Land Use Impacts on Water Quality in Oak Creek Watershed

by
Keira Johnson

A THESIS

submitted to

Oregon State University

Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Environmental Science
(Honors Scholar)

Presented May 29, 2020
Commencement June 2020

AN ABSTRACT OF THE THESIS OF

Keira Johnson for the degree of Honors Baccalaureate of Science in Environmental Science presented on May 29, 2020. Title: Land Use Impacts on Water Quality in Oak Creek Watershed.

Abstract approved:_____

Carlos Ochoa

Understanding the relationships between land use, water quality, and groundwater is crucial for ecological, economic, and water management decisions. This study aims to provide a comprehensive analysis of the land use activities and hydrologic processes influencing the water quality of Oak Creek watershed. Objectives of this study were: 1) to determine land use influence on stream water anion concentration along a longitudinal gradient; 2) to assess potential effects of stream-aquifer interaction on stream water quality; and 3) to determine potential origins and seasonal variability of surface water flow. Water samples were collected between January 2018 and November 2019 from 22 stream sites and 19 shallow groundwater wells in Oak Creek watershed spanning forested, agricultural, and urban land use. All samples were analyzed for anion (i.e., chloride, sulfate, nitrate, phosphate) concentrations and stable isotopes of water. Results indicate that: 1) Oak Creek acts as an integrator of precipitation received in high elevations and incoming ground and surface water sources as it moves downstream driving overall stability of isotopic compositions but leading to increasing chloride and sulfate concentrations; 2) shallow groundwater in agricultural settings exhibits high spatial variability; and 3) land use – water quality relationship are complex and temporally variable.

Key Words: land use, water quality, water isotopes, groundwater-surface water interaction

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APPROVED:

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J Renée Brooks, Committee Member, representing Pacific Ecological Systems Division, EPA

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I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

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Keira Johnson, Author

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1 Introduction

1.1 Motivation for Research

Declining water quality has become a global issue as land is developed for agricultural and urban activities to support our growing population. One of the most prevalent aspects of water quality is nutrient loading, which can cause harmful algal blooms detrimental to ecosystems. Anthropogenic sources of nutrients, including agricultural runoff, domestic sewage, and industrial effluents, may enter waterways through point or non-point source surface transport, as well as through subsurface transport. The United States Geological Survey (USGS) and the Oregon Department of Environmental Quality (ODEQ) have conducted studies to understand water quality issues and trends in Oregon, including in the Willamette River and its tributaries. Sections of the Willamette River mainstem and tributaries are water quality limited for temperature, dissolved oxygen and chlorophyll a indicating high nutrient loads and increasing eutrophication conditions (DEQ, 2012). A study by USGS showed that Willamette River tributaries with high phosphorus and nitrate concentrations generally drained predominantly agricultural land (USGS, 1998). Understanding the nutrient origin, pathways they enter surface and groundwater, and associated management practices affecting these pathways is important for maintaining aquatic habitat now and in the future.

To further understand the water quality – agricultural land relationship in the Willamette Valley, the Oregon State University (OSU) Ecohydrology lab, along with other stakeholder groups including, but not limited to, the Oregon Farm Bureau and the Oregon Dairy Farmers Association, has developed a study to investigate field, catchment, and watershed scale impacts of multiple land use-environment relationships within the Willamette Valley. The broader goals of this study are to characterize biophysical and land use relations influencing water quality and quantity to provide information to improve land management practices and inform policy related to water management. The Oak Creek watershed, located on the leeward side of the coast range, was chosen for a long-term research site because it reflects typical land use gradients (i.e., forest, agriculture, urban) of Willamette River sub-watersheds, and includes agricultural land managed by OSU that is accessible for research. Similar to other watersheds in the Willamette Valley, Oak Creek watershed exceeds EPA limits for temperature and bacteria. Ongoing research in Oak Creek includes investigation of the stream temperature gradient along Oak Creek, assessment of water transport in the vadose zone, characterization of the hydrogeologic framework, examination of grazing impacts on soil properties and water quality in pastures, evaluation of water quality indicators in Oak Creek, and investigation of riparian area surface water and groundwater interactions influencing stream water quality. This research focuses specifically on understanding the impacts of land use on water quality indicators and nutrient transport within the Oak Creek watershed.

1.2 Watershed Overview

Watersheds provide many functions to the ecosystem including water capture, storage, and release. Humans, and our land use activities, are intimately related to the ability of a watershed to carry out these functions. Water capture is the movement of water from the atmosphere into the soil. Infiltration is the trapping of precipitation in the upper layers of the soil, and percolation is the movement of water into deeper layers of the soil or groundwater. Capture rate is determined by nonanthropogenic factors such as soil type, underlying geology, climate, and also by anthropogenic factors such as soil compaction and vegetation cover. Water storage takes place in the space between soil particles. Management of land and vegetation, along with soil texture,

structure, and depth, impact water storage ability. Soil moisture can be lost due to transpiration, percolation, and evaporation. Water release occurs when groundwater enters the surface water system within the watershed or when groundwater exits through cross watershed percolation. The rate and amount of water released depends on both the water already stored in soil and underlying bedrock, and also on overland flow (water that did not infiltrate). Riparian vegetation also directly affects the rate and amount of release; it acts as a buffer between groundwater and surface water and slows and reduces groundwater discharge by uptake and transpiration.

The isotopic composition of water varies depending on geographic location. Ecosystems are influenced by different hydrologic processes creating variation in the isotopic signature of water. The isotopic composition of water refers to the proportion of stable isotopes of water (O_{18}:O_{16} and H_2:H_1) within a sample. Water isotopic composition varies within watersheds as well. For example, water found in the upper reaches of a watershed will generally differ from that in the lowlands. Precipitation has a large influence on the isotopic composition of water, especially along an elevation gradient. As elevation increases, the isotopic composition of water decreases because of the preferential condensation of heavier isotopes. This means that the lowlands of a watershed tend to be isotopically heavier than the uplands.

Chemical composition of water also varies within a watershed. Headwaters are predominately composed of rainwater and groundwater and is therefore less disturbed by the addition of chemical, biological, and physical contaminants. As surface water flows out of the uplands towards the lowlands, runoff from agricultural and urbanized land can contribute nutrient pollution (e.g., chloride, nitrate, sulfate) and sediment to the stream. Furthermore, groundwater collects nutrients as it moves through soil and rock that are then deposited into surface water via groundwater discharge.

1.3 Land Use – Water Quality Interactions

Investigating land use-water quality interactions at a watershed scale is beneficial for understanding the influence of different land uses and related activities (e.g. forest, agriculture, urban) within the watershed, and for involving all stakeholders in the study. Several studies have documented the influence of land use on water quality. Some authors have examined if riparian zone land use has a different influence on stream water quality compared to watershed land use on stream water quality. Results have varied; Sliva and Jones (2001) and Mello et al. (2018) stated that overall the entire watershed has a larger influence while Tran et al. (2010) concluded that the riparian zone has a larger impact. However, the dominant finding is that some parameters are better correlated with the whole catchment while other parameters are more correlated with the riparian zone (Johnson et al., 1997). Other studies have investigated seasonal change by analyzing water quality during different times of the year, concluding that there are temporal changes in the relationship between land use and water quality. Yu et al. (2016) indicated that water quality and land use were strongly correlated in the dry season in the Wei River Basin in China. Collins and Jenkins' (1996) study of agricultural dominated basins in the Middle Hills of the Himalayas concluded that the wet season led to lower concentrations of cations in the stream due to dilution from monsoon rains, but a higher concentration of anions and ammonium due to fertilizer leaching was observed. Both of these studies determined that agricultural land has the highest impact on water quality; in the Wei Basin the positive correlation between agricultural land and physicochemical and nutrient variables indicated that agricultural practices were a source of pollution, and in the Middle Hills higher percentage agriculture catchments were associated with higher concentrations of nitrate, sulfate, chloride,

and base cations revealing the impacts of agricultural practices. Other studies have shown similar results to those by Collins and Jenkins (1996). For example, Mello et al. (2018) concluded that total suspended solids (TSS), total nitrogen (TN), total phosphorus (TP), and fecal coliform (FC) were all positively correlated with agriculture-dominated catchments. Ahearn et al. (2005) also linked TSS with agricultural land. However, a study conducted by Lee et al. (2009) to examine how special patterns of land use relate to water quality indicated low correlation between water quality degradation and agricultural land.

Several studies have been conducted in the Pacific Northwest region to better understand the relationship between land use and water quality. For example, in the Little Bow River in Alberta, Canada, Little et al. (2003) investigated the land use-water quality relationships and concluded that a positive relationship exists between TN, TP, and nitrate-nitrogen and high intensive agricultural practices. This conclusion led to concern about the negative implications of confined animal feeding operations (CAFO) and manure application for ecosystem health. In the Abbotsford Aquifer in British Columbia, Canada elevated nitrogen concentrations were determined to be originating from agricultural practices, especially animal operations (Zebarth et al., 1998). In the Yakima River Basin in Washington, US, Cuffney et al. (1999) studied the impairment of different ecoregions and determined that agricultural practices were the primary factor associated with ecosystem impairment. In the Calapooia River Basin in Oregon, US, high levels of nitrogen concentration and nitrogen export were associated with agricultural dominated catchments (Lin et al., 2018). Compton et al. (2019) also examined seasonal nitrogen export in the Willamette River Basin in Oregon, US, based on crop cover and fertilizer input recommendations, indicating that agriculturally dominated catchments had the highest concentrations of nitrogen due to fertilizer inputs. Both of these studies indicated that seasonality had a large impact on origin and amount of nitrogen export; winter months were consistently associated with high stream export due to fertilizer leaching from heavy rains. Studies by Compton et al. (2014) and Greathouse et al. (2014) investigated red alder as a nitrogen source in the Willamette Basin originating from forested regions and concluded that nitrogen concentrations are positively correlated with red alder populations and high stream flows.

The Oak Creek Watershed is located in the western area of the Willamette Basin and is the focus for our study. Various other studies (Li and Kegley, 2005; Haggerty 2013, Katz 2016) have been conducted in Oak Creek Watershed. For example, Brown (2000) investigated the potential for pasture, poplar stand, and native Oak forest to act as a nutrient buffer. Denitrification and nitrogen uptake rates were measured, and Brown concluded that an integrated buffer of all three vegetation types would be most successful as a nutrient buffer because of the enhanced denitrification ability of poplar stand and pasture in conjunction with the vegetative uptake of nitrogen associated with native forest. Poor (2006) investigated the influence of storm events on nitrate concentrations and export rates in sub catchments in the Oak Creek Watershed, determining that nitrogen export rates increased with increased flow and development. In the upper Oak Creek Watershed, Royer (2006) investigated the impact of forest roads and concluded that storm runoff from roads is not significantly impactful at the mouth of the watershed.

1.4 Stream-Aquifer Interactions

To gain a comprehensive understanding of a watershed, the storage and movement of groundwater and its influence on surface waters must be studied. Groundwater is formed when precipitation or surface water from streams, lakes, and wetland infiltrates into the ground. The rate of infiltration depends on climate, land cover, soils, and geology. Groundwater percolates

through the unsaturated (vadose) zone and is stored in soil or rock structures in the zone of saturation. At this depth, the water flows horizontally with little vertical mixing and according to the hydraulic gradient (i = dh/dl) and gravity. Aquifers are permeable geologic layers that store groundwater. The upper layer of the aquifer determines whether the aquifer is confined or unconfined. Confined aquifers are characterized by a relatively impermeable upper strata while unconfined aquifers' upper strata are the water table. The saturated thickness of an aquifer is the vertical depth of an aquifer which is able to store water and significantly impacts the potential yield of an aquifer. Groundwater and surface water, while usually viewed as separate entities, are interdependent. Groundwater has the ability to move laterally, vertically, or horizontally, and therefore is often connected to and/or feeds surface water bodies. Baseflow is the groundwater that sustains surface water. Surface water may also influence groundwater patterns with change in land use patterns that alter infiltration rates causing changes in groundwater quantities.

The majority of groundwater-surface water interactions occur in the riparian zone of a stream. The riparian zone performs a vital role in a watershed; it connects the surrounding land to the stream. Benefits of well-functioning riparian zones include erosion control, nutrient and toxin uptake, flood control, and improved habitat. In the northwestern United States, riparian zones play a crucial role in maintaining the integrity of the channel during the wet season when heavy rains are routine. In the summer when rainfall is infrequent, riparian zones help to maintain a steady stream flow through the slow release of stored groundwater. The interactions between stream water and groundwater can be classified as either gaining or losing conditions, although a stream can both gain and lose water along different reaches. If groundwater is discharged into the stream channel, the stream is classified as gaining. For this to occur, the water table must be higher than the surface of the stream water. Conversely, a losing stream is characterized by a relatively lower water table and water movement from the stream into the ground.

Several studies have documented the interactions between groundwater and surface water. For example, in the Murray-Darling Basin in Australia, Parsons et al. (2008) studied surface-groundwater interactions to better understand the impact of climate change and continued agricultural practices on the water resources. They concluded that surface and groundwater systems have been and will continue to reflect reduced river gains and increased river loses. On Kangaroo Island in South Australia, water level and salinity were monitored to determine the conditions of a stretch of the Rocky River in relation to the greater catchment. The river system was characterized as a losing connected type, driven by high evapotranspiration characteristic of riparian vegetation. Krause et al. (2007) studied surface-groundwater interactions along a temporal and spatial scale in the Hazel River catchment in Germany and concluded significant temporal variation in exchange fluxes existed. While the Hazel River was determined to have net gaining conditions, riparian groundwater was determined to be recharged via streamflow in the winter when flow is high. Groundwater typically exhibited low net exfiltration; however a significant portion of the river discharge in the summer was contributed from riparian groundwater. Rozemeijer and Broers (2007) studied the contribution of groundwater to surface water pollution in Noord-Brabant in The Netherlands, determining that poor water quality of shallow groundwater leads to poor surface water quality, especially during low flow seasons. The results of this study imply that surface water management must be integrated with groundwater management to improve quality system-wide. In New Mexico, surface-groundwater interactions were monitored by Fernald et al. (2010) in an irrigated valley along the Rio Grande. Results indicated that the surface water irrigation system and shallow

aquifer both store water underground and release it into the river, effectively increasing flow later in the year. It was predicted that changes in water use or irrigation practices would result in higher flows in spring as opposed to fall and winter due to less contribution from groundwater. Schilling et al. (2005) studied surface-groundwater interactions of an incised stream in Iowa to determine nitrogen contribution to the stream via riparian groundwater. Nitrate concentrations were highest along the incised stream where the unsaturated zone was the thickest, and results indicated that riparian zones could contribute nitrogen to streams during the spring groundwater recharge period when stream banks are unvegetated. In Oregon, several studies have been conducted on surface-groundwater interactions (Herrera et al., 2015; La Marche and Wood, 2011; Petrides Jiménez, 2008). Durfee (2018) studied Fifteenmile Creek in northcentral Oregon and used temperature as an indicator for surface-groundwater interactions, concluding that groundwater was generally cooler in the summer and warmer in the winter compared to stream water, and that groundwater may have a moderating impact on surface water. Caruso et al. (2019) used a hydrogeologic framework to study the surface-groundwater interactions of the Deschutes Basin and found that the groundwater system was shallow and comprised of unconfined aquifers due to low permeability underlying geology. These aquifers are replenished via winter rainfall and spring snowmelt, and feed springs and subsurface flow. The conclusions of this study will help to inform management decisions in central Oregon.

1.5 Stable Isotopes of Water

Isotopes are commonly used in the assessment of water resources. Water stable isotopes, deuterium ($\delta^{2}H$) and oxygen-18 ($\delta^{18}O$), can be used alongside geochemical tracers (e.g., ions, organic carbon) to determine specific interactions within a watershed (Gibson et al., 2005). Isotopes are atoms of the same element that have different numbers of neutrons. The variation in neutrons means that isotopes vary in mass. Isotopes can be either stable or unstable. Unstable (radioactive) isotopes decay over time to form other isotopes and in the process emit alpha or beta particles. Stable isotopes are not radioactive and do not decay, however they may be the product of isotopic decay.

Rainwater, groundwater, and stream water have differing isotopic signatures due to isotopic fractionation. Fractionation is the relative partitioning of isotopes based on atomic mass, bond energy, and nuclear structure. Biological, chemical, and physical processes can cause fractionation leading to isotopic ratios that give insight into the history of the water. Fractionation causes spatial and temporal variations in water stable isotopes that allows for analysis of flow paths and component mixing based on differing signatures. Mass dependent fractionation is caused by the difference in atomic masses between isotopes resulting in changes in relative proportions of different isotopes. Phase change is an example of mass-dependent fractionation; when water evaporates isotopically lighter water is favored leaving isotopically heavier water in liquid form and when water is condensed, isotopically heavier water will precipitate out first. The Rayleigh rain out effect describes how precipitation becomes isotopically depleted the further away from its original vapor source it falls due to mass-dependent fractionation. As a vapor cloud moves across a land mass, the first precipitation event will be isotopically heavier relative to the remaining vapor in the cloud because heavier isotopes (^{18}O and ^{2}H) are condensed into liquid before lighter isotopes (^{16}O and ^{1}H). Isotopic compositions of precipitation samples from around the world can be linearly plotted relative to one another ($\delta^{18}O$ vs $\delta^{2}H$) on the Global Meteoric Water Line (GMWL). The GMWL, given

below, represents the mean relationship between $\delta_{18}O$ and $\delta_{2}H$ based on isotopic compositions of precipitation samples from all over the world:

$\delta_{2}H = 8\ \delta_{18}O + d$

where *d* is the deuterium excess factor. Ocean water, from which the majority of atmospheric water is sourced, has a d = 0, but water evaporated over the ocean is neither in perfect equilibrium nor 100% humidity (air above the ocean averages 85% humidity) and therefore the global mean value of d for freshwater sources is +10‰ to account for the effects of non-equilibrium fractionation. Evaporation in humid environments results in fractionation rates closer to equilibrium fractionation, while low humidity results in more kinetic fractionation and a slope < 8 (Figure 1). Thus, d-excess can be used to indicate deviations from the GMWL.

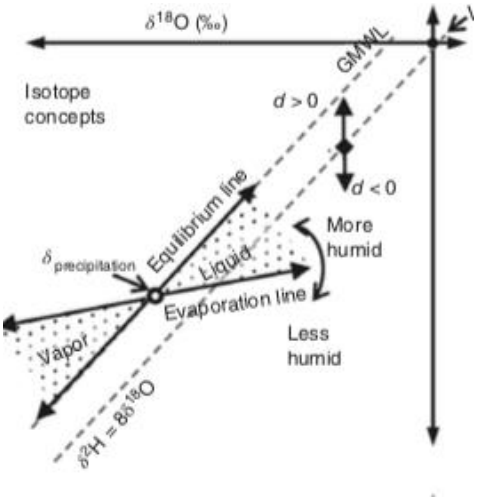

Figure 1: GMWL, d-excess, and the effects of kinetic and equilibrium fractionation on precipitation. Figure from Allen et al. (2017).

Several studies have used water stable isotopes to determine contributions to and the origin of stream water (Nickolas et al., 2017; Brooks et al., 2012; Koeniger et al., 2009; Mountain et al., 2004; Schulte et al., 2011; Wang et al., 2009). In the Weser Basin, Germany, a strong seasonal effect was observed; winter was associated with more negative values while summer was associated with more positive values (Koeniger et al., 2009). Similar results were obtained in the Heihe River Basin, China; however, seasonal variations in river water were different than variations in precipitation (Wang et al., 2009). In Taiwan, summer stream water was determined to be mainly supplied by moisture recycling, enforcing the importance of forested watershed maintenance (Peng et al., 2015). Brooks et al. (2012) study of the Willamette Valley, Oregon observed little seasonal variation in small tributaries in the watershed but found significant seasonality in the Willamette River due to changes in elevation of source water throughout the year. A dominant finding is the existence of a relationship between elevation and isotopic signature (Wang et al., 2009, Brooks et al., 2012; Peng et al., 2015). The Rayleigh rain out effect accounts for less enriched isotopic compositions at higher elevations. Contrary to the Rayleigh effect, the leeward side of the Coast Range in Western Oregon lacks a relationship between elevation and isotopic signature (Brooks et al., 2012). This discrepancy may be due to cross-basin water exchange from the more isotopically enriched windward side of the Coast Range through permeable underlying geology (Nickolas et al., 2017). Understanding the

temporal origin of water sources is important to inform management strategies surrounding water use and conservation.

1.6 Study Objectives

Understanding the complexity and integrated nature of watersheds is important to our ability to make purposeful regulatory laws, conduct economic activity in an environmentally sound manner, and to protect the biodiversity of the ecosystem. Studies investigating land use and water quality relationships and groundwater – surface water interactions have become increasingly prevalent as urbanization and agricultural land encroach on once undeveloped land, and surface and ground water patterns change. As part of a larger project examining land use – water quality relationships in the Willamette Valley, this study aims to provide a comprehensive analysis of the land use activities and hydrologic processes influencing the water quality of Oak Creek watershed. The objectives of this study are: 1) to determine land use influence on stream water anion concentration along a longitudinal gradient; 2) to assess potential effects of stream-aquifer interaction on stream water quality; and 3) to determine potential origins and seasonal variability of surface water flow. Understanding the relationships between land use, water quality, and groundwater is crucial for future ecological, economic, and domestic water management decisions within Oak Creek watershed and the greater Willamette Valley, especially as precipitation and snow melt timing change and the prevalence of drought increases.

2 Methods

2. 1 Study Site

This study was conducted in Oak Creek watershed located in Oregon's western Coast Range in the greater Willamette River Basin (Figure 2). Oak Creek (44.5885467, -123.33775) is a 24 km long stream with a drainage area of 32.63 km2. Elevation within the watershed ranges from 63 m where Oak Creek flows into the Mary's River up to 649 m at McCulloch Peak. The watershed is characterized by a Mediterranean climate with dry, warm summers and wet, mild winters. Mean annual precipitation is 1043 mm (NOAA).

The upper Oak Creek watershed is dominated by Paleocene/Eocene age Siletz River basalt with intrusions of Eocene/Oligocene age Western Cascade Volcanics. The Corvallis Fault lies northwest of Corvallis and marks the contact of the Siletz River Basalt with the Eocene age Tyee formation. The Tyee formation is overlain by Quaternary Surficial Deposits in the lower watershed. Based on data from Oregon Water Resources Groundwater Information System sedimentary deposit thickness ranges from less than 6 meters near the fault and generally thickens towards Mary's River with depths of up to 61 meters. These sedimentary deposits overlie the Siletz formation in the upper watershed floodplain of Oak Creek as well (DOGAMI).

Oak Creek watershed can be characterized by three main land use categories: forest, agriculture, and urban development. The basin is dominated by forest (63%), with the uplands vegetated by Douglas-Fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*), and western redcedar (*Thuja plicata*) and the lowlands vegetated by Oregon white oak (*Quercus garryana*), red alder (*Alnus rubra*), Oregon ash (*Fraxinus latifolia*), and bigleaf maple (*Acer macrophyllum*). Agricultural land, dominated by hay, pasture, and grazing livestock, occupies 23% of the basin. Urban development comprises 11% of the total land area. Highest density of urban development is located at the confluence of Oak Creek and the Mary's river, associated with the city of Corvallis (2010 US census population: 54,462).

2.2 Field Methods

Water samples were collected at 39 sites within the watershed; 22 stream sites and 19 shallow groundwater wells. Of the stream sites, 18 were located on the mainstem and 4 were located on tributaries (Figure 2a). Catchments for each stream sampling location were delineated using USGS StreamStats (https://streamstats.usgs.gov/ss/). These catchments range in size from 0.24 km^2 to 32.63 km^2 and in mean elevation from 360.1 m to 149.4 m. Sites were selected based on land use and accessibility. Three surface water sites were associated with forested land use (>90% forest), fifteen surface water sites were associated with agriculture land use (>10% agriculture), and four surface water sites were associated with urban land use (>10% urban). Out of Oak Creek's 125 tributaries, three of the principle contributors (e.g., Mulkey Creek, Lamprey Creek, Alder Creek) as well as one unnamed forest tributary were selected. Fifteen of the shallow wells were located on hay and pasture agriculture fields (Figure 2b). Fields 1 and 2 were used for cattle grazing in the spring, summer, and fall, while Field 3 was used for hay production. Both fields received applications of both liquid manure from the OSU Dairy Farm and synthetic 40-0-0-6 NPKS fertilizer (Table 1). Four wells were located in the riparian area at 6 (RW1), 9 (RW4), 16 (RW5), and 24 (RW6) meters from Oak Creek. Shallow wells were installed throughout the course of the study (Table 2).

Table 1: Field management practices during study period.

Field	Field Use	Synthetic Fertilizer Application Dates	Manure Application Dates
Field 1	Cattle grazing	2017, 2018	2017, 2018, 2019
Field 2	Cattle grazing	2017, 2018	n/a
Field 3	Hay production	2017, 2018	2018

2. 3 Water Sampling Methods

Data collection occurred between January 2018 and November 2019 (Table 3). Surface water samples were collected in the thalweg of a well-mixed zone of the stream. Sampling sites were visited approximately monthly to measure temperature and specific conductivity using a Multiparameter Sonde (AquaTROLL 600, In-Situ Inc., Fort Collins, CO, USA). At each site, the sonde was deployed for 90 seconds. Prior to sampling, the sonde was calibrated for specific conductivity using a solution of 1413 $\mu S\ cm^{-1}$.

Water samples for anion and isotope analysis were collected quarterly. To collect surface water samples for anion analysis, water was extracted from the thalweg of the stream using a 60 mL plastic syringe. The syringe was rinsed with water from the current sampling site before collecting the sample. Each sample was filtered in the field using a disposable 25mm x 0.45 μm nylon filters. At least 30 mL of water was filtered into a 60 mL HDPE acid-washed bottle. Bottles were rinsed with a small amount of filtered water from the current sampling site before filling with the sample. Samples were stored in the freezer until they were analyzed at the Institute for Water and Watershed Collaboratory.

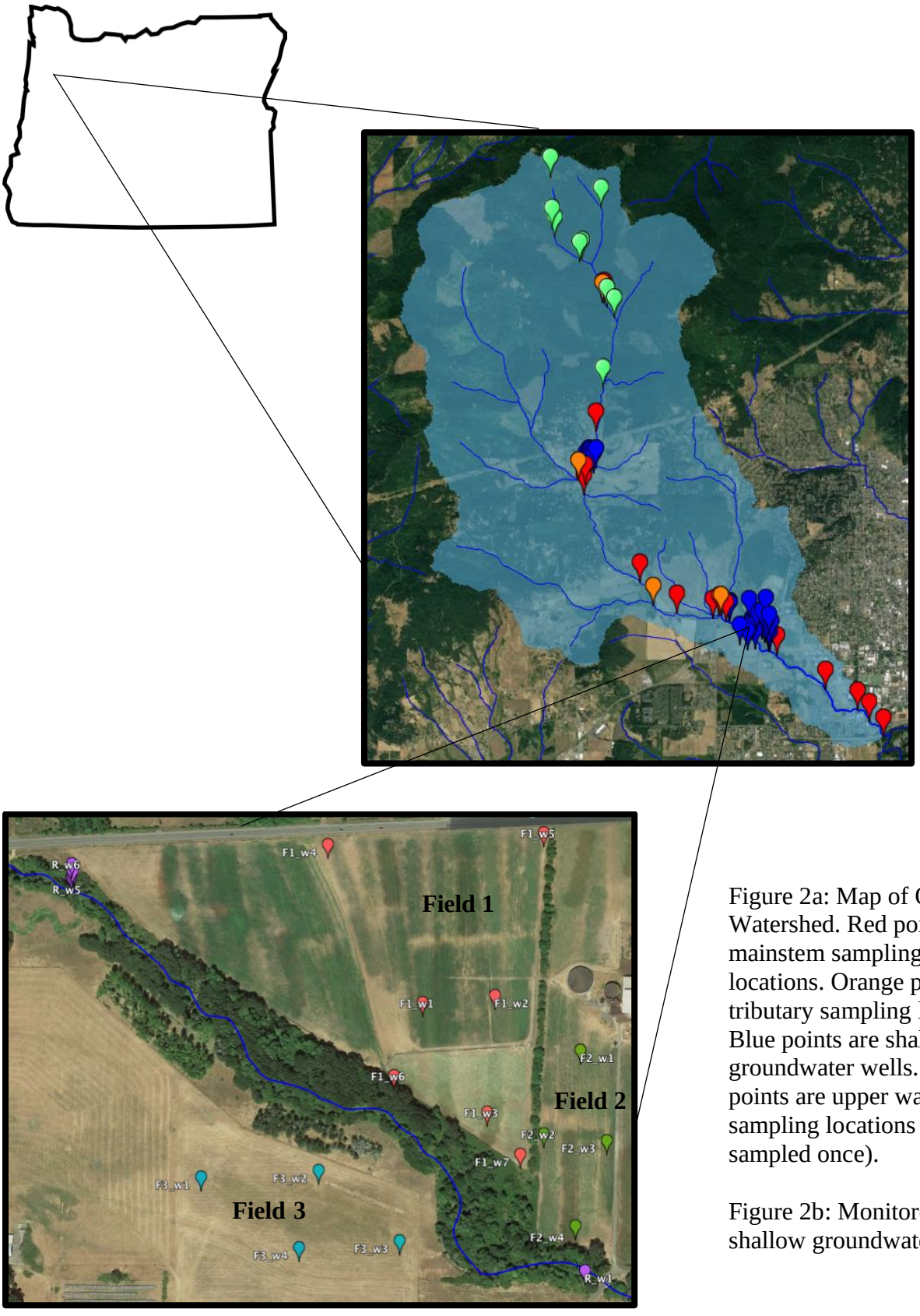

Figure 2a: Map of Oak Creek Watershed. Red points are mainstem sampling locations. Orange points are tributary sampling locations. Blue points are shallow groundwater wells. Green points are upper watershed sampling locations (only sampled once).

Figure 2b: Monitored shallow groundwater wells.

Table 2: Location, structural characteristics, and data collection start date for each shallow groundwater well.

Well ID	Latitude	Longitude	Well Diameter (mm)	Material	Depth to Water Table (m)	Depth to Water Data Date Collected	Data Collection Start Date
F1W1	44.5696	-123.3041	50	PVC	0.4	12/4/18	1/15/18
F1W2	44.5697	-123.3030	50	PVC	1.4	12/4/18	1/15/18
F1W3	44.5684	-123.3030	50	PVC	0.8	12/4/18	1/15/18
F1W4	44.5713	-123.3055	50	PVC	0.6	12/4/18	1/31/19
F1W5	44.5715	-123.3023	50	PVC	0.3	12/4/18	1/31/19
F1W6	44.5688	-123.3045	50	PVC	0.5	12/4/18	1/31/19
F1W7	44.5680	-123.3025	50	PVC			1/31/19
F2W1	44.5691	-123.3016	50	PVC	0.8	9/4/19	11/22/19
F2W2	44.5682	-123.3022	50	PVC	0.2	12/4/18	1/31/19
F2W3	44.5682	-123.3012	50	PVC	0.1	12/4/18	1/31/19
F2W4	44.5672	-123.3017	50	PVC	1.4	9/4/19	11/22/19
F3W1	44.5677	-123.3074	50	PVC	1.9	12/4/18	1/31/19
F3W2	44.5678	-123.3056	50	PVC	2.1	12/4/18	1/31/19
F3W3	44.5670	-123.3043	50	PVC	2.0	12/4/18	1/31/19
F3W4	44.5669	-123.3059	50	PVC	1.6	12/4/18	1/31/19
RW1	44.5668	-123.3015	32	Cast Iron	1.9	12/4/18	1/15/18
RW4	44.5709	-123.3094	32	Cast Iron	2.0	12/4/18	1/31/19
RW5	44.5710	-123.3094	50	PVC	1.9	12/4/18	1/31/19
RW6	44.5710	-123.3094	32	Cast Iron	2.7	12/4/18	1/31/19

Bottles were acid washed prior to reuse to minimize sample contamination. Individual bottles were filled to the brim with 10% HCl and capped. Bottles were soaked overnight, then HCl was poured back into the carboy for reuse and bottles were rinsed five times with deionized (DI) water, filled to the brim with DI water, and soaked overnight. The specific conductivity of rinsed out water from 20% of acid washed bottles was measured, and if any values exceeded 0.6 $\mu S\ cm^{-1}$ all bottles were rinsed and filled with DI water and soaked overnight. The procedure was repeated until the conductivity of the RO water from the selected 20% of bottles was below 0.6 $\mu S\ cm^{-1}$. Once within the acceptable limit, all bottles were rinsed once with DI water and left to dry in a reverse flow hood before being capped and stored.

Surface water samples for isotope analysis were collected by dipping a 20 mL glass vial into the thalweg of Oak Creek. Samples were sealed with conical insert caps without headspace to prevent evaporation and stored upside down until they were processed at the Pacific Ecological Systems Division of the EPA for $\delta_{18}O$ and $\delta_{2}H$.

Table 3: Parameters and locations sampled for each sampling date. SC indicates specific conductivity; T indicates temperature; GW indicates groundwater samples from shallow wells; SW indicates surface water samples from Oak Creek.

Date	Parameters	Location
1/15/18	T, anions	GW, SW
2/28/18	isotopes	GW, SW
4/18/18	SC, T, anions	GW, SW
5/19/18	SC, T	SW
7/13/18	SC, T	GW, SW
7/27/18	SC, T	SW
9/10/18	SC, T, anions, isotopes	SW
1/31/19	SC, T, anions, isotopes	GW, SW
3/20/19	SC, T	GW, SW
4/19/19	SC, T	GW, SW
5/17/19	SC, T, anions, isotopes	GW, SW
6/10/19	SC, T	GW, SW
7/22/19	SC, T	GW, SW
8/28/19	SC, T, anions, isotopes	GW, SW
9/27/19	SC, T	GW, SW
10/30/19	SC, T	GW, SW
11/22/19	SC, T, anions, isotopes	GW, SW

Groundwater was extracted from wells using a peristaltic pump (Model 410, Solinst Canada Ltd., Georgetown, ON, Canada) with 20 ft of 3/8" diameter silicone tubing. To measure temperature and specific conductivity, water was pumped into a flow through cell with a suction gasket fit to the sonde. To collect anion and isotope samples, water was pumped directly from the 3/8" tubing into a 60 mL plastic syringe and 20 mL glass vial, respectively. Identical procedures as stream water anion and isotope collection were used for groundwater anion and isotope collection and filtration.

2.4 Water sample analysis

2.4.1 Anion Analysis

All samples were analyzed for chloride, sulfate, bromide, phosphate, fluoride, and nitrate using an Ion Chromatograph (Model ICS-1500, Dionex Corporation, Sunnyvale, CA, USA) at the Collaboratory at the Institute of Water and Watersheds in Corvallis, OR. Samples were allowed to thaw completely before analysis. Quality assurance/quality control was ensured during lab analysis, which included check standards, blanks, and duplicates. The detection limit for all anions analyzed was 0.01 mg L^{-1}. Samples that reported concentrations higher that 5.0 mg L^{-1} for any of the anions were diluted to the proper factor and run through the Ion Chromatograph. For example, samples with a concentration between 5 and 9 ppm required a dilution factor of two, samples with a concentration between 9 and 19 required a dilution factor of 5, samples with a concentration between 19 and 40 required a dilution factor of 20. Only the

data pertaining to the anion with the concentration greater that 5.0 mg L^{-1} was used from the dilution results.

2.4.2 Isotope Analysis

All samples were analyzed for water isotopes ($\delta^{2}H$, $\delta^{18}O$) on a Laser Absorption Water-Vapor Isotope Spectrometer (Model 908-0004, Los Gatos Research, Mountain View, CA, USA) located at the Integrated Stable Isotope Research Facility at the Pacific Ecological Systems Division of the U.S. Environmental Protection Agency, Corvallis, OR. The equation given below denotes the equation used to derive a delta (δ) value for a given isotope:

$$\delta \text{ (in ‰)} = (R_x / R_s - 1) \bullet 1000$$

where R is the ratio of a heavy isotope to light isotope (e.g. $^{18}O/^{16}O$), R_x is the sample and R_s is the standard Vienna Standard Mean Ocean Water (VSMOW)). Measurement precision (1 standard deviation) for the Laser Spectrometer was determined on 17 duplicates of study samples spanning the range of sample values and was 0.36 and 0.15 ‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively. Accuracy based on the mean ± standard deviation of 8 quality-control standards analyzed with the study samples was 0.01 ± 0.30 and 0.02 ± 0.11 ‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively.

2.5 Data Analyses

Data was selected based on consistency and accuracy for analysis. In 2018, groundwater data was sparsely collected because wells were dry the first summer after installation, and between 2018 and 2019, 11 new wells were installed. Therefore, groundwater data from 2018 does not provide sufficient temporal nor spatial information for analysis, and only 2019 groundwater data was used. All collected surface water data was used as the sampling locations stayed consistent throughout the study period.

Approximately 60 temperature and specific conductivity measurements were recorded by the sonde at each sampling location for each sampling date. After sampling, the first 15% and last 10% of data measurements were removed and the median value from the remaining measurements was used as the value for each sampling location. All specific conductivity values below 50 μS cm^{-1} were removed.

In multiple samples, bromide and fluoride had concentrations that were below the detection limit and therefore did not provide consistent data for analysis. Chloride, sulfate, nitrate, and phosphate were identified as parameters of interest given their potential to identify land use effects on water quality.

Two isotope samples exhibiting strong evaporated signatures were removed from analysis. Both samples were collected in stagnant tributaries in the summer.

Analyses were performed to investigate both temporal and spatial trends. Stream meter (0 meters at the mouth), delineated using Google Earth Pro version 7.3.3.7699 (Google LLC, Mountain View, CA, USA), was used to analyze how measured surface water parameters changed spatially. For specific conductivity and temperature, data was divided into three seasons (i.e., winter, spring, summer) for temporal analysis. Anion and isotope temporal analysis use the sampling dates because fewer samples were collected, and stream conditions and recent precipitation have a more direct effect on measured isotopic results. Correlations between variables were investigated using linear regression models. All analyses were performed using R and RStudio version 1.1.463 (RStudio, PBC, Boston, MA, USA).

3 Results

3.1 Hydrologic Setting

Precipitation totaled 732 and 845 mm in water year 2018 and 2019, respectively, (Figure 3), which is lower compared to the mean annual precipitation (1043 mm). Stage at stream meter 2500 along Oak Creek ranged from 0.23 to 1.21 m, with the highest values observed between November and April and lowest values observed between July and September (stage data courtesy of Mary Santlemann, OSU, College of Earth, Ocean, and Atmospheric Sciences). Generally speaking, 2019 exhibited flashier winter stage, and by inference discharge, and higher summer baseflow conditions than 2018.

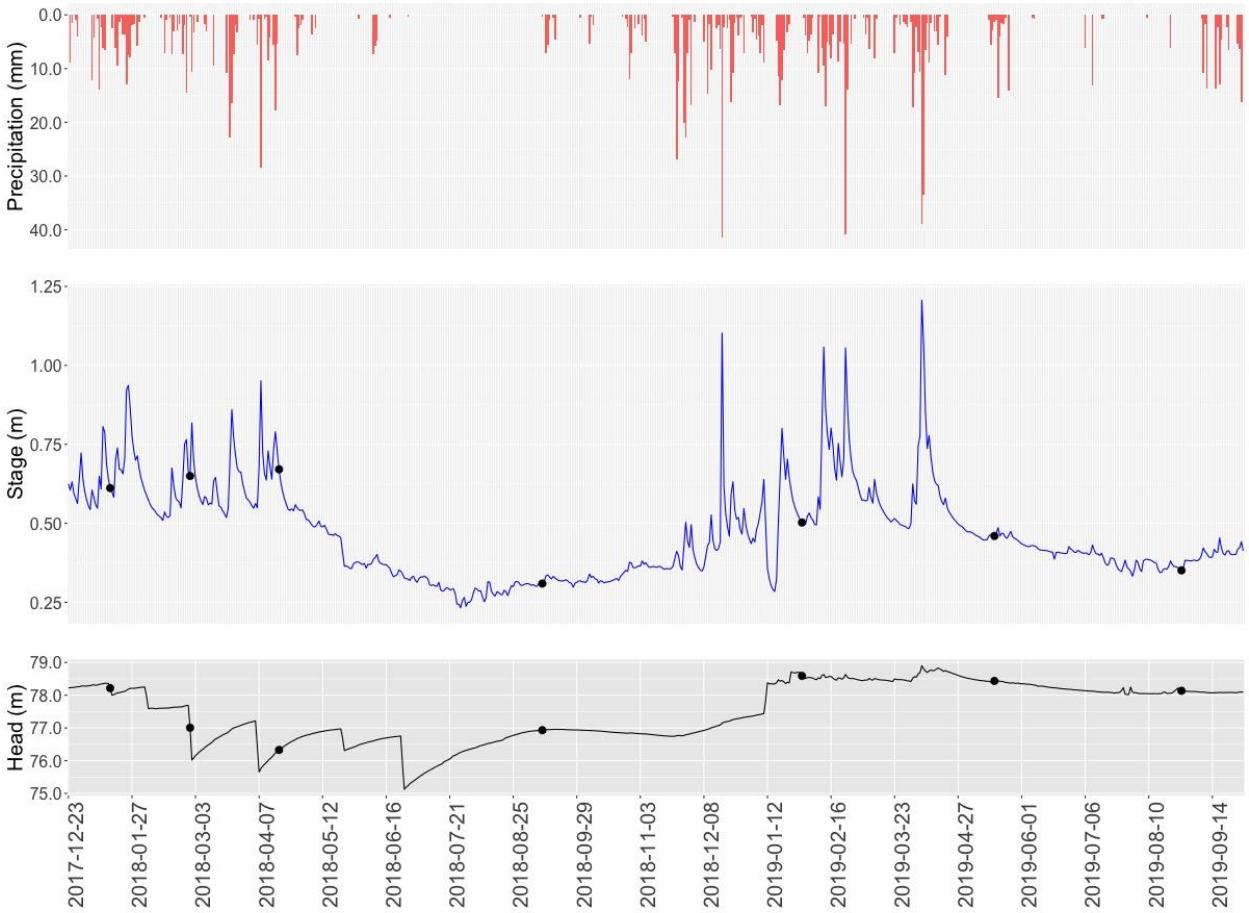

Figure 3: Corvallis precipitation (top), stage curve for Oak Creek (middle), and head from shallow groundwater monitoring well (bottom). Black dots indicate anion and isotope sampling dates.

3.2 Field Parameters

Mainstem stream temperature ranged from 4.0 °C to 22.6 °C with a mean of 12.3 °C (SE ± 0.3 °C), while tributary stream temperature ranged from 4.9 °C to 22.0 °C with a mean of 12.6 °C (SE ± 0.6 °C). As expected, stream temperature fluctuated seasonaly, with warmer temperatures observed in the summer compared to the winter (Figure 4). Summer stream temperatures from 2018 were higher, on average, than stream temperatures from 2019, which correlates with warmer mean ambient temperatures and lower stage. In the winter, the stream

temperature decreases with movement downstream until around stream meter 5000, where it then begins to increase. Urban stream reach showed a stronger downstream increase in the winter compared to other stream reach sections and seasons. Both spring and summer show a relatively consistent increase in temperature with movement downstream along all reach sections (i.e., forest, agriculture, and urban) at a mean rate of by 0.16 °C km^{-1} and 0.26 °C km^{-1}, in spring and summer respectively. In spring and summer Mulkey Creek (triangle slightly downstream of 5000 meters, Figure 4) is consistently warmer than surrounding stream measurements which may be due to its stagnant nature.

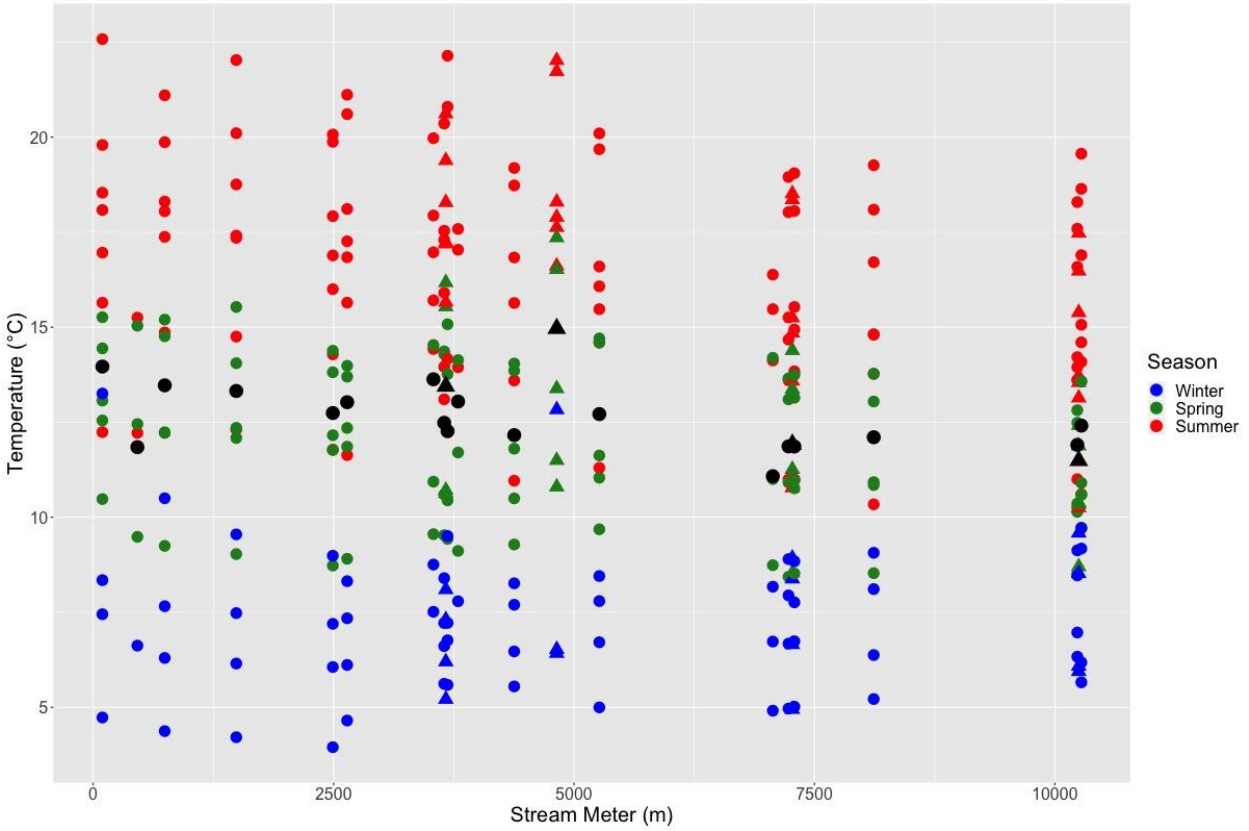

Figure 4: Temperature by stream meter. Stream meter 0 represents the mouth of the Oak Creek. Black points represent mean values for each site. Mainstem sites are shown as circles and tributary sites are represented by triangles.

Mainstem specific conductivity ranged from 145.3 µS cm^{-1} to 458.9 µS cm^{-1} with a mean of 242.5 µS cm^{-1} (SE ± 3.2 µS cm^{-1}), while tributaries had a slightly higher range and mean, 146.3 µS cm^{-1} to 596.9 µS cm^{-1} and 280.2 µS cm^{-1} (SE ± 12.1 µS cm^{-1}), respectively. Consistent with stream temperature, a seasonal difference was measured between conductivity values. Summer measurements are consistently higher than spring values, while winter values exhibit less consistent behavior and often fell between summer and spring values (Figure 5). Across all three seasons, an increase in conductivity with movement downstream was measured, with a mean slope of 4.52 µS cm^{-1} km^{-1}. Specific conductivity in the agricultural tributaries was consistently higher than the surrounding stream measurements, although specific conductivity does not increase at sites directly downstream of the tributaries.

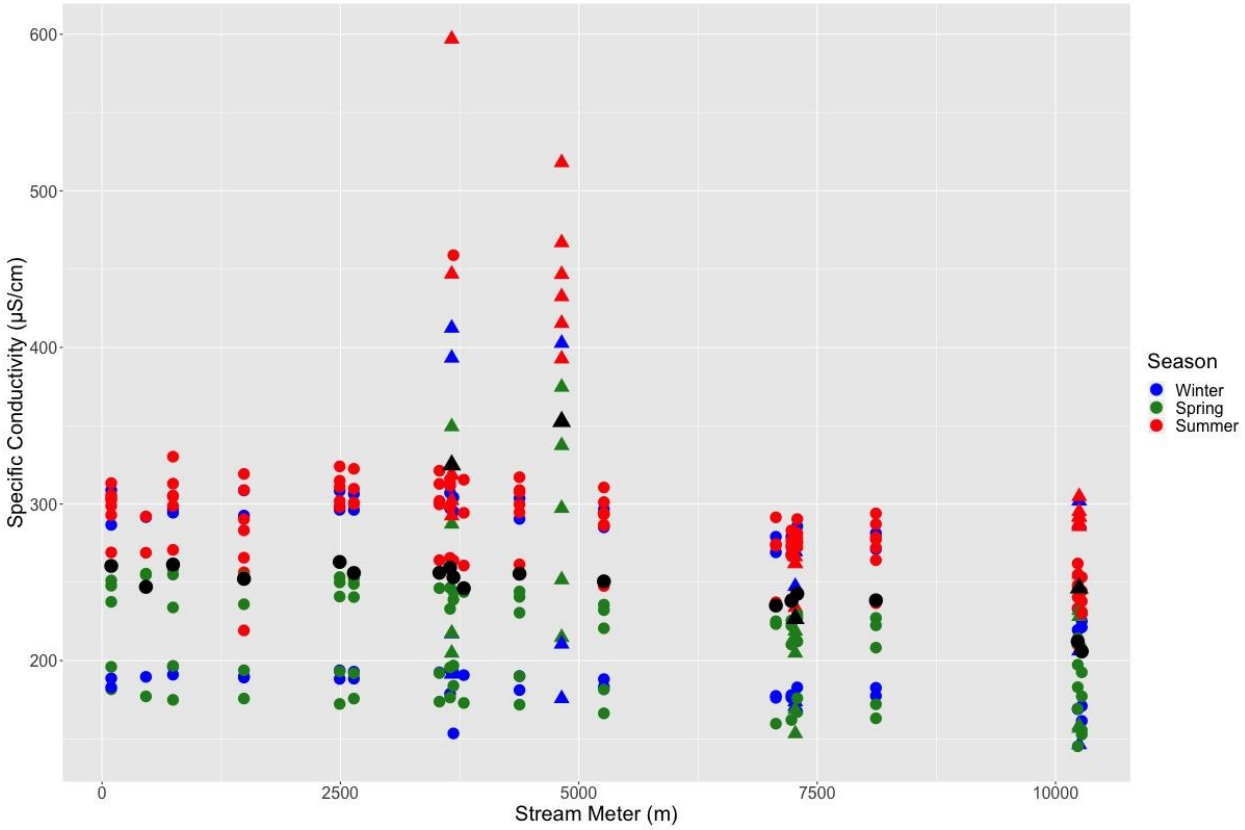

Figure 5: Specific conductivity vs stream meter. Stream meter 0 represents the mouth of the Oak Creek. Black points represent mean values for each site. Mainstem sites are shown as circles and tributary sites are represented by triangles.

3.3 Stable Isotopes of Water

The isotopic ratio of weekly precipitation inputs mainly falls along the GMWL (Figure 6), with a long term (since 2002) volumetric weighted mean of -9.3‰ (SE ± 0.1‰) and -63.9‰ (SE ± 0.8‰) for $\delta_{18}O$ and $\delta_{2}H$, respectively (precipitation data courtesy of J. Renée Brooks, US EPA, Corvallis). The isotopic ratio of weekly precipitation inputs during the study period were highly variable (red circles, Figure 6), and had volumetric weighted mean values of -9.3‰ (SE ± 0.4‰, range from 2.1‰ to -18.7‰) and -62.2‰ (SE ± 2.8‰, range from -11.4‰ to -140.4‰), for $\delta_{18}O$ and $\delta_{2}H$, respectively.

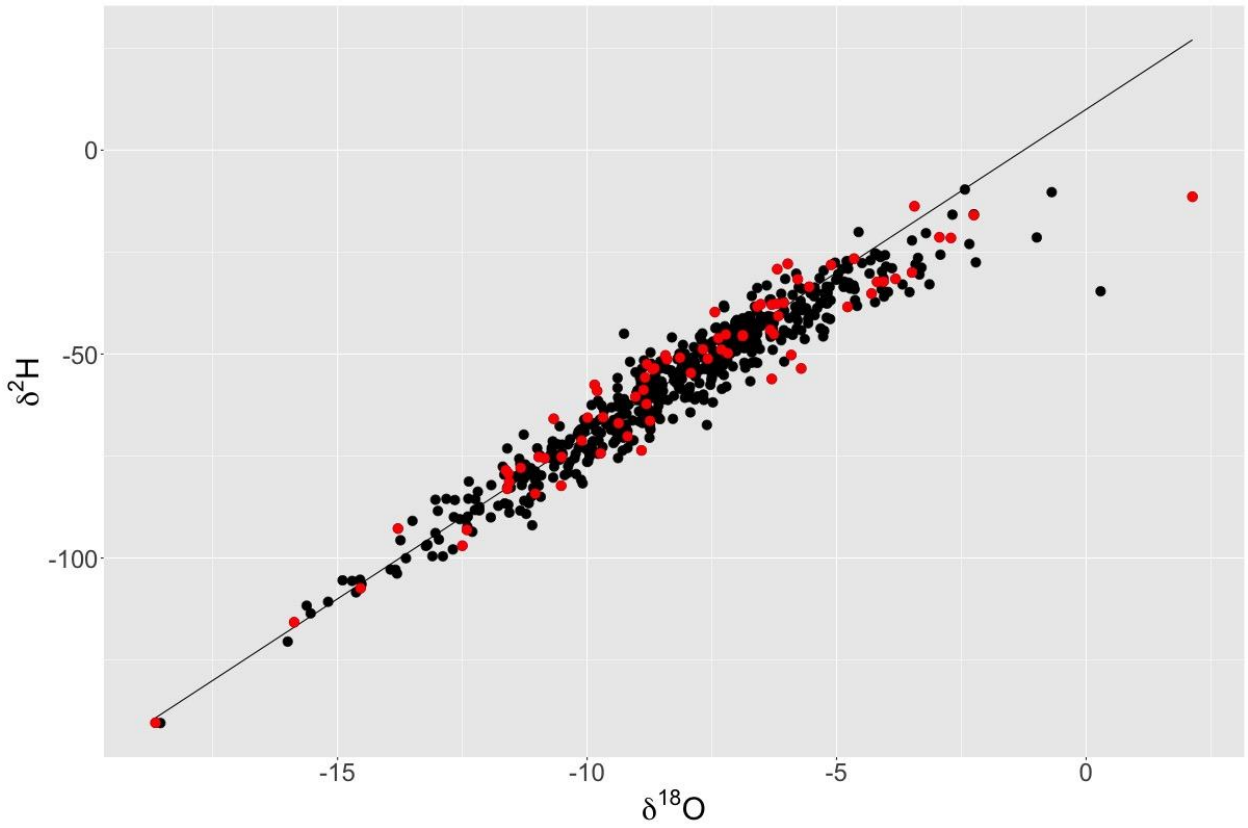

Figure 6: Dual isotope plot ($\delta_{18}O$ and δ_2H) of precipitation data from November 2002 – February 2020 collected in Corvallis, OR. Data from September 2017 to November 2019 is shown in red. GMWL is shown in black.

Mainstem surface water isotopes within Oak Creek ranged from -10.0‰ to -8.4‰ for $\delta_{18}O$ with a mean of -9.2‰ (SE ± 0.0‰) and from -66.9‰ to -58.4‰ for δ_2H with a mean of -60.4‰ (SE ± 0.1‰). Tributary surface water isotopes range from -9.6‰ to -8.6‰ for $\delta_{18}O$ with a mean of -9.0‰ (SE ± 0.1‰) and from -62.5‰ to -57.0‰ for δ_2H with a mean of -60.2‰ (SE ± 0.4‰). All but one mainstem sample fell above the GMWL, indicating no significant evaporation (Figure 7). Tributary samples generally fell closer to or below the GMWL, showing a signature more similar to groundwater. D-excess values of mainstem sites ranged from 8.4 ‰ to 17.4‰ with a mean value of 12.8 ‰ (SE ± 0.2‰), while d-excess values of tributary sites ranged from 8.6‰ to 17.8‰ with a mean value of 12.2‰ (SE ± 0.5‰). Variation in the surface water for a given sampling date was predominately in $\delta_{18}O$, while variation between sampling dates is predominately in δ_2H. Samples from higher elevations in the watershed (139 – 455 meters) (green points, Figure 2a) were collected once on February 7, 2020 to determine if upstream sources were the origin of high d-excess water. These samples showed a more enriched δ_2H signature (-60.5‰ to -58.0‰) than most other stream samples but fell within the range of stream $\delta_{18}O$ signatures (-9.3‰ to -8.9‰), and thus do not explain the origin of high d-excess in Oak Creek.

Groundwater isotopes from shallow wells had a greater range for each isotope than surface waters, but values fell on or below the GMWL, giving groundwater a unique isotopic signature compared to surface water (Figure 7). Groundwater isotope ratios ranged from -9.8‰

to -7.5‰ for $\delta_{18}O$ with a mean of -8.6‰ (SE ± 0.1‰) and -68.2‰ to -52.9‰ for $\delta_{2}H$ with a mean of -60.0‰ (SE ± 0.4‰). D-excess values range from 2.3‰ to 14.1‰. Less temporal separation was observed in groundwater compared to surface water; surface water samples exhibited distinct grouping based on sampling event while groundwater samples were more evenly distributed along the GMWL. However, samples collected on November 22, 2019 fall further below the GMWL compared to other sampling events.

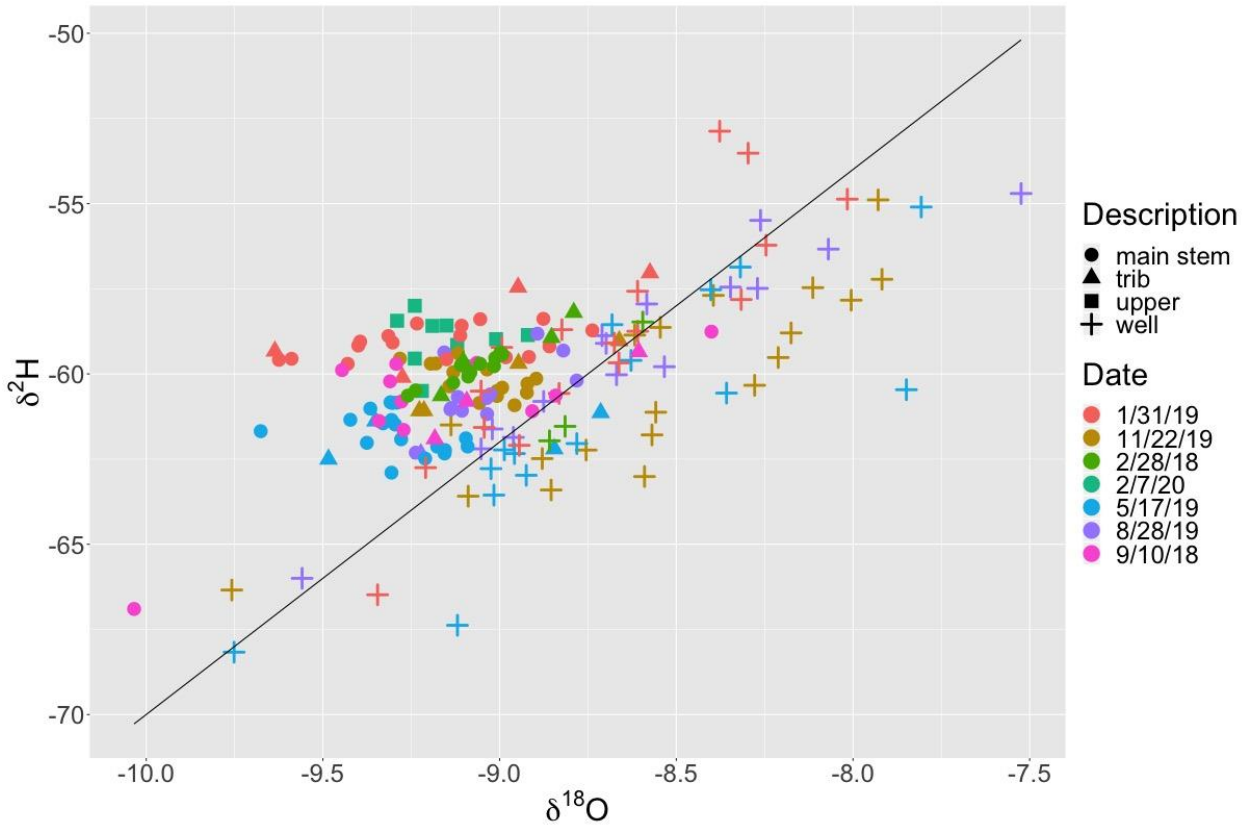

Figure 7: Dual isotope plot ($\delta_{18}O$ and $\delta_{2}H$) of water samples collected during the project. GMWL is drawn in black.

Stream samples were more enriched than long term precipitation isotope value (purple square, Figure 8). The mainstem mean value across all sampling events and locations was -9.2‰ and -60.4‰ for $\delta_{18}O$ and $\delta_{2}H$, respectively, which was 3.5‰ more enriched in $\delta_{2}H$ and 0.1‰ more enriched in $\delta_{18}O$ compared to the long-term precipitation isotope value. The two sampling events that diverged in $\delta_{2}H$ from the mainstem mean (January 31, 2019 and May 17, 2019) were skewed towards precipitation values from 2 months, 3 months, and 1 year, indicating that water that fell >1 month ago may be impacting the signature of the stream. The February 28, 2018 sampling event took place during a wet period and the stream isotope values fall more parallel to the GMWL than other sampling event data. The values are offset from the GMWL, but unlike in other sampling events they show a similar d-excess along the entire stream.

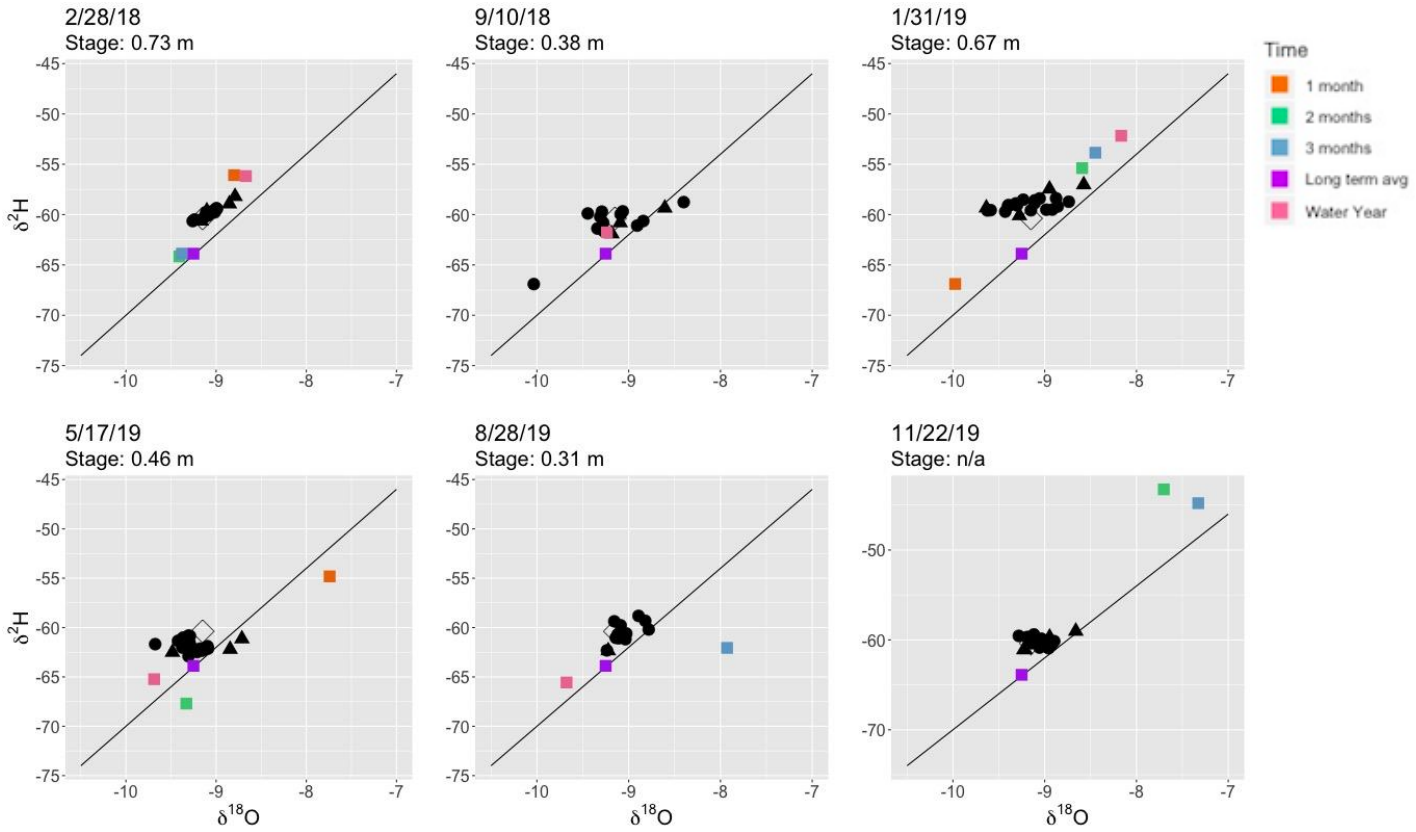

Figure 8: Stream samples shown in black; circles are mainstem sites and triangles are tributary sites. The mean isotopic signature of mainstem sites is shown as an open diamond. Precipitation means (integrated over different time periods) are shown as colored squares, where weekly measures were integrated precipitation amount-weighted means since the sampling date. GMWL shown as black line.

Groundwater isotopic ratios averaged 8.6‰ and -60.0‰ for $\delta_{18}O$ and $\delta_{2}H$, respectively, and varied more spatially but less temporally compared to stream isotopic values (Figure 8). In addition, mean groundwater isotopic ratios were more enriched compared to long term mean precipitation (purple square, Figure 9) (0.6‰ and 3.9‰ higher for $\delta_{18}O$ and $\delta_{2}H$, respectively) and mainstem (only elevated for $\delta_{18}O$ at 0.5‰ greater). The isotopic composition of groundwater varied in relationship to mean precipitation integrated over different time periods (Figure 9) indicating a potential distribution in groundwater residence times (e.g., young to old). For example, on January 31, 2019, groundwater from some wells had similar isotopic values as the two- and three - month precipitation means indicating influence by recent precipitation, while others are clustered around the mean groundwater isotopic value (open diamond, Figure 9), indicating older water, more influenced by recent precipitation. Samples from 11/22 mostly fell below the GMWL indicating a slight evaporated signature, which may be the result of evaporated irrigation water from summer.

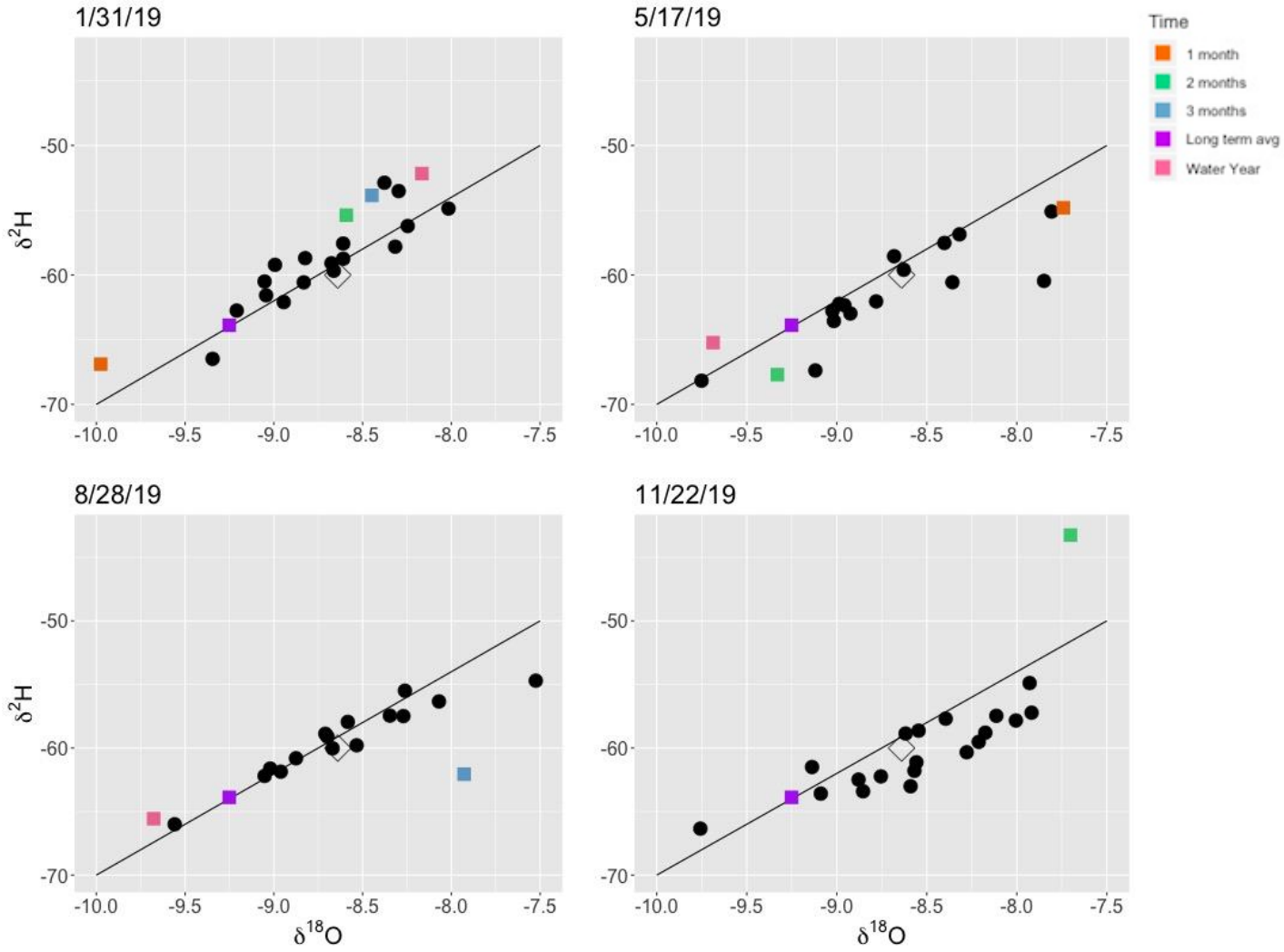

Figure 9: Shallow groundwater samples shown as black circles. The mean isotopic signature of shallow groundwater sites is shown as an open diamond. Precipitation means (integrated over different time periods) are shown as colored squares, where weekly measures were integrated precipitation amount-weighted means since the sampling date. GMWL shown as black line.

3.3.1 Surface Water Trends

Isotopic shifts in water as it moves downstream come from mixing of new water sources entering the stream. δ_2H values do not show a large range of values with movement downstream (Figure 10). Summer sampling events show the most variation in δ_2H values, 8.1‰ for September 10, 2018 and 3.5‰ for August 28, 2019. The stream water in agricultural areas has similar δ_2H values to the groundwater sampled from agricultural areas. Sampled tributaries account for some of the variation in the δ_2H values, but changes in δ_2H were measured in Oak Creek that are not explained by tributaries, indicating that other unmeasured sources, either groundwater or surface water, are mixing into the stream.

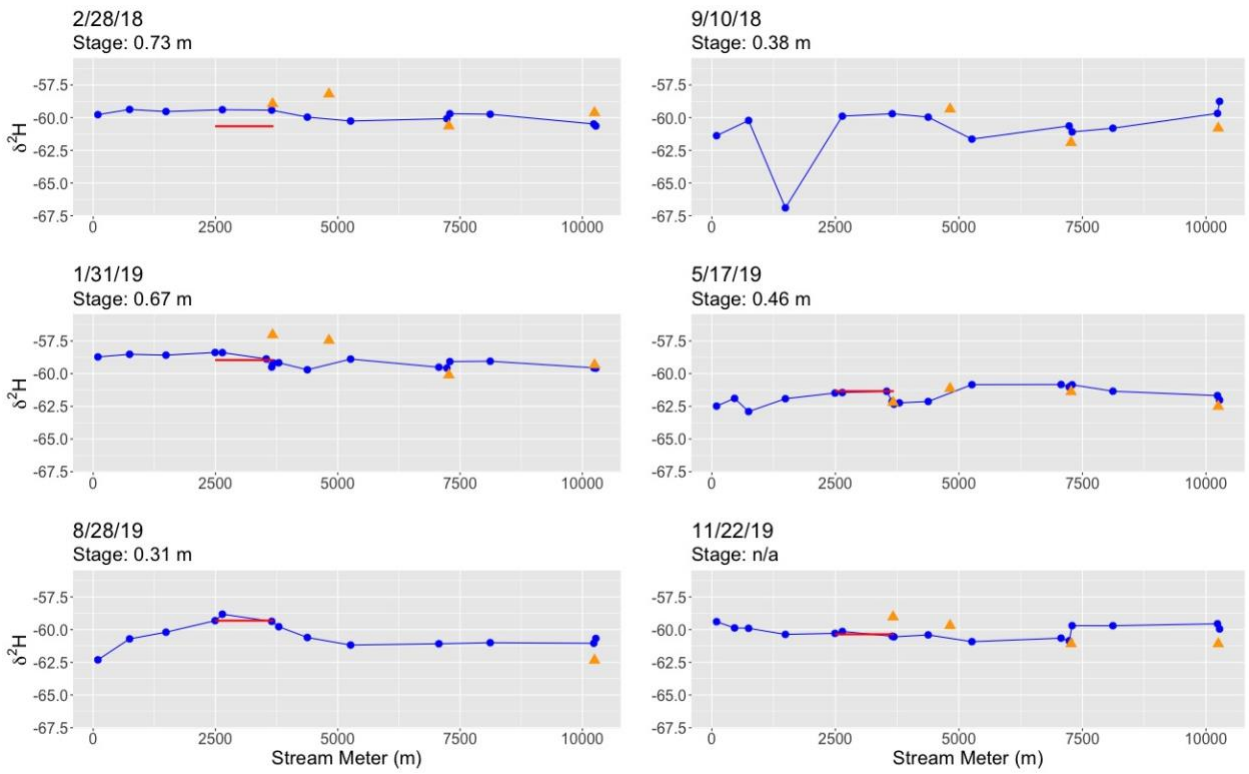

Figure 10: Changes in δ_2H signatures with distance along creek for each sampling event. Mainstem samples are blue circles. Blue line connects mainstem samples from headwaters of Oak Creek (10,275 m) to mouth (0 m). Tributaries are shown as orange triangles at the distance where they enter the mainstem. Red line represents mean groundwater δ_2H value and spans the length of the stream which passes through the area where shallow groundwater wells are installed.

Changes in temporal variability were examined by looking at the standard deviation of each sampling location (Figure 11). Standard deviation of δ_2H generally increased with movement downstream. The two headwater forest sites (at 10,275 and 10,248 m) had slightly higher variation than the ones directly downstream, possibly due to the variability of precipitation signatures between sampling dates (Figures 8 and 9). Downstream locations showed greater variation indicating mixing of more variable sources, which may be indicative of groundwater mixing, considering the larger range measured δ_2H values in groundwater. Three of the four tributaries were more variable than the surrounding mainstem sites, and the two tributaries draining agricultural catchments are especially variable. The standard deviation of δ_{18}O at each site was within the analytical error range (<0.2 ‰), with the exception of TS22 (stream meter 1,488 m). This site also showed the highest variation in δ_2H and irregular activity in the September 10, 2018 sampling event (Figure 10), most likely caused by a nearby point source.

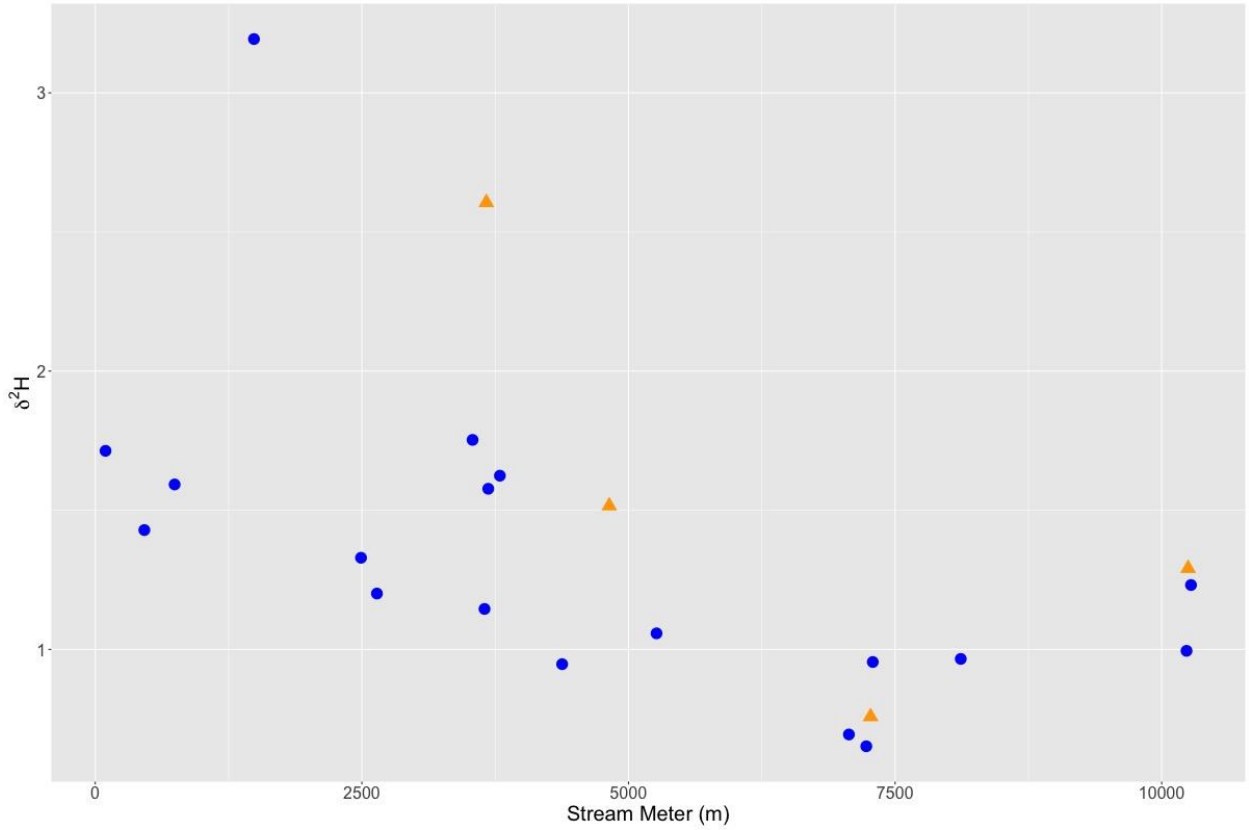

Figure 11: Standard deviation of $\delta_{2}H$ over all six sampling events at sampling locations along the stream length. Stream meter 0 is the mouth of Oak Creek. Blue points are mainstem sites, orange triangles are tributary sites.

$\delta_{18}O$ varied more with movement downstream relative to $\delta_{2}H$. Generally, the stream became more enriched with movement downstream, with the exception of September 10, 2018 where the opposite was true (Figure 12). Consistent with $\delta_{2}H$, downstream mixing occurred that cannot be explained by the measured tributaries or groundwater wells. However, unlike $\delta_{2}H$, the mean shallow groundwater $\delta_{18}O$ signature does not match that in the stream, indicating that the water entering the stream was not shallow groundwater. In five of the six sampling events, the stream becomes more depleted at the beginning of the agricultural section where we would expect it to become more enriched if measured groundwater were contributing to the stream (Figure 12).

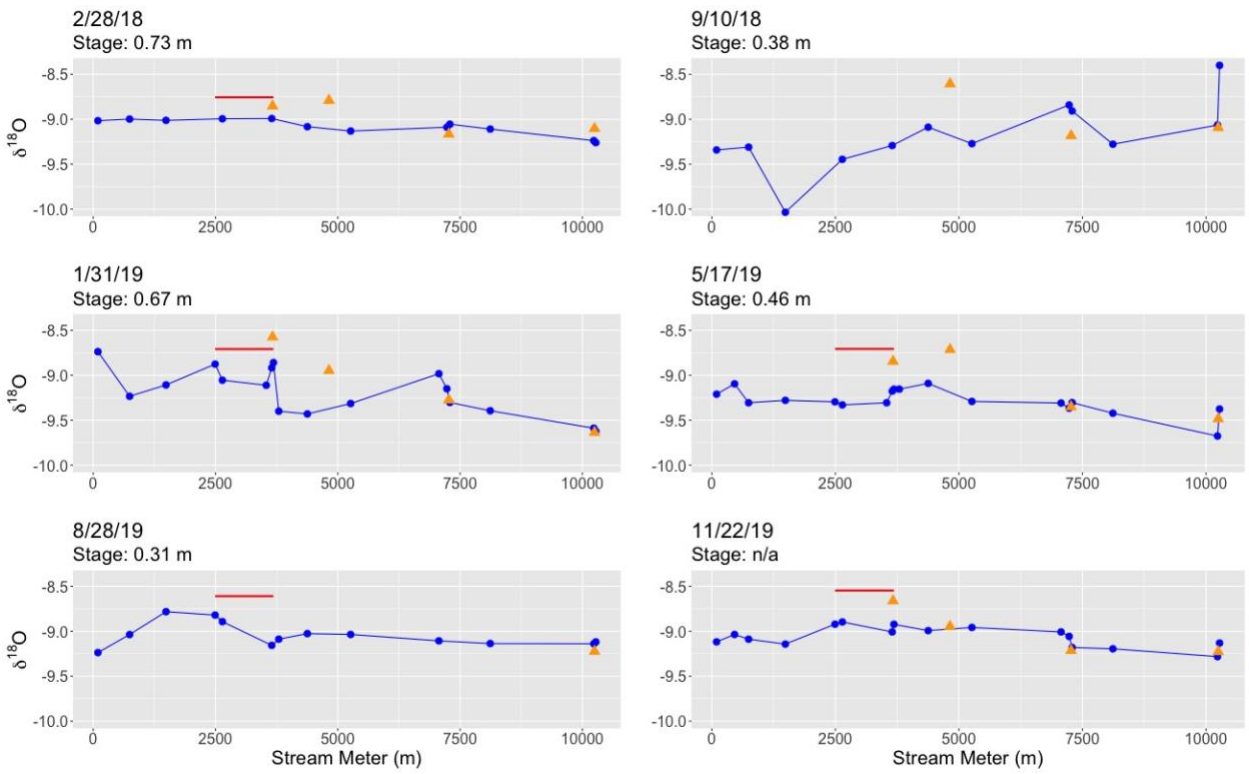

Figure 12: $\delta_{18}O$ signatures by sampling event. Mainstem samples are blue circles. Blue line connects mainstem samples from headwaters of Oak Creek (10, 275 m) to mouth (0 m). Tributaries are shown as orange triangles. Red line represents mean groundwater $\delta_{18}O$ value and spans the length of the stream which passes through the area where shallow groundwater wells are installed.

Surface water had a much higher d-excess than the measured shallow groundwater (Figure 13). Thus d-excess might reveal mixing of shallow groundwater as surface water moves downstream. The mean d-excess of groundwater falls below the GMWL in all but one sampling event and almost all stream samples fall above the GMWL and move both closer to and further to the GMWL along the stream meter gradient. Groundwater inflows may be occurring where stream samples move closer to the mean shallow groundwater d-excess. Sampling sites do not follow the same pattern between sampling dates, indicating that contributing sources change over time. In general, d-excess tends to decrease from headwaters to downstream (Figure 14). However, the large differences between sites relatively close to each other indicate that multiple sources with varying d-excess must be contributing to the stream.

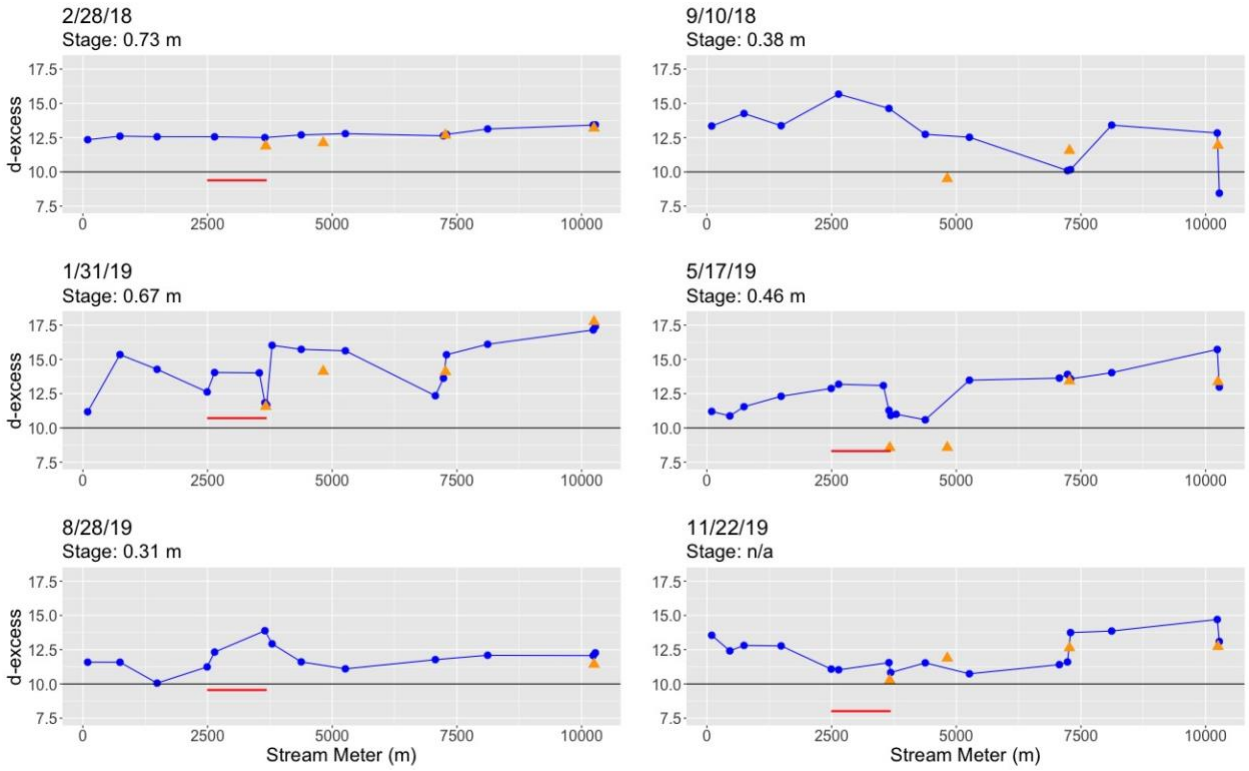

Figure 13: D-excess values by sampling event. Mainstem samples are blue circles. Blue line connects mainstem samples from headwaters of Oak Creek (10, 275 m) to mouth (0 m). Tributaries are shown as orange triangles. Red line represents mean groundwater d-excess value and spans the length of the stream which passes through the area where shallow groundwater wells are installed. D-excess of the GMWL (10 ‰) is shown in black.

D-excess variation also decreased slightly moving downstream (Figure 14). Variation in stream samples within each sampling date was predominantly in $\delta^{18}O$, not $\delta^{2}H$, and therefore spatial variation in d-excess indicates variation in $\delta^{18}O$ sources (Figure 7). Higher variation in the headwaters may be due to temporal precipitation variability; the headwaters are mostly fed by recent precipitation while the downstream sites are a mix of recent precipitation and other ground and surface water sources, both of which exhibit less variation than precipitation signatures. Precipitation events have varied isotopic signatures, which in a precipitation-fed system, causes variation between sampling dates (Figures 8 and 9). With movement downstream, groundwater sources with comparatively lower d-excess signatures enter the stream therefore reducing the variability (Figure 14). Although measured groundwater sources move up and down along the GMWL, the values fall on or close to the GMWL giving them a mean d-excess that is lower than stream water d-excess.

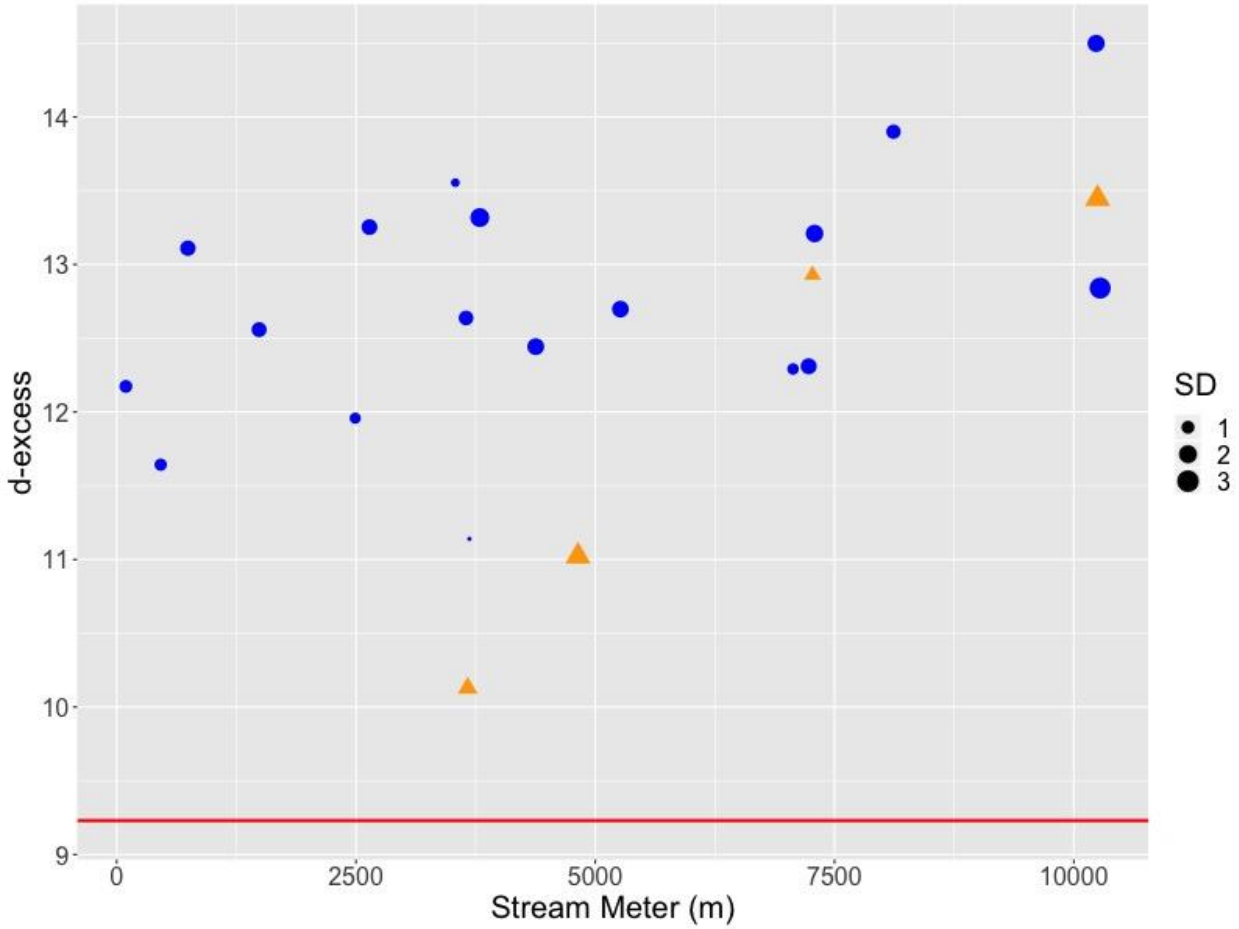

Figure 14: Mean d-excess values at each sampling location. Stream meter 0 represents the mouth of the Oak Creek. Blue points are mainstem sites, orange triangles are tributary sites. Red line represents mean groundwater d-excess value. Size of points reflects d-excess standard deviation.

3.3.2 Groundwater trends

Groundwater isotopes fall more evenly along the GMWL compared to stream isotope values. Wells within the same field do not have similar isotopic signatures, indicating that groundwater flow paths within the same proximity are carrying water from different sources (Figure 15). The variability of each well between sampling events indicate that the residence times are likely not the same between wells within the same field. The variation in signatures of groundwater on both a temporal and spatial scale mean that shallow groundwater cannot be considered as one large, static source, but rather that it varies with residence time and precipitation inputs. Riparian groundwater wells shift in $\delta_{18}O$ and d-excess values, sometimes falling below and other times above the GMWL, indicating that riparian wells are more influenced by stream water than wells in other fields. The $\delta_{18}O$ shift is consistent with higher variability of $\delta_{18}O$ than $\delta_{2}H$ in stream water.

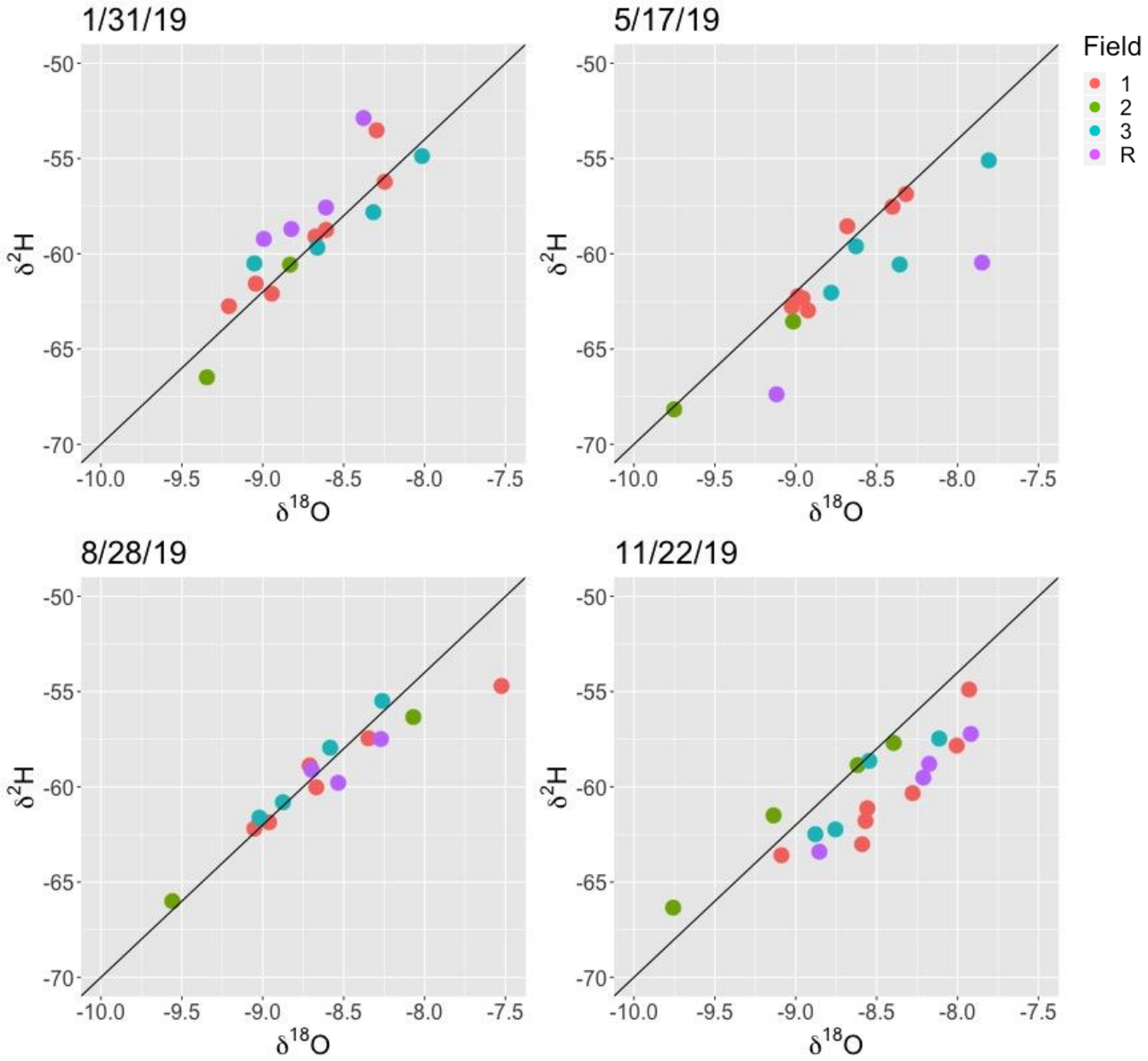

Figure 15: Dual isotope plot of groundwater samples collected during the project. GMWL is drawn in black.

3.4 Anion Concentration

Concentrations of chloride, sulfate, nitrate, phosphate, bromide, and fluoride were measured at selected stream and well locations from January 2018 through November 2019. In multiple samples, bromide and fluoride had concentrations that were below the level of detection (0.01 ppm) and therefore did not provide consistent data for analysis and were not further explored. Chloride, sulfate, nitrate, and phosphate were identified as parameters of interest given their potential to identify land use effects on water quality.

3.4.1 Surface water trends

Chloride concentrations ranged from 3.4 ppm to 13.0 ppm with a mean of 7.3 ppm (SE ± 0.25 ppm) in the main steam and from 3.5 ppm to 25.8 ppm with a mean of 8.3 ppm (SE ± 1.03 ppm) in tributaries. chloride concentrations generally showed higher values in late summer and "wetting up" period (e.g., August – November) compared to winter and spring values, which exhibited similar concentrations. Chloride concentration increased (mean = 0.43 ppm km^{-1}) with movement downstream across all sampling dates, and consistently showed a step increase in concentrations between the forest headwaters and other sites (8,000 meters, Figure 16a).

Sulfate concentrations ranged from 1.56 ppm to 13.06 ppm with a mean of 2.77 ppm (SE ± 0.15 ppm) in the main steam and from 1.62 ppm to 5.94 ppm with a mean of 2.86 ppm (SE ± 0.20 ppm) in tributaries. Similar to chloride, sulfate also tended to exhibit the highest concentrations between August and November, and increased in concentration with movement downstream (mean = 0.25 ppm km^{-1}). In summer sampling events, there was a steep increase in sulfate concentration at downstream sites. Unlike the chloride behavior downstream, sulfate did not show a step function in concentrations at the inception of agriculture fields, though the two agricultural tributaries (triangles at stream meter 5000 and 3750; Figure 16b) show elevated chloride and sulfate values compared to the surrounding mainstem sites.

Nitrate concentrations ranged from 0.01 ppm to 1.21 ppm with a mean of 0.50 ppm (SE ± 0.03 ppm) in the main steam and from 0.02 ppm to 1.15 ppm with a mean of 0.35 ppm (SE ± 0.06 ppm) in tributaries. Mean nitrate concentrations were consistent from the headwaters to stream meter 3500, where the stream transitions into an urban setting, however, below stream meter 3500 nitrate concentration increased with movement towards the mouth (Figure 16c). Unlike sulfate and chloride, highest nitrate concentrations were observed during winter; elevated concentrations of nitrate were also observed during the summer in the urban reach. In winter, nitrate concentrations increase consistently with movement downstream, while spring nitrogen concentrations decrease with movement downstream until reaching the urban area, where they then increase in concentration. In summer, agricultural areas exhibit lower nitrate concentrations compared to forested sites, followed by higher concentrations in urban areas.

Phosphate concentrations ranged from 0.01 ppm to 0.22 ppm with a mean of 0.06 ppm (SE ± 0.003 ppm) in the main steam and from 0.02 ppm to 0.13 ppm with a mean of 0.06 ppm (SE ± 0.006 ppm) in tributaries. In contrast to chloride and sulfate, mean phosphate concentrations do not significantly change with movement downstream, with the exception of August 28, 2019 which showed an increasing concentration with movement downstream (Figure 16d). High concentrations for other anions (i.e., chloride, sulfate, nitrate) were also measured for this event. phosphate concentrations generally exhibit similar temporal changes to chloride, sulfate, and nitrate with higher values observed in the summer months.

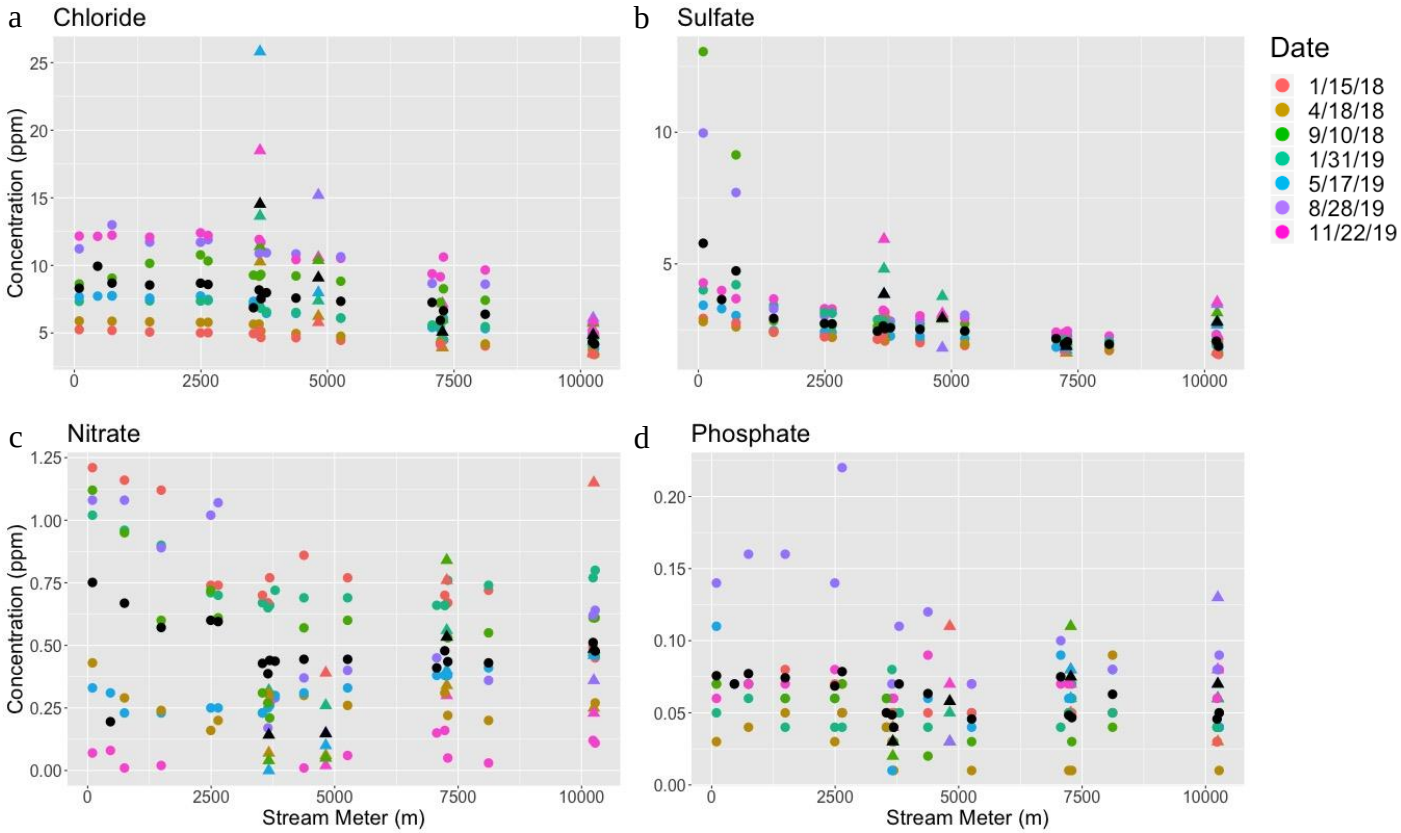

Figure 16: Concentrations of chloride (a), sulfate (b), nitrate (c), and phosphate (d) vs stream meter. Stream meter 0 represents the mouth of the Oak Creek. Colored points represent different sampling events. Black points are the mean values for each site.

Examining standard deviation of anion concentration provides insight into the source of each anion in Oak Creek. Low variability suggests a constant source, while high variability indicates temporally varying sources, or that outside processes may be impacting concentration. Across all four anions, downstream sites exhibit more variability than headwater sites (Figure 17). Chloride, nitrate, and phosphate exhibit a general increase in variability with movement downstream. Interestingly, chloride shows a step increase in variability between the forested headwaters and more downstream sites, suggesting that chloride concentrations in the headwaters are driven by a constant source while downstream sites are influence by anthropogenic activity (Figure 17a). Nitrate concentrations also exhibit a step increase, similar to chloride, however the increase was measured between agricultural and urban areas, indicating more variation in urban nitrate sources than forest and agricultural sources (Figure 17c). In contrast to other measured anions, sulfate variability does not exhibit a significant increasing trend and exhibits the lowest variation in concentration, except for two downstream sites, indicating that sulfate sources are consistent year-round and thus, are not likely governed by anthropogenic activity (except two urban sites) (Figure 17b).

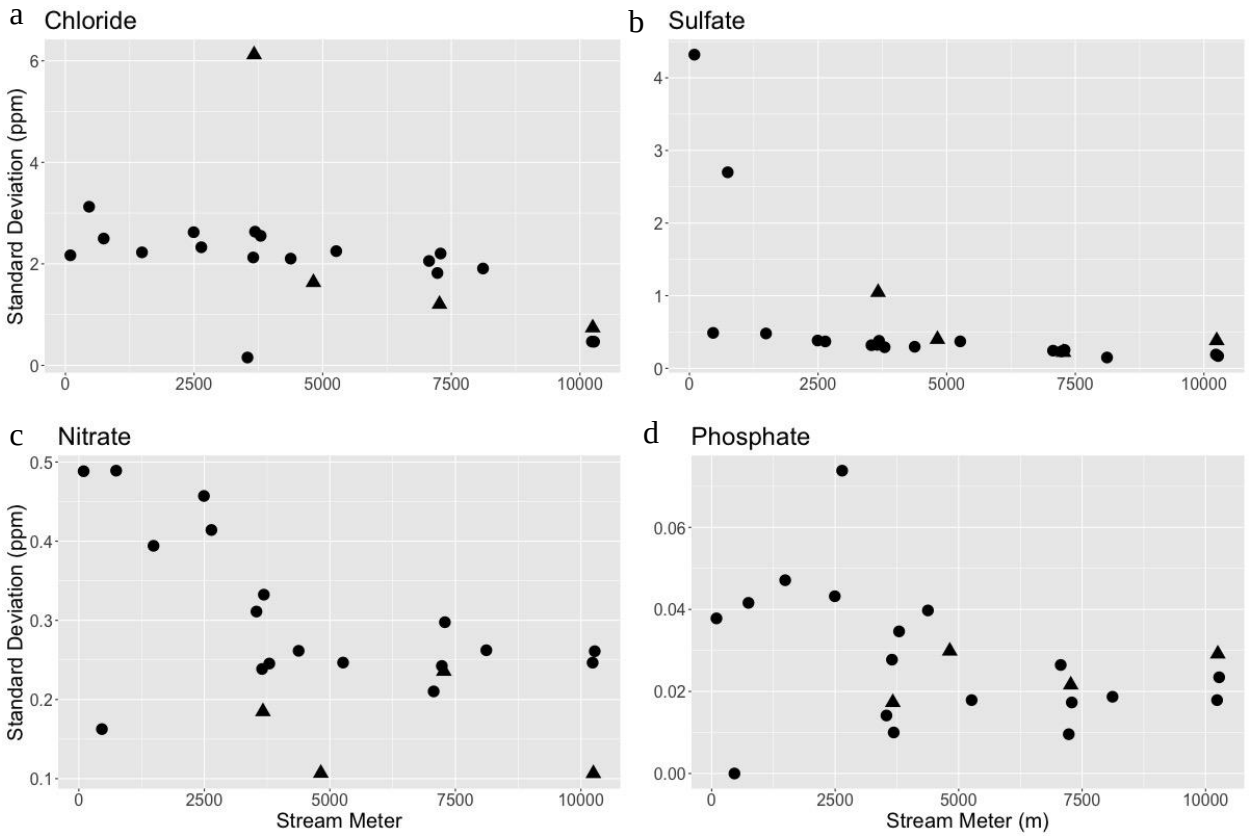

Figure 17: Standard deviation of chloride (a), sulfate (b), nitrate (c), and phosphate (d) along stream meter. Mainstem sites are shown as circles and tributaries are shown as triangles. Stream meter 0 represents the mouth of Oak Creek.

3.4.2 Groundwater trends

Groundwater chloride concentrations were higher than surface water concentrations (Figure 18a) while groundwater nitrate concentrations were significantly lower than surface water concentrations (Figure 18c). Phosphate and sulfate concentrations were not significantly different between the groundwater and surface water samples, although groundwater sulfate concentrations were generally higher than surface water concentrations (Figure 18b). Temporal trends were not observed in groundwater concentrations. Only one year of continuous data has been collected for groundwater analysis and trends may emerge over the course of the long term study.

Groundwater chloride concentrations range from 2.34 ppm to 530.59 ppm with a mean of 68.40 ppm (SE ± 15.26 ppm), which is mainly driven by significantly higher concentrations observed in Field 3 (mean = 242.68 ppm, SE ± 48.51 ppm) as compared to the other two fields (mean = 17.73 ppm, SE ± 1.61 ppm).

Nitrate concentrations range from 0.01 ppm to 54.76 ppm with a mean of 7.00 ppm (SE ± 2.81 ppm). Again, Field 3, and specifically F3W3 had nitrate concentrations consistently higher than all other wells (mean = 43.78 ppm, SE ± 4.08 ppm). Higher concentration (>1 ppm) of nitrate were measured in Field 1 on August 28, 2019. Besides these occurances, all data fell below 1 ppm with nitrate concentrations below the detection level in 58.2% of samples.

Phosphate concentrations range from 0.01 ppm to 2.45 ppm with a mean of 0.19 ppm (SE ± 0.06 ppm). 31.6% of groundwater phosphate concentrations were below detection level.

Concentrations are generally consistent across all three fields, with the exception of consistently high concentrations (>0.25 ppm) in F2W3 and F3W2. Phosphate concentrations may be elevated in F2W3 due to its close proximity to the dairy operation drainage channel.

Groundwater sulfate concentrations range from 0.03 ppm to 67.04 ppm with a mean of 9.12 ppm (SE ± 1.40 ppm). Concentrations are higher in Fields 1 and 2 (mean = 9.14 ppm, SE ± 0.25 ppm), compared to Field 3 (mean, excluding F3W3 = 1.55 ppm, SE ± 0.06 ppm). Similar to nitrate, F3W3 had substantially elevated sulfate concentrations (mean = 45.56 ppm, SE ± 6.73 ppm).

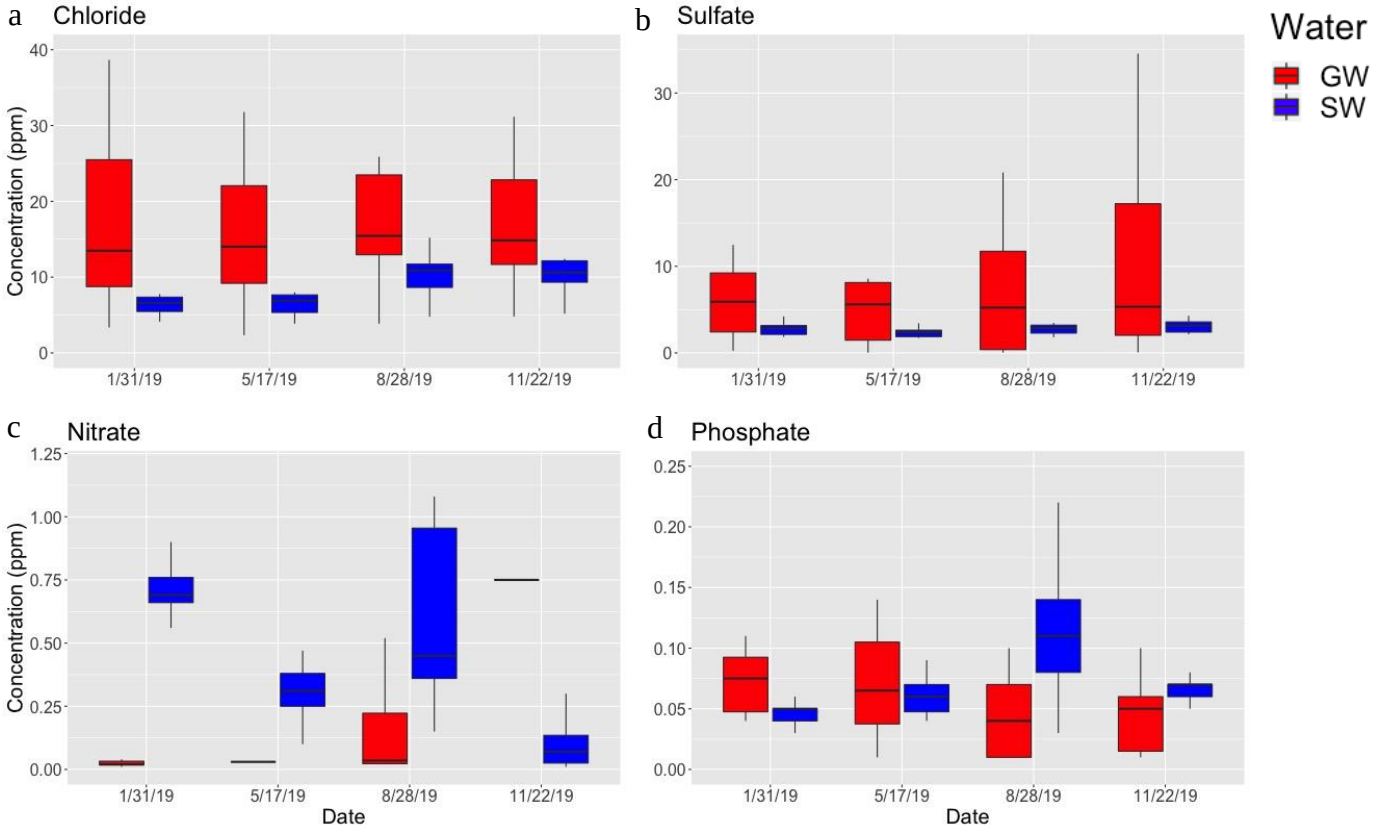

Figure 18: Surface water and groundwater concentrations of chloride (a), sulfate (b), nitrate (c), and phosphate (d) for all sampling dates. Outliers not shown.

Of the four measured anions, chloride differs most, and most consistently, between fields. Chloride exhibits a strong, positive, log-linear relationship with specific conducivity (slope = 0.34 µS ppm^{-1}) (Figure 19a). Field 3 is characterized by distinctly higher chloride and specific conductivity values than Field 1, Field 2, and the riparian area, which exhibit similar ranges of both parameters. Since specific conductivity is measured monthly while chloride is measured quarterly, conductivity can be used as a proxy for chloride concentrations.

Contrary to specific conductivity, sulfate and chloride exhibit a strong, negative, log-linear relationship (slope = -1.15 ppm ppm^{-1}) if the behavior or F3W3 (blue points in upper right, Figure 19b) is removed from the analysis. Field 3, aside from F3W3, is characterized by high chloride and low sulfate values, whereas fields 1 and 2 are characterized by low chloride and high sulfate values. Riparian wells have chloride concentrations similar to fields 1 and 2, but lower relative sulfate values.

Neither phosphate nor nitrate show strong correlations with chloride nor clustering of points by field.

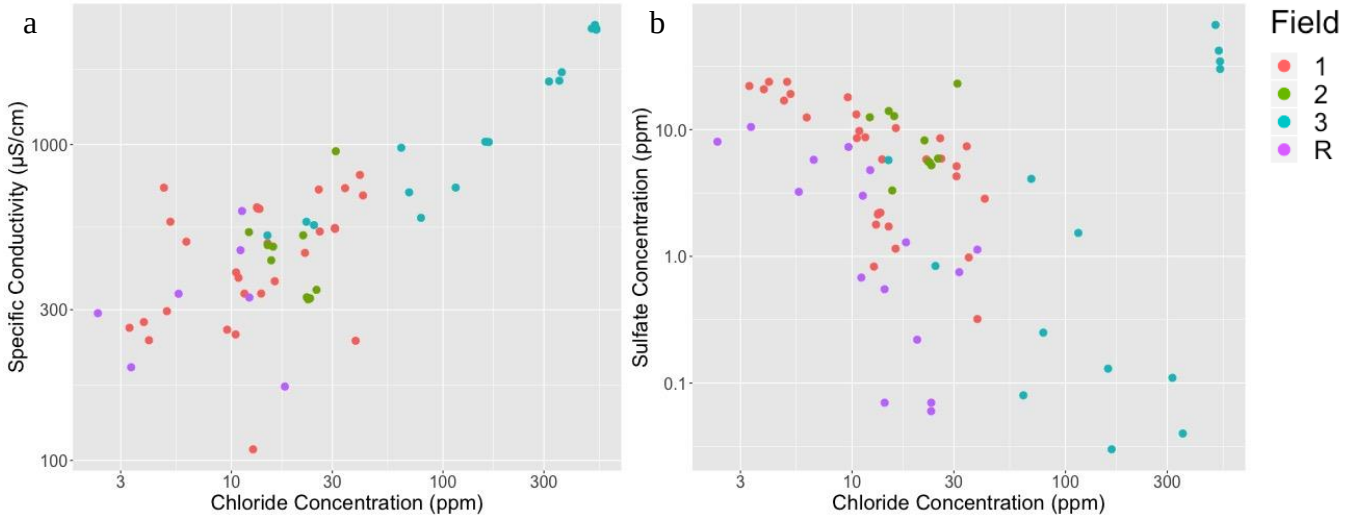

Figure 19: Relationship between chloride concentrations and specific conductivity (a) and chloride and sulfate concentrations (b) in groundwater. Axes are on a log scale.

3.4.3 Groundwater – surface water interactions in agricultural areas

Stream water consistently increases in chloride and sulfate as it passes through the agricultural area (red and purple points, respectively, Figure 20). Increase in chloride is highest on August 28, 2019 and September 10, 2018, while increase in sulfate is highest in January 31, 2019 and August 28, 2019. In comparison, nitrate and phosphate show more variability, with both anions exhibiting decreasing concentrations on April 18, 2018 and January 31, 2019, respectively (blue and green points, respectively, Figure 20). Interestingly, significant nitrate increases were only measured on August 28, 2019 and September 10, 2018, which coincides with the elevated inputs of concentration chloride.

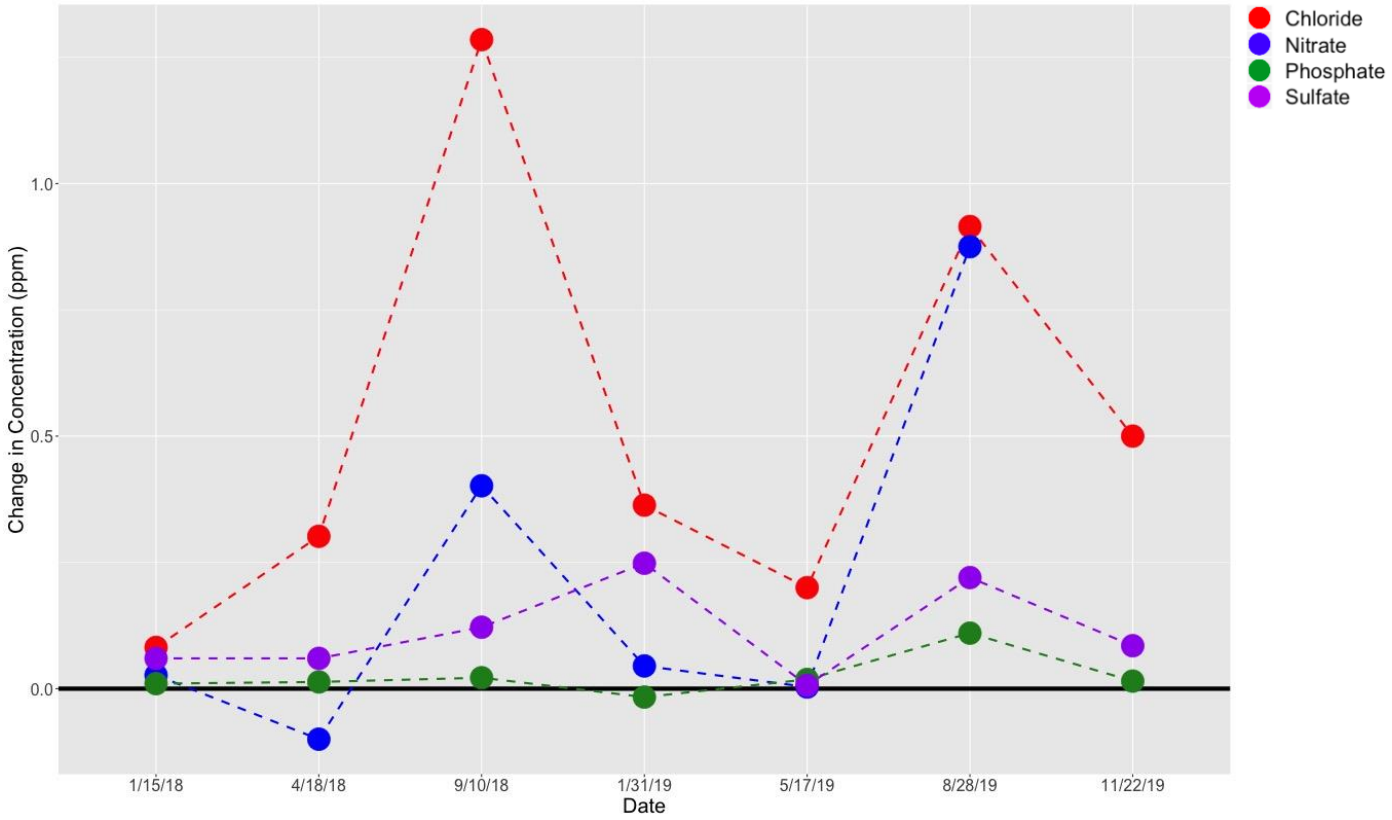

Figure 20: Change in stream water anion concentrations before and after agricultural groundwater monitoring area. Black line drawn at 0 ppm.

3.5 Correlations

Chemical parameters and factors that may be influencing them (e.g., elevation and stream meter) show more and stronger correlations in winter compared to summer sampling events (Figure 21). In winter, chloride is positively correlated with sulfate, conductivity, and $\delta_{18}O$, and negatively correlated with nitrate, stream temperature, elevation, and stream meter. Like chloride, sulfate is also positively correlated with $\delta_{18}O$, and negatively with elevation and stream meter. Nitrate has a strong negative correlation with conductivity and positive correlation with temperature. Interestingly, $\delta_{2}H$ and $\delta_{18}O$ are not strongly correlated in winter, however, $\delta_{18}O$ is correlated with elevation and stream meter (Figure 21a). In the summer, many of the correlations exhibited in winter sampling events weaken and fall away (Figure 21b). However, chloride is more strongly correlated with elevation and stream meter in the summer compared to the winter. Unlike winter, $\delta_{18}O$ and $\delta_{2}H$ exhibit a correlation in the summer, and the correlation between $\delta_{18}O$ and elevation and stream meter falls away (Figure 21b), indicating that stream water source differs between the summer and winter.

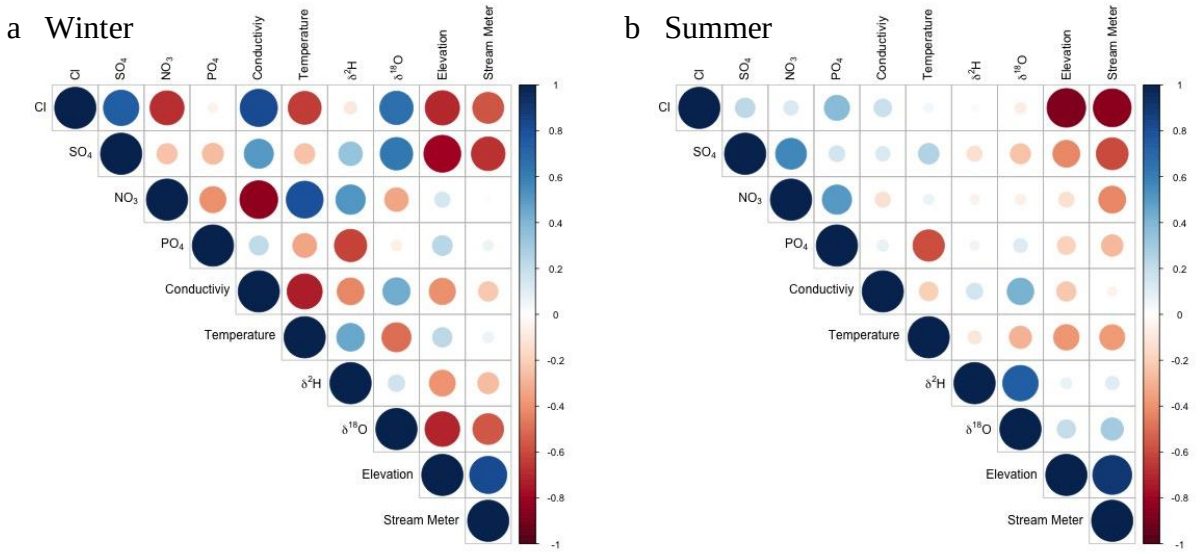

Figure 21: Correlation matrix of all mainstem values for measured variables. Left matrix includes winter sampling events (a) and right matrix includes summer sampling events (b). Size of circle indicates correlation coefficient.

Chemical parameters exhibit the most and strongest correlations in Field 3 compared to other monitored groundwater areas (Figure 22). In Field 3, chloride, sulfate, nitrate, specific conductivity, $\delta_{18}O$, and $\delta_{2}H$ are all positively correlated with each other (Figure 22c). Phosphate is the only parameter that shows significant negative correlations, with chloride and conductivity. Field 3 clearly exhibits different behavior than the other measured groundwater areas (Figure 19). However, when Well 3 is removed the negative correlations associated with phosphate become stronger, and many of the positive correlations weaken, or in the case of sulfate and water isotopes, reverse altogether, indicating that the behavior of Well 3 is driving many of the exhibited relationships (Figure 22c inset).

Other groundwater sampling areas do not show consistent patterns in correlations. Fields 1 and 2 have more negative correlations than Field 3 and the riparian area. Field 1 exhibits negative correlations between chloride and $\delta_{18}O$ and $\delta_{2}H$, and between sulfate and chloride and conductivity (Figure 22a). Positive correlations are exhibited between chloride and phosphate and conductivity, and between sulfate and $\delta_{18}O$ and $\delta_{2}H$. This suggests that water source is influencing sulfate and chloride concentration within Field 1; more isotopically enriched water is higher in sulfate concentration while isotopically depleted water is higher in chloride concentration.

Field 2 exhibits negative correlations between chloride and $\delta_{18}O$ and $\delta_{2}H$ (consistent with Field 1), nitrate with sulfate and temperature, and phosphate with sulfate, conductivity, $\delta_{18}O$, and $\delta_{2}H$, while positive correlations are exhibited between sulfate and conductivity, $\delta_{18}O$, and $\delta_{2}H$ (Figure 22b).

The riparian zone exhibits the fewest correlations of groundwater sampling areas (Figure 22d). Positive correlations were observed between chloride and phosphate, and nitrate and sulfate, $\delta_{18}O$ and $\delta_{2}H$, and negative correlations were observed between chloride and sulfate, nitrate, and conductivity, and phosphate and conductivity. The lack of correlations may stem

from greater stream water influence, which tends to show fewer correlations than groundwater in the summer (Figure 21b), compared to wells in other areas (i.e., Fields 1-3).

Unlike winter stream data, all four groundwater sampling locations exhibited a positive correlation between $\delta_{18}O$ and $\delta_{2}H$ indicating that the water is not enriched in $\delta_{18}O$ as seen in stream water. Summer stream data exhibits a positive correlation between $\delta_{18}O$ and $\delta_{2}H$ which indicates that summer flows are more influenced by groundwater than winter flows. However, the $\delta_{18}O$-$\delta_{2}H$ correlation in the riparian zone is weaker than that observed in other three fields which further indicates that there may be a greater influence in stream water.

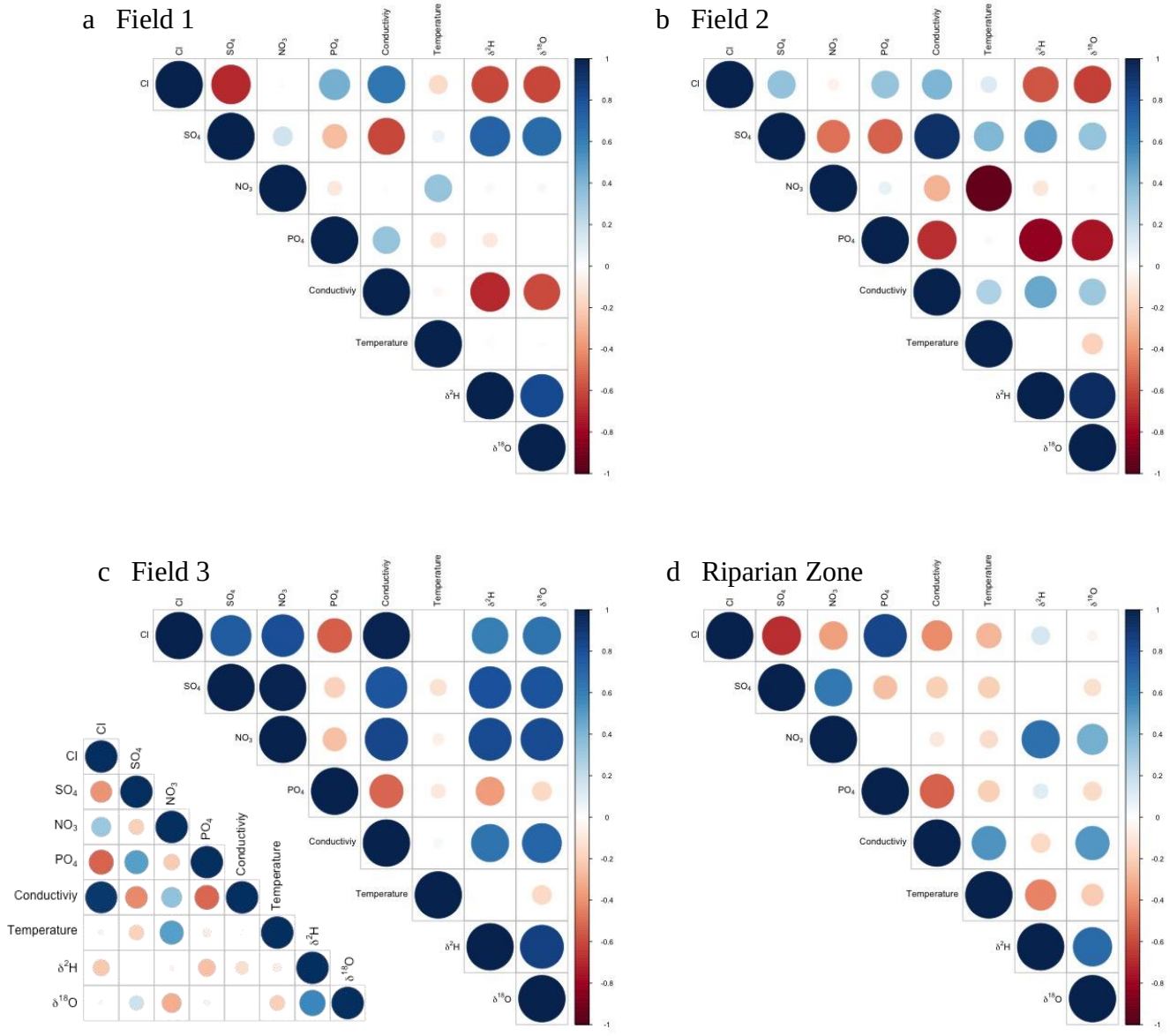

Figure 22: Correlation matrix of all groundwater values for measured variables. Field 3 inset excludes F3W3. Size of circle indicates correlation coefficient.

4 Discussion

Stream water and groundwater isotopic values and anion concentrations in Oak Creek that cross the topographic (63m-649m) and land use (urban, agriculture, and forested) gradients from January 2018 to November 2019 show three major phenomena: 1) Oak Creek acts as an integrator of precipitation received in high elevations and incoming ground and surface water sources as it moves downstream driving overall stability of isotopic compositions but leading to an increasing chloride and sulfate concentrations; 2) shallow groundwater in agricultural settings exhibits high spatial variability; and 3) land use – water quality relationship are complex and temporally variable. Overall the message that emerges is that Oak Creek watershed is governed by spatially variable hydrologic, land use, and biological processes. I discuss these three key findings below.

4. 1 Oak Creek acts as an integrator

4.1.1 Precipitation as a source of isotopic variability

Stream water exhibited only a fraction of the variability measured in precipitation (Figure 8), indicating that the stream acted as an integrator of recent precipitation and other sources, including shallow groundwater and other non-measured surface water sources. Stream water deviated from the mean mainstem isotopic values (white diamond in Figure 8) towards recent precipitation, which suggests that these sampling events were influenced by their respective recent (as in a few months to a year) precipitation events. For example, the samples from January 31, 2019 were above the long-term stream mean towards the enriched recent precipitation, while the samples from May 17, 2019 were below the long-term mean towards more depleted recent precipitation (Figure 8). However, stream samples throughout the study never deviate far from the long-term mean value, and they are skewed towards time-integrated precipitation values from two months to the water year, suggesting that recent (as in days to one month) precipitation is not the main contributor to the stream, but rather slower (months to a year) pathways dominate such as recently infiltrated groundwater. The one exception to this is the February 28, 2018 sampling event which, unlike other events, was collected on the rising limb of the hydrograph indicative of increased inputs of young water (Figure 3). Additionally, samples from this event exhibit a slope similar to the GMWL and appear to be skewed away from the long-term stream water mean towards one-month precipitation. With movement downstream, d-excess stays consistent and the isotopic composition of the samples become more enriched. The previous month received 120.9 mm of rain which had a mean isotopic signature with a similar d-excess, but more enriched than, the long-term mean stream water (Figure 8). Bankfull storage from recent high flows may be contributing to the stream, therefore enriching isotopic values of the stream while maintaining a stable d-excess.

All sampling events had stream water with high d-excess, and because stream samples vary more in $\delta_{18}O$ within a sampling date than $\delta_{2}H$, d-excess is driven by variation in $\delta_{18}O$ (Figure 7). High d-excess values were measured in the headwaters and were not measured in precipitation nor shallow groundwater, indicating that this could be an elevation effect. Consistent with Oak Creek data, high d-excess values were measured most consistently in spring and summer in the Marys River watershed, while fall and summer exhibited some values below, rather than above, the GMWL (Nickolas et al., 2017). Interestingly, when the Marys River watershed was divided based on underlaying geology, sandstone dominated catchments exhibited more seasonal variation in d-excess values. Oak Creek exhibits similar seasonal variation, despite being underlaid by basalt, although comparably less than to the Marys River.

One potential explanation for the high d-excess values is the upwelling of a high d-excess groundwater source in the upper watershed. However, samples were collected from sites further upstream of sampling sites did not show the highest d-excess, although they were still depleted in $\delta_{18}O$. Furthermore, if the source of high d-excess were groundwater, we would expect summer sampling events dominated by groundwater to show high d-excess water, but the upper watershed sites show the lowest measured d-excess in the summer. Lastly, sampling events on January 31, 2019 and May 17, 2019 show more depleted $\delta_{18}O$ values compared to both the samples collected further upstream of sampling sites and other sampling events, indicating that the high d-excess water cannot be from a constant source. Given the variation in $\delta_{18}O$ and $\delta_{2}H$ values of the high d-excess water, a process rather than constant source is likely causing depletion in $\delta_{18}O$ relative to $\delta_{2}H$. One process that may explain high d-excess values in the upper watershed is re-evaporation of precipitated water caught by canopy interception on the windward side of the coast range (Allen et al., 2017). Low clouds are common in the upper elevations of the coast range, creating an environment where evaporated water can contribute to local precipitation. Thick coastal canopies intercept precipitation, which is then evaporated, contributing high d-excess vapor back to the atmosphere. As the cloud moves over the coast range, precipitation is higher in d-excess compared to that which did not come from re-evaporated vapor. The slope of the evaporation line determines the d-excess and is driven by relative humidity, and the variability of humidity may help to explain why some events show water with a higher d-excess than others (Figure 1). For example, samples collected from sites further upstream did not show the highest d-excess, and sampling events on January 31, 2019 and May 17, 2019 show more depleted $\delta_{18}O$ values. The higher variability of d-excess in the upper watershed relative to downstream sites indicates that they are influenced more by re-evaporated vapor variability than downstream sites, which supports the hypothesis that upper watershed high d-excess water originates from precipitation that contains more re-evaporated vapor. The process must also be contained to the upper watershed because precipitation and shallow groundwater samples collected at lower elevations did not exhibit high d-excess. More research is needed to determine the exact cause of high d-excess in the stream water.

4.1.2 Groundwater as a source of isotopic stability

Unlike stream water, groundwater samples fell on or below, rather than above, the GMWL (Figure 7), and exhibited similar $\delta_{2}H$ values (Figure 10), but more enriched in $\delta_{18}O$ (Figure 12). No high d-excess water was measured in the shallow groundwater, and it had a consistently lower d-excess than stream water, indicating that shallow groundwater is not impacted by the same high elevation precipitation that may cause high d-excess stream water. Decreasing d-excess and d-excess variability with movement downstream (Figure 14) indicates mixing of lower d-excess waters, which may be caused by mixing of shallow groundwater with stream water. Shallow groundwater can explain the deviations towards lower d-excess values; however, all sampling events, except February 28, 2018, exhibited deviations towards high d-excess values as well (Figure 13), which cannot be accounted for by measured groundwater. For example, on August 28, 2019, $\delta_{18}O$ values increased through the agricultural section of the stream causing a decrease in d-excess shifting the stream values closer to measured groundwater values indicating a contribution of shallow groundwater to Oak Creek (Figure 13). However, downstream of this location, the stream exhibits an increase in d-excess, but no incoming sources were measured nor can it be explained by any measured shallow groundwater. This event, and other similar deviation thus indicate that other sources that we did not measure are clearly

mixing with stream water as it moves downstream. Furthermore, the large difference between stream and groundwater $\delta_{18}O$ values indicates that there is not enough shallow groundwater contributing to alter the isotopic signature of stream water. Deeper aquifer contributions may be the origin of the non-measured sources and could carry depleted $\delta_{18}O$ water to lower elevations from higher elevations through deeper flow paths, thus contributing high d-excess water seen in Figure 13.

On a broader scale, seasonal isotopic trends can also be used to examine potential groundwater contributions to Oak Creek. Groundwater consistently exhibits strong, positive correlations between δ_2H and $\delta_{18}O$ (Figure 22). Interestingly, stream water δ_2H and $\delta_{18}O$ exhibit a positive correlation in the summer, but lack correlation in the winter (Figure 21), indicating higher contributions of groundwater to surface water in the summer

4.1.3 Groundwater as a source of sulfate and chloride in stream water

Both sulfate and chloride concentrations increased with movement downstream across all sampling events indicating integration of downstream sources. Sulfate concentration exhibited very little variation between sampling events indicating that a constant process may be the source of stream water sulfate (Figure 17b). The sampling events that deviated from the trend and exhibited elevated sulfate concentrations were not consistent in location nor season: elevated concentrations in urban areas were measured in the summer while those in agricultural tributaries were measured the winter, indicating that agricultural and urban sulfate inputs are different. If agricultural inputs were the cause of elevated sulfate concentrations in the tributaries, we would expect to see higher concentrations of agriculturally associated inputs in the summer. The forest tributary also exhibits elevated concentrations of sulfate in the winter, indicating elevated concentrations are likely associated with natural processes, not only associated with development. One possible explanation for elevated sulfate concentrations is the leaching of secondary sulfate from soil into stream water. In the Sleepers River watershed in Vermont, US, Mayer et al. (2010), found that during the second re-wetting phase, re-oxidation of sulfides in soil and bedrock doubled sulfate concentration in streams. Increasing downstream concentrations may also be driven by groundwater contributions to Oak Creek, as shallow groundwater values generally exhibited higher sulfate concentrations than stream water.

In contrast to sulfate, chloride exhibits more seasonal variability (Figure 17a), with the highest concentrations measured in summer and fall. Chloride is often naturally occurring from input of sea salt spray integrated into precipitation and minerals, however, can originate from anthropogenic sources as well (e.g., agricultural discharge, urban runoff, and/or sewage effluents) (Brandt et al., 2017). Given that the highest rate of increase is observed through the agricultural area, and high concentrations of chloride were measured in the agricultural tributaries, Mulkey Creek (31% agricultural) and Lamprey Creek (32% agricultural), small scale farm practices in the watershed are likely the main contributor to chloride in Oak Creek. However, downstream locations of these tributaries do not show drastically higher concentrations of chloride indicating that they must not be contributing a significant amount of water to the mainstem. Furthermore, shallow groundwater chloride concentrations measured in agricultural areas were consistently higher than surface water concentrations, suggesting that agricultural practices contributing to groundwater chloride concentrations may also be contributing to surface water chloride. For both chloride and sulfate, regardless of anthropogenic or natural source, higher concentrations in groundwater compared to surface water along with

increasing surface water concentrations with movement downstream indicates that Oak Creek acts as an integrator of incoming flows.

4.2 Shallow groundwater exhibits high spatial variability

4.2.1 Residence time varies between close proximity wells

Groundwater isotopic values were more spread out along the GWML and more representative of measured precipitation variability than surface water (Figure 9). The larger range in isotopic values indicates that groundwater is more variable than surface water; however, each well was not consistently variable, which suggests differing residence times between wells. Higher variability, and shorter residence time, is driven by changing water sources between sampling events indicating that water is moving more quickly into and out of the well than wells with low variability, which have a more consistent water source, and longer residence time. Figure 9 shows that some wells are more influenced by recent precipitation (one, two, or three months), while others are clustered around the mean well isotopic value. Wells that are skewed more towards recent precipitation have a shorter residence time than those that show an isotopic composition more similar to the long-term mean. Within each field, isotopic values did not cluster spatially for each given sampling date (Figure 15), indicating that even at close proximity there is high variability between the wells. Riparian wells exhibited the most fluctuation between sampling dates which may be explained by converging flow paths as different groundwater sources are entering the stream. The idea of heterogeneity and variability between measured groundwater sources in close proximity upsets the idea that groundwater is a stable, homogenous source, and suggests that, at least in shallow aquifers, groundwater is not consistently integrating over space nor time.

4.2.2 Land use practices influence groundwater nutrient concentrations

Compared to surface water, groundwater anion concentrations vary less temporally but more spatially. Significant differences in sulfate and chloride concentration between Fields 1 and 2 and Field 3 were observed, but not nitrate or phosphate, indicating that land use practices influence some nutrient concentrations more than others. Riparian wells exhibited concentrations most similar to Fields 1 and 2, which is expected considering they are adjacent to Field 2 (i.e., RW1) and land managed with the same practices as Field 1 (i.e., RW 4, RW5, RW6). Field 3 is characterized by high chloride and low sulfate values, while other monitored groundwater areas are characterized by low chloride and high sulfate values (Figure 19b). The different behavior exhibited between fields may be explained by geographic location; Field 1, Field 2, and the riparian wells are located north of Oak Creek while Field 3 is located south of Oak Creek. Thus, Field 3 is receiving water from a contributing area different from, and influenced by land use practices different from, Field 1, Field 2 and the riparian wells. Across all three fields, nitrate exhibited low values (generally <1 ppm), and over half of the samples taken exhibited concentrations below the level of detection, which may be indicative of denitrification (Huno et al., 2018). F3W3 is the exception, consistently showing nitrate concentrations over 30 ppm. Sulfate concentrations were also consistently over 30 ppm, and chloride concentrations over 500 ppm in F3W3, indicating that this well is not influenced by the same flow paths as other wells. Higher concentrations in F3W3 may be due to overapplication of manure in the NE corner of the field in the spring of 2018. Furthermore, F3W3 is 1.1 to 4.5 meters shallower than other Field 3 wells, and thus may be more influenced by field inputs and measuring a shallower aquifer. Another possibility is that the residence time of W3 is longer than other wells within the field

and therefore nutrients concentrate within the groundwater. Further research is needed to determine why Well 3 exhibits different behavior.

4.3 Land use and instream processes drive variance in nutrient concentrations

4.3.1 Surface water nutrient concentrations

As discussed in section 4.1.3, both chloride and sulfate increase with movement downstream across all sampling events. Other measured nutrients (i.e., nitrate and phosphate) exhibited lower concentrations and fewer trends than chloride and sulfate making it more difficult to identify land use impacts on stream water concentrations. Furthermore, both nitrate and phosphate are used for biological activity making them more prone to biological processes and thus introducing other sources of variability.

Nitrate concentrations exhibit the most temporal and spatial variation of all measured anions indicating that they may be influenced by more than one land use and/or process. A consistent spatial pattern was not observed, however when temporal patterns were examined, spring concentrations were consistently lowest across all three land uses and decreased with movement downstream which indicates biological uptake (Munn and Meyer, 1990). While both spring and summer are periods of high biological activity, spring may have a higher uptake rate than summer because the canopy is more open allowing for sunlight penetration through to the stream. Furthermore, summer uptake may be offset by anthropogenic inputs such as urban drainage, causing higher summer concentrations of nitrate in urban areas. Interestingly, mean winter and spring concentrations are similar in the forest, however, unlike spring concentrations, winter concentrations increase with movement downstream. Furthermore, a few high nitrate concentrations were measured in the forest in the winter, which may be explained by nitrate leaching from red alder trees. Compton et al. (2003) found that N_2-fixing red alder are positively correlated with nitrate concentrations in the Oregon Coast Range, and nitrate concentrations peak in late fall through winter. High winter nitrate concentrations further downstream may be driven by winter fertilizer application, or runoff from earlier applications (Compton et al. 2019).

Phosphate concentrations exhibit the fewest trends compared to other measure anions, indicating that land use may not influence phosphate concentrations significantly. The sampling event on August 28, 2019 is the exception; consistently higher concentrations across all three land uses were exhibited, which may have been driven by breakdown of organic matter in low flows, although we would expect to see high concentration from the summer of 2018, as well. Lower agricultural and urban sites exhibit much higher concentrations indicating that elevated concentrations may be from sources such as fertilizer and manure runoff or urban discharge.

Further indication of biological processes impact on nitrate and phosphate come from comparing winter and summer correlations between measured parameters. Summer sampling events showed fewer and weaker correlations than winter sampling events which could be explained by hot spots and moments in the stream leading to more heterogeneity in the stream in the summer compared to the winter. As reported by Simon et al. (2005), uptake rates in New Zealand streams are highest in spring and summer, although little correlation between nutrients was exhibited indicating that different factors influence each nutrient. In the summer, warmer weather and slower flows increase the biological productivity of streams and allow more time for ecosystem processes, such as nutrient cycling, to occur between sampling sites, therefore causing variation in concentration between sites. Interestingly, chloride and sulfate, as well as other measured parameters (i.e., specific conductivity, temperature, $\delta^{18}O$ and $\delta^{2}H$) also showed fewer and weaker correlations in the summer compared to winter. As discussed above, groundwater

contributions make up a larger portion of the stream in the summer compared to winter, and measured shallow groundwater was highly variable both isotopically (Figure 15) and in nutrient concentration (Figure 19) thus contributing to stream heterogeneity.

4.3.2 Groundwater – surface water interactions through agricultural areas

To further investigate interactions between shallow groundwater and stream water, the stream reach that flows through the monitored agricultural area (3685 m to 2492 m) was analyzed for changes in anion concentration between upstream and downstream of the agricultural area. In the winter and spring, intermittent drainage ditches flow into Oak Creek through this reach, however in the summer, the only incoming flows are groundwater contributions. Anion concentrations generally increase between upstream and downstream, indicating contributions from drainage points and/or groundwater. Interestingly, summer sampling events, especially August 28, 2019, exhibited the greatest increase in anion concentration for all four anions suggesting that shallow groundwater impacts the water quality of Oak Creek most in the summer. Summer was the only period in which higher concentrations of all four anions were measured in groundwater compared to surface water; groundwater phosphate and nitrate concentrations were often lower than stream concentrations during other seasons. Although high concentrations were measured in summer, this water would not immediately contribute to the Oak Creek concentrations. While shallow flow paths could possibly be quick and therefore elevated concentrations from earlier in the summer might contributing to stream water, the lack of consistent high (relative to surface water) groundwater concentrations indicates a deeper groundwater source. Flow volume may help explain why anion concentration increases were more evident during summer events. While groundwater contributes to stream flow year-round, higher winter flows likely it diluted out, and therefore anion concentrations from groundwater inflows are not significant. However, in summer, streamflow is dominated by groundwater, and therefore groundwater anion contributions are measurable.

Consistent with increasing anion concentrations on August 28, 2019 in the monitored agricultural reach, deviations in surface water $\delta_{18}O$ and d-excess towards mean shallow groundwater further support contributions from shallow groundwater. Although groundwater data was not collected on September 10, 2018, stream water isotopic composition through the monitored agricultural area deviated towards higher d-excess, rather than low d-excess, which is characteristic of shallow groundwater thus indicating that shallow groundwater is not the contributing source of anion concentration increase (Figure 12).

Our ability to infer groundwater – surface water interactions are extremely limited. Groundwater wells were only installed to read the uppermost aquifer, and therefore I lack information on the water chemistry of deeper groundwater flow paths. Large proportions of groundwater contribution to surface water come from deeper flow paths (Gilmore et al., 2016) and are therefore important to holistically understand groundwater contributions to surface water.

5 Conclusions

For this study, water samples were collected between January 2018 and November 2019 from 22 stream sites and 19 shallow groundwater wells in Oak Creek watershed. Stream sites spanned forested, agricultural, and urban land use, and groundwater wells were installed in fields fertilized with both manure and synthetic fertilizer. Water samples were analyzed for anion (i.e., chloride, sulfate, nitrate, phosphate) concentrations and stable isotopes of water. Data was used

to investigate land use influence on stream and groundwater anion concentrations and groundwater - surface water interactions within Oak Creek watershed. Results from this study show three major phenomena: 1) Oak Creek acts as an integrator of precipitation received in high elevations and incoming ground and surface water sources as it moves downstream driving overall stability of isotopic compositions but leading to an increasing chloride and sulfate concentrations; 2) shallow groundwater in agricultural settings exhibits high spatial variability; and 3) land use – water quality relationship are complex and temporally variable.

Stream water exhibited only a fraction of the variability measured in precipitation, indicating that the stream acted as an integrator of recent precipitation and other sources, including shallow groundwater and other non-measured surface water sources. During winter sampling events, stream water was influenced more by recent (1-3 month) precipitation, while summer sampling events exhibited stream water isotopic compositions similar to water year and long-term precipitation isotopic values. The headwaters of Oak Creek exhibited water with the highest d-excess and most temporal variability, and isotopic variability generally decreased with movement downstream indicating mixing of less variable sources with a lower d-excess than stream water. Concentrations of chloride and sulfate consistently increased downstream along the mainstem of Oak Creek further indicating source mixing. Sulfate concentrations were relatively steady at each site year-round and therefore are likely due to a constant, natural source, such as leeching from soils. Chloride concentrations exhibited the fastest rate of downstream increase through the agricultural area, compared to forest and urban areas, suggesting that chloride originates from agricultural practices. This also is supported by higher chloride concentrations in groundwater compared to stream water.

Groundwater isotopic values were more representative of measured precipitation variability than surface water. The larger range in isotopic values indicates that shallow groundwater is more variable than surface water; however, each well was not consistently variable, which suggests differing residence times between wells. Within each field, isotopic values did not cluster spatially for each given sampling date, indicating that even at close proximity there is high variability between the wells. Anion concentration also varied between fields, with significant differences observed in sulfate and chloride concentrations between Fields 1 and 2 and Field 3, but not nitrate or phosphate, indicating that land use practices influence some nutrient concentrations more than others.

In contrast to chloride and sulfate, nitrate and phosphate results did not exhibit consistent patterns, suggesting that natural processes, such as in stream uptake and leeching from the surrounding watershed, may be driving temporal variation. However, both nutrients exhibited high concentrations in urban areas during summer that are likely driven by anthropogenic activity, rather than natural processes. During summer, fewer correlations between measured parameters were observed, indicating more heterogeneity between sampling locations likely due to instream processes, groundwater contributions, and watershed activities (e.g., recreation, lawn care, commercial agriculture). Influence of groundwater on the water quality in the agricultural reach of Oak Creek was most evident during summer months. On August 28, 2019, concentrations of chloride, sulfate, nitrate, and phosphate increased along an 1193-meter agricultural reach with no known surface water inputs. Consistent increases along this reach were not observed during other seasons, possibly due to higher flows in Oak Creek that masked groundwater contribution. Further research and the installation of deeper groundwater wells are required to better understand the origin and variability of groundwater contributions in Oak Creek.

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