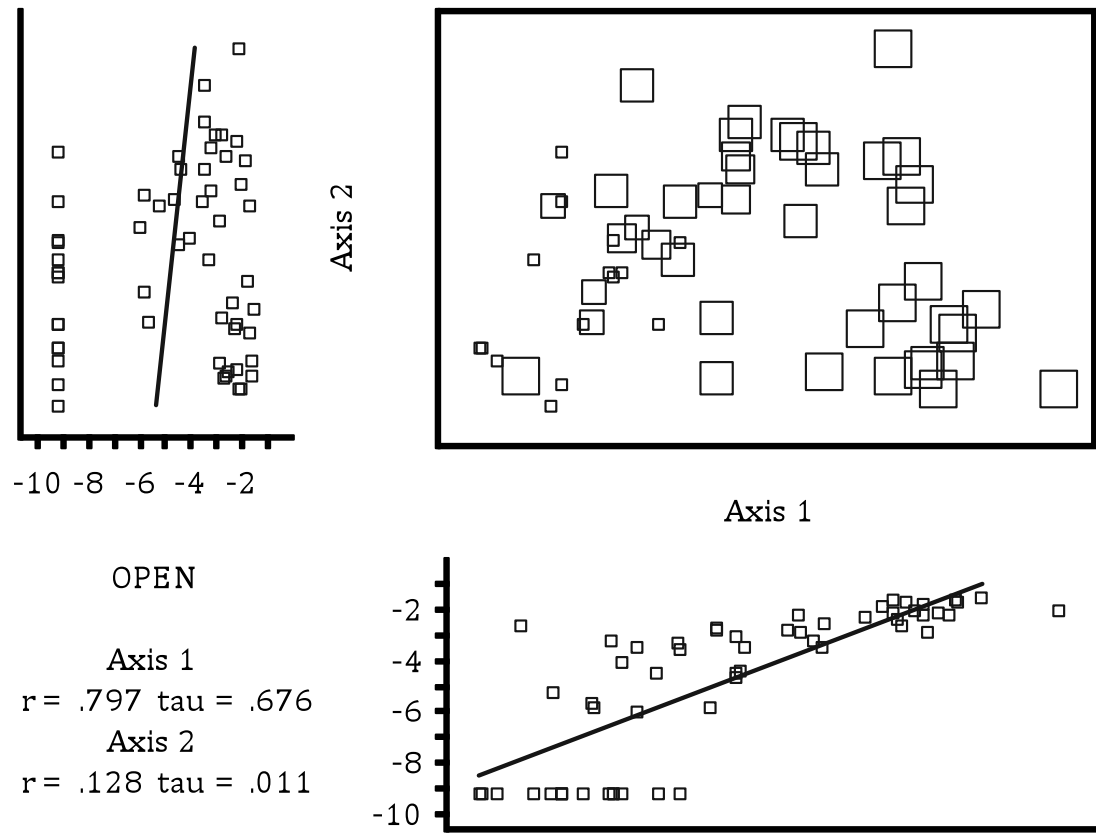
# Appendix E2. Principal Components Analysis with Watershed Area Overlay



## Appendix E3. Principal Components Analysis with Elevation Overlain



#### Appendix E4. Principal Components Analysis with Percent Open Overlain



# Appendix E5. Principal Components Analysis with Percent Wet Overlain

