May 2017

Terroir Studies in Washington and Wisconsin American Viticultural Areas

Snejana Karakis
University of Wisconsin-Milwaukee

Recommended Citation

Karakis, Snejana, "Terroir Studies in Washington and Wisconsin American Viticultural Areas" (2017). *Theses and Dissertations*. 1495.
https://dc.uwm.edu/etd/1495

TERROIR STUDIES IN WASHINGTON AND WISCONSIN AMERICAN VITICULTURAL AREAS

by

Snejana Karakis

A Dissertation Submitted in

Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

in Geosciences

at

The University of Wisconsin-Milwaukee

May 2017

ABSTRACT

TERROIR STUDIES IN WASHINGTON AND WISCONSIN AMERICAN VITICULTURAL AREAS

by

Snejana Karakis

The University of Wisconsin-Milwaukee, 2017
Under the Supervision of Professor Barry Cameron

The concept of terroir has been evaluated since the 12th century, when Cistercian monks from Burgundy realized that the physical environment in which grapes are grown has a major influence on the character and quality of the resulting wine. These environmental conditions affecting grape and wine quality are known as terroir in viticulture and have become increasingly important in the grape growing and wine industry. In this dissertation, three studies investigating the terroir of vineyards located in Washington and Wisconsin American Viticultural Areas (AVAs), which are defined by the Alcohol and Tobacco Tax and Trade Bureau (TTB) as delimited grape-growing regions having distinguishing features and defined boundaries, are presented. The research objective was to understand and evaluate the interplay of the environmental factors that influence the character and quality of grapes and wines produced in vineyards from Washington and Wisconsin AVAs. These two AVAs have drastically different climates, with the Washington site hosting a xeric to aridic soil moisture regime, and the Wisconsin site having an udic soil moisture regime, allowing for the assessment of climate influence on the interrelated properties of the soil and vine.

In Chapter 2, the terroir of historic Wollersheim Winery, the only winery within the confines of the Lake Wisconsin AVA, is examined to understand the interplay of environmental

factors influencing the character and quality as well as the variability of Wollersheim wines. Soil texture, chemistry, and mineralogy in conjunction with precision viticulture tools such as electromagnetic induction and electrical resistivity tomography surveys, are utilized in the Wollersheim Winery terroir characterization and observation of spatially variable terroir at the vineyard scale. Establishing and comparing areas of variability at the plot level for two specific vineyard plots (Domaine Reserve and Lot 19) at Wollersheim Winery provides insight into the effects of soil properties and land characteristics on grape and wine production using precision viticulture tools.

In Chapter 3, the source of water acquired by grapevines during the critical phenological stages of the 2015 growing season is evaluated using stable isotopes oxygen and hydrogen in water at Wollersheim Winery's vineyard plot Lot 19. The stable isotope analyses of source and vine water provide insight into seasonal water use, vine water uptake processes, and active rooting zones and the role of water in the vine ecological and physiological processes during the growing season to support development of efficient irrigation strategies while managing grape and wine quality. The seasonal vine water use trend supports a variable functional rooting depth for water acquisition by the vines during the different phenological stages, with rain water as a preferential source during the spring months and a root system developed to reach for water progressively deeper as the growing season advances as greater storage of water is found in deeper soil in the autumn months.

Chapter 4 presents a regional scale reconnaissance survey that examines the relationships between soil characteristics and the phenolic compound concentrations of Syrah grapes collected during the 2014 harvest from 11 vineyards planted across four different terroirs in the Walla Walla Valley AVA in an assessment of the useful application of the terroir construct at this scale. Soil

properties, including drainage, depth, available water-holding capacity (AWC), texture, bulk and plant available chemistry, and mineralogy in conjunction with concentrations of grape phenolic compounds, including tannin, polymeric and total anthocyanins, quercetin glycosides, and catechin are assessed to explore the link between vineyard soil and grape chemistry. The relationships between soil characteristics and phenolic compounds of Syrah grapes from the Walla Walla Valley AVA vineyards, generally indicate that although the four terroirs have distinctly different soil properties, the grape phenolic concentrations reveal only subtle variations; overall, these minor differences show higher concentrations of phenolics may be associated with vineyards that feature soils exhibiting the influence of basalt from weathered basalt bedrock or basalt-derived alluvium. The study demonstrates that large scale characterizations at the AVA level can be limited by the variability of soil properties at the vineyard level.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

Upon the successful completion of this dissertation, I look back with a great sense of gratitude toward this remarkable institution, which has supported my endeavors since the time I first stepped into it more than 15 years ago. I extend my sincere appreciation to all the faculty, staff, and graduate and undergraduate students for making the department such a terrific place to learn and work. I would like to express my earnest gratitude to my advisors Dr. Barry Cameron and Dr. Erik Gulbranson, whose brilliance, enthusiasm, and encouragement have been instrumental in the completion of this study, from the field work adventures to the most difficult interpretations. I express my heartfelt thanks to Dr. Kevin Pogue (Whitman College, Walla Walla, WA) for his assistance in the field and constant enlightening throughout the Walla Walla Valley trip and beyond. I am obliged to Dr. William Kean, Dr. Julie Bowles, and Michael Baierlipp for assistance with the geophysical surveys and sharing their knowledge of geophysics and geoelectrical methods, and I also wish to graciously acknowledge Dr. Lindsay McHenry for guidance on the XRF and XRD analyses, and to Dr. Elmo Rawling for the laser grain size analysis. I also take this privilege to express my regard and appreciation to Dr. John Valley and Mike Spicuzza (University of Wisconsin - Madison) for the cryogenic vacuum line expertise and support with the water extraction process.

I would like to thank Philippe Coquard, winemaker at Wollersheim Winery, and the Wollersheim team for sharing our passion for terroir, providing vineyard access and samples, stimulating terroir conversations, and great tastings; and the Walla Walla Valley AVA winery owners, vineyard managers, and winemakers for their kindness and generosity in providing not only access to their vineyards, but very enjoyable and informative terroir discussions. Lastly, I would like to thank all my friends and family for their support, and an especially enormous thanks

to my husband John who helped me maintain focus, encouraged and supported me during the longest of days.

I dedicate this dissertation to my daughter Stephanie Roxanne Parfitt - may you always desire more than you can accomplish in your quest for knowledge.

1.0 Chapter I: General Introduction

1.1 Terroir Background

The cultivation of grapes and production of wine have a long history. Wine residue on 7000-year-old pottery jars found in a Neolithic village in Iran is evidence that viticulture and winemaking date back as far as civilization itself (McGovern et al. 1996). The term "terroir" has its origin in the vineyards of 12th century Burgundy, France, and can be defined as the unique characteristics of a vineyard imparting their essence into the character and quality of the grapes grown and wine produced in that vineyard. This unique collection of physical attributes includes factors such as the geology, soils, landscape, and climate of a place. In addition to these physical environment elements, the human factors involved in winemaking, such as vineyard management, viticultural practices, and vinification techniques also contribute to the character and quality of a wine. Terroir is the result of the relationship and interaction of the physical elements and human factors involved in the making of a wine. Simply stated, terroir is the distinct “taste of place”, the quality that gives a wine its unique character.

The conceptual development of terroir is best exemplified by the simple occurrence of adjacent vineyards in the Burgundy region of France, examined since the 12th century by Cistercian monks who created the “Clos de Vougeot,” Burgundy's largest stonewall surrounded vineyard. The French monks of Burgundy were the first to notice that different vineyard plots produced consistently different wines (Wilson 1998; Haynes 1999; White et al. 2009). Through trial and error, they realized that certain grape varieties produce better wines if planted in certain areas. The legacy of the French monks of Burgundy shaped the development of the Burgundy vineyards hierarchy of appellations, including the Grand Cru, Premier Cru, and Commune, which are indicative of relative quality.

In the Old World, which includes the European regions with a long documented history of wine making, the emphasis is placed on the vineyard site, allowing the natural components of terroir to be expressed in the wines. The Old World wine regions have some of the most distinctive terroirs, each producing very diverse styles of wine even within their own boundaries. In the Old World, the vineyard site is much more important than the winemaker, and the role of terroir dominates. In the New World of wine, which includes wine regions such as the United States, Australia, South America, and South Africa, where the role of terroir is still developing, the emphasis is placed on applying the best viticultural management practices and wine technology to produce great wines (White et al. 2009). These practices have significantly improved the quality of wines, although they have resulted in a more homogenized style of wines, often lacking the distinguishing characteristics or expressiveness of terroir.

Although high quality wines are produced in various terroirs across the world's grape-growing regions, there are some generally-established factors for high terroir potential. For example, vines grow best at latitudes within the world's temperate climate belts, at elevations that allow full ripening at the end of the growing season; thus, cultivated varieties selected according to the appropriate climatic conditions (i.e., early ripening varieties in cool climates and late ripening varieties in warm climates) will produce the highest quality grapes. Steep, south facing slopes (in the Northern hemisphere, north facing slopes in the Southern hemisphere) maximizing solar radiation; close proximity to bodies of water, moderating the climate; and well drained soils, inducing a moderate water deficit, are all recognized desirable terroir factors.

Initially, the concept of terroir was evaluated simply based on empirical knowledge, as grape growers and winemakers observed the variation in the quality of grapes and wines produced in certain areas within and between vineyards. Subsequently, terroir studies took a more scientific, analytical approach in examining the interaction between the physical and environmental conditions of a vineyard site and the quality of grapes and wine. The first scientific studies assessing the concept of terroir originated in France in the early 1970s with publications by Dr. Gerard Seguin of the University of Bordeaux. Currently, terroir research studies are conducted in most wine regions of the world. Many studies have been focused on the various aspects of terroir, such as climate (Winkler et al. 1974, Gladstones 1992, Jones 2006), soil (Seguin 1986, White, R. 2009), and cultivated varieties (van Leeuwen 2004), while more recent studies have been concentrated on wine chemistry, sensory attributes and wine composition, and fingerprinting and geographical origin identification of wines.

Some of the most notable terroir publications include James Wilson's textbook *Terroir – The Role of Geology, Climate, and Culture in the Making of French Wines* published in 1998, in which the role of vineyard geology is emphasized as the foundation of the soil and subsoil through which the vines grow and the defining factor for topography and landforms, which collectively influence the drainage and microclimate environment of vines. Another publication, *Fine Wine and Terroir*, dedicated to Dr. Simon Haynes, who is regarded as the godfather of terroir studies in North America, is a collection of nineteen papers that highlight the significance and history of terroir, and evaluate particular aspects of terroir or terroir components. These studies established a scientific approach and some of the first quantitative methods of studying terroir.

Haynes (1999) established the scientific basis for terroir studies, noting that there are five fundamental groups of variables influencing terroir: meteorological, physiographic, pedological, geological, and viticultural. The meteorological aspect consists of variables such as the temperature maxima and minima, hours of sunlight, wind conditions, and rainfall. Factors such as the landform type, elevation, slope aspect and grade, and slope drainage define the physiographic element of terroir. The pedological aspect includes the soil type, composition, texture, grain size, and porosity, soil mineralogy and chemistry, and clay mineralogy. The geological aspect of terroir consists of the bedrock geology type, geochemistry, petrology, and texture, and the surface water and ground water flow rates and chemistry. The components of the viticultural aspect of terroir include the trellising methods, row spacing, grape-bunch thinning and allowable production, use of fertilizers, tile draining, irrigation, and addition of soil or rock material.

Taylor et al. (2002), Greenough et al. (2005), and Eggers et al. (2005) established a methodology for the identification of wines by geographical origin through geochemistry. Trace element abundances and isotope ratios of soils and wines and organic compounds of wines were used in the chemical fingerprinting of wines based on region. The authors demonstrated the use of several trace elements to identify the geographical origin of wines, linking wines to soil and grape variety. The natural pattern of trace element diffusion from parent material to soil and to grapes, allows for the differentiation of wines based on the provenance of their soils. Similarly, traces of strontium in wine can be used to track its origin, as rubidium decays into strontium in soil over time, the ratio of strontium to rubidium will vary in the soil, grapes, and wine from region to region.

Bowen et al. (2004) and Jones et al. (2005) used geographic information systems (GIS) methods to assess site suitability by mapping viticultural areas based on the most desirable terroir environments. GIS tools were applied in modelling viticultural settings by combining spatial information, such as zoning, elevation, slope, aspect, soil, bedrock, and climate, into a viticultural suitability map. A GIS analysis can help determine the best areas of land suitable for vineyards and wine production, the best layout for rows, and the extent of most suitable land to expand current vineyards. Identifying areas with the most desirable viticultural conditions can assist with vineyard planning and management, which can result in improved grape and wine quality.

Hubbard et al. (2003) demonstrated the use of precision viticulture methodologies in mapping vineyard variability. Geophysical methods (ground penetrating radar) were applied to assess the variations in soil characteristics such as soil texture and associated soil water distribution, which can vary significantly at the vineyard or plot level. These techniques facilitate the delineation of areas with similar characteristics within a vineyard, allowing differently customized management strategies and processes such as pruning, fertilizing, and irrigation to be implemented separately for different areas within a vineyard, in the interest of increasing the quality of fruit production and ultimately the quality of wine.

These studies investigating the concept of terroir, refined our understanding for how fundamental terroir variables influence the factors governing grape and wine quality. The studies presented in this dissertation build from these earlier works by integrating multiple different types of data collection strategies in vineyards of two distinct climates, semi-arid (Washington) and humid (Wisconsin), to address research questions concerning the role of soil hydrology, climate, landform, and cultivar on grape quality. These studies use terroir as a scientific method, provide readily applicable information for grape growers to better understand the specific influences on seasonal fluctuations in grape quality, and further our understanding of the external controls on secondary metabolite development in grapes. Through refining the understanding of explicit terroir influences on grapes prior to fermentation, these studies provide scientific evidence to demonstrate how grape quality varies as a function of environmental factors (soil, topography, landscape age, physiology of grapevines) and climate (year-to-year deviations from a climate normal) in two distinct AVAs. These insights provide highly transferrable information for grape growers and have a direct impact on vineyard land and crop management practices in both warm and humid temperate latitude climates and Mediterranean climates.

1.2 Research Objectives and Significance

The research objective was to understand and evaluate the interplay of the environmental factors that influence the character and quality of wines produced in vineyards from Washington and Wisconsin AVAs, which have drastically different climates. The Washington study site has a xeric to aridic soil moisture regime, and the Wisconsin site has an udic soil moisture regime, allowing for the assessment of climate influence on the interrelated properties of the soil and grapevine.

Terroir as a concept lends itself well to scientific study, as it is a state factor model, which expresses the state of a system as a function of a set of state factors or physical conditions, which are independent of the system under study and theoretically may vary independently. This set of physical conditions concerning terroir are often auto-correlated and include the soil and all its properties, the grape variety, the climate (temperature, hours of sunlight, precipitation), the landscape (elevation, slope, aspect), the organisms (bacterial, fungal, plant, animal interactions), and the vitiviniculture (vineyard management, viticultural practices, and vinification techniques). Thus, terroir is a function of the soil (S) grape variety (G), climate (C), landscape (L), organisms (O), and vitiviniculture (V).

$$\text{Terroir} = f\,(S, O, G, C, L, V)$$

This framework guided the development of hypotheses of these studies and influenced the set of tests applied to each hypothesis. In this manner, the terroir for each study site was defined, and the explicit variables influencing grape and wine quality were identified.

In Chapter 2, the terroir of historic Wollersheim Winery, the only winery within the confines of the Lake Wisconsin AVA, is examined to understand the interplay of environmental factors influencing the character and quality as well as the variability of Wollersheim wines. In Chapter 3, a focused study on vineyard plot Lot 19 at Wollersheim Winery evaluates the source of water acquired by grapevines during key phenological stages over the 2015 growing season using stable isotopes oxygen and hydrogen in water. Chapter 4 presents a regional scale reconnaissance survey that examines the relationships between soil characteristics and the phenolic compound concentrations of Syrah grapes collected during the 2014 harvest from 11 vineyards planted across four different terroirs in the Walla Walla Valley AVA in an assessment of the useful application of the terroir construct at this scale.

2.0 Chapter II: Terroir of Historic Wollersheim Winery, Lake Wisconsin AVA, Prairie du Sac, Wisconsin

Based on: Karakis, S., Cameron, B., and Kean, W., 2016. Geology and Wine 14. Terroir of Historic Wollersheim Winery, Lake Wisconsin American Viticultural Area. Geoscience Canada, 43(4), 265-282. doi: https://doi.org/10.12789/geocanj.2016.43.107

2.1 Abstract

The viticultural history of Wisconsin started in the 1840s, with the very first vine plantings by Hungarian Agoston Haraszthy on the Wollersheim Winery property located in the Lake Wisconsin American Viticultural Area (AVA). This study examines the terroir of historic Wollersheim Winery, the only winery within the confines of the Lake Wisconsin AVA, to understand the interplay of environmental factors influencing the character and quality as well as the variability of Wollersheim wines. Soil texture, chemistry, and mineralogy in conjunction with precision viticulture tools such as electromagnetic induction and electrical resistivity tomography surveys, are utilized in the Wollersheim Winery terroir characterization and observation of spatially variable terroir at the vineyard scale. Establishing and comparing areas of variability at the plot level for two specific vineyard plots (Domaine Reserve and Lot 19) at Wollersheim Winery provides insight into the effects of soil properties and land characteristics on grape and wine production using precision viticulture tools.

The viticultural future of Wisconsin looks quite favorable, as the number of wineries keeps rising to meet the demand for Wisconsin wine and local consumption. As climate change continues to affect the grape varieties cultivated across the world's wine regions, more opportunities arise for Wisconsin to cultivate cool-climate European varieties, in addition to the American and French-American hybrid varieties currently dominating grape production in this glacially influenced wine region.

2.2 Introduction

The state of Wisconsin is perhaps best known for cheese and beer, invoking placid images of lush pastureland, clear lakes, and the north woods, but in the last decade, there has been a significant increase in the number of wineries established across this Midwestern state. Although Wisconsin has a long winemaking history, the Wisconsin grape growing and wine industry has experienced rapid growth in recent years. The viticultural history of the state of Wisconsin extends back to the 1840s, when the illustrious nobleman Agoston Haraszthy, a Hungarian-born immigrant who subsequently became a pioneer in California's grape and wine industry, first settled in south-central Wisconsin. Haraszthy planted the first vines in 1847 and 1848 and built a 40-foot cellar on the prairie bordering the Wisconsin River − the current location of Wollersheim Winery, which has become a National Historic Site. The traditional European vines planted by Haraszthy did not survive the harsh Wisconsin winters. At the end of 1848 he followed the gold rush to California, where he founded some of the first productive vineyards (including Buena Vista Winery in Sonoma), introduced over 300 varieties of imported European vines, and ultimately became known as the founder of the California wine industry (Pinney 1989). Agoston Haraszthy's vine planting and cellar digging efforts on the hill of Wollersheim Winery in Prairie du Sac, Wisconsin, mark the humble beginning of the state's viticultural history.

Wine production in Wisconsin has always been minimal due to its climate, which is susceptible to extremes of temperature (the record low of –48.3°C, or –55°F, was reported in February 1996), making Wisconsin's mesoclimates incompatible with the cultivation of most Vitis Vinifera varieties. Overall, average annual minimum temperatures in the state of Wisconsin range between –2°C and 3°C, and average annual maximum temperatures vary from 10°C to 14°C. Data from the Wisconsin State Climatology Office show that Wisconsin's continental climate, moderated by Lake Michigan and Lake Superior, is characterized by a short growing season of 140 to 150 days in the east-central Lake Michigan coast and southwestern valleys and even shorter in the central portion of the state, as a result of inward cold air drainage. These cool-climate conditions commonly limit yield and quality of grapes because of occasional spring freezes, which can occur from early May in southern counties and Lake Michigan coastal areas to early June in northern counties, and fall frosts, which can occur from late August/early September in northern and central lowlands to mid-October along the Lake Michigan coastline. Based on a long-term climatological temperature average (calculated using the 1981−2010 U.S. Climate Normals), a total of 2264 Growing Degree Days (GDD, base 10°C or 50°F) were calculated for Wisconsin from April 1st to October 31st, which puts Wisconsin in Winkler's Region I (2500 or less GDD). The Winkler scale, which is a method of classifying climate of grape growing regions based on heat summations (one degree day per degree Fahrenheit over 50°F), includes five climate regions: Region I (≤2500 GDD); Region II (2501–3000 GDD); Region III (3001–3500 GDD); Region IV (3501–4000 GDD); and Region V (>4000 GDD). Because Vinifera vines typically cannot survive the cold Wisconsin winters, mostly cold-resistant native American and French-American hybrid varieties, such as Marechal Foch, Leon Millot, Edelweiss, La Crosse, Frontenac, St. Peppin, Seyval Blanc, Marquette, and many other resilient varieties, are cultivated in Wisconsin. Many Wisconsin winemakers procure grapes from other areas of the USA (California, Washington, New York), and also make wine from other types of fruit, including cherries, strawberries, blueberries, raspberries, cranberries, peaches, apples, and pears. Most Wisconsin wineries make a combination of grape and fruit wines, and increasingly more producers make wine from locally grown cold-climate grapes.

In spite of the Midwestern USA climatic challenges, the Wisconsin grape industry has expanded exponentially in the last decade, as most vineyards were planted between 2005 and 2010. The number of Wisconsin wineries keeps climbing, with over 100 wineries to date (2016) across the state, according to the Wisconsin Winery Association. As global temperatures continue to increase, the current areal extent of grape growing regions will shift accordingly, allowing new varieties to be cultivated in certain regions, as well as limiting the production and affecting the quality of established cultivars in other regions. As climate change continues to affect the selection of grape varieties that can be cultivated in Wisconsin, some grape growers are starting to experiment with Vitis Vinifera varieties; cool-climate Riesling is the frontrunner.

In 2012, Wisconsin grape growers and winery owners were surveyed regarding grape-growing practices, winery operating practices, and sales and production performance in order to establish industry baselines and quantify economic contribution. The survey was conducted by Tuck and Gartner (2014) as part of the United States Department of Agriculture (USDA)-funded Northern Grapes Project. Based on the survey results, approximately 708 acres of vines were planted and approximately 1400 tons of grapes harvested in 2011. Of the 71,699 planted vines in the state, the majority (58,300) are cold hardy vines, comprising 34,400 red cultivars and 24,000 white cultivars. The top three red cultivars are Marquette, Frontenac, and Marechal Foch, constituting 42%, 26%, and 9%, respectively, of the total planted cold-hardy red varieties. The top three white cultivars are Frontenac Gris, Brianna, and La Crescent, representing 27%, 19%, and 15%, respectively, of the total planted cold-hardy white varieties (Tuck and Gartner 2014). As evidenced by these survey results, Wisconsin is a very small grape producer. For comparison, the top 13 United States grape producers are listed in Table 2-1, based on data from the Crop Production Report (ISSN: 1936-3737) released on August 12, 2015, by the National Agricultural Statistics Service (NASS), Agricultural Statistics Board, USDA. California leads the way with 6,822,000 tons (89%), followed by Washington with 512,000 tons (5%), and New York with 188,000 tons (2%) of total production in 2014.

State	**Total Grape Production (tons)**
California	6,822,000
Washington	512,000
New York	188,000
Pennsylvania	91,000
Michigan	63,300
Oregon	58,000
Texas	9,400
Virginia	8,800
North Carolina	6,000
Missouri	4,030
Georgia	4,000
Ohio	3,810
Arkansas	1,490

Table 2-1: Summary of 2014 US Grape Production. Source: Crop production report released August 12, 2015, by the National Agricultural Statistics Service, Agricultural Statistics Board, United States Department of Agriculture

The state of Wisconsin is divided into five distinctive wine regions: the Northwoods Region, Fox Valley Region, Glacial Hills Region, Door County Region, and Driftless Region, and within these five wine regions, there are three established American Viticultural Areas (AVAs), including the Lake Wisconsin AVA, the Upper Mississippi River Valley (UMRV) AVA, and the Wisconsin Ledge AVA (Fig. 2-1). The Lake Wisconsin AVA, established on February 4, 1994, is situated in the south-central part of the state and encompasses approximately 130 square kilometers (km^2) in two counties. It includes within its boundaries the location of the historic Wollersheim Winery. The UMRV AVA, established on June 22, 2009, is the largest designated appellation in the world, stretching approximately 78,000 km^2 across southeastern Minnesota, southwest Wisconsin, northwest Illinois, and northeast Iowa, and it includes within its boundaries the Lake Wisconsin AVA. The Wisconsin Ledge AVA, established on March 22, 2012, is located in the northeastern part of the state, covering approximately 9800 km^2 in 11 counties, and is part of the Niagara escarpment corridor, stretching along the Lake Michigan shores. This research study examines the terroir of historic Wollersheim Winery, the only winery within the confines of the Lake Wisconsin AVA, to understand the interplay of environmental factors influencing the character, quality, and variability of Wollersheim wines.

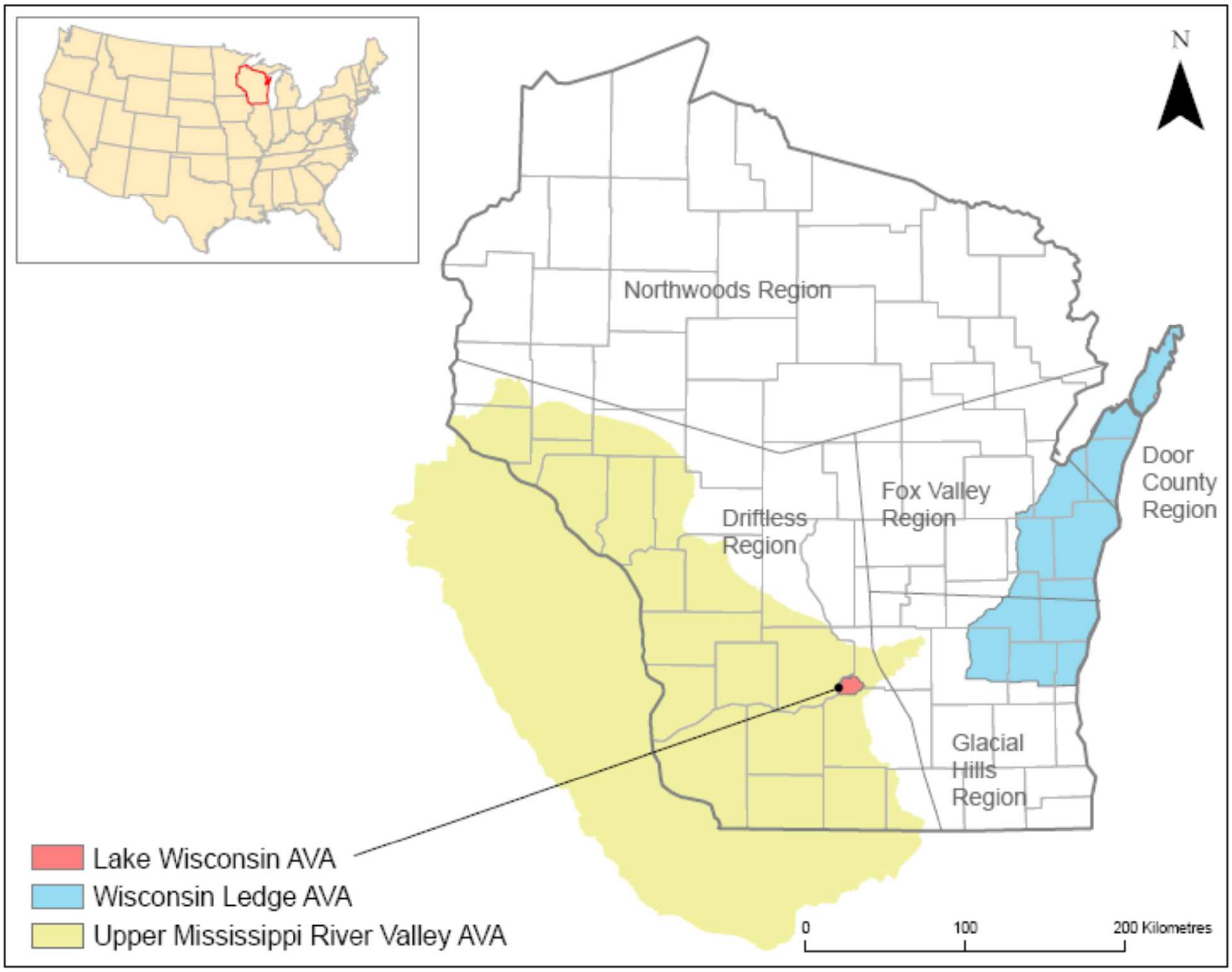


Figure 2-1. The five Wisconsin Wine Regions (Northwoods, Fox Valley, Glacial Hills, Door County, and Driftless) and the three AVAs (Lake Wisconsin, the Upper Mississippi River Valley, and the Wisconsin Ledge)

2.2.1 Overview of The Terroir of Lake Wisconsin AVA

Lake Wisconsin AVA is situated in south-central Wisconsin, approximately 70% in Columbia County and 30% in Dane County. The AVA is bordered to the west and north by the Wisconsin River and Lake Wisconsin, respectively, to the east by Spring Creek and State Highway

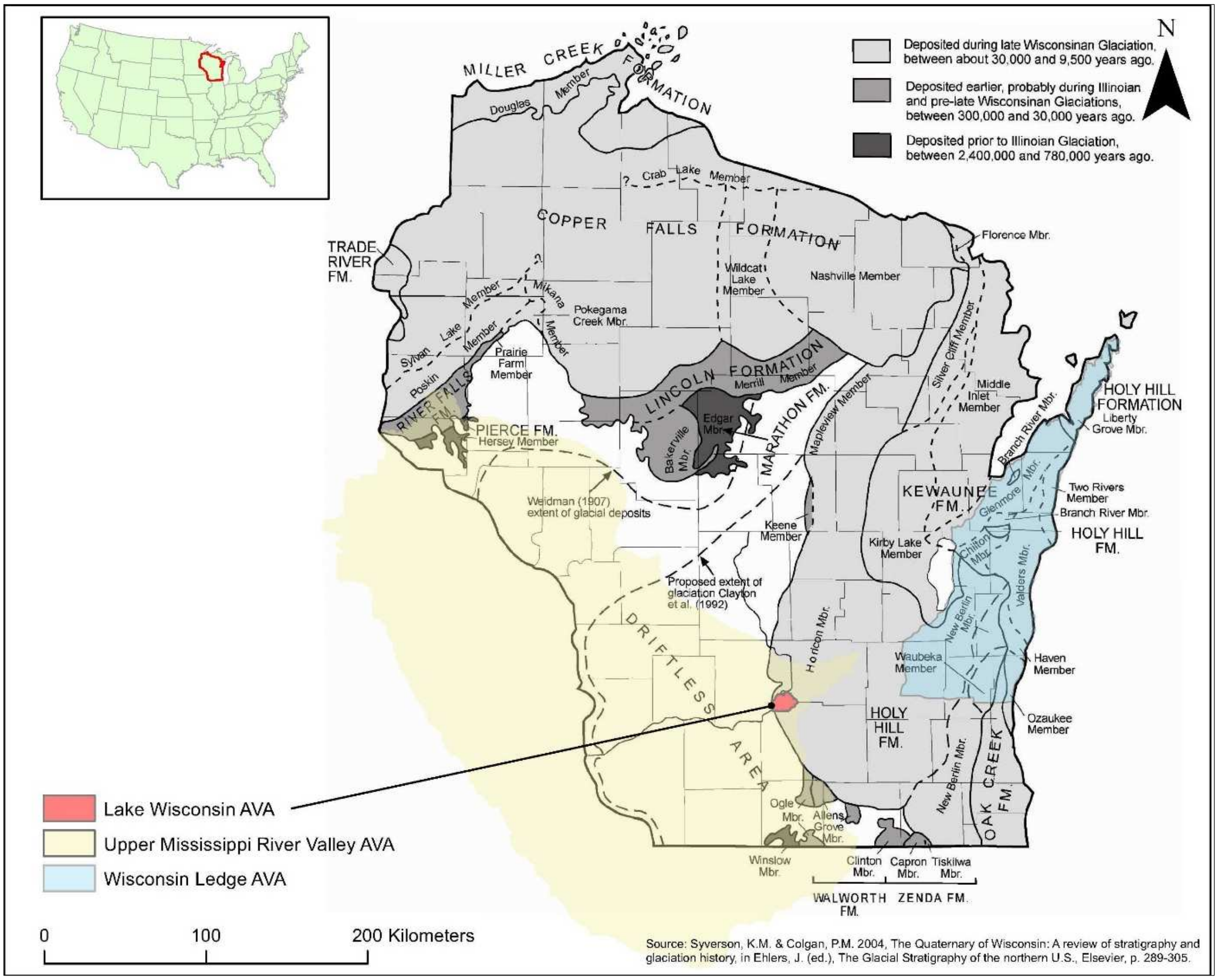
113, and to the south by Mack Road and State Highway Y (Fig. 2-2); its boundaries are defined by federal regulations (GPO Electronic Code of Federal Regulations 2015).

Content may not reflect National Geographic's current map policy. Sources: National Geographic, Esri, DeLorme, HERE, UNEP-WCMC, USGS, NASA, ESA, METI, NRCAN, GEBCO, NOAA, Increment P Corp.

Figure 2-2. Map depicting the boundaries of the Lake Wisconsin AVA and the location of historic Wollersheim Winery, the only winery in the Lake Wisconsin AVA

The climate within the Lake Wisconsin AVA displays minor variability. The Wisconsin River and Lake Wisconsin moderate the temperatures, and average annual precipitation ranges from approximately 762 to 813 mm, which is lower than most of the state. The number of frost-free days ranges from 125 to 170 across the AVA and represents the number of days in the interval between the last spring day and the first autumn day with freezing temperatures. Based on a 30-year climatological temperature average using data from Columbia and Dane counties weather stations, Lake Wisconsin AVA falls in the low range of the Winkler Region II (2501−3000 GDD), with an average of 2555 GDD.

The geology of the Lake Wisconsin AVA comprises Precambrian bedrock units consisting of crystalline igneous and metamorphic rocks, overlain by lower Paleozoic (Cambrian and Ordovician) sedimentary rocks. Specifically, Cambrian sandstone interbedded with secondary dolostone and shale constitute the Elk Mound, Tunnel City, and Trempealeau groups, whereas Ordovician dolostone with secondary sandstone and shale is assigned to the Prairie du Chien Group (Oneota and Shakopee formations). The Lake Wisconsin AVA extends along the eastern margin of the Driftless Area or Paleozoic Plateau, which remained unglaciated during the last glacial advance. The USA upper Midwest region was covered by ice during three glacial stages: the Pre-Illinoian, Illinoian, and Wisconsinan. The most recent major glacial advance of the North American Laurentide Ice Sheet was the Wisconsinan, which lasted from approximately 25,000 to 15,000 years ago (Attig et al. 2011). The glacial lobes of the Laurentide Ice Sheet extended down into the northern and eastern parts of the state, covering its terrain in glacial drift, but never reached the Driftless Area in the western and southern parts of the state. The Driftless Area is characterized by a lack of glacial drift and an erosional topography consisting of flat-topped hills, steep forested slopes, and a well-developed, dendritic drainage system. The landscape is dissected by a network of steeply-cut valleys developed by stream erosion during the roughly 420 million years between the Silurian and Quaternary periods. In contrast, to the east of the Driftless Area, the land was glaciated, and the topography consists of small, gently undulating hills, a less developed drainage system, and numerous lakes, wetlands, and marshes. Although glaciers never reached the Driftless Area during the Quaternary (Mickelson et al. 1982), the effects of glaciation are observed in its peripheral deposits and landscapes, which were affected by periglacial processes (Stiles and Stensvold 2008).



Source: Syverson, K.M. & Colgan, P.M. 2004, The Quaternary of Wisconsin: A review of stratigraphy and glaciation history, in Ehlers, J. (ed.), The Glacial Stratigraphy of the northern U.S., Elsevier, p. 289-305.

Figure 2-3. Map depicting the glacial features of the state of Wisconsin in relation to the locations of the state's three AVAs (from Syverson and Colgan 2004).

The Lake Wisconsin AVA is situated in the transitional zone between the glaciated topography to its east and the unglaciated, driftless topography to its west. Its landscapes are part of the glacially-derived Holy Hill Formation, comprising the Horicon and Mapleview members (Fig. 2-3). The deposits consist of terminal moraines − large ridges of glacial debris that accumulated at the glacial limit − and outwash deposits of stratified sand and gravel found in the valleys of rivers that carried large volumes of glacial meltwater. Generally, postglacial deposits include sand, silt, clay, and organic materials deposited in stream valleys and lowlands, whereas glacial stream deposits include outwash and hummocky sand and gravel. Silt-sized loess, windblown from the floodplains of glacial meltwater rivers, was deposited on top of the land surface during the Wisconsinan Glaciation, but was subsequently eroded from many areas, and is now present as a thin discontinuous cover on uplands and slopes (Clayton and Attig 1997). Figure 2-3 depicts the glacial features across the state of Wisconsin, including the extent of the Horicon and Mapleview members of the Holy Hill Formation, as well as the non-glaciated Driftless Area, in relation to the locations of the state's three AVAs.

The soils across the Lake Wisconsin AVA were developed on top of various types of parent materials, ranging from sandstone and dolostone bedrock to glacial till, outwash, and loess deposits. The parent materials covering the largest proportions of the AVA are calcareous sandy loam till, loess over glacial loamy till, silty sediments over stratified silts and sands, loess and/or silty slope alluvium, loess over calcareous sandy loam till, and loess over glacial till (USDA Natural Resources Conservation Service, Web Soil Survey data). Most cultivated soils in the region have developed in loess, making these windblown silt deposits the foundation of agriculture (Clayton and Attig 1997).

2.2.2 Glacially Influenced Terroir in Other Vine-Growing Regions

Worldwide, many wine regions located where soils developed on glacially transported parent materials are known for producing outstanding wines. Generally, ice and glacial meltwater are the primary agents of deposition of the soil parent material, generating glacial till and glaciofluvial/glaciolacustrine deposits, respectively. Windblown silt-sized loess deposits can also be generated from the floodplains of glacial meltwater rivers.

In New Zealand, vast portions of the North and South islands are covered by Quaternary glacial and fluvial sediments, and extensive outwash deposits are distributed across the lowlands. The majority of vineyards are planted on alluvium and outwash gravels. In the Central Otago region, nearly half of the planted vineyards are located on glacial gravels; in Hawkes Bay, which includes the Gimblett Gravels wine region, approximately 63% of vineyards are located on outwash deposits; and in the Marlborough and Waipara wine regions, most vineyards are planted on alluvium and outwash gravels (Imre and Mauk 2009).

In Canada, the soils of the Niagara Peninsula wine region developed on glacial till resulting from the advance and retreat of ice during Quaternary continental glaciations, and on glaciolacustrine and glaciofluvial deposits formed during interglacial periods. The Niagara vineyards planted on these soils define two distinctive terroirs: the flat area of the Lake Iroquois (a prehistoric glacial lake) Plain extending between Lake Ontario and former lakeshore of Glacial Lake Iroquois, and the Escarpment, consisting of the Glacial Lake Iroquois bench terraces and the slopes above the Niagara Escarpment (Haynes 2000). In the Canadian Okanagan and Similkameen valleys of British Columbia, many glacial advances generated soil parent materials consisting of unconsolidated glacial deposits. In the Okanagan Valley, the thickness of Pleistocene glacial deposits is nearly 100 m, and glaciofluvial deposits cover the sides of the valley (Taylor et al. 2002). Most vineyards in the Okanagan and Similkameen valleys are planted on soils derived from these glacial sediments, which include glaciofluvial, fluvial fan, and glaciolacustrine deposits (Bowen et al. 2005).

In the USA, the Columbia Valley AVA, which encompasses several other AVAs in Washington and Oregon, has soils derived from Quaternary glacial sediment and aeolian deposits. Recurring Pleistocene glacial outburst flooding events, known as the Missoula floods, generated glacial flood sediment deposits known as Touchet beds, which accumulated in river valleys and covered the landscape (Meinert and Bussaca 2000, 2002; Pogue 2009). Deposits of windblown loess of varying thickness overlie the Touchet beds. Most vineyards in the Columbia Basin are planted on soils derived from deposits of loess and glacial flood sediments (Pogue 2009). In the Finger Lakes AVA of New York state, vineyards are planted on soils consisting of varied accumulations of gravel, sand, silt, and clay produced by glacial processes (Swinchatt 2012). The Devonian bedrock, which is now covered by Pleistocene glacial deposits, was scoured repeatedly during glacial advances. The retreating glaciers generated the glacial meltwater that formed the Finger Lakes and carved a landscape of moraines, glacial till, and glacial outwash (Meinert and Curtin 2005).

In France, the landscapes of the Rhone Valley and Bordeaux wine regions have abundant glacial sediments originating from the Alps. In the Rhone Valley, alpine glaciers descended from the Alps, scouring valleys and leaving behind an assortment of glacial till and moraine deposits. Meltwater and subsequent glacial floods re-sorted some of these deposits into extensive terraces and gravel plateaus where many vineyard sites are located (Wilson 1998). In the Bordeaux wine region, Medoc and Graves vineyards are located on gravel terrace mounds. The gravel-rich soils of these areas developed on the outwash deposits associated with the Garonne River interglacial floods and the moraine deposits generated during the Pleistocene glaciation (Wilson 1998).

These glacially influenced wine regions produce exceptional wines in a unique terroir consisting of soils developed on transported, glacially derived parent materials. The glacial soils provide distinct vineyard sites and are characterized by good internal drainage and moderate fertility and water-holding capacity, controlling vine vigor and promoting grape ripening.

2.3 Terroir Characterization of Wollersheim Winery

Wollersheim Winery is a National Historic Site, with a history extending back to the 1840s, when the legendary Hungarian nobleman Agoston Haraszthy first settled on the estate. One of Wisconsin's largest wineries, top wine producers, and a leader in the Midwestern wine industry, Wollersheim Winery produces approximately 240,000 gallons or 1.2 million bottles annually, which corresponds to approximately 1410 tons of grapes. Most are custom-grown grapes, including Sangiovese, Chardonnay, Riesling, Pinot Noir, Seyval Blanc, Carignan, and Muscat from Washington (335 tons), California (10 tons), and New York (783 tons); however, approximately 20% (282 tons) are Wisconsin-grown grapes, including 25 acres of vineyards located on site. Four winter-hardy hybrid grape varieties are cultivated on the Wollersheim Winery estate, including two French-American red hybrids (Marechal Foch and Leon Millot) and two Wisconsin-native American white hybrids (St. Pepin and LaCrosse), producing eight different estate wines made entirely from Wisconsin-grown grapes. Specifically, the grapes grown in the young, flat vineyards produce light-bodied wines (Prairie Blush, Eagle White, Prairie Sunburst Red, and Ice Wine); grapes from the medium-aged vines planted on medium-sloped vineyards produce medium-bodied wines (Ruby Nouveau, Bon Vivant, and Domaine du Sac); and grapes from the oldest and steepest-sloped vineyard produce the rich, full-bodied Domaine Reserve wine.

Best known for its distinctive regional wines, Wollersheim Winery has received numerous medals and awards in national and international wine competitions. Some of the most recent Wollersheim Winery accolades include the 2012 Winery of the Year award at the San Diego International Wine Competition and the 2015 Small Winery of the Year award at the Riverside International Wine Competition. It has also won many awards for its estate wines, such as the 2015 Prairie Blush, which most recently was awarded the Chairman's Trophy at the 2016 Ultimate Wine Competition in Hawthorne, New York, and gold medals at the 2016 New World International

Wine Competition in Ontario, Canada, the 2016 Winemaker Challenge International Wine Competition in San Diego, California, and the 2016 Dan Berger's International Wine Competition in Sonoma County, California. Other estate wines, including Domaine Reserve, Domaine du Sac, Eagle White, and Prairie Sunburst Red, have consistently won awards at numerous competitions; a listing of the various awards can be found on the winery's website (http://www.wollersheim.com).

This research study provides a terroir characterization of the Wollersheim Winery vineyards, and utilizes analyses of soil type, texture, geochemistry, and mineralogy to understand the interaction of environmental factors influencing the character and quality of Wollersheim wines. The study further examines local-scale vineyard variability between two plots (Domaine Reserve and Lot 19) that are cultivated with the same grape variety (Marechal Foch) to determine the controls on small-scale variability in grape quality and Wollersheim wines.

2.4 Materials, Methods, and Data Acquisition

Total major and select minor and trace element compositions were determined on powdered rock samples and on the fine fraction of vineyard soil samples, which were powdered and fused for x-ray fluorescence (XRF) analysis. Loss on ignition (LOI) was determined by heating 1 gram of sample for 10 minutes in a muffle furnace at 1050°C and calculating the mass difference. The major element and select minor and trace element abundances were obtained from glass disks fused at 1050°C in a Claisse M4 fluxer and analyzed using a Bruker S4 Pioneer XRF in the Department of Geosciences, University of Wisconsin–Milwaukee. Plant-available soil chemistry analysis was conducted by the University of Wisconsin Soil Testing Laboratory in Madison, Wisconsin, to determine concentrations of phosphorus, potassium, calcium, magnesium, sulfur, zinc, manganese, and boron, as well as pH, cation exchange capacity, and organic matter. Soil texture was determined by grain size analysis using a Malvern Mastersizer 2000E laser diffraction particle-size analyzer. In the laser diffraction method, a laser beam is passed through a sample to measure the angular variation in scattered light intensity, which is used to evaluate the particle size distribution within a sample. Soil and rock mineralogy were determined non-quantitatively on a portion of each powdered sample by x-ray diffraction (XRD) analysis. Random mounts were prepared by gently smoothing the surface of a fine powder poured into a flat surface onto a cavity mount sample holder. Samples were analyzed in the Department of Geosciences at the University of Wisconsin–Milwaukee using a Bruker D8 Focus XRD system (Cu Ka radiation, 1 s per 0.02° 2θ, 2°–60° range, scintillation detector). Minerals were identified by searching the International Centre for Diffraction Data (ICDD) PDF-2 database of standard X-ray powder diffraction patterns for a match with the pattern of the unknown, using Bruker's EVA software for peak matching.

Vine trunk circumferences were measured at two plots, Lot 19 and Domaine Reserve, on September 14, 2014. Vine trunk circumference measurements can be used as an indicator of vine vigor variation (Imre and Mauk 2011). The measurements were collected from every vine at every other row, approximately 20 cm from the ground surface at the narrow part of the vine.

Geophysical surveys, including electromagnetic induction (EM) and electrical resistivity tomography (ERT) were conducted at two plots, Lot 19 and Domaine Reserve, on May 18, 2014. The EM surveys were carried out with a Geonics EM-31-MK2 ground conductivity meter, which has a fixed coil spacing (3.66 m) and a single frequency (9.8 kHz) generating the primary magnetic field, with depths of exploration of approximately 3 m in the horizontal dipole mode and approximately 6 m in the vertical dipole mode. The Geonics EM-31-MK2 ground conductivity meter is calibrated for a standard operating height of 1 m above the ground, which is approximately waist height. The EM surveys were performed at walking speed, and apparent electrical conductivity (ECa) measurements were collected from 104 locations at each plot along alternating transects between every other row of vines, for a total of 9 transects completed at each plot. ECa measurements in the horizontal and vertical dipole modes were read directly from the integrated data logger, and the measurement locations were georeferenced by means of a GPS receiver. The ECa datasets for both plots were downloaded with the Geonics DAT31W software program and interpolated using the ordinary kriging method with the Esri ArcGIS Desktop software program.

The ERT survey was conducted using a GF Instruments ARES-G4 unit, with a standard survey line of 115 m consisting of three cables and a total of 24 electrodes. The electrodes were spaced 3 m apart in the Wenner array, attaining a maximum exploration depth of 14 m. The Wenner array consists of four electrodes spaced equally in a straight line at ground surface; current is applied to the two outer (current) electrodes and the potential difference measured at the two inner (potential) electrodes. The ERT method records the contrast in apparent electrical resistivity (ER) in soil, providing an estimate of the horizontal and vertical lithological variations. Two profiles were completed at each plot, one near the top row and one near the bottom row of vines. The profiles were used to determine lateral changes in resistivity, identifying the lateral continuity of layers. The ER data for all profiles were downloaded with the GF Instruments ARES v5.0 program and exported into RES2DINV (Geotomo) inversion program for processing. A common logarithmic scale was applied to all profiles for appropriate comparison.

2.5 Results and Discussion

The Wollersheim Winery vineyards are located on a hill overlooking the Wisconsin River, at elevations between approximately 213 and 306 m, on south and southwest-facing gentle slopes. The vines are planted 2 m apart and the distance between rows is 3 m, which allows sufficient space for farming equipment. The 25 acres of bearing vineyards consist of approximately 700 vines per acre for a total of 17,500 vines on site. The landforms are streamlined hills and valleys shaped by glaciers and glacial stream deposits consisting of outwash and hummocky sand and gravel (Mickelson 2007). The glacial deposits are part of the Horicon Member of the Holy Hill Formation, which is characterized by glacial till comprising brown gravelly, clayey, silty sand, and dolomite derived from Ordovician formations; these glacial deposits are overlain by loess (Clayton and Attig 1997).

The climate is moderated by the Wisconsin River, and air drainage in the river valley inhibits frost in the vineyards. In the Wollersheim Winery area, where the average growing season ranges from April 1st to October 31st, a total of 2382 (base 50°F) GDD were recorded in 2014. Based on a 30-year climatological temperature average (1981−2010), Wollersheim Winery falls in the low range of the Winkler Region II (2501−3000 GDD) with an average of 2652 GDD. In comparison, Napa, California falls in the middle range of the Winkler Region III (3001−3500 GDD) with an average of 3297 GDD, and Walla Walla, Washington falls in the high range of the Winkler Region II (2501−3000 GDD) with an average of 2959 GDD.

2.5.1 Vineyard Soil Properties

To characterize the terroir and assess vineyard variability at Wollersheim Winery, a total of 12 soil profiles were examined and sampled throughout the vineyards (Fig. 2-4). Two rock samples were also collected in the vicinity of the vineyards. The first was from a sandstone outcrop exposed along Highway 60, approximately two kilometers to the north-northeast of the Wollersheim vineyards; the second was from a representative dolostone boulder (approximately 2 x 4 x 2 m) at the top of the Domaine Reserve plot that was transported from the Ordovician Prairie du Chien Group dolostone bedrock bordering the east boundary of the vineyards. The elevations of the soil sample locations range from 236 to 286 m, and the maximum depths of the soil profiles range from 50 to 70 cm below ground surface, across horizons A, E, and B.

Figure 2-4. Location map of Wollersheim Winery vineyards illustrating the distribution of soil types, and soil sample and resistivity profile locations.

Based on the USDA taxonomic classification, the vineyard soils are Alfisols, which is a soil order characterized by moderately weathered and leached clay-rich soils having high to medium base saturation, relatively high native fertility, and abundant iron and aluminum. The soils are further classified as the subgroup Udalfs (Alfisols found in humid climates) and the great group Hapludalfs (Udalfs with minimum horizonation). Specifically, the soils are Typic and Mollic Hapludalfs in a mesic soil temperature regime and udic soil moisture regime, indicating that the soils are similar to other Alfisols (Typic) or have a darkened and organic-rich surface horizon (Mollic).

Based on a water budget analysis using the National Oceanographic and Atmospheric Administration's National Climate Data Center climate normals and the USDA Official Soil Series descriptions (textures and profile thicknesses) to determine the water status of soils over the growing season, the soils are seasonally moist in normal years, and generally experience a surplus throughout the year. Recharge periods extend from April through October, when temperatures are generally above 5°C. Although droughts likely alter the water balance, drought years do not represent ‘normal years’ in this region. Based on the USDA Official Soil Series descriptions, the soils are part of the Gaphill−Rockbluff complex, and Boyer, Kegonsa, and Seaton Series, which are characterized by very deep, well-drained soils.

Based on the grain size analysis, silt- and sand-sized grains dominate the soil samples collected throughout the vineyards, with average silt and sand compositions of 59% and 34%, respectively. The soils plot in the silty loam and sandy loam fields of the USDA soil texture triangle (Fig. 2-5), and these textures are in general agreement with the USDA taxonomic classification for these soils. Soil samples collected from the highest elevations in the northern and eastern parts of the property (DR-1, DR-2, and Lot 10A/B) contain the highest silt content (79-80%) and correspond to areas of steeper slope, thinner soil, and shallower depth to bedrock. Most of the vineyard soils are silty loams developed on parent materials consisting of windblown loess deposits; these soils are represented by 8 of the 12 soil samples collected and cover approximately 42% of the property.

The vineyard soils in the northern and central parts of the property, represented by soil samples Lot 10A/B, Lot 14, and Lot 20, underlie approximately 27% of the property, and consist of sandy loams derived from loamy outwash and glaciofluvial deposits underlain by outwash. Along the eastern property boundary, in a small area covering approximately 4% of the property and characterized by the highest elevations and steepest slope, soil sample DR-1 is a sandy loam developed on loamy colluvium and sandy deposits overlying sandstone bedrock. The remainder of the property (approximately 25%) consists mostly of a centrally located gravel pit developed in gravelly outwash.

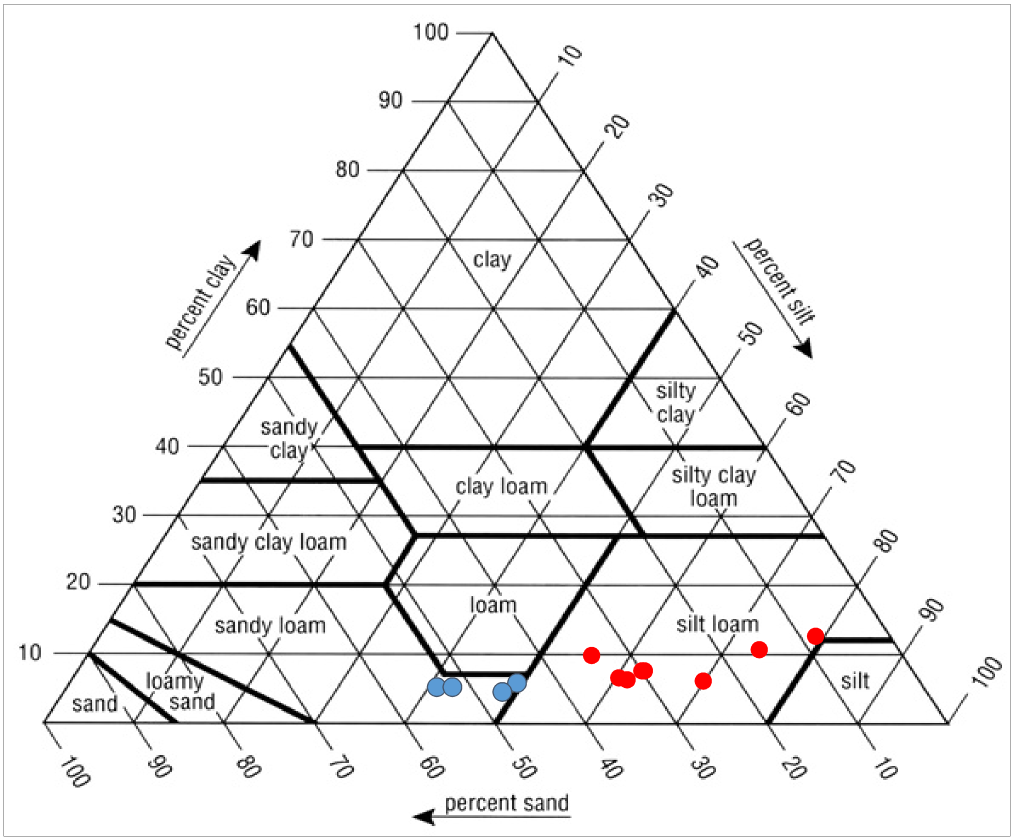


Figure 2-5. Ternary diagram showing the vineyard soil textures plotting in the silt loam and sandy loam fields of the USDA Soil Texture Triangle.

2.5.2 Vineyard Soil Chemistry and Mineralogy

Soil chemical analyses were carried out for organic matter, cation exchange capacity, and pH, along with plant-available macronutrients (potassium, calcium, magnesium, phosphorus, and sulfur) and micronutrients (boron, manganese, and zinc) that are essential elements necessary for completion of the plant life cycle (Table 2-2). All these elements have important roles in the metabolic functions of vines and require that minimum levels be maintained. The physical and chemical characteristics of the vineyard soils, such as texture, pH, organic matter, and cation exchange capacity, affect the nutrient pool, availability, adsorption, and retention potential.

Fine-grained, clayey soils can reduce the availability of potassium to vines, whereas coarse-grained, sandy soils are prone to leaching and can drain nutrients from the soils (Lambert et al. 2008). The silty loam and sandy loam vineyard soil samples are dominated by silt- and sand-sized grains, providing a good balance between drainage and water holding capacity.

The pH values of the vineyard soil samples, ranging from 5.6 to 7.6, indicate moderately acidic to slightly alkaline conditions, which provide good nutrient availability and balance for the health of the vines. Soils rich in organic matter are generally high in available nutrients, as decomposition of organic matter adds nutrients to soil and improves water-holding capacity. Cation exchange capacity, which is influenced by the soil’s organic matter and clay content, affects the ability of soil to hold positively charged nutrients for plant uptake (Dami et al. 2005). The highest organic matter percentages and cation exchange capacities, ranging from 1.1−1.3% and 12−13 cmol/kg, respectively, correspond to vineyard soil samples containing the highest silt content collected from the vineyards located in the northern and eastern parts of the property.

TABLE 2-2 - Summary of Soil Plant-Available Chemistry and Texture

Sample ID	DR-1	DR-2	Lot 5	Lot 6	Lot 7	Lot 8	Lot 9	Lot 10A/B	Lot 14	Lot 19-1	Lot 19-2	Lot 20
Depth (cm)	50	50	65	65	70	60	55	50	55	50	50	50
Soil Type	1145F	SmC2	SmB	SmB	SmB	SmB	SmC2	BoD2	BoD2	KeB	KeB	BoC2
Parent Material (USDA WSS)	Loamy colluvium over sandy residuum weathered from sandstone	Loess and/or silty slope alluvium	Loess and/or silty slope alluvium	Loess and/or silty slope alluvium	Loess and/or silty slope alluvium	Loess and/or silty slope alluvium	Loess and/or silty slope alluvium	Loamy outwash over sandy and gravelly outwash	Loamy outwash over sandy and gravelly outwash	Loess over sandy and gravelly outwash	Loess over sandy and gravelly outwash	Fine-loamy glacio-fluvial deposits over sandy-gravelly outwash
Clay	5.8	12.3	7.3	7.3	5.0	5.5	4.2	10.4	6.3	4.9	6.0	9.5
Silt	70.3	79.6	62.4	63.0	41.0	49.7	48.7	74.2	60.6	42.7	61.7	56.0
Very Fine Sand	10.0	4.2	10.8	7.8	12.4	12.5	12.9	8.3	10.0	7.1	11.7	7.6
Fine Sand	8.7	2.0	14.6	12.0	26.4	20.5	20.0	5.0	9.9	17.3	11.0	12.7
Medium Sand	5.0	1.8	4.8	9.3	14.7	11.5	13.0	2.1	6.8	21.4	7.3	11.3
Coarse Sand	0.21	0.1	0.0	0.59	0.46	0.34	1.2	0.006	5.9	6.4	2.2	2.9
Very Coarse Sand	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56	0.06	0.10	0.03
pH	7.6	5.6	5.7	6.0	6.1	5.9	5.9	6.0	7.1	7.0	7.3	7.0
OM %	1.3	1.1	0.7	0.6	0.3	0.4	0.7	1.1	1.0	0.7	1.0	1.3
CEC (cmol/kg)	12	9	3	4	2	2	2	13	9	4	9	10
P (ppm)	7	28	35	28	34	28	49	8	28	24	16	8
K (ppm)	70	95	50	49	34	24	37	112	79	44	63	79
Ca (ppm)	1587	994	465	567	278	354	482	1384	1234	689	1172	1211
Mg (ppm)	469	373	96	150	68	62	66	658	442	225	515	586
B (ppm)	0.5	0.3	0.3	0.3	0.2	0.2	0.2	0.4	0.4	0.3	0.4	0.6
Mn (ppm)	13	27	36	25	14	21	89	35	30	43	29	28
Zn (ppm)	0.9	0.4	1.5	0.7	0.4	0.4	2.1	0.5	1.2	1.5	1.0	1.0
S (ppm)	3.5	2.0	3.3	1.2	1.0	2.3	3.5	2.3	5.0	2.3	2.3	1.8

Notes:
1145F - Gaphill-Rockbluff complex, 30 to 60 percent slopes
SmC2 - Seaton silt loam, 6-12% slopes, eroded
SmB - Seaton silt loam, 2-6% slopes
BoD2 - Boyer sandy loam, 12-20% slopes, eroded
KeB - Kegonsa silt loam, 2-6% slopes
BoC2 - Boyer sandy loam, 6-12% slopes, eroded
USDA WSS - United States Deprtment of Agriculture Web Soil Survey (http://websoilsurvey.nrcs.usda.gov)
OM - Organic matter
CEC - Cation exchange capacity

The concentrations of plant-available macronutrients potassium (24–112 ppm), calcium (278–1587 ppm), magnesium (62–658 ppm), phosphorus (7–49 ppm), and sulfur (1–5 ppm), and micronutrients boron (0.2–0.6 ppm), manganese (13–89 ppm), and zinc (0.4–2.1 ppm), indicate significant variability in the vineyard soils. Some of these nutrient concentrations are outside the ranges specified by Moyer et al. (2014) in their pre-plant soil fertility guidelines for establishing productive vineyards, and by Dami et al. (2005) in the Midwest Grape Production Guide. However, when assessing the nutrient requirements of established vineyards, analyzing vine tissue samples in conjunction with soil samples is critical for determining vine nutrient status and identifying potential deficiencies (Moyer et al. 2014).

Overall, the plant-available soil chemistry shows the most variability for calcium, magnesium, and potassium; the highest concentrations of these elements are found in soils having the highest silt content in the northern and eastern parts of the property, i.e. in areas of steeper slope, thinner soil, and shallower depths to bedrock, where the vineyards producing the lowest yields and highest quality grapes are planted.

XRF total elemental analysis conducted on the fine fraction (silt and clay) of the soil samples indicates some variation in the chemical composition of the vineyard soils (Table 2-3). These elemental abundances represent the total concentrations in the soil and are indicative of the general vineyard soil conditions, whereas plant-available essential elements (Table 2-2), which are necessary for the completion of the plant life cycle, must be dissolved in an ionized water solution to allow uptake into the metabolism of the vines.

TABLE 2-3 - Summary of Total Elemental Analysis and Mineralogy

Sample ID	DR-1	DR-2	Lot 5	Lot 6	Lot 7	Lot 8	Lot 9	Lot 10A/B	Lot 14	Lot 19-1	Lot 19-2	Lot 20	Dolostone	Sandstone
Elevation (m)	286	276	275	274	272	272	264	276	261	236	236	244	286	286
SUM	99.04	98.71	99.11	98.96	99.01	98.59	98.68	99.37	99.07	98.8	98.73	97.68	100.46	100.99
LOI	12.25	4.21	3.66	3.64	3.17	2.99	3.43	5.21	5.07	5.84	19.09	7.95	43.4	21.7
SiO_2	59.29	73.37	77.46	76.20	76.80	77.18	78.73	71.95	72.11	71.50	45.16	62.09	2.25	53.77
Al_2O_3	9.70	11.18	9.18	9.83	9.49	9.27	8.13	11.60	10.47	10.08	8.96	13.30	0.62	0.59
TiO_2	0.57	0.73	0.76	0.74	0.77	0.71	0.72	0.74	0.65	0.79	0.47	0.75	0.02	0.06
Fe_2O_3	3.63	3.77	2.70	3.13	3.15	2.90	2.36	4.21	3.87	4.47	4.97	7.22	0.32	0.88
K_2O	3.14	2.55	2.46	2.48	2.57	2.51	2.37	2.52	2.40	2.68	2.21	2.73	0.27	0.19
MgO	4.01	0.85	0.67	0.77	0.74	0.70	0.50	0.99	1.32	0.90	6.94	1.27	20.72	9.51
CaO	5.43	0.67	0.72	0.69	0.78	0.77	0.83	0.79	1.61	1.08	9.82	1.14	32.77	14.12
Na_2O	0.65	1.04	1.14	1.16	1.18	1.23	1.20	1.05	1.20	0.97	0.62	0.72	0.0	0.0
P_2O_5	0.16	0.11	0.12	0.10	0.12	0.10	0.13	0.07	0.14	0.17	0.21	0.20	0.03	0.09
MnO	0.10	0.10	0.08	0.08	0.06	0.08	0.14	0.12	0.10	0.19	0.21	0.19	0.09	0.05
Zr	427	441	491	511	557	526	617	497	484	510	250	458	<11	62
V	75	81	58	68	65	72	47	101	63	77	81	151	<14	<15
Zn	47	68	66	69	58	59	50	59	73	66	87	116	<17	<16
Ni	33	32	15	35	11	6	7	28	35	30	19	52	<13	<14.2
Cr	59	80	68	69	62	67	67	55	56	51	62	96	19	18
Ce	123	144	146	131	126	141	77	139	235	237	181	162	<50	107
Sr	144	130	126	122	175	192	123	128	139	118	119	111	126	50
Ba	410	588	647	614	626	605	684	520	500	542	370	493	<47	<47
Quartz	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	x	xxx
Plagioclase[1]	x	x	xx	xx	x	x	xx	xx	x	xx	-	x	-	-
Orthoclase[2]	xx	xx	x		x	xx	x	xx	x	xx	x	xx	-	-
Dolomite	xx	-	-	-	-	-	-	-	-	-	xx	x	xxx	xxx
Biotite	x	x	x	x	x	x	x	x	x	x	-	x	-	-
Hornblende	-	x	-	-	-	-	-	x	x	-	x	x	-	-
Clay[3]	x	x	x	x	x	x	x	x	x	x	x	x	x	x

Notes:

Concentrations are in weight % for oxides and ppm for elements.

[1] Plagioclase - Albite, Anorthite, Labradorite

[2] Orthoclase - Microcline, Sanidine, Adularia

[3] Clay - Vermiculite, Montmorillonite

Relative mineral abundance based on visual evaluation of peak height and intensity (xxx = most abundant; x = least abundant; - = absent)

Overall, the most variability in total concentrations is noted for SiO_2 (45.16–78.73%), CaO (0.67–9.82%), MgO (0.5–6.94%), Al_2O_3 (8.13–13.30%), and Fe_2O_3 (2.36−7.22%). The vineyard soils contain average total concentrations of K_2O, CaO, MgO, and P_2O_5 of 2.55%, 2.03%, 1.64%, and 0.14%, respectively; and Fe_2O_3, MnO, Ni, and Zn are present in the vineyard soils in average total concentrations of 3.87%, 0.12%, 1200 parts per million (ppm), 25.2 ppm, and 67.5 ppm, respectively. The dolostone rock sample consists primarily of CaO (32.77%), MgO (20.72%), and SiO_2 (2.25%), whereas the sandstone sample is dominated by SiO_2 (53.77%), CaO (14.12%), and MgO (9.51%). The variation in the chemical composition of the vineyard soils reflects the diversity of parent materials in which the soils have developed.

The XRD analysis indicates that the soil mineralogy is dominated by quartz, plagioclase (albite/anorthite/laboradorite), orthoclase (microcline/sanidine/adularia), dolomite, and minor biotite, hornblende, and various clay minerals (vermiculite, montmorillonite). The dolostone consists primarily of dolomite, along with minor quartz and clay minerals, whereas the sandstone is composed of quartz and dolomite, and minor clay minerals, indicating that it is a dolomite-rich sandstone. Unpublished field notes from Road Materials Investigations Reports prepared by the Wisconsin Geological and Natural History Survey show that dolomite is the most common pebble lithotype in the Holy Hill Formation, based on analyses of rock types present in deposits of sand and gravel throughout Dane County. East of Sauk City (Fig. 2-2), more than 50% of the pebbles in glacial till consist of coarse-grained, mafic igneous rock to depths of at least 15 m (Clayton and Attig 1997). Consistent with chemical analyses indicating elevated MgO and CaO, soil samples DR-1, Lot-19-2, and Lot 20 contained dolomite, which may indicate the influence of weathered dolostone and dolomite-rich sandstone in the soils located in closest proximity to the bedrock outcrops. The relatively high Fe_2O_3 content in the soils relative to the rock samples may result from the oxidation of ferromagnesian minerals such as hornblende and biotite from mafic igneous rocks. The compositional variation of the soils is illustrated graphically on plots of major element oxides versus SiO_2 (Fig. 2-6), and spatially on maps depicting interpolated concentrations across the study area (Fig. 2-7). The plots show that SiO_2 has a strong inverse correlation with CaO and MgO; high coefficients of determination (R^2) explain 80% of the variation. The soils are highly depleted in CaO and MgO relative to the dolostone sample and slightly depleted relative to the dolomite-rich sandstone sample. Fe_2O_3, P_2O_5, and MnO are also inversely correlated with SiO_2, and have lower coefficients of determination that account for 40–60% of the variation. The soils are highly enriched in Fe_2O_3, slightly enriched in P_2O_5, and have similar MnO compositions relative to the dolostone and sandstone samples. TiO_2 and SiO_2 are positively correlated, with a coefficient of determination that accounts for 70% of the variation. The soils are significantly enriched in TiO_2 relative to the bedrock samples. Additionally, SiO_2 has a strong positive correlation with Zr and Ba; high coefficients of determination explain 80–90% of the variation (not shown). Again, these compositional differences reflect the diversity of parent materials, which include windblown loess, loamy outwash and glaciofluvial deposits underlain by outwash, and loamy colluvium and sandy deposits overlying sandstone bedrock.

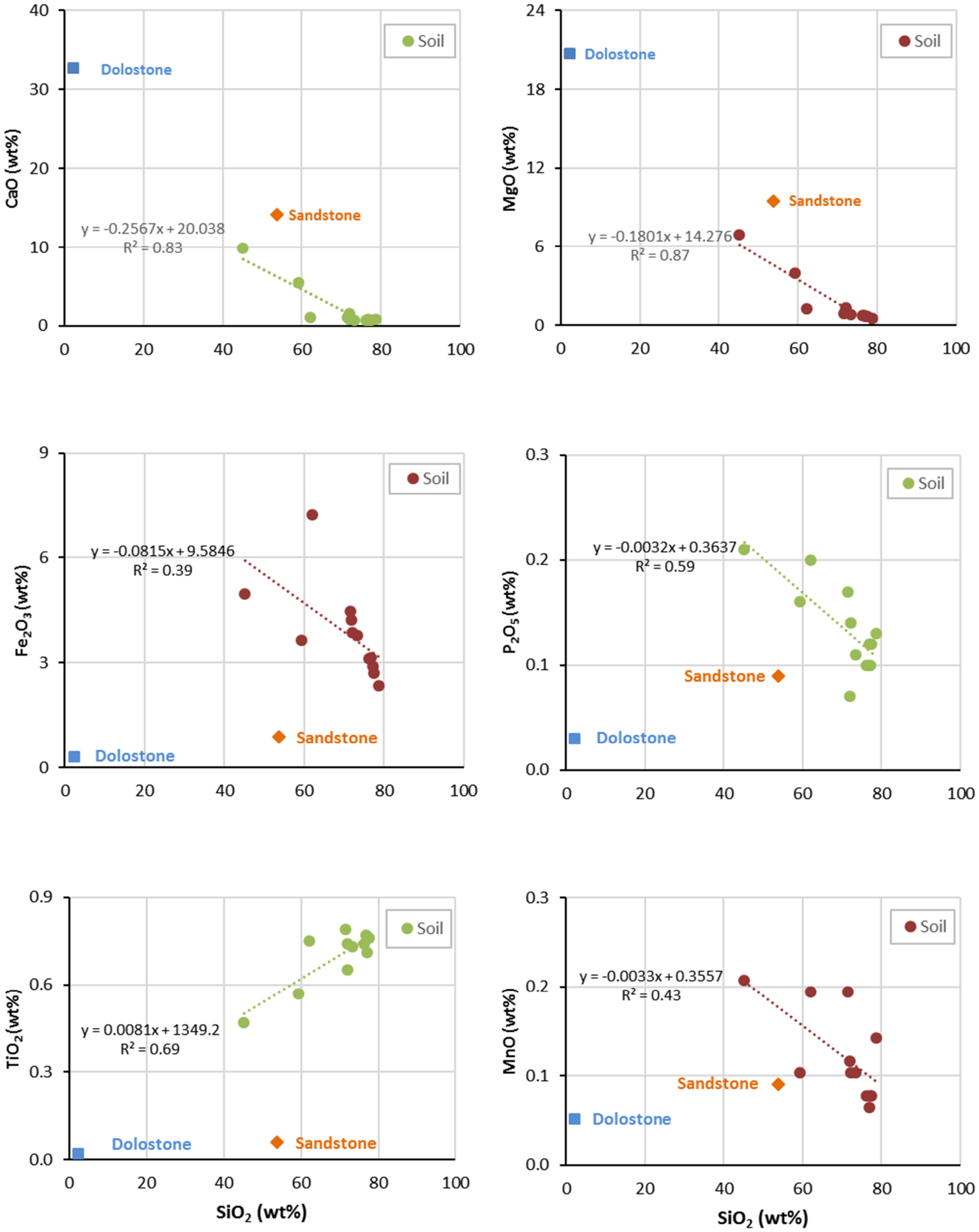


Figure 2-6. Harker diagrams depicting the compositional variation of selected major elements in soils relative to bedrock samples, reflecting the diversity of soil parent materials and the influence from the dolostone and dolomite-rich sandstone bedrock.

Figure 2-7 depicts the spatial compositional variability in soils, based on interpolated concentrations across the study area. Overall, the soils with the highest SiO_2 contents are found in the southern half, whereas the lowest SiO_2 contents occur in the northwest corner of the study area. Conversely, the soils with the highest CaO and MgO contents are present in the northwest corner and the lowest CaO and MgO contents are in the southern half of the study area. The highest Fe_2O_3 and Al_2O_3 compositions are found in soils from the west and north-central parts of the study area, and the highest P_2O_5 contents are located in the west and northwestern corner. Of note are soil samples DR-1, Lot-19-2, and Lot 20, which contain the lowest percentages of SiO_2 (62.09−45.16%), the highest LOIs (7.95−19.09%), and elevated concentrations of MgO (1.27−6.94%) and CaO (1.14−9.82%) relative to the rest of the soil samples. These compositions reflect the dolostone and dolomite-rich sandstone bedrock influence on the soils of these vineyard plots, caused by dissolution of primary minerals during rock weathering. Forested ridges underlain by dolostone of the Ordovician Prairie du Chien Group border the east boundary of the vineyards, and weathered outcrops of dolomite-rich sandstone are observed approximately 2 km to the northeast, along Highway 60. Wollersheim Winery winemaker, Philippe Coquard, states that the grapes from these vineyard plots (Lots 10A/B, 11 [not sampled], and Domaine Reserve) consistently produce the lowest yields and reach the highest sugar levels. With average Brix (estimated concentration of dissolved sugar) values of 21.5, average pH values of 3.31, and average yields of approximately 5 to 6 tons per acre, these grapes consistently achieve a perfect balance of sugar and pH levels at harvest, and produce wines with robust fruit flavors and concentrated aromas (P. Coquard personal communication March 15, 2016).

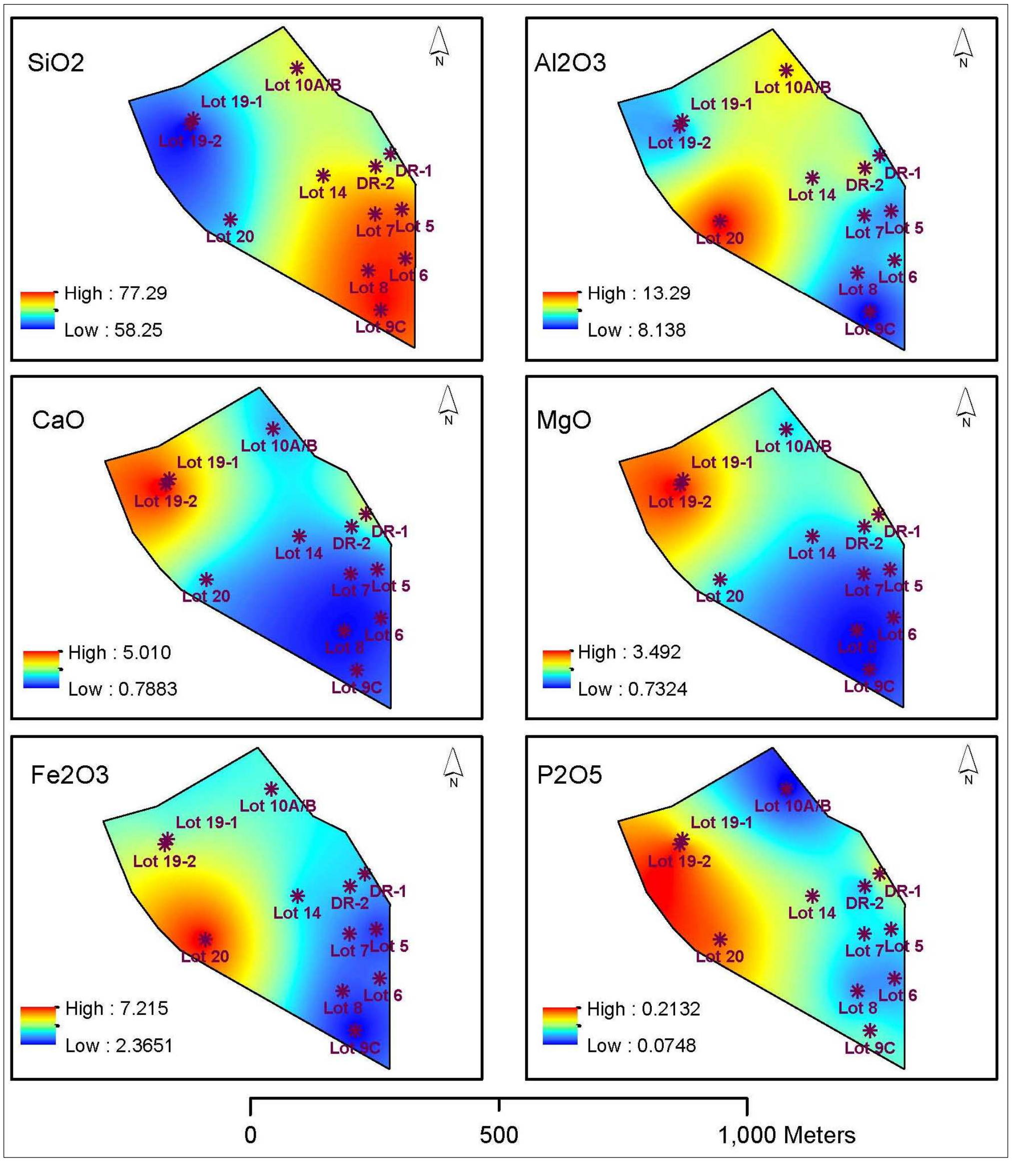


Figure 2-7. Spatial distribution of selected major elements in Wollersheim Winery vineyards (see Figs. 2-2, 2-4), reflecting the variety of parent materials in which the soils formed.

In the southern part of the property, the vineyards are characterized by soils with higher sand content, intermediate elevations, and flatter slopes; these vineyards produce the highest grape yields (approximately 7 to 8 tons per acre) and softer wines with delicate, lighter flavors (P. Coquard personal communication March 15, 2016). Overall, these are typical economic crop yields for hybrid grapes that have been optimized and proven successful for Wollersheim Winery in terms of maintaining a balance between profitability and grape and wine quality, while meeting the demand for sensible local wines.

2.5.3 Vineyard Variability Study at Domaine Reserve and Lot 19

The 1.6-acre Domaine Reserve and 1.4-acre Lot 19 plots, both planted with Marechal Foch grapes, were selected for further investigation by means of geophysical methods and vine trunk circumference measurements. Both plots have a southwesterly aspect, with slopes of 21% at Domain Reserve and 10% at Lot 19. The geophysical surveys provide measurements of apparent ECa and its inverse, ER, which are correlated with soil moisture, clay content and mineralogy, rock fragments, bulk density, porosity, and other soil properties (André et al. 2012). Vine trunk circumference measurements can be used to assess subsurface variability at the plot level and as a proxy for vine vigor, which can be correlated with grape characteristics (Imre and Mauk 2011).

2.5.4 Vine Trunk Circumferences

Vine trunk circumferences were measured at Domaine Reserve and Lot 19 in September 2014. The Domaine Reserve vines were planted in 1974, and the Lot 19 vines were planted in 1987. Measurements were collected from every vine on every other row, for a total of nine rows at each plot. The number of measurements collected was 437 at Domaine Reserve and 477 at Lot 19. Generally, vine trunk circumferences were similar between the two plots: median circumferences were 170 mm at Domaine Reserve and 190 mm at Lot 19 (Fig. 2-8). The Domain Reserve vine circumference data displayed slightly more variation, with a range of 300 mm compared to a range of 260 mm for the Lot 19 data.

Smaller vine trunk circumferences were observed at the uppermost three rows, at higher elevations near the top of the slope at Domaine Reserve. As uniform management practices are implemented at both plots, the variation in vine trunk circumferences between them reflects vine age, soil conditions (type, texture, and drainage), and topographic conditions (slope, elevation); it is also observed in grape yields, which are approximately 5 tons per acre at Domaine Reserve and 6 tons per acre at Lot 19. Wollersheim Winery's Philippe Coquard considers the age of the vines to be the dominant factor in the variation of vine trunk circumferences, although he insists that it is the combination of these factors (vine age, soil conditions, and topographic conditions) that ultimately creates these differences (personal communication, March 15, 2016). Larger circumferences in older vines may be expected if vine age alone were a determining factor, but the actual average measurements indicate that the younger vines of Lot 19 have the larger circumferences; it is clear, therefore, that the effects of age, soil, and topographic conditions combined outweigh the effects of vine age by itself.

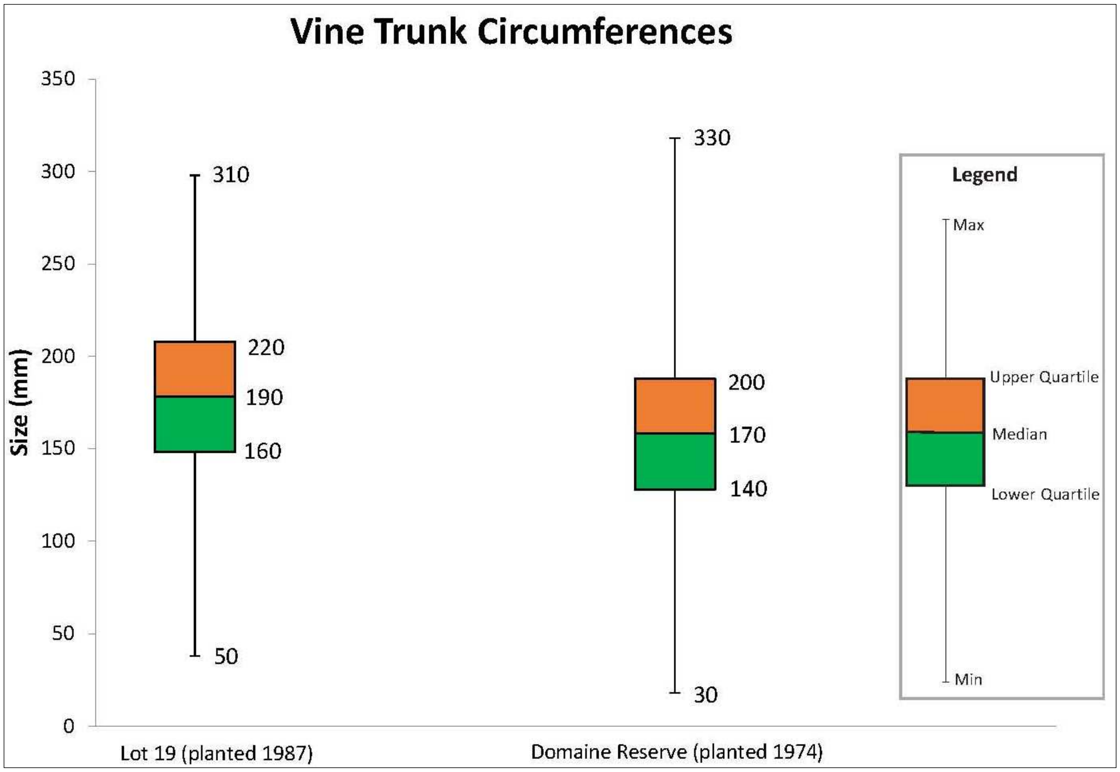


Figure 2-8. Box and whisker plots showing the trunk circumference measurements collected from Domaine Reserve and Lot 19; variations between the plots are a result of different vine ages, soil conditions, and topographic conditions.

2.5.5 Geophysical Surveys

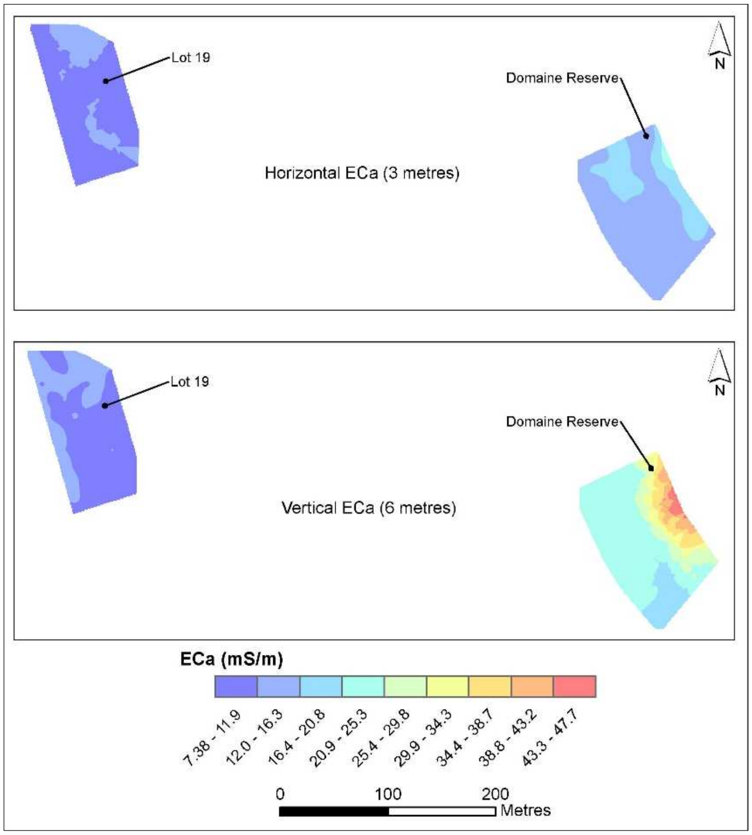
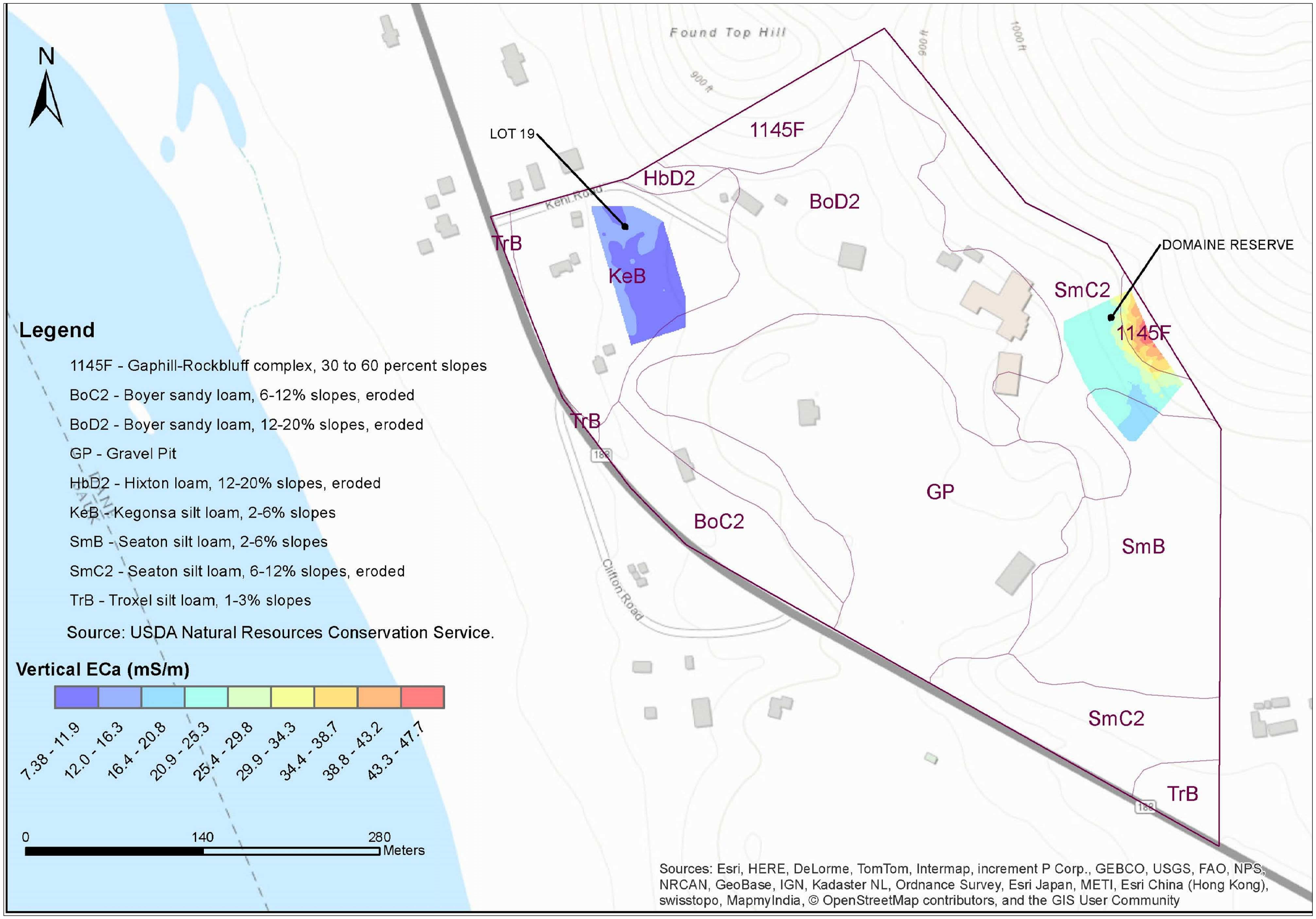


Figure 2-9. Horizontal (3 m) and vertical (6 m) apparent electrical conductivity (ECa) measurements in soils at Domaine Reserve and Lot 19, demarcating areas of similar soil type at each plot. mS/m: millisiemens per metre

EM and ERT surveys were completed at Domaine Reserve and Lot 19 in May 2014. The survey measurements were used to determine spatial variations in the subsurface that can be used to map soil variations within each plot. The soils were likely saturated by spring precipitation at the time of the survey. Figure 2-9 presents the horizontal (3 m) and vertical (6 m) soil ECa at 9.8 kHz measured in May 2014. Overall, the ECa values were relatively low, ranging from 7 to 68.75 millisiemens per meter (mS/m), and spatially correlated areas of similar ECa were noted at both plots. These areas generally coincide with the distribution of different soil types, as established by the USDA.

The horizontal ECa measurements were generally similar between the two plots, ranging from 5 to 27.25 mS/m at Lot 19 and from 7 to 30.75 mS/m at Domaine Reserve, indicating relatively sandy surficial soils. Vertical ECa values ranged from 7.25 to 18 mS/m at Lot 19 and from 8 to 68.75 mS/m at Domaine Reserve. The highest vertical ECa values were encountered at Domain Reserve in the northeastern corner of the plot, which is underlain by the Gaphill − Rockbluff complex (well-drained sandy loams developed from loamy or sandy colluvium), and has steeper slopes and shallower soil (Fig. 2-10). An inverse relationship between ECa and depth to bedrock is observed here because soils developed from the underlying bedrock are generally more conductive than the bedrock, and groundwater at or above the bedrock interface may also increase conductivity. Philippe Coquard of Wollersheim Winery confirms that the shallow depth to bedrock restricts rooting depth and limits grape yields in this northeast portion of the plot, which also coincides with smaller vine trunk circumference measurements in this area.



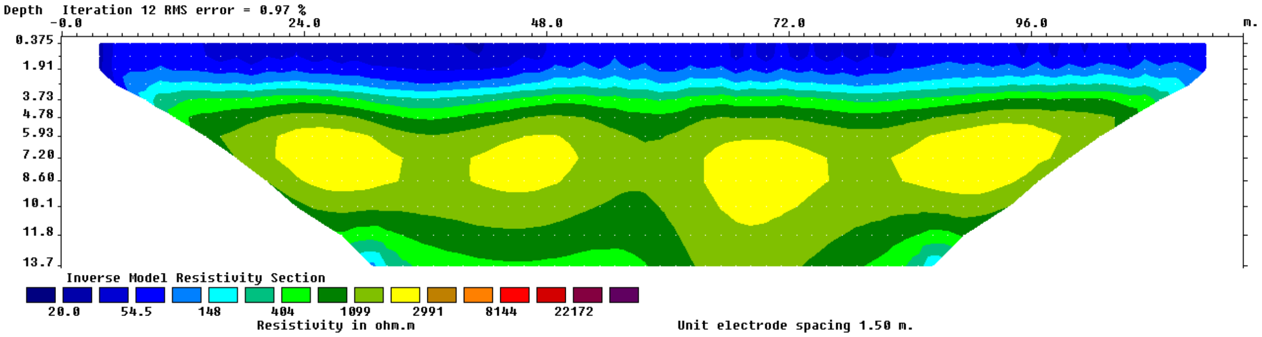
Source: USDA Natural Resources Conservation Service.

Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

Figure 2-10. Vertical (6 m) apparent electrical conductivity (ECa) measurements and soil types at Domaine Reserve and Lot 19; the area of highest ECa (the Domaine Reserve plot) coincides with steeper slope and shallower soil depth, restricting rooting depth and limiting crop yields in this area. mS/m: millisiemens per metre.

Figures 2-11 and 2-12 illustrate the two resistivity profiles completed at each plot: one profile near the top row, and one profile near the bottom row of vines. Overall, the ER measurements can be correlated with the ECa data of the plots, with areas of high conductivity corresponding to low resistivity and vice versa. At Lot 19, the ER values were generally similar between the top (53–7433 ohm-m) and bottom (51−3850 ohm-m) rows. Although the top row of the Domaine Reserve plot revealed ER measurements (26−2821 ohm-m) similar to those observed at Lot 19, much higher resistivity values (25−31,551 ohm-m) were noted for the bottom row of vines, indicating the presence of a more resistive layer at lower elevations, near the foot of the slope. This highly resistive layer is encountered at a depth of approximately 12 m near the bottom row of vines at Domaine Reserve, indicating an increase in coarser soil textures with depth.

Domaine Reserve Top Row



Domaine Reserve Bottom Row

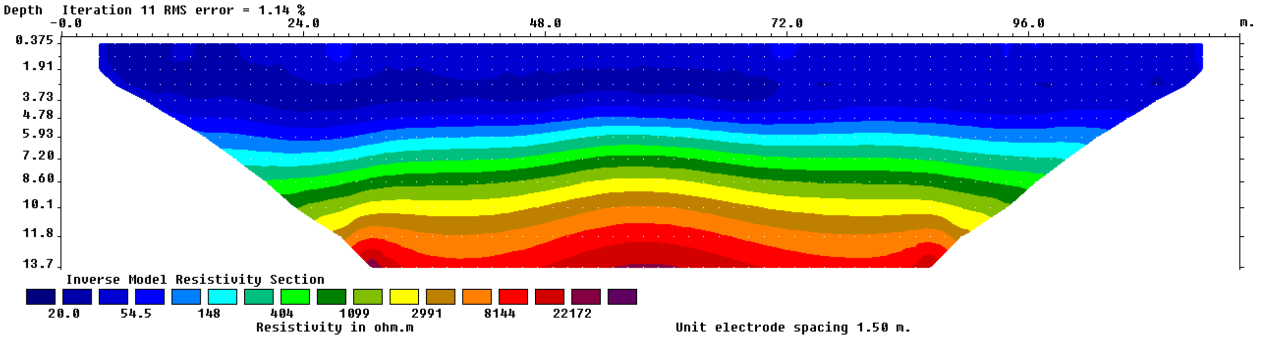
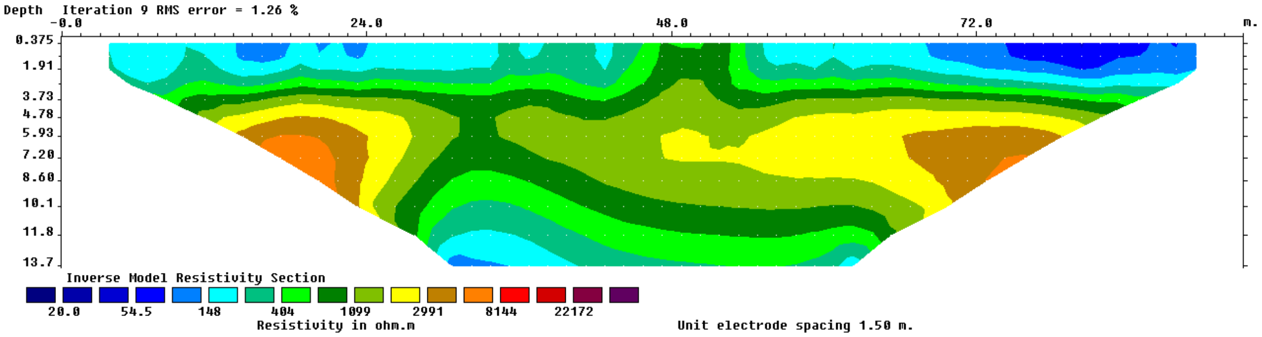


Figure 2-11. Soil electrical resistivity measurements for the two resistivity profiles completed at Domaine Reserve.

Lot 19 Top Row



Lot 19 Bottom Row

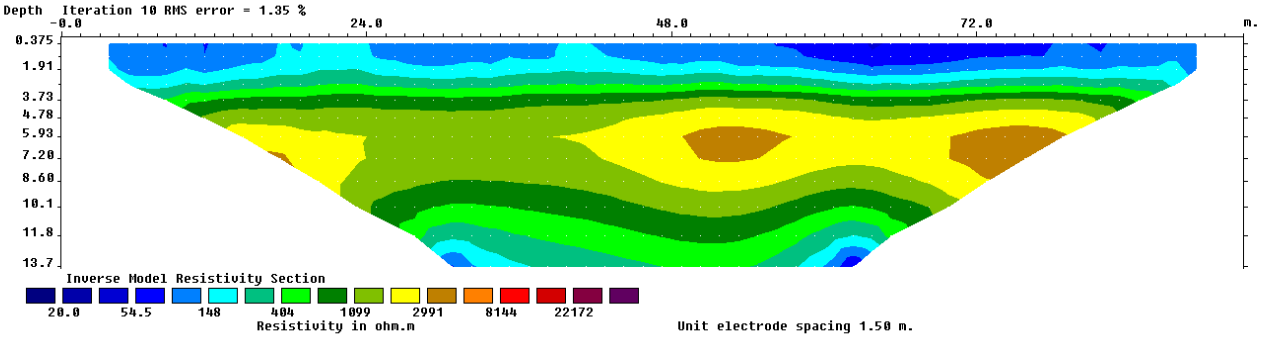


Figure 2-12. Soil electrical resistivity measurements for the two resistivity profiles completed at Lot 19.

These coarser textures at depth coincide with the centrally located gravel pit, consisting of stratified sand and gravel, and covering approximately 25% of the property. Based on well-log information from private wells drilled on the property, the stratified sand and gravel layer is laterally continuous and extends from 2 to 29 m below ground surface in the center of the property and from 9 to 15 m below ground surface in the northeast part of the property. Based on the ER data, Lot 19 has a more homogeneous subsurface, compared to the Domaine Reserve plot, which shows much more variability between the top and bottom rows. Overall, the ECa data corroborate the ER data at the Domaine Reserve plot, depicting more conductive/less resistive soils near the top row of vines, proximal to the Gaphill−Rockbluff complex, and more resistive/less conductive soils approximately 12 m deep near the bottom row of vines at Domaine Reserve. This indicates an increase in coarser soil textures with depth and coincides with the location of the stratified sand and gravel pit.

In addition to the differences established by geoelectrical methods, other plot characteristics such as elevation, slope, and vine age variations further differentiate the two plots. Specifically, the Domaine Reserve plot is situated at elevations of 259−305 m, has an average slope of approximately 20%, more soil textural variability across the plot, higher average clay and silt content, and vines approximately 42 years old. The grapes from Domaine Reserve have consistently higher sugar levels, with average Brix values of 21.13, average pH values of 3.29, and average yields of approximately 5 tons per acre, producing the best wines with robust fruit flavors and bold, concentrated aromas. In contrast, Lot 19 is located at lower elevations (213−259 m), has a gentler average slope of ca. 10%, less soil textural variability across the plot, higher average sand content, and younger vines approximately 29 years old. The grapes from Lot 19 attain intermediate sugar levels, have average Brix values of 20.07, average pH values of 3.28, average yields of approximately 6 tons per acre, and produce medium-bodied wines with pleasant fruit flavors and balanced aromas.

2.6 Conclusions

Wollersheim Winery is the birthplace of Wisconsin viticulture, a National Historic Site, and a leader in the Midwestern USA wine industry. Its location on a hill bordering the Wisconsin River marks the transition zone from glaciated terrain to the east to non-glaciated terrain to the west. The Wollersheim vineyards, with south and southwest-facing slopes and good air drainage, have well-drained soils dominated by silt- and sand-sized grains (silty loams and sandy loams). The vineyard soils are developed on parent materials consisting of windblown loess deposits, loamy outwash and glaciofluvial deposits underlain by outwash, and loamy colluvium and sandy deposits overlying sandstone bedrock.

The plant-available chemistry of the vineyard soils shows that the most variability and highest concentrations of calcium, magnesium, and potassium correspond to vineyard soils having the highest silt content in the northern and eastern parts of the property. The XRF total elemental chemistry of the vineyard soils reveals the most variability in SiO_2, CaO, MgO, Al_2O_3, and Fe_2O_3, reflecting the variety of parent materials in which the soils have developed. The soil mineralogy consists primarily of quartz, plagioclase, orthoclase, and dolomite, minor biotite and hornblende, and various clay minerals. The soil samples with the lowest SiO_2 compositions and the highest LOIs have elevated MgO and CaO contents, indicating a contribution from the weathering of dolostone or dolomite-rich sandstone bedrock in the soils of these plots, which are located in closest proximity to the bedrock outcrops. Vineyard geophysical surveys at the Domaine Reserve and Lot 19 plots demonstrate spatial variations within the subsurface at the plot level, demarcating soil variations within each plot. The ECa data are consistent with the ER data, indicating more soil textural variability and higher average clay and silt content for the Domaine Reserve plot, and less textural variability and higher average sand content for Lot 19. Additional characteristics, such as elevation, slope, and vine age variations further differentiate the two plots. Thus, the terroir of the Domaine Reserve plot, consisting of more heterogeneous soils, higher elevation, steeper slope, and older vines, produces the lowest yields, the best quality grapes, and the rich, full-bodied Domaine Reserve wine, whereas the terroir of Lot 19, comprising more homogeneous soils, lower elevation, gentler slope, and younger vines, produces slightly higher yields, good quality grapes, and the medium-bodied Domaine du Sac wine.

With an increasing demand for wine and an expanding local consumption movement across the state, the future of viticulture in Wisconsin looks promising, with new wineries opening and larger acreage of grapes being cultivated throughout the state to meet the demand for Wisconsin wine. As climate change continues to affect the selection of cultivated grape varieties, Wisconsin holds a great potential for cultivating quality cool-climate European varieties, in addition to the American and French–American hybrids currently dominating the state’s grape production. Future work focused on selecting the proper hybrid not only for the appropriate climatic conditions, but also for the specific soil type, will aid in further refining our understanding of the optimal terroir conditions for cultivating quality cold-climate grapes.

3.0 Insight into Grapevine Source Water Acquisition during Key Phenological Stages Using Stable Isotope Analysis

3.1 Abstract

Stable isotope analyses of grapevine water provide insight into seasonal water use trends, soil depths of active water/nutrient uptake, and the role of water in the physiological processes of the grapevines during the growing season to support development of efficient irrigation strategies while managing grape and wine quality. The water acquired by the grapevines of Lot 19 at Wollersheim Winery during the 2015 growing season originated from various soil depths and was derived from a combination of meteorological sources prior to recharging the soil water reservoir. The isotopic composition of grapevine water demonstrates that the functional rooting depth for water uptake is highly variable during the different phenological stages of the grapevines over the growing season. The hydrogen stable isotope ratio (δD) values of vine water identify rain as the principal water source in the spring months during budbreak and flowering/fruit set, and various combinations of rain and groundwater in the summer and autumn months, with an increasing percentage of groundwater in the mixture, as the veraison/ripening stages continue and fruit maturity is achieved at harvest. The seasonal vine water use trend demonstrates a variable functional rooting depth for grapevine water acquisition over time, with the shallow roots utilizing rain water as a main source in spring and a root system that can reach progressively deeper into the soil profile for water as the growing season advances. The preferential vine water use over the growing season in this area allows irrigation recommendations to be made or forecasted to maximize water uptake efficiency from the soil and water conservation. This study site is under an udic soil moisture regime, potentially providing insensitive isotopic variations due to the evenness of rainfall; thus, the success of this approach in an udic regime suggests that that deployment of

these methods will be highly effective in identifying seasonal water uptake patterns in ustic and xeric moisture regimes.

3.2 Introduction

Vineyard terroir is recognized as a critical component of assessing grape and wine quality (Wilson 1998; Haynes 1999; White et al. 2009). Terroir, as a state factor model, incorporates the synergistic interaction of the unique physical characteristics of a vineyard, such as the geology, soils, geomorphology, biologic organisms, grape variety, and climate; in order to understand how the combination of these factors is imparted into the character and quality of the grapes produced in that vineyard. In addition to the physical environment elements that influence the unique attributes of grapes and wine, human factors involved in viticulture and winemaking, such as vineyard management, viticultural practices, and vinification techniques, also contribute to the character and quality of the grapes and resulting wine. Therefore, terroir is a function of the soil (S), organisms (O), grape variety (G), climate (C), landscape (L), and vitiviniculture (V), [Terroir = f (S, O, G, C, L, V)]. The vineyard soil, in particular, is one of the most influential terroir factors due to its critical role in the grapevines' absorption of water and nutrients affecting the synthesis and accumulation of secondary metabolites in grapes (Bergqvist et al. 2001; Chone et al. 2001; Van Leeuwen et al. 2004; Cortell et al. 2005; Cortell and Kennedy 2006; Koundouras et al. 2006; Morlat and Bodin 2006; De Andrés-de Prado et al. 2007; Gómez-Míguez et al. 2007; Cohen and Kennedy 2010; Ubalde et al. 2010; Van Leeuwen 2010; Shange and Conradie 2012; Teixeira et al. 2013; Tramontini et al. 2013); and soil heterogeneity at the vineyard level has been directly related to variability of grape quality, indicating that soil properties exert a substantial control on the availability of water and nutrients to the vines (Bramley et al. 2011; Scarlett et al. 2014). In turn, soil water content is correlated to matric potential, which varies with soil texture. Coarse textured soils have large pores and lose most pore water at low matric potentials, while finer textured soils have a mixture of pore sizes and lose water more slowly reaching higher matric potentials (Chapman et al. 2012; Whalley et al. 2013). Soil textural heterogeneity has an impact on the vine water source, as demonstrated by ecohydrologic separation of environmental water studies, which show partitioning of water in the soil, challenging the assumption that water is thoroughly mixed in the soil (Hewlett and Hibbert 1966). These studies demonstrate that soil water separates into mobile and stationary water; mobile water filters through the soil and eventually reaches surface water bodies, while stationary water, which is stored in soil zones with high matric potential and remains tightly bound in small pores, thus limiting potential mixing with other water, is acquired by plants (Jackson et al. 1999; Meinzer et al. 1999; Brooks 2009; Philips 2010; Goldsmith et al. 2011; Moreno Gutiérrez et al. 2012; McDonnell 2014; Brooks 2015; Evaristo et al. 2015).

The source of vine water may include a mixture of water from precipitation and groundwater, and during a growing season, vine water use varies depending on factors such as precipitation inputs, temperature, humidity, and evapotranspiration. The isotopic composition of the vine water reflects that of the source water (i.e., local precipitation inputs, groundwater, or a combination of these). We hypothesize that the location of soil water accessed by a plant fluctuates over the growing season according to weather variations, soil moisture status, and physiologic demand of the plant. Approximately 60% of grapevine roots are encountered in the top 60 cm of soil (Smart et al. 2006); as the growing season progresses, grapevines extract water from shallow soil depths where the highest root densities exist, and if moisture becomes depleted in the shallow soil, vine water extraction proceeds to different soil depths, where higher water availability and lower root densities are present (Prichard et al. 2004).

The stable isotope analyses of source and vine water can provide insight into seasonal water use, vine water uptake processes, active rooting zones, and the role of water in the vine ecological and physiological processes during the growing season (Wershaw et al. 1966; Ehleringer and Dawson 1992; Brunel et al. 1995). Soil water includes a mixture of waters from precipitation (rain, snowmelt) and groundwater; in addition, water in soils used for agriculture may include irrigation water as an additional component of the soil water mixture. In viticulture, however, irrigation must be carefully managed in accordance to the needs of the vines during its critical phenological stages to maintain an optimal balance between mild water stress, which is known to influence grape quality via the phenylpropanoid metabolic pathway, and vine development (Jones and Davis 2000; Deluc et al. 2009; Van Leeuwen et al. 2009; Chaves et al. 2010; Martínez-Lüscher et al. 2016). Irrigation may be necessary from budbreak to flowering and fruit set, whereas during the ripening period from veraison through harvest, limited water supply stimulates the vines to direct more energy into fruit development versus excess vegetative growth (Moyer et al. 2013). In regions with seasonal drought, deficit irrigation strategies are implemented to maximize efficiency of vine water use while conserving water resources. Deficit irrigation is recognized as an effective approach in refining vine water use while controlling grape quality, allowing vines to tolerate mild water stress with a positive impact on grape quality (Wample and Smithyman 2002; Prichard et al. 2004; Chaves et al. 2010).

The stable isotopic composition of water extracted from suberized plant tissue, prior to reaching leaves, has been shown to be a faithful record of the source of water uptake by a plant (Ehleringer and Dawson 1992). Thus, the stable isotopes of water in precipitation, soil, and vines can be utilized in evaluating the variation in the water source selected by vines over the growing season. The stable isotopes of oxygen and hydrogen in precipitation covary in a predictable fashion, being controlled by temperature, the extent of evaporation, the amount of rainout, etc., indicating that the stable isotopes of water are an excellent reference for the geographic place of origin of a given parcel of water (Gat 1996). Because plants take up water from soil quantitatively, there is no net isotopic fractionation in the isotopic composition of water during plant uptake and transport through roots and stems. Therefore, plant water in suberized tissue that has not undergone evapotranspiration and exchange with biosynthetic compounds in leaves, should reflect the isotopic composition of the water source (Wershaw 1966; Zimmerman et al. 1967; Dawson and Ehleringer 1991; Dawson 1993; Dawson et al. 2002). Thus, given appreciable differences in isotopic compositions of rainwater during a growing season, variable residence times of water in a soil (Buhay and Edwards 1995), and distinct isotopic compositions of groundwater relative to ambient precipitation, it is possible to determine the source(s) of water acquired by vines during the growing season. This is in contrast to the well-studied isotope effects on plant water during evapotranspiration and biosynthesis, which impart significant fractionations of oxygen and hydrogen isotopes (Barbour et al. 2001; Roden et al. 2002), but these are processes that occur at the leaf-level, in non-suberized tissues.

Studies using the variation of natural abundance of water-stable isotopes in soil water and suberized tissue plant water demonstrated that the piston flow model or the concept of translatory flow is imperfect, as reservoirs of water (with distinct isotope compositions) remained in discrete pockets of soil with high matric potential despite percolation of rainwater (Brooks et al. 2009; Goldsmith et al. 2011; McDonnell 2014; Evaristo et al. 2015). In a soil with textural contrasts, the high and low matric potential regions influence where vines access water in the soil and, in turn, provide considerable heterogeneity in isotope composition, reflecting a mixture of waters from precipitation (rain, snowmelt) from different seasons and storm tracks, groundwater, and/or irrigation, as well as different residence times for soil water components. Although the mechanism(s) controlling isotopic heterogeneity in soil water is poorly understood, the potential isotopic stratification of soil water could be leveraged to test the depth regions of soil accessed by vines for water uptake during the growing season.

As soil water contains a combination of waters, each with their unique isotopic signature, the isotopic composition of the grapevines will reflect that of the source water utilized. This study examines the source of the water acquired by grapevines during the critical phenological stages of the 2015 growing season using stable isotopes oxygen and hydrogen in water at Wollersheim Winery, one of Wisconsin's best-known wine producers.

3.3 Materials and Methods

3.3.1 Study Site

The only winery in the Lake Wisconsin America Viticultural Area (AVA), Wollersheim Winery is a national historic site located in Prairie du Sac, Dane County, Wisconsin. The studied vineyard plot, Lot 19, is located on a hill overlooking the Wisconsin River (Fig. 3-1). Situated at elevations between approximately 213-259 meters, Lot 19 is a 0.6-hectare plot planted in 1987 with 18 rows of Marechal Foch vines trending northwest-southeast on a southwesterly aspect slope of approximately 10% grade. The vines are planted 2 meters apart with a distance of 3 meters between the rows, allowing sufficient space for farming equipment, and typical yields for Lot 19 are approximately 11 tons per hectare.

Figure 3-1. Map of Wollersheim Winery, illustrating the location of study vineyard Lot 19 and the distribution of soil types based on USDA Official Soil Series.

3.3.2 Rain Water, Soil Water, and Root/Stem Water

The precipitation isotopic signatures were assessed in relation to the critical phenological stages of the grapevines over the growing season (Coombe 2004), spring precipitation representing the budbreak, flowering, and fruit set stages; summer precipitation characterizing veraison and ripening; and autumn precipitation representing the fruit maturity and harvest phenological stages. The 2015 growing season dataset represents an average range of isotopic compositions for spring, summer, and autumn season precipitation.

During the months of May through September 2015, rain water was collected in a precipitation collector designed for obtaining a monthly cumulative stable isotope sample. The precipitation collector, consisting of a 13-liter high-density polyethylene (HDPE) bucket with an o ring sealed lid and a HDPE funnel glued in the bucket lid, containing a 1-centimeter thick layer of light mineral oil to prevent evaporation, was utilized to collect cumulative monthly rain water samples from May through September 2015. Rain water samples were collected utilizing a 30-milliliter syringe to draw up a sample of water from below the oil layer in the precipitation collector, wiping off the oil from the outside of the syringe, ejecting the water sample through a funnel lined with several coarse paper filters into a 20-milliliter glass sample vial, with minimum head space, and sealed with a screw-cap. The precipitation collector was emptied following each sampling event, and the rain water samples were refrigerated until isotopically analyzed. In addition, a groundwater sample was collected from the winery's water supply well, which is approximately 56 meters deep, has a static water level of approximately 26 meters below ground surface, and is the source of irrigation water for the vines. Groundwater samples were collected at the beginning (May) and end (September) of the growing season.

Soil and stem/root samples were collected concurrently with the monthly rain water samples. Smart et al. (2006) reviewed grapevine root distributions reported by various researchers, and found that generally, 60% of grapevine roots are encountered in the top 60 cm of soil, and more than 80% of roots are found in the top 120 cm of soil, or less, depending on the presence of root limiting horizons. Thus, during each sampling event, a 50-cm deep soil pit was dug near the selected study vine, and soil samples were collected from depths of 10, 30, and 50 cm below ground surface. Soil samples were collected into 20-mL glass vials, and were stored in a freezer pending water extraction and isotope analysis. Stem samples were collected in May and June from shoots located closest to the trunk of the selected study vine, and in order to prevent damage to the vine, root samples encountered during the advancement of the soil pit were collected in July, August, and September. The stem/root samples were placed into 20-mL glass vials, and sealed with a screw cap. The vials containing the soil and stem samples were placed in zipped plastic bags and transferred to a freezer for storage pending water extraction and analysis.

3.3.3 Cryogenic Vacuum Water Extraction and Isotopic Analysis

The water from soil and stem/root samples was extracted using a cryogenic vacuum extraction line (Ehleringer and Osmond 1989) at the University of Wisconsin Madison's Stable Isotope Laboratory. A small portion of each sample was placed into a glass tube (27 mm outside diameter, 178 mm long) compatible with the cryogenic vacuum line. Samples were extracted for 1 hour (West et al. 2006), after which the extracted water was immediately transferred into a 2-mL screw top glass vial and stored in a refrigerator until analyzed.

The rain water and extracted soil and stem/root water samples were analyzed at the University of Wisconsin Milwaukee School of Freshwater Sciences using a Picarro L2130-I $\delta D/\delta^{18}O$ Ultra High-Precision Isotopic Water Analyzer with a precision of 0.100 ‰ for hydrogen stable isotope ratios (δD) and 0.025 ‰ for oxygen stable isotope ratios ($\delta^{18}O$). Soil moisture was quantified on the remaining soil and stem/root samples, which were weighed, dried at 105 °C over 48 hours, and re-weighed to calculate percent moisture content. All isotopic ratios are reported in the conventional delta notation (δ) relating the isotopic composition of the samples to that of an internationally accepted reference standard (Vienna Standard Mean Ocean Water, V-SMOW) on a per mil (‰) basis: $\delta = (R_{sample}/R_{standard} - 1) \times 1000$, where R is the molar ratio of heavy to light isotopes (Gat 2005).

3.4 Results

3.4.1 Terroir Overview

Wollersheim Winery's Lot 19 is located within a landscape that is part of the streamlined hills and valleys shaped by glaciers and glacial stream deposits consisting of outwash and hummocky sand and gravel (Mickelson et al. 1982; Mickelson 2007). The glacial deposits are part of the Horicon Member of the Holy Hill Formation (Syverson and Colgan 2004), which is characterized by glacial till comprising brown gravelly, clayey, silty sand, and dolomite derived from Ordovician formations, and are overlain by loess (Clayton and Attig 1997; Stiles and Stensvold 2008; Attig et al. 2011). Based on the United States Department of Agriculture (USDA) Official Soil Series description, the soils are silt loams, part of the Kegonsa Series (type locality) characterized by very deep, well drained Alfisols. Specifically, the soils are Mollic Hapludalfs in a mesic soil temperature regime and udic soil moisture regime, indicating the soils have a darkened and organic-rich surface horizon, and a high base status clay-rich subsurface horizon. Locally, the soil texture observed within the sampled profiles became consistently coarser with depth, from silt and clayey silt in the surficial depths to progressively more sandy textures encountered toward the terminal depth of the soil pit (50-cm).

The climate is moderated by the Wisconsin River, and air drainage in the river valley inhibits frost in the vineyards. In the Wollersheim Winery area, where the average growing season ranges from April 1st to October 31st, a total of 2382 (base 50°F) GDD were recorded in 2014. Based on a 30-year climatological temperature average (1981-2010), Wollersheim Winery falls in the low range of the Winkler Region II (2501-3000 GDD) with an average of 2652 GDD. In comparison, Napa, California falls in the middle range of the Winkler Region III (3001-3500 GDD) with an average of 3297 GDD, and Walla Walla, Washington falls in the high range of the Winkler Region II (2501-3000 GDD) with an average of 2959 GDD.

Based on a water budget analysis using the National Oceanographic and Atmospheric Administration's (NOAA) National Climate Data Center climate normals and the USDA Official Soil Series descriptions (textures and profile thicknesses) to determine the water status of soils over the growing season, the soils are seasonally moist in normal years, largely experiencing a surplus throughout the year, with recharge periods from April through October, when temperatures are generally above 5º C (Fig. 3-2). Although droughts likely alter the water balance, drought years do not represent "normal years" in this region.

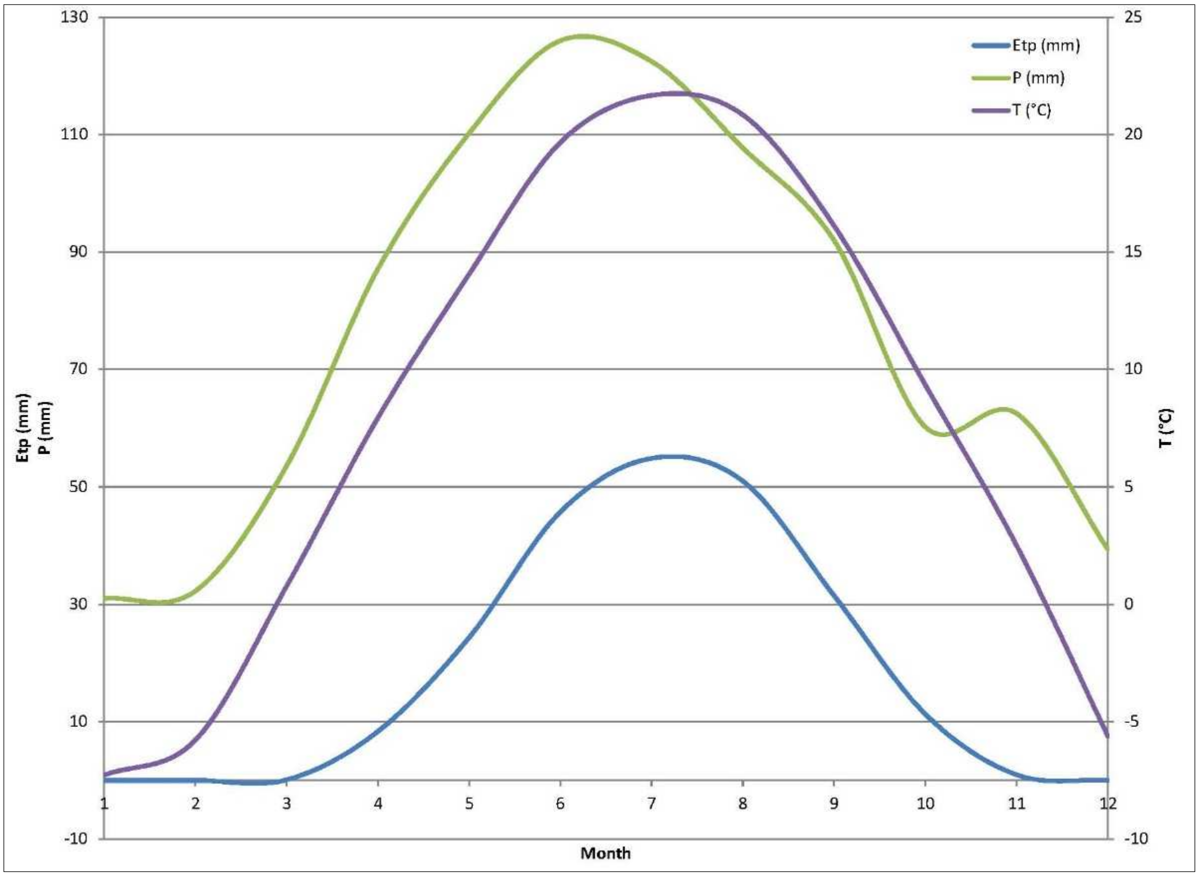


Figure 3-2. Water budget graph illustrating potential evapotranspiration, precipitation, and temperatures calculated using climate normals and the USDA Official Soil Series descriptions.

3.4.2 Grapevine Phenological Stages

The typical timing and duration of the critical phenological stages for the vines of Lot 19 include budbreak in late April/early May as temperatures increase; flowering in mid-to-late June, after which the flowers set and the berries begin to grow during the fruit set stage in late June; veraison, marking the beginning of coloration in mid-to-late July with complete color change by early August; and fruit maturity and harvest in early-to-mid September. Depending on the local weather variations of the growing season, the timetable of the vines' phenological stages can fluctuate by as long as two to three weeks; however, the time interval between the flowering and harvest stages has been consistently 85 to 90 days (Philippe Coquard personal communication January 9, 2017). After fruit maturity/harvest and leaf fall, the vines prepare for dormancy from November/December to March/April, when there is no active photosynthesis and the vines store carbohydrates in the trunk and roots.

3.4.3 Rain Volumes and Soil Moisture

Over the 2015 growing season, a total rain volume of 412 mm was recorded, which is in the mid-range of water requirements (250 to 750 mm) for a mature vineyard grown on medium to heavy textured soils (Goldammer 2015). Monthly rain volumes over the five sampling events (May through September) of the 2015 growing season ranged from 158 to 42 mm, decreased progressively from May to July, then increased slightly in August and September (Table 3-1, Fig. 3-3).

Table 3-1. Monthly rain and percent soil moisture at the 10, 30, and 50-cm depths over five monthly sampling events representing the phenological stages of the 2015 growing season.

Sample	Spring		Summer		Autumn	Mean ± SD
	May	June	July	August	September	
	Budbreak	Flowering & Fruit Set	Veraison/ Ripening	Veraison/ Ripening	Fruit Maturity/ Harvest	
Rain (mm)	158	99	42	53	59	82 ± 47
Soil Moisture 10 cm	12.4	11.5	9.02	7.43	9.57	10 ± 2.0
Soil Moisture 30 cm	10.3	10.9	10.3	7.29	8.72	9.5 ± 1.5
Soil Moisture 50 cm	6.95	8.03	7.55	5.24	3.90	6.3 ± 1.7
Soil Moisture Mean ± SD	9.9 ± 2.7	10 ± 1.9	9.0 ± 1.4	6.7 ± 1.2	7.4 ± 3.1	

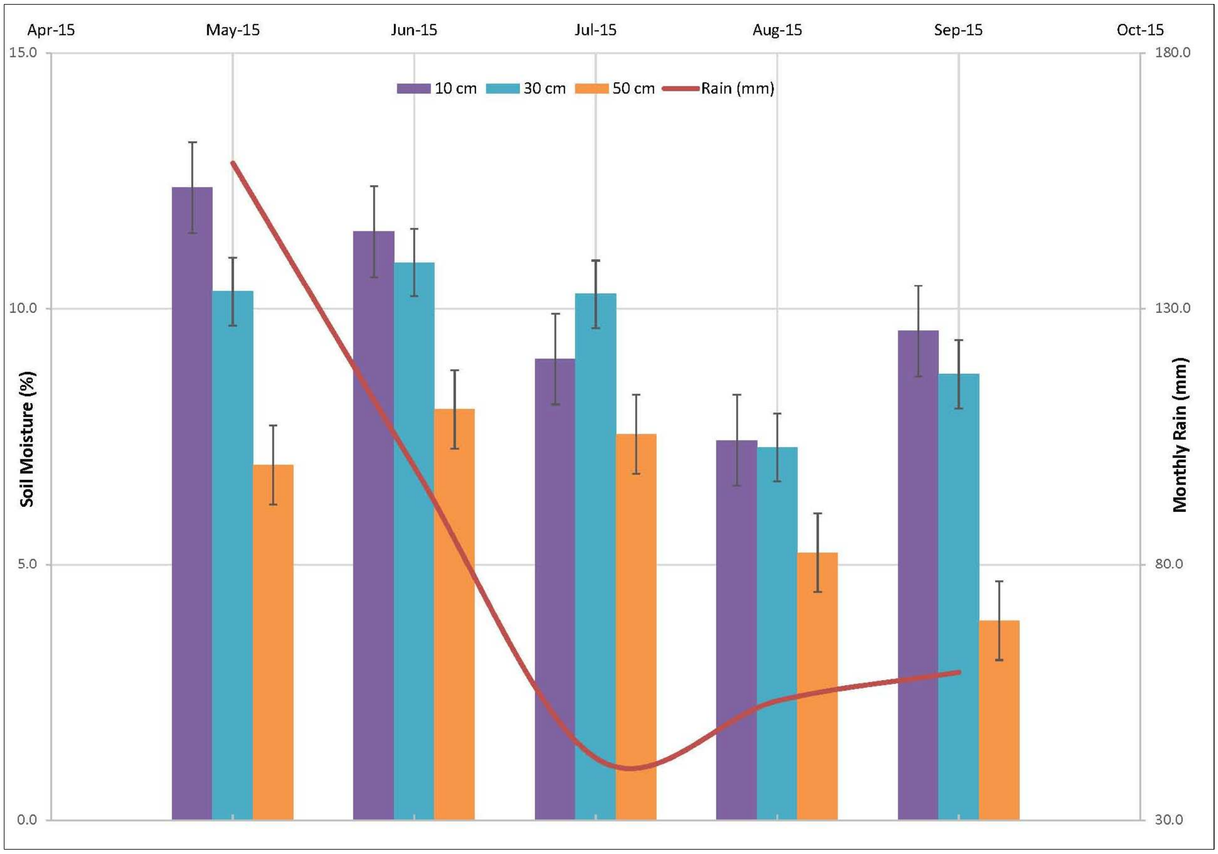


Figure 3-3. Graph of percent soil moisture at 10, 30, and 30-cm depths and monthly rain over the growing season.

The highest monthly rain volume (158 mm) occurred in May and corresponds to the highest soil moisture value (12.4%) identified in the shallow (10-cm) soil sampling depth. Generally, the mean soil moisture of the soil profile across the three soil sampling depths was highest in May and June (9.9 and 10.2%) and lowest in August and September (6.7% and 7.4%). Similarly, mean soil moisture for each sampling depth over the growing season was highest (10.0%) in the shallow (10-cm) soil and lowest (6.3%) in the deep (50-cm) soil. Across the five monthly sampling events, soil moisture typically decreased with depth, with the exception of the July sampling event, which coincides with the lowest monthly rain volume (42 mm) of the growing season, when the soil moisture at the intermediate sampling depth of 30-cm was higher than at the shallow sampling depth of 10-cm. Although soil moisture can be influenced by severe events (i.e., heavy rains, flooding), generally the soil moisture values, which were obtained from soil samples collected at the end of each month, correlate with the monthly rain volumes recorded at the end of each month over the growing season.

3.4.4 δD Results of Groundwater, Rain, Soil, and Vine Water

Monthly rain δD values ranging from -21.5 to -51.9 ‰ over the five monthly sampling events, the most negative δD values occur in June and most positive δD occur in July; concomitantly, vine water δD values ranging from -29.3 to -51.0 ‰ reflect a parallel trend for these months, being most negative in June and most positive in July (Table 3-2, Fig. 3-4).

Table 2. δD (‰) values for groundwater, monthly rain, soil water from 10, 30, and 50-cm depths, and vine water over five monthly sampling events representing the phenological stages of the 2015 growing season.

Sample	Spring		Summer		Autumn	Mean ± SD
	May	June	July	August	September	
	Budbreak	Flowering & Fruit Set	Veraison/ Ripening	Veraison/ Ripening	Fruit Maturity/ Harvest	
Groundwater δD (‰)	-56.65					
Rain Water δD (‰)	-40.97	-51.87	-21.54	-27.56	-31.96	-34.8 ± 11.9
Vine Water δD (‰)	-38.52	-51.01	-29.32	-45.09	-42.78	-41.3 ± 8.1
Soil Water 10-cm δD (‰)	-31.08	-56.31	-40.96	-39.95	-35.24	-40.7 ± 9.6
Soil Water 30-cm δD (‰)	-59.30	-64.42	-53.34	-46.53	-39.98	-52.7 ± 9.8
Soil Water 50-cm δD (‰)	-63.90	-59.89	-47.99	-47.97	-41.60	-52.3 ± 9.3
Soil Water δD (‰) Mean ± SD	-51.4 ± 17.8	-60.2 ± 4.1	-47.4 ± 6.2	-44.8 ± 4.3	-38.9 ± 3.3	

In contrast to the variability observed in δD values of rain and vine water, a progressively enriched trend is noted for mean δD values of soil water across the three sampling depths, becoming consistently more positive (δD enriched) over the growing season, with mean δD values ranging from -60.2 ‰ in June and -38.9 ‰ in September. Generally, the δD values of the soil water from the shallow 10-cm depth interval correspond most closely to the δD of the rain water during the five monthly sampling events, while the δD values of the deeper soil water from the spring sampling months (May and June) are more similar to the δD value of the groundwater or potentially a combination of groundwater and more depleted snowmelt.

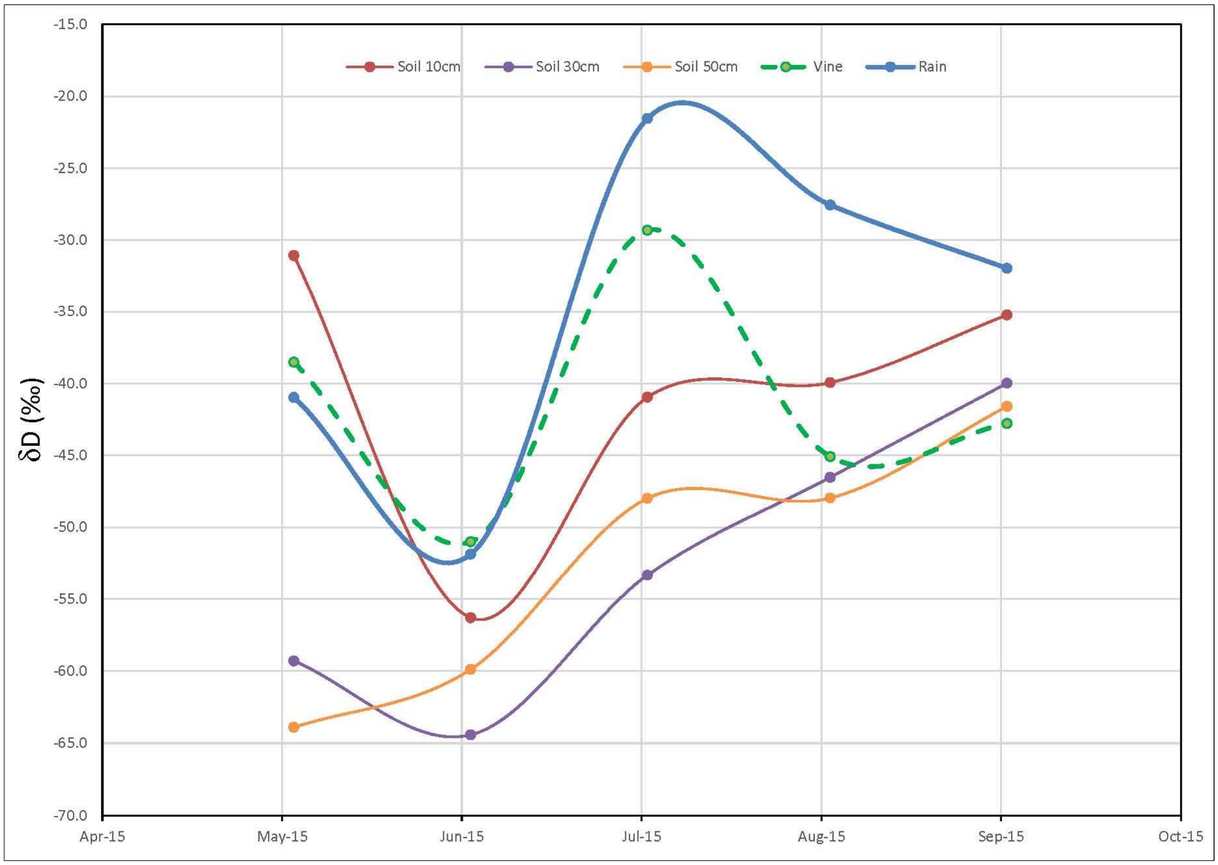


Figure 3-4. Graph of δD values for rain, soil, and vine water over the growing season.

The deeper soil water from the summer and autumn sampling months (July, August, and September) reflect a combination of rain and groundwater, with an increasing proportion of the groundwater component over time. Although, the soil water samples show systematic isotopic changes relative to the monthly rain water samples, with consistently more δD depleted values than the rain, an inconsistency is noted for the soil water samples from 10-cm collected during the May 2015 sampling event, which is significantly δD enriched (-31.1 ‰) relative to the May rain (-41.0 ‰) (Table 3-2, Fig. 3-5).

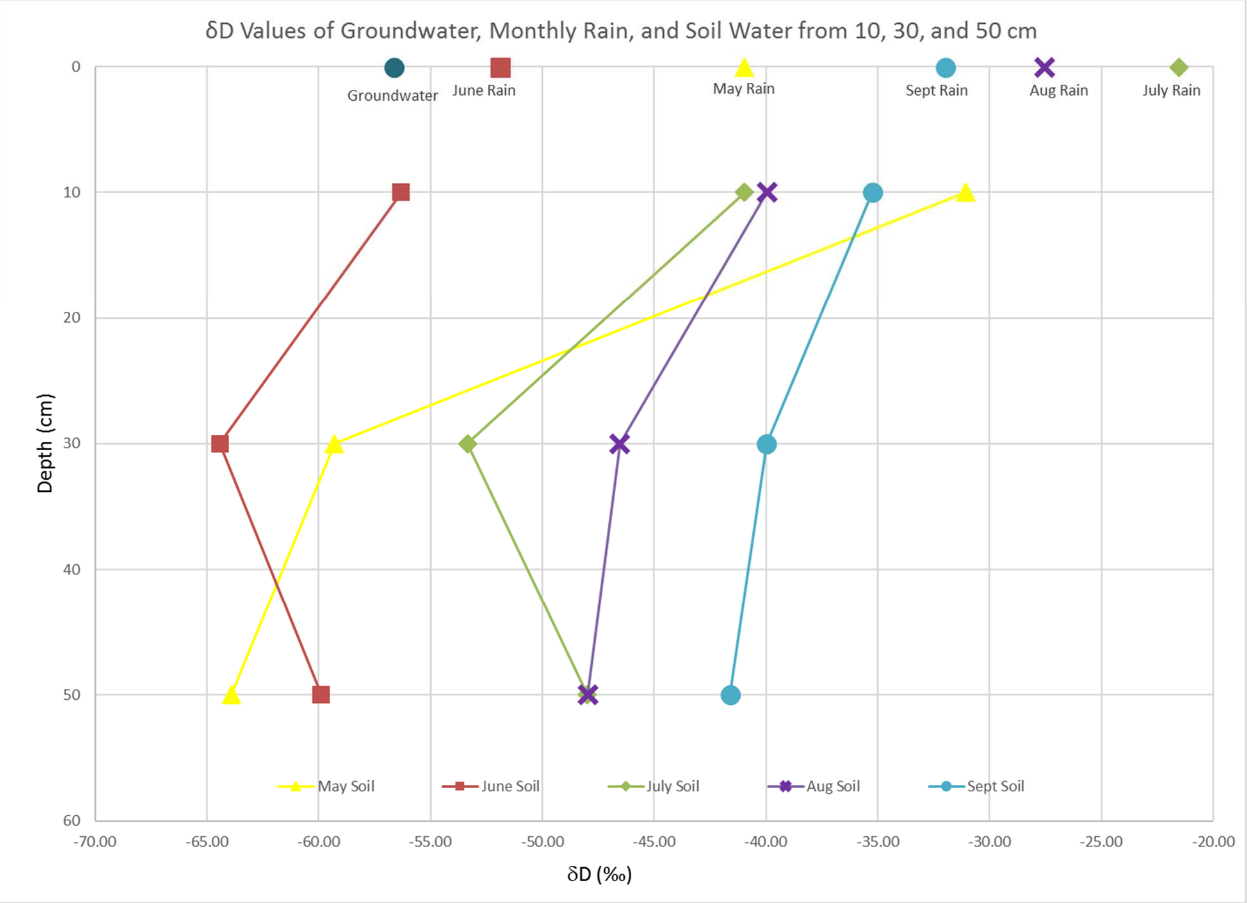


Figure 3-5. Graph showing δD values of soil versus depth along with δD values of groundwater and monthly rain.

3.5 Discussion

During the 2015 growing season, the vines obtained water from different soil depths (Table 3-2, Fig. 3-4). Despite similarity in the range of δD values of vine water and soil water over the growing season, vine water δD values are variable when compared between individual sampling time points, indicating water uptake from various sources and combination of sources. In the spring months (May and June) during the budbreak and flowering/fruit set phenological stages, the δD signature of vine water is similar to that of the corresponding rain water (with δD values within 94% and 98% of the rain δD values, respectively). This indicates that the water source of the vines was primarily rain water during these spring months, which correspond to the highest rain volumes (158 and 99 mm, respectively) of the growing season; consequently, with rain water readily available in the root zone, the vines do not reach deep into the soil profile in search of water and preferentially utilize rain water. During these incipient phenological stages, water uptake by the roots is necessary for plant development via nutrient solubility facilitating nutrient transport from the soil to the vines.

In the summer months of veraison and ripening stages, the δD signature of vine water reflects a combination of rain and shallow soil water from the 10-cm depth in July, while in August the δD signature of vine water reflects the intermediate soil water from the 30-cm depth, indicating that the vine water source is a combination of rain water and groundwater, with nearly equal proportions of each component in early summer, and groundwater as the dominant component in the mixture in late summer. This indicates that as the growing season advances, temperatures increase and rain volumes decrease during the summer months, and the availability of rain water to vines is limited, which prompts the vine roots to search deeper into the soil profile for their water source. These summer months correspond to the lowest rain volumes (42 and 53 mm, respectively) of the growing season, which is optimal, as excess water during these stages can result in berry splitting or dilution of sugars and flavors.

In autumn (September) at fruit maturity/harvest, the δD signature of vine water is more depleted than the rain and soil water from all sampling depths, indicating that the vine obtained its water from even deeper in the soil profile (Fig. 3-4), where the source is a combination of rain water and groundwater, with groundwater as the dominant component in the mixture. This trend further suggests that in the later stages of vine phenological development, increasingly warmer temperatures resulting in increased evapotranspiration, as soil water is lost to the atmosphere via evaporation from the ground surface and from the vines' leaves, along with gradually decreasing and limited precipitation supply during the summer months, stimulate the vines to reach progressively deeper for their water source.

Generally, rain water is consistently more δD enriched than the soil water, which demonstrates a depth dependent trend, with shallow soil water (10-cm) being most δD enriched across the growing season; intermediate soil water (30-cm) being most δD depleted in the spring and early summer months; followed by a transition to most δD depleted deep soil water (50-cm) in the late summer and autumn months. The sources of water acquired by the vines include rain water in spring and combinations of rain and groundwater in the summer and autumn months, with an increasing percentage of groundwater in the mixture over time. These trends indicate that among the soil water components, the spring rain water is likely stored in small pores in areas of high matric potential in the soil and doesn't mix with other water components, having the longest residence time in the soil. This is corroborated by the observed soil textures within the sampled profile, which became consistently coarser with depth; from a zone of high matric potential in the near surface (10 to 20-cm) characterized by silt and clayey silt to lower matric potential zones toward the terminal depth of the soil pit (50-cm) characterized by progressively sandier textures. Accordingly, episodes of rainfall over the growing season would likely be reflected in the shallow soil water (10-cm) isotope data.

Overall, soil water samples show systematic isotopic changes relative to the rain water samples, with the exception of the May 2015 sampling event, when the soil water sample at the 10-cm depth was significantly δD enriched (-31.1 ‰) relative to the May rain (-41.0 ‰). This inconsistency points to the presence of an additional water source with a significantly enriched isotopic signature in the shallow soil water mixture. According to the NOAA Storm Data Report for May 2015, a hail storm occurred on May 3, 2015, in Dane and surrounding counties. The isotopic signature of the hail may have contributed to the isotopic enrichment the 10-cm soil water collected during the May 2015 sampling event via equilibrium fractionation that accompanies chemical reactions and phase changes. Although no apparent physical damage to the vines was observed, hail is an example of a climatic extreme detrimental to agricultural crops. Hail forms during thunderstorms when upward motion of air carries water droplets above the freezing level forming hailstones, and as additional water freezes onto them, the hailstones grow until they become too heavy for the updrafts to support them, dropping to the ground.

Generally, as air masses move across continents and lose water by rainout, they become depleted in the heavy isotope species because the liquid phase is enriched in the heavy isotopes relative to the vapor phase during equilibrium fractionation (Gat 2005; Clark 2015). Similarly, the solid phase is enriched in the heavy isotopes relative to the liquid phase during equilibrium fractionation; thus, during the hail forming phase change (i.e., liquid to solid), the heavier isotopes are preferentially removed from the air mass as liquid water, and then once more in the phase change to solid water. During this process, as water freezes and hail forms, the heavier isotopes (^{18}O and ^{2}H) become enriched in the hail. Additionally, unlike the liquid phases, the solid phases do not participate in isotope exchange with atmospheric moisture, preserving the isotopic signature as originally developed in the cloud (Gat 1996).

The fractionation associated with the equilibrium exchange reaction of the ice-water phase transition can be expressed using the isotope fractionation factor alpha (α), which is equivalent to the ratio of the heavy to light isotope ratio (i.e., $^{2}H/^{1}H$, $^{18}O/^{16}O$) in ice and water. Another relationship using isotope fractionation δ values is given by the equation:

$$\alpha_{\text{ice-liquid}} = (1000 + (\delta D_{\text{ice}}) / (1000 + (\delta D_{\text{liquid}}).$$

Since 1955, several authors have determined theoretical and experimental values for the fractionation factor α of D between ice and water ranging from 1.0171±0.0005 to 1.0211±0.0007 (Weston 1955; Posey and Smith 1957; O'Neil 1958; Craig and Horn 1968; Arnason 1969); Lehmann and Siegenthaler's (1991) published experimental value for the fractionation factor α of D for the ice-water transition is 1.0212±0.0004. To evaluate the premise that hail contributed to the isotopic enrichment the 10-cm soil water collected during the May 2015 sampling event and that the soil water is a mixture of rain water and hail meltwater, an apparent fractionation factor was calculated using the rain and 10-cm soil water isotopic data,

$$\alpha_{\text{ice-liquid}} = (1000 + (-31.0778)) / (1000 + (-40.9746)) = 1.01032.$$

The calculated α value of 1.01032 is lower than the published values for equilibrium fractionation factors, which is consistent with the premise that the 10-cm soil water isotopic composition is a mixture of meltwater from hail and rain, and not simply related to meltwater derived from hailstones, nor solely derived from rainfall. An $\alpha_{\text{ice-liquid}}$ value greater than 1 indicates that the first phase (ice) is more enriched than the second phase (liquid); thus, for an apparent $\alpha_{\text{ice-liquid}}$ calculated value of 1.01032, the δD of hail is +10.32‰ higher than the δD value of hail meltwater at equilibrium. Using the measured δD values of rain and soil water from the 10-cm depth, a δD value of -9.90 ‰ was calculated for the hail meltwater, which indicates that the δD value of hail is 0.42 ‰. A binary mixing model was utilized to calculate the relative proportions of each component (rain and hail meltwater) of the soil water mixture isotopic composition in the 10-cm soil depth, indicating a 76% contribution from rain and a 24% contribution from hail meltwater in the soil water mixture. Thus, only water with an isotopic composition of -9.90 ‰ would be able to shift the δD value of the soil water by this value, and given the hail storm event that occurred in May 2015, hail is the most likely component in the soil water.

Over the 2015 growing season, the grapevines obtained water from various sources and combination of sources, reaching progressively deeper for their water source as the growing season advanced. Specifically, in spring during budbreak and flowering/fruit set, the vines used primarily rain water, in early summer at the beginning of veraison/ripening, the vines used a combination of rain and shallow soil water (10-cm), in late summer at the end of veraison/ripening, the vines used intermediate soil water (30-cm depth), and in autumn at fruit maturity/harvest, the vines used water from even deeper (>50-cm) in the soil profile.

Vine water management is an important consideration for vineyards, and vine water use can be manipulated to control vegetative and reproductive growth and focus on enhanced fruit quality. Typically, over a growing season, vineyards planted in silt and clay rich soils require 250 to 750 mm of rainfall, whereas vineyards planted in sandy soils require 900 to 1200 mm of rainfall (or its equivalent in irrigation); and during grapevine development, water consumption is highest from fruit set to harvest and from fruit set to veraison, with 35% and 36%, respectively, and lowest from budbreak to flowering and from flowering to fruit set, with 9% and 6% respectively, of the season's total (Goldammer 2015). However, as vines utilize water for different physiological processes, water use can be controlled during certain phenological stages to improve grape quality. Specifically, although water requirements are low between budbreak and flowering/fruit set, the vines undergo critical developmental changes that are sensitive to water levels. Between flowering/fruit set and veraison water levels can be manipulated as vine and grape development progresses and excessive canopy growth can sometimes result in shading of the developing grape clusters; and after veraison, grape development is unaffected by water levels, and excess water can cause dilution of flavors or sugars (Moyer et al. 2013). Deficit irrigation is utilized to control grape quality by limiting water after fruit set to promote smaller grape berries and a greater skin to pulp ratio, and after veraison to increase sugar and phenolic concentrations; however, vineyard irrigation strategies are highly variable, as the effects of deficit irrigation on grape quality depend on climatic variables (i.e., amount of rainfall, evaporative demand), cultivar, soil types and textures, cover crops, rooting zones, and grapevine phenological stages (Winkler et al. 1974; Gladstones 1992; Deloire et al. 2004; Prichard et al. 2004; Cohen and Kennedy 2010). The results of this study show that in an udic/mesic climate, a vineyard planted with Marechal Foch grapevines in silt loam soils has a relatively shallow effective root zone depth, and in drought conditions, irrigation would be focused in the surficial upper 10-cm of soil in spring and the upper 30-cm of soil in summer, and progressively deeper into the soil profile into the late summer and autumn months, as evidenced by the preferential vine water uptake over the growing season. In arid, semi-arid, and Mediterranean climates, where grape growing areas have an increased risk of water deficit, such as in ustic, aridic, and xeric moisture regimes in which the available water capacity is limited, irrigation strategies will be affected by increased evapotranspiration, greater effective root zone depths, as well as soil texture variations, which affect soil hydrology and rooting depths via factors such as limited infiltration in the dry, coarse-textured, shallow soils of aridic climates, rapid infiltration in the freely drained soils with typical calcic horizons of ustic climates, and root restricting horizons in the intensely leached soils of xeric climates that often exhibit silica cemented duripans.

3.6 Conclusions

The observed trends of vine water uptake from the soil over the growing season can be utilized in developing irrigation strategies to maximize efficiency of vine water use as well as water conservation. The findings of this study suggest that the water acquired by vines during grape development originated from various sources and combination of sources. The isotopic composition of vine water demonstrates that the functional rooting depth for water acquisition by the vines is highly variable during the different phenological stages of the vines over the 2015 growing season. The vine water δD values indicate rain is the main water source in the spring months during budbreak and flowering/fruit set, and as the growing season advances, progressively deeper water sources within the soil profile are sought by the vines as ripening ensues and fruit maturity is achieved. Over the summer months during the veraison/ripening stages, the δD signature of vine water reflects a combination of rain and shallow soil water in July, and intermediate soil water in August. In September at the fruit maturation/harvest stage, the most depleted vine water δD value points to a deeper source of water for the vines beyond the deepest soil depth interval sampled (50-cm).

The seasonal vine water use trend supports a variable functional rooting depth for water acquisition by the vines during the different phenological stages, with the shallow roots utilizing rain water as a preferential source during the spring months and a root system developed to reach for water progressively deeper as the growing season advances as greater storage of water is found in deeper soil in the autumn months. The preferential vine water uptake performance over the growing season indicates that in drought conditions, the top 10-cm and 30-cm of soil would require irrigation in spring and summer, respectively, followed by progressively deeper intervals in the soil profile requiring to be wetted over the growing season.

Future research focused on sampling deeper into the soil profile (beyond the 50-cm depth interval sampled) would provide more precise insights on functional rooting depth for these vines. The variation in water availability and its effects on the phenological stages of the vines are important in determining a grape growing region’s potential for production of quality grapes and wines within the limits of its climatic regime. Thus, in a changing climate affecting precipitation patterns and water availability, consistent production of quality grapes is challenged, as vine phenology and grape ripening are highly dependent on the vine water status, and maintaining an optimal water balance for grapevines is imperative.

4.0 Chapter III: Effects of Vineyard Soil Properties on Phenolic Compounds in Syrah Grapes from the Walla Walla Valley AVA, Washington

4.1 Abstract

The phenolic compounds that develop in grapes over the growing season are sensitive markers of differences between vineyards and associated variations in grape and wine quality, and vineyard soils affect the phenolic composition of grapes via their control on the uptake of vine nutrients and water. This study is a regional scale reconnaissance survey that examines the relationships between soil characteristics and the phenolic compound concentrations of Syrah grapes collected during the 2014 harvest from 11 vineyards planted across four different terroirs in the Walla Walla Valley American Viticultural Area (AVA) in an assessment of the useful application of the terroir construct at this scale. Soil properties, including drainage, depth, available water-holding capacity (AWC), texture, bulk and plant available chemistry, and mineralogy in conjunction with concentrations of grape phenolic compounds, including tannin, polymeric and total anthocyanins, quercetin glycosides, and catechin are assessed to explore the link between vineyard soil and grape chemistry across the Walla Walla Valley AVA's four terroirs. No significant differences were noted at this regional scale, and the relationships between soil characteristics and phenolic compounds, generally indicate that although the four terroirs have distinctly different soil properties, the grape phenolic concentrations reveal only subtle variations. Overall, the minor differences discerned indicate that higher concentrations of phenolics may be associated with coarser-textured, well to somewhat excessively drained soils of limited depth and lower AWC, and within the Walla Walla Valley AVA, these characteristics are most common in vineyards that feature soils exhibiting the influence of basalt from weathered basalt bedrock or basalt-derived alluvium. The study demonstrates that large scale

characterizations at the AVA level can be limited by the variability of soil properties at the vineyard level.

4.2 Introduction

Vineyard terroir has been viewed as a critical component of wine quality since the 12th century, when the Cistercian monks of Burgundy realized that the physical environment in which grapes are grown has a major influence on the character and quality of grapes and resulting wine. The unique characteristics of a vineyard, including factors such as the geology, soil, landscape, and climate contribute collectively to the quality of the grapes and sensory attributes of the wine produced in that vineyard (Wilson 1998; Haynes 1999; White et al. 2009). Grape phenolic compounds, which are secondary metabolites that develop in the skin and seeds of grapes during ripening are one measure of grape and wine quality. The transformations that occur in the skin and seed phenolics during grape berry maturation have a fundamental influence on wine quality because the phenolic composition of grapes ultimately influences the balance, taste, color, consistency, and aroma of wines. The biosynthesis of phenolic compounds proceeds from the essential amino acid, phenylalanine, following the phenylpropanoid biosynthetic pathway, and the functional roles of phenolics include pigmentation, attraction of pollinator and seed dispersal organisms, UV-light protection, and pathogen protection (Cortell et al. 2007; Imre et al. 2012; Teixeira et al. 2013). Phenolics are also known to provide various human health benefits due to their antioxidant and anti-inflammatory properties (Cortell and Kennedy 2006; Koundouras et al. 2006; Di Majo et al. 2008; Kennedy 2008; Teixeira et al. 2013; Anesi et al. 2015). Grape phenolic compounds are classified into non-flavonoids and flavonoids. The two most well-known non-flavonoid classes are the hydroxycinnamates (e.g., caftaric acid) and stilbenes (e.g., resveratrol); and the three main classes of flavonoids include the anthocyanins, flavonols, and flavan-3-ols. The principal flavonols in grapes are present as glycosides of quercetin, kaempferol, myricetin, and isorhamnetin; and the flavan-3-ols include monomeric (catechins) and polymeric (proanthocyanidins or condensed tannins) structures (Kennedy et al. 2002; Cortell et al. 2005; Cortell and Kennedy 2006; Teixeira et al. 2013).

The phenolic synthesis and accumulation in grapes and therefore grape berry composition, including phenolic content, are influenced by terroir factors. The processes that control the synthesis and accumulation of grape phenolic compounds and the effects of the vineyard environment and viticultural practices on these processes have been the subjects of considerable research. These studies generally conducted at the vineyard level have concluded that the most influential factors in the synthesis of grape phenolic compounds are solar radiation and sunlight exposure, temperature, cultivated variety, as well as environment conditions that affect absorption of water and nutrients (Bergqvist et al. 2001; Cortell and Kennedy 2006; Gómez-Míguez et al. 2007; Koundouras et al. 2006; Cohen and Kennedy 2010; Ubalde et al. 2010; Van Leeuwen 2010; Teixeira et al. 2013). In particular, variability of grape quality at the vineyard level has been directly related to soil heterogeneity, indicating that soil properties exert a substantial control on the availability of water and nutrients (Bramley et al. 2011; Scarlett et al. 2014).

Although some phenolic compounds in wine arise from microbial activity and oak used in the vinification process, most are derived from grapes and their concentrations are controlled by grape variety, vineyard physical environment, vineyard management, and vinification techniques (Kennedy 2008). Koundouras et al. (2006) compared the phenolic composition of grapes and associated wines produced using the same vinification techniques over two vintages, and found that grapes with high concentrations of phenolic compounds produce wines with high phenolic content. As wine quality is driven by the phenolic content of grapes, the concentrations of phenolics that can be extracted into wines are dependent on the concentrations of phenolics available in the grapes (Cortell et al. 2005); and maximizing the grape phenolic content promotes enhanced organoleptic properties and overall quality of wines. Thus, harvest and wine making decisions are governed by the synthesis and accumulation of phenolics in grapes, which in turn depend on the availability of water and nutrients from the vineyard soil.

4.2.1 The Role of Soil in the Development of Grape Phenolics

The transfer of water through the grapevine, by absorption through the roots and evapotranspiration through leaves, influences grape berry quality. In a study investigating the concurrent effects of climate, soil, and cultivated variety, Van Leeuwen et al. (2004) found that the grape berry composition depends significantly on the soil, which in turn affects the vine water status through its texture, water holding capacity, and depth. Generally, mild water stress results in lower vine vigor through reduced foliage production and lower fruit yield through decreased berry number and size, and is associated with higher grape phenolic content (Smart, 2014). As soil is the foundation of the grapevine, supplying water and nutrients required for plant growth, its properties strongly influence vine vigor, grape berry yield, and the attendant grape phenolic composition.

4.2.2 Soil Properties Influencing Phenolics

Studies largely conducted at the vineyard scale determined that soil properties, including parent materials, fertility, texture, rooting depth, and water holding capacity are important components of terroir that govern water stress and associated vine vigor and grape berry size via their influence on nutrient and water absorption, ultimately influencing the development of phenolics in grapes and wines.

Parent materials influence grape phenolic content by contributing different mineral compositions, textures, and degrees of weathering to the soil; thus affecting the available nutrients and water holding capacity of the soil. Shange and Conradie (2012) evaluated grapevine function relative to different soil parent materials and found that soils originating from shale have significantly more fine sand than granite-derived soils, which have a higher proportion of gravel and coarse sand, highlighting the textural differences resulting from diverse parent materials. Shale-derived soils were found to have higher water holding capacity, higher total potassium content, as well as higher nitrogen content in the grape juice. Morlat and Bodin (2006) studied the composition and quality of Chenin Blanc and Cabernet Franc grape berries based on soil depth, clay content, and degree of weathering of the parent rock, and found that grapes cultivated in weakly-weathered rock (associated with lower water holding capacity) were significantly smaller in size, had higher sugar and anthocyanin content, lower titratable acidity, and a higher Total Phenolic Index than grapes cultivated in strongly-weathered rock, which had higher water holding capacity.

Soil fertility influences the vigor and productivity of grapevines and therefore the quality of the resulting wine. Vineyard soils have low agricultural requirements, and generally, lower soil fertility has been associated with higher grape quality. Soil fertility is typically evaluated based on the concentrations of soil organic matter, carbon, nitrogen, phosphorus, and potassium. Although these elements are essential in the development of the vines, high soil fertility can lead to higher vigor and yields, reducing grape quality. In a study by de Andrés-de Prado et al. (2007), Grenache planted in more fertile soils (higher organic matter, organic carbon, and potassium composition), with higher water-holding capacity produced wines with considerably lower total phenolic content and lower color intensity. Chone et al. (2001) investigated vine nitrogen status on four vineyard blocks planted with Cabernet Sauvignon in the Medoc area of Bordeaux, by conducting weekly estimates of vine nitrogen uptake from veraison through harvest, and found that reduced vine vigor, smallest grape berries, and highest phenolic content for must and wine were produced under nitrogen deficiency.

Soil texture, which is determined through grain size analysis and expressed as percentages of clay, silt, sand, and/or gravel, is used to classify soils and estimate soil water holding capacity, which is lower for soils with coarser textures. Generally, coarse textured soils with lower water holding capacity have been associated with higher concentrations of grape and wine phenolics (van Leeuwen et al. 2004, de Andrés-de Prado et al. 2007, Ubalde et al. 2010, Imre et al. 2012). De Andrés-de Prado et al. (2007) assessed the effects of soil on the quality of wine at two vineyards planted with Grenache over two vintages and determined that loam-clayey soils, with finer texture/less coarse fraction and higher fertility and water holding capacity, yielded wines with lower color intensity and lower total phenolic composition. Ubalde et al. (2010) found that coarser-textured soils abundant in sand and gravel, somewhat excessively drained, and with a low water holding capacity inhibited vine root development and produced smaller grape berries with higher sugar content and wines with higher color intensity, total polyphenols, tannins, and anthocyanins. Similarly, a study by Imre et al. (2012) comparing three vineyards with varying proportions of gravel in their soils determined that under the same irrigation stress regime, the soils with the finer texture and lower proportion of gravel produced wines with lower color intensity, fewer total red pigments and monomeric pigments than the soils with coarser texture and a higher proportion of gravel. Van Leeuwen et al. (2004) evaluated vine development and grape berry composition in soils with different textures, including a gravelly soil with low water holding capacity associated with high water deficit potential, a soil with a heavy clay subsoil associated with moderate water stress potential, and a sandy soil with no water stress potential due to vine roots within reach of the water table. Although a sandy soil texture can provide good drainage, the presence of a shallow water table can preclude the vines from undergoing beneficial mild water deficit. The authors determined that the gravelly and clayey soils produced grapes with higher anthocyanin concentrations than the sandy soils. Furthermore, grape berry weight and yield were highest for the sandy soils as a result of the unrestricted water availability from the shallow water table in the sandy soils.

Soil depth is generally evaluated in terms of vine rooting depth. Limiting the soil depth reduces soil water holding capacity, which in turn can increase phenolic content and ultimately enhance wine quality. Overall, on most substrates, shallow soils enhance terroir expression. Generally, a negative correlation has been found between grape or wine phenolics and effective soil depth, which is the depth from the soil surface to the hardpan or restrictive layer (Choné et al. 2001, Cortell et al. 2005, Koundouras et al. 2006). Choné et al. (2001) studied four vineyard blocks with different soil types in the Medoc area of Bordeaux, and, in spite of a rainy vintage, observed mild water deficits associated with a shallow root depth gravelly soil, as well as slight negative correlations for finer textured soils (between root zone depths of 0.7, 1.0, 1.5, and 2 meters) and concentrations of anthocyanins and tannin in must and wine. Cortell et al. (2005) evaluated the spatial variations of vine growth parameters in a Pinot Noir vineyard as a function of grape berry and wine phenolic composition using precision viticulture techniques, and found a strong correlation between soil depth, water-holding capacity, and vine vigor. Specifically, the study showed that areas of shallow soil depth, lower soil water-holding capacity, and lower vine vigor corresponded to areas of higher skin proanthocyanidin in grape berries at harvest. Shallow soil depth and associated low water-holding capacity resulted in reduced vine vigor and canopy structure, increasing sunlight exposure and temperature, which enhanced the accumulation and synthesis of grape phenolic compounds and the resulting wine quality. Another study by Koundouras et al. (2006) in southern Greece at three non-irrigated vineyards over two vintages found significantly lower yield and vine vigor in the vineyard plot where vine water uptake was limited due to shallow soil depth and vine rooting. Overall, this vineyard plot yielded grape berries with the highest anthocyanin content and total phenolics index through ripening, had the highest must sugar content, and produced wines with consistently higher total phenolics than the other two vineyards with deeper soils.

This study provides an appraisal of the useful application of the terroir concept at the regional scale via a reconnaissance survey that evaluates the relationships between soil characteristics (parent material, depth, texture, chemistry, mineralogy, and water holding capacity) and the classes and concentrations of phenolic compounds (catechin, tannin, quercetin glycosides, polymeric anthocyanins, total anthocyanins, as well as soluble solids) developed in Syrah grapes at harvest from 11 vineyards located in the Walla Walla Valley AVA, where soils can be categorized into four distinctive terroirs.

4.3 Geologic Setting and Overview of Walla Walla Valley AVA

The study area is located in the Walla Walla Valley American Viticultural Area (AVA), which encompasses approximately 1,300 km^2. Straddling the border of southeastern Washington and northeastern Oregon, the Walla Walla Valley AVA includes within its boundaries the newly approved Rocks District of Milton–Freewater AVA (The Rocks AVA), which is located entirely in Oregon (Fig. 1). A detailed study of the Walla Walla Valley AVA highlighting the variability of its terroirs has been carried out by Meinert and Busacca (2000).

The terroir of the Walla Walla Valley AVA is influenced by the rain shadow effect of the Cascade Mountains and a warm, semi-arid climate. Elevations across the Walla Walla Valley AVA range from 122 meters (400 feet) to 610 meters (2000 feet) and annual rainfall varies from 178 millimeters (mm) (7 inches) at the western end of the AVA to 559 mm (22 inches) along the foothills of the Blue Mountains to the east. With an average growing season ranging from April 1st to October 31st, a total of 3,444 Growing Degree Days (GDD, base 50°F) were recorded in 2015 for the Walla Walla Valley AVA (based on data from the Walla Walla airport weather station). Based on a long-term (24-year) climatological temperature average, the Walla Walla Valley AVA fits in the middle range of the Winkler Region II (2500-3000 GDD) with an average of 2835 GDD (50°F).

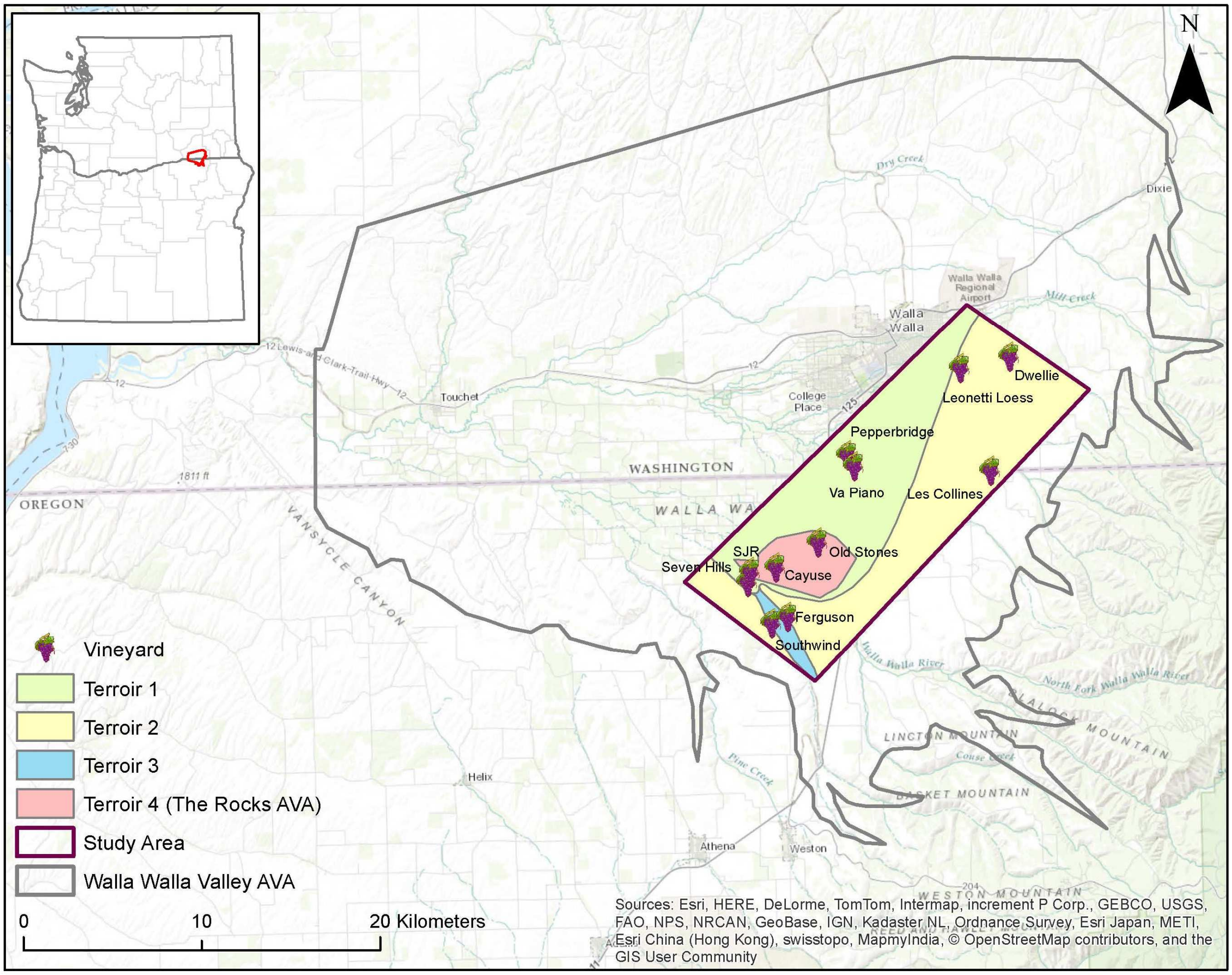
The tumultuous geological history of the Walla Walla Valley comprises extensive basaltic lava eruptions, vast glacial outburst floods, and wind-blown loess deposits of various thicknesses. The entire Walla Walla River basin is underlain by massive flood basalts known as the Columbia River Basalt Group mostly erupted during the Miocene (17-15 Ma), covering an area of approximately 163,700 km^2 and having an estimated volume of 174,300 km^3 (Carson and Pogue 1996; Meinert and Bussaca 2000). Recurring Pleistocene glacial outburst flooding events (Missoula floods) that occurred between 15,300 and 12,700 years ago deposited sediment at elevations below 366 meters (1200 feet) throughout the area (Meinert and Bussaca 2000; Pogue 2009). The glacial flood events deposited a sequence of graded beds, known as the Touchet beds. Subsequent fluvial and aeolian processes have altered the deposits of glacial flood sediments in many parts of the valley. The silt fraction of the flood sediment deposits generated by each Missoula flood was eroded by the prevailing southwesterly winds, which carried the silt to the northeast, covering the landscape with deposits of windblown loess of varying thicknesses.

Most vineyards in the Columbia Basin are planted on soils derived from deposits of loess and glacial flood sediments (Pogue 2009). Across the valley floor (below 366 meters or 1200 feet) cobblestone river gravels, flood sediments, and loess deposits mantle the landscape and overlie the basalt bedrock, and in the foothills (above 366 meters or 1,200 feet) the bedrock is overlain by loess.

According to the Washington State Wine Commission, the Walla Walla Valley AVA has experienced tremendous expansion in the last fifteen years, having the largest number of wineries in Washington, with over 100 wineries and over 800 hectares of vineyards. The leading grape variety planted is Cabernet Sauvignon, with Merlot, Chardonnay, and Syrah as the other predominant varieties. Gewurztraminer, Cabernet Franc, Sangiovese, Grenache, Malbec, Petit Verdot, Tempranillo, Pinot Gris, Riesling, Sauvignon Blanc, Semillion, and Viognier are also cultivated.

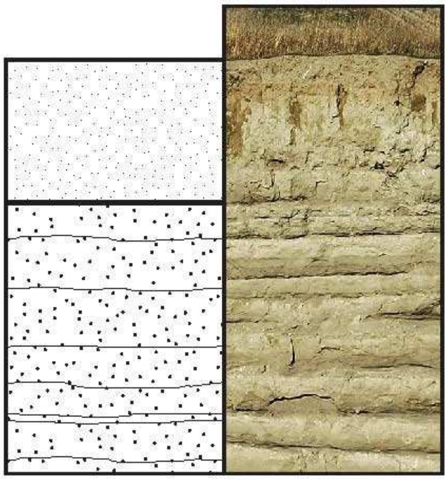
4.3.1 Study Area

The study area encompasses approximately 194 km^2 in the southeast quadrant of the Walla Walla Valley AVA, with 57% of the study area in Washington and 43% of the study area in Oregon (including The Rocks AVA). The study was focused on 11 vineyards planted with Syrah grapes across different terroirs (Fig. 4-1). Four distinctive terroirs are defined within the study area (Fig. 4-2). Terroir 1 is restricted to elevations below 366 meters (1200 feet) and consists of 0.6 to 1.2 meters (2 to 4 feet) of loess over Missoula flood sediments. In Terroir 1, represented by Pepperbridge, Seven Hills, and VaPiano vineyards, grapevine roots typically penetrate loess into underlying Missoula flood deposits. Terroir 2 is restricted to elevations above 366 meters (1200 feet), consists of thick loess ($\geq$3 meters) overlying basalt bedrock, and is represented by Les Collines, Leonetti Loess, and Dwelley vineyards. Terroir 3 is situated on steeper slopes in the foothills and canyons of the Blue Mountains and consists of thin loess (<1 meter) over weathered basalt bedrock. In Terroir 3, represented by Ferguson and South Wind vineyards, grapevine roots penetrate the thin loess and encounter basalt bedrock. Terroir 4 lies within the alluvial fans of the Walla Walla River, and consists of basalt cobblestone river gravels in a sand and silt matrix. This terroir is enclosed by the boundaries of The Rocks AVA, and is represented by Cayuse, SJR, and Old Stones vineyards.

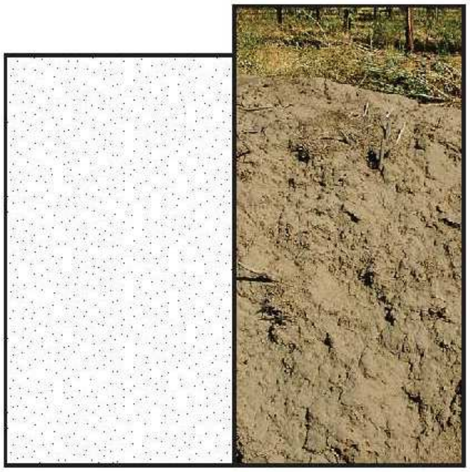


Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

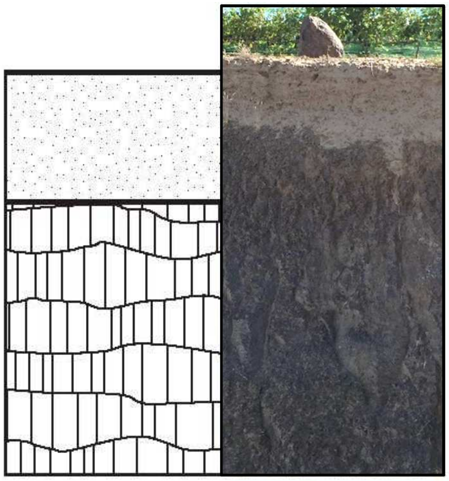
Figure 4-1. Map showing the study area in the southeast quadrant of the Walla Walla Valley AVA, and the study vineyards planted with Syrah grapes across different terroirs



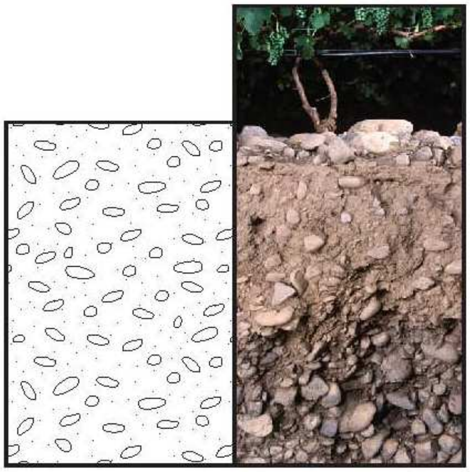
Terroir 1: Loess over Missoula Flood sediments (Pepperbridge, Seven Hills, Va Piano)



Terroir 2: Thick loess (>3m) over basalt bedrock (Les Collines, Leonetti Loess, Dwelley)



Terroir 3: Thin loess (<1 m) over weathered basalt bedrock (Ferguson, South Wind)



Terroir 4: Basalt cobblestone river gravels in a sand and silt matrix (Cayuse, SJR, Old Stones)

Figure 4-2. Four distinctive soil terroir categories in the Walla Walla Valley AVA

4.4 Materials and Methods

4.4.1 Soil Assessment

To minimize flattening of microscale variation, collocated soil and grape samples were collected from the study vineyards in each of the four terroirs in September 2014. Soil profiles were examined to maximum depths of 50 centimeters below ground surface, across horizons A, E, and B, and soil samples were collected from the bottom of each pit. Soil texture was determined through grain size analysis via a Malvern Mastersizer 2000E laser diffraction particle-size analyzer.

Total major and select minor and trace element compositions were determined on the fine fraction of the vineyard soil samples, which were powdered and fused for x-ray fluorescence (XRF) analysis. Loss on ignition (LOI) was determined by heating 1 gram of sample for 10 minutes in a muffle furnace at 1050 °C and calculating the mass difference. The major element and select minor and trace element compositions were obtained from glass disks fused at 1050°C in a Claisse M4 fluxer and analyzed using a Bruker S4 Pioneer XRF in the Department of Geosciences, at University of Wisconsin – Milwaukee (UWM). Plant-available soil chemistry analysis was conducted by the University of Wisconsin Soil Testing Laboratory in Madison, Wisconsin, and includes concentrations of phosphorus, potassium, calcium, magnesium, sulfur, zinc, manganese, and boron, as well as pH, cation exchange capacity (CEC), and organic matter (OM).

Soil mineralogy was determined non-quantitatively on a portion of each powdered sample by x-ray diffraction (XRD) analysis. Random mounts were prepared by gently smoothing the surface of a fine powder poured into a flat surface onto a cavity mount sample holder. Samples were analyzed in the Department of Geosciences at the University of Wisconsin–Milwaukee using a Bruker D8 Focus XRD system (Cu Ka radiation, 1 s per 0.02° 2θ, 2°–60° range, scintillation detector). Minerals were identified by searching the International Centre for Diffraction Data (ICDD) PDF-2 database database of standard X-ray powder diffraction patterns for a match with the pattern of the unknown, using Bruker's EVA software for peak matching.

4.4.2 Grape Phenolic Panel

Grape samples were collected from the east side of the row at each study vineyard during the September 2014 harvest. Two to three grape clusters were collected from each vineyard, and approximately 250 grams of loose berries were weighed, placed in sealable plastic bags, and frozen prior to being submitted to the laboratory for analysis. Grape phenolic profile analyses were performed by ETS Laboratory in Saint Helena, California by high performance liquid chromatography on a one-day turnaround time. The grape phenolic panel analysis entailed a wine-like extraction of whole grape berries and an analysis of major grape phenolic compounds associated with wine color and tannin development, including catechin, tannin, quercetin glycosides, polymeric anthocyanins, total anthocyanins, as well as degrees Brix (°Brix), which provide estimated concentrations of the dissolved sugar in the resulting extract.

4.4.3 Data and Maps

Vineyard-specific data collected during the September 2014 harvest, as well as data from the United States Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS), Web Soil Survey (WSS) (http://websoilsurvey.nrcs.usda.gov/) were incorporated in this study. Data were plotted using the geographic information system software program Esri ArcGIS Desktop to geospatially characterize the study area vineyards. WSS soil properties were assessed utilizing the USDA NRCS Soil Data Viewer tool built as an extension to ArcMap, which facilitates spatial mapping of soil properties from the WSS attribute database. The maps were generated using the Washington State Plane South Coordinates FIPS 4602 (meters), in the

North American Data system of 1983 (NAD 1983); and ordinary kriging, which allows statistical interpolation of spatial data, generating predictions about the spatial extent of the evaluated variable.

4.5 Results and Discussion

4.5.1 Study Area Soils

The spatial distribution of the WSS soil properties, including parent material, surface texture, soil depth, drainage class, available water holding capacity (AWC), and frost action are depicted on Figures 4-3a through 4-3f. The vineyard soils across the study area developed from various glacially-derived parent materials, including loess, silty loess over calcareous lacustrine, and glacio-fluvial deposits (Terroir 1), loess deposits (Terroir 2), loess mixed with colluvium from basalt deposits (Terroir 3) and mixed, very gravelly alluvium deposits (Terroir 4) (Fig. 4-3a). The surface textures of the vineyard soils consist of silt loam across Terroirs 1 and 2, very stony loam in Terroir 3, and very cobbly loam in Terroir 4 (Fig. 4-3b). The soil depths range from 46 to 201 cm, with the best vine conditions represented by the shallower soil of vineyards located in Terroir 3 (Fig. 4-3c), and the soil drainage classes indicate overall good conditions for the vines in the study area, with well drained soils across Terroirs 1, 2, and 3, and somewhat excessively drained soils in Terroir 4 (Fig. 4-3d). The soil AWC values, ranging from 0.1 to 0.2 cm H_2O per cm soil, are lower in Terroirs 3 and 4 (Fig. 4-3e); and the soil frost action is low to moderate for Terroirs 3 and 4 and high for Terroirs 1 and 2 (Fig. 4-3f). The pre-agricultural vegetation in southeast Washington consisted of native grasslands, ranging from sagebrush-steppe, to meadow steppe, to coniferous forest distributed according to the precipitation gradient across the area, and consisting of xerophytic and mesophitic shrubs, perennial grasses, conifers, and various annual and perennial grasses and forbs (Meinert and Busacca 2000).

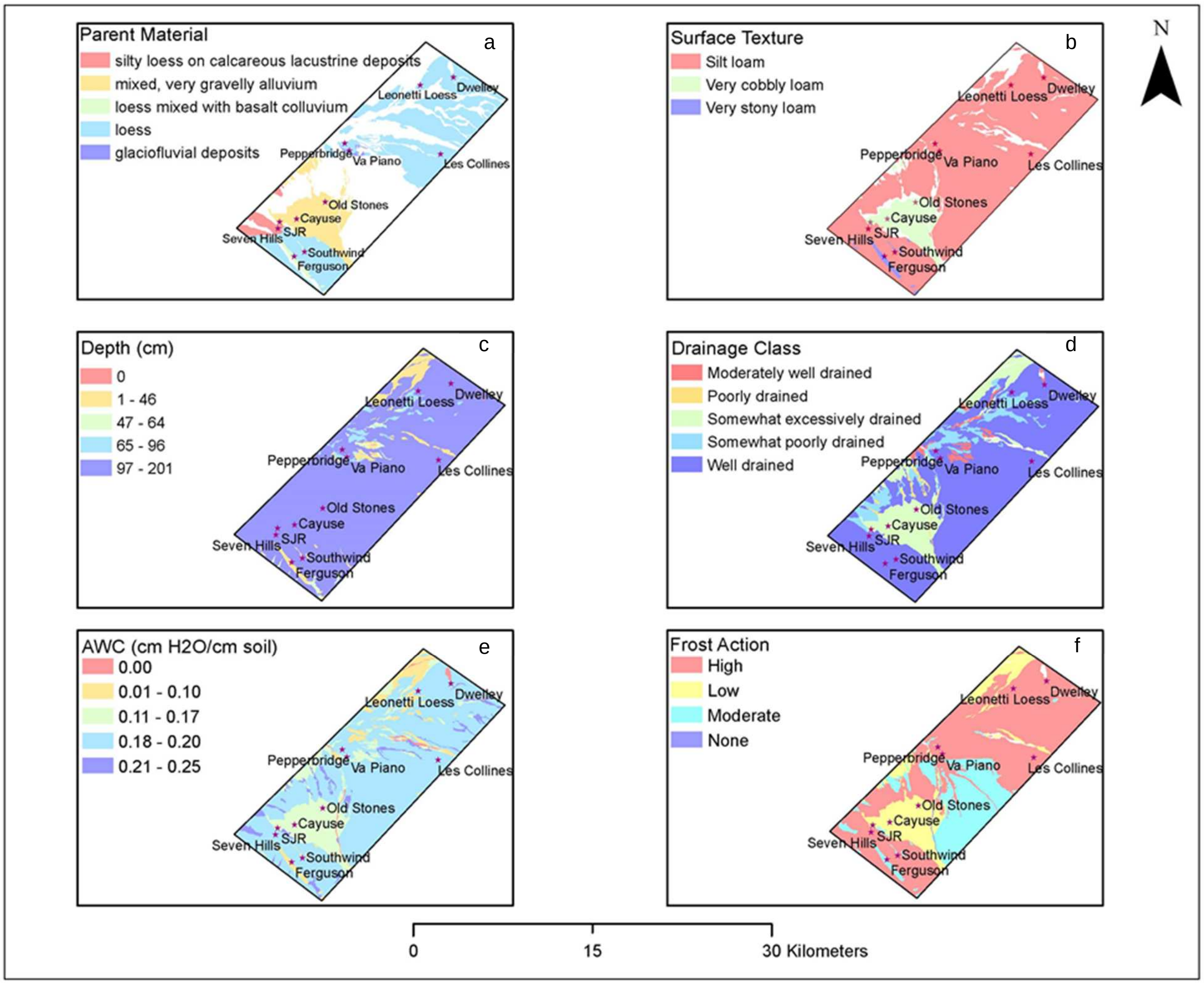


Figure 4-3a-f. Map depicting the spatial distribution of soil properties, including parent material, surface texture, soil depth, drainage class, available water holding capacity, and frost action Source: http://websoilsurvey.nrcs.usda.gov.

Based on the USDA taxonomic classification, the soils across the study area are Mollisols, which is a soil order characterized by a deep, high organic matter, nutrient-enriched surface horizon (mollic epipedon) resulting from the long-term addition of organic materials derived from plant roots, and typically have soft, granular, soil structure. Mollic epipedons typically form where the natural vegetation produces more below-ground biomass than above-ground biomass, such as grasslands in temperate climates (Buol et al. 2003). The transition to vineyards from native grasslands likely changed the organic matter cycling in these soils, as biomass production shifted from being predominantly in the subsurface grass roots to above-ground biomass production in leaves and fruit, and this transition is evidenced by the general absence of high organic matter mollic epipedons in the sampled vineyard soils across the study area. Based on a water budget analysis using the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center (NCDC) climate normals and the USDA Soil Series descriptions (textures and profile thicknesses) to determine the water status of soils over growing seasons under normal year conditions, the soils are prone to intense leaching. This type of soil hydrology creates a drought-sensitive environment, with the soils generally experiencing a period of utilization in the month of June, followed by a deficit during the months of July through September, and a recharge period during October through December. The water deficit allows for controlled irrigation, which in turn controls vine vigor.

The sampled vineyard soils are mapped as Terrace Escarpments, Ellisforde, Walla Walla, Lickskillet, and Freewater Series, which are characterized by well drained to overly drained soils, although soil series maps are notably coarse in resolution and dependent upon the accuracy of model-generated predictions of soil properties from landforms. The Terrace Escarpments consist of very steep or severely eroded banks or escarpments, and are represented by Terroir 1 vineyard Va Piano. The soils of the Ellisforde series are generally found on terraces and consist of very deep soils developed in loess overlain by lacustrine sediments, and are represented by Terroir 1 vineyard Seven Hills. The Walla Walla series soils are generally found on hills, consisting of deep and very deep soils developed in loess, and are characterized by vineyards of Terroir 2 and Terroir 1 vineyard Pepperbridge. The Lickskillet series soils, represented by the vineyards of Terroir 3, are found on plateaus and uplands and are shallow soils developed in stony colluvium, consisting of weathered fragments of basalt and rhyolite mixed with loess. The soils of the Freewater series, characterized by the vineyards Terroir 4, are deep soils developed on high stream terraces in gravelly alluvium that is combined with loess in the upper portion. These diverse soils have different dominant processes that can impart distinct controls on grape quality as a result of texture-induced differences in water holding capacity, exchangeable cations, and nutrient status.

4.5.2 Vineyard Soil Texture, Mineralogy, and Chemistry

4.5.2.1 Soil Texture

Based on the grain size analysis, silt sized grains dominate the textures of the soil samples, with a silt content ranging from 60% to 81%, sand content ranging from 10% to 35%, and clay content ranging from 6% to 10%. (Table 4-1). The soils plot in the silt loam (Terroirs 1, 3, and 4) and silt (Terroir 2) fields of the USDA soil texture triangle (Fig. 4-4), and these textures are in general agreement with the USDA taxonomic classification for these soils.

Among the four terroirs, the vineyard soil samples containing the highest average clay content (9%) were collected from Terroir 3, where soils developed from loess mixed with colluvium from basalt, and correspond to the highest mean elevations. The vineyard soil samples containing the highest average sand content (22%) were collected from Terroir 4, where soils developed from mixed, very gravelly alluvium.

4.5.2.2 Soil Mineralogy and Chemistry

The XRD analysis indicates a primarily uniform soil mineralogy dominated by quartz, plagioclase (albite/anorthite/laboradorite), and/or orthoclase (microcline/sanidine), with minor muscovite, biotite, amphibole, apatite, and clay minerals (vermiculite, montmorillonite) (Table 4-2). Although overall the mineralogy of the vineyard soils is indicative of a mixture of minerals typical of glacially derived materials, generally, the mafic minerals biotite and amphibole are predominantly present in the vineyard soils from Terroir 3 and Terroir 4. As basalt is composed predominantly of ferromagnesian minerals and with lesser amounts of calcium-rich plagioclase feldspar, the mineralogy of the vineyard soils from Terroir 3 and 4 may represent the influence of the weathered basalt bedrock underlying the thin loess and the basalt cobblestone river gravels, respectively, that characterize these terroirs, in addition to the influence of loess and glacial sediments, as evidenced by the abundant quartz.

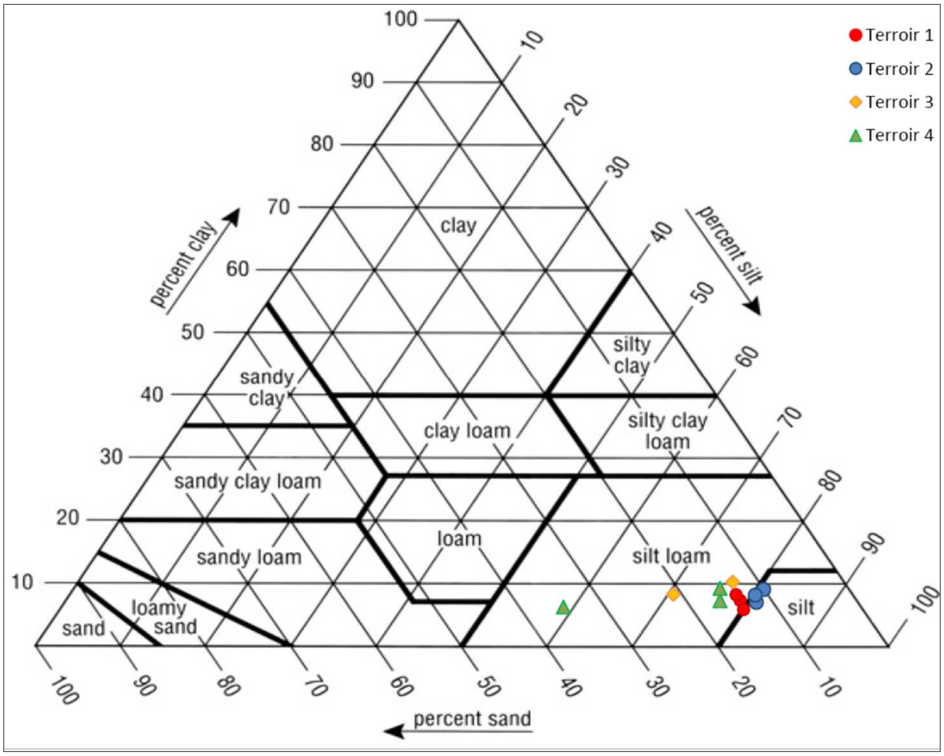


Figure 4-4. Ternary diagram showing the vineyard soil textures plotting in the silt loam and silt fields of the USDA Soil Texture Triangle.

TABLE 4-1 - Summary of Soil Total Elemental Analysis, Plant-Available Elements, and Texture

Terroir		1			2			3		4			Terroir 1	Terroir 2	Terroir 3	Terroir 4
Vineyard		Pepperbridge	Seven Hills	Va Piano	Les Collines	Leonetti Loess	Dwelley	Ferguson	Southwind	Cayuse	SJR	Old Stones	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Elevation (m)		248.7	266.7	254.2	371.6	332.5	407.5	430.4	391.1	269.7	255.1	273.4	256.5 ± 9.2	370.5 ± 37.5	410.7 ± 28	266.1 ± 9.7
Major Oxides (wt %)	SUM	98.46	98.67	98.35	99.34	98.81	98.72	99.16	99.35	98.71	98.87	100.05	98.49 ± 0.16	98.96 ± 0.34	99.3 ± 0.13	99.21 ± 0.73
	LOI	4.25	4.6	4.81	4.72	4.97	4.42	5.08	7.70	5.34	5.47	7.53	4.55 ± 0.28	4.7 ± 0.28	6.4 ± 1.85	6.1 ± 1.23
	SiO2	62.73	62.23	64.18	64.69	64.28	64.53	64.18	59.59	57.92	59.20	55.40	63.05 ± 1.01	64.5 ± 0.21	61.9 ± 3.2	57.5 ± 1.93
	Al2O3	13.77	13.51	13.66	14.08	13.82	13.78	13.32	12.68	13.41	13.51	13.99	13.65 ± 0.13	13.89 ± 0.16	13 ± 0.45	13.6 ± 0.31
	TiO2	1.20	1.20	0.96	1.00	1.03	1.00	1.11	1.05	1.58	1.44	1.67	1.12 ± 0.14	1.01 ± 0.02	1.1 ± 0.04	1.6 ± 0.12
	Fe2O3	7.02	6.92	5.48	6.32	6.17	6.25	6.74	6.79	9.61	8.95	10.17	6.47 ± 0.86	6.25 ± 0.08	6.8 ± 0.04	9.6 ± 0.61
	K2O	2.20	2.18	2.19	2.22	2.09	2.22	1.96	1.89	1.55	1.65	1.45	2.19 ± 0.01	2.18 ± 0.08	1.93 ± 0.05	1.6 ± 0.1
	MgO	1.98	2.19	1.49	1.62	1.54	1.68	1.74	2.03	2.31	2.18	2.37	1.89 ± 0.36	1.61 ± 0.07	1.89 ± 0.21	2.3 ± 0.097
	CaO	2.81	3.46	2.50	2.27	2.41	2.36	2.61	5.29	4.25	3.83	4.62	2.92 ± 0.49	2.35 ± 0.07	3.95 ± 1.9	4.2 ± 0.395
	Na2O	2.02	1.90	2.64	1.96	2.03	2.01	1.95	1.84	2.23	2.14	2.23	2.19 ± 0.4	2 ± 0.04	1.9 ± 0.08	2.2 ± 0.05
	P2O5	0.23	0.23	0.20	0.20	0.22	0.22	0.20	0.23	0.23	0.24	0.32	0.22 ± 0.02	0.21 ± 0.01	0.22 ± 0.02	0.26 ± 0.05
	MnO	0.12	0.10	0.09	0.09	0.10	0.10	0.12	0.12	0.14	0.13	0.15	0.1 ± 0.01	0.1 ± 0.01	0.12 ± 0	0.1 ± 0.01
Trace Elements (ppm)	Zr	300	335	274	331	328	327	341	320	242	243	201	303 ± 31	230 ± 2	331 ± 15	229 ± 24
	V	134	131	99	94	112	101	117	108	230	193	241	121 ± 19	75 ± 9	112 ± 7	221 ± 25
	Zn	84	75	77	81	85	71	87	73	102	106	115	79 ± 5	57 ± 7	80 ± 10	107 ± 7
	Ni	21	18	15	35	38	30	23	33	24	32	17	18 ± 3	25 ± 4	28 ± 7	25 ± 8
	Cr	39	57	44	61	61	73	45	55	41	60	34	47 ± 10	44 ± 7	50 ± 7	45 ± 13
	Ce	222	160	200	176	155	117	160	147	137	107	178	194 ± 31	121 ± 30	154 ± 10	141 ± 36
	Sr	249	252	260	263	257	259	255	251	275	262	269	254 ± 6	175 ± 3	253 ± 3	269 ± 7
	Ba	617	652	647	663	673	661	684	673	601	612	531	639 ± 19	452 ± 7	678 ± 7	581 ± 44
Plant-Available Elements (ppm)	P	12	12	20	25	20	32	42	22	20	34	55	14.7 ± 4.6	25.7 ± 6	32 ± 14.1	36.3 ± 17.6
	K	202	253	191	252	254	237	240	231	220	229	276	215 ± 33.1	248 ± 9.3	236 ± 6.4	242 ± 30.1
	Ca	1719	4306	1359	1704	1645	1692	1921	4940	2538	2269	2672	2461 ± 1608	1680 ± 31	3431 ± 2135	2493 ± 205
	Mg	399	208	264	409	317	359	452	245	564	535	499	290 ± 98	362 ± 46	349 ± 146	533 ± 33
	B	1.3	0.7	0.7	1.8	0.7	1.1	0.9	0.9	0.5	0.6	0.4	1 ± 0.3	1.2 ± 0.6	0.9 ± 0	0.5 ± 0.1
	Mn	3	1	3	5	4	5	7	2	4	5	6	2.3 ± 1.2	4.7 ± 0.6	4.5 ± 3.5	5 ± 1
	Zn	1.2	4.2	1.8	1.8	1.2	1.3	3	1.8	4.2	5.1	8.1	2.4 ± 1.6	1.4 ± 0.3	2.4 ± 0.8	5.8 ± 2
	S	8.7	9.5	4.7	4.5	5.5	8.7	7.1	4.1	11.5	3.5	8.9	7.6 ± 2.6	6.2 ± 2.2	5.6 ± 2.1	8 ± 4.1
	CEC	15	27	12	16	14	15	17	32	20	18	24	18 ± 7.9	15 ± 1	24.5 ± 10.6	20.7 ± 3.1
	pH	7.8	8.5	7.6	7.2	7	7.2	6.7	8.3	7.1	7.4	6.5	8 ± 0.5	7.1 ± 0.1	7.5 ± 1.1	7 ± 0.5
	O.M.	1.6	1.3	2.1	1.5	1.6	1.5	1.9	2.3	1.9	1.9	3.1	1.67 ± 0.4	1.53 ± 0.1	2.1 ± 0.3	2.3 ± 0.7
Texture (%)	Clay	7.1	7.9	5.6	8.8	6.7	7.9	9.9	7.6	7.2	8.9	5.5	6.9 ± 1.2	7.8 ± 1	8.7 ± 1.6	7.2 ± 1.7
	Silt	79.4	78.5	80.5	81.3	81.4	80.7	76.8	71.7	77.2	75.8	59.9	79.5 ± 1	81.1 ± 0.4	74.2 ± 3.6	71 ± 9.6
	Sand	13.6	13.6	13.9	9.9	11.9	11.4	13.3	20.7	15.6	15.3	34.6	13.7 ± 0.2	11.1 ± 1	17 ± 5.2	21.9 ± 11

Notes:
OM - Organic matter (%); CEC - Cation exchange capacity (cmol/kg)
SD-Standard Deviation

TABLE 4-2 - Summary of Soil Parent Material, Type, and Mineralogy

Terroir	1			2			3		4		
Vineyard	Pepperbridge	Seven Hills	Va Piano	Les Collines	Leonetti Loess	Dwelley	Ferguson	Southwind	Cayuse	SJR	Old Stones
Parent Material (USDA WSS)	Loess	Silty loess over calcareous, lacustrine deposits	Glacio-fluvial deposits	Loess	Loess	Loess	Loess mixed with colluvium from basalt	Loess mixed with colluvium from basalt	Mixed, very gravelly alluvium	Mixed, very gravelly alluvium	Mixed, very gravelly alluvium
Soil Type	WIB	24B	Tc	8B	WaD	WaD	114B	48E	29A	29A	29A
Mineralogy											
Quartz	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx
Plagioclase[1]	xx	xx	-	xx	xx	xx	xx	xx	xx	xx	xx
Orthoclase[2]	-	-	xx	-	-	-	-	-	-	-	-
Biotite	-	-	-	-	-	-	x	x	x	x	x
Muscovite	x	x	x	x	x	x	-	-	-	-	-
Amphibole	-	x	-	-		-	x	x	x	x	x
Apatite	-	-	x	-	x	-	-	-	x	x	-
Clay[3]	x	x	x	x	x	x	x	x	x	x	x

Notes:

WIB - Walla Walla silt loam, lacustrine substratum, 0 to 8 percent slopes
24B - Ellisforde silt loam, 1 to 7 percent slopes
Tc - Terrace Escarpments
8B - Athena silt loam, 1 to 7 percent slopes
WaD - Walla Walla silt loam, 8 to 30 percent slopes
29A - Freewater very cobbly loam, 0 to 3 percent slopes
114B - Walla Walla silt loam, 1 to 7 percent slopes
48E - Lickskillet very stony loam, 7 to 40 percent slopes
USDA WSS - United States Deprtment of Agriculture Web Soil Survey (http://websoilsurvey.nrcs.usda.gov)
Relative mineral abundance based on visual evaluation of peak height and intensity (xxx = most abundant; x = least abundant; - = absent)
[1] Plagioclase - Albite, Anorthite, Labradorite
[2] Orthoclase - Microcline, Sanidine
[3] Clay - Vermiculite, Montmorillonite

The XRF analysis of total major and select trace elements conducted on the fine fraction (silt and clay) of the soil samples indicates some variation in the chemical composition of the vineyard soils (Table 4-1). These bulk elemental abundances represent the total concentrations in the soil and are indicative of the general vineyard soil composition in terms of the chemical evolution of the soils over their developmental history. The variation in the chemical composition of the vineyard soils reflects the diversity of parent materials in which the soils have developed. Overall, the most variability in total concentrations is noted for the following major oxides: SiO_2 (55.4 – 64.7%), Fe_2O_3 (5.48 – 10.17%), and CaO (2.27 – 5.29%).

The compositional variation of the vineyard soils is illustrated graphically on plots of major element oxides versus SiO_2 content (Figures 4-5a and 4-5b) and compared to the loess, glacial flood sediment (Touchet), as well as the basalt and granite chemical composition data from Meinert and Busacca (2000). All vineyard soil compositions are generally similar to the Meinert and Busacca (2000) loess (loess regular, loess calcic, and loess soil) and shallow glacial flood sediment (Touchet 2m) data, plotting between the basalt and granite end-members. The soils are depleted in K_2O and CaO, enriched in TiO_2, FeO, and MgO, and have similar P_2O_5 and MnO compositions relative to the granite erratic sample; and are highly depleted in TiO_2, P_2O_5, MnO, FeO, K_2O, CaO, and MgO compositions relative to the basalt sample. The plots show strong negative correlations with SiO_2 for CaO, MgO, and FeO in the soil samples, with high coefficients of determination (R^2) explaining 80% of the variation (Fig. 4-5a). Conversely, soil K_2O (Fig. 4-5b) has a positive correlation with SiO_2 with a coefficient of determination that accounts for 80% of the variation.

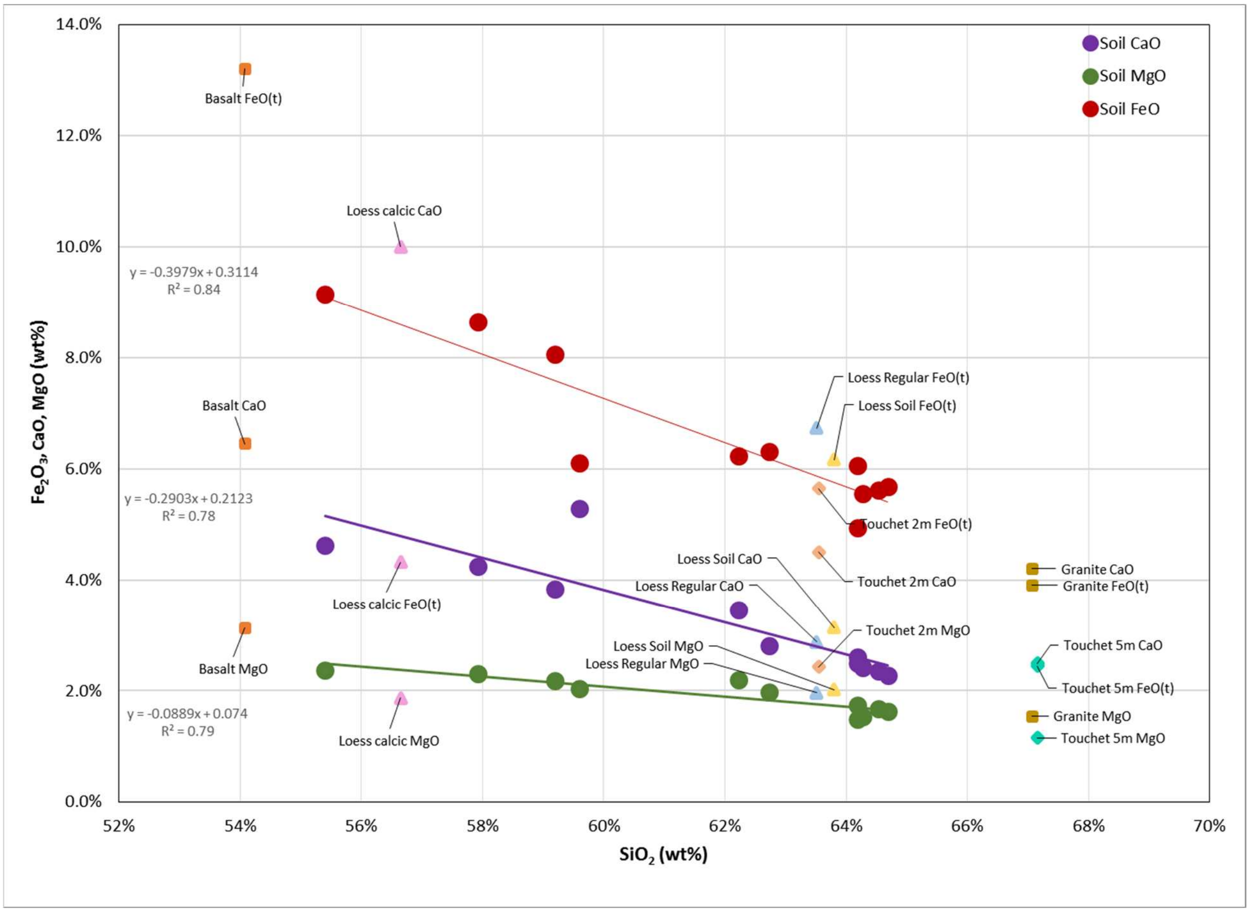


Figure 4-5a – Variation diagram depicting the FeO, CaO, and MgO versus SiO_2 composition of soils relative to loess, glacial flood sediment, basalt, and granite chemical composition data from Meinert and Busacca (2000), reflecting the diversity of soil parent materials and the influence from the basalt bedrock. Linear regression analysis indicates major oxides vary linearly with SiO_2 (R^2=0.84, 0.78, and 0.79).

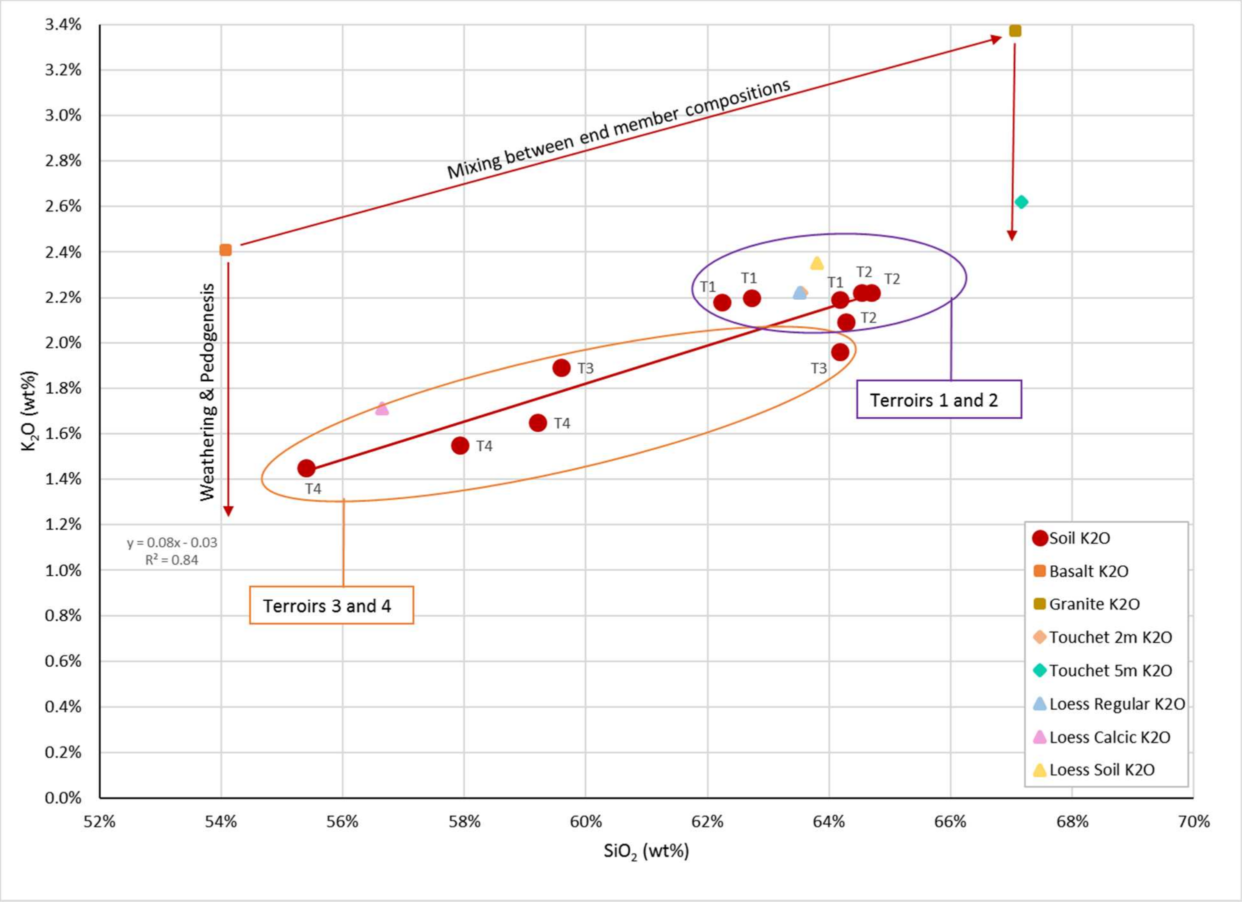


Figure 4-5b – Variation diagram depicting the K_2O versus SiO_2 composition of soils exemplifying the mixing trend between the basalt and granite end members and the influence soil forming processes that alter the inherited geochemistry. Linear regression analysis indicates K_2O varies linearly with SiO_2 (R^2=0.84).

Overall, the soil chemical compositions are indicative of a mixing trend between the basalt and granite end members, and Figure 4-5b exemplifies this trend, illustrating the K_2O composition of the soils across the four terroirs relative to the basalt, granite, loess, and flood sediment K_2O compositions. Specifically, the Terroir 3 and Terroir 4 soil K_2O compositions exhibit a mixing trend between basalt and loess, whereas the Terroir 1 and Terroir 2 soil K_2O compositions demonstrate mixing between granite and shallow flood sediment/loess. Overall, these compositional differences reflect the diversity of parent materials from which the soils developed, including loess, silty loess over calcareous lacustrine, and glacio-fluvial deposits (Terroir 1), loess (Terroir 2), loess mixed with colluvium from basalt (Terroir 3) and mixed, very gravelly alluvium (Terroir 4), and the compositional influence of the end members basalt and granite across the different terroirs.

The compositional variation of the soils is illustrated spatially on maps depicting interpolated concentrations across the study area (Fig. 4-6). Overall, the soils with the highest SiO_2, K_2O, and Al_2O_3 (not shown) and lowest TiO_2, Fe_2O_3, CaO, and MgO compositions correspond to the vineyards of Terroir 2. Conversely, the soils with the lowest SiO_2 and K_2O and highest TiO_2 and Fe_2O_3 content are present near the southwest part of the study area in Terroir 4. These soils also coincide with the highest Na_2O, P_2O_5, and MnO content. The soils with the highest CaO and MgO compositions also coincide with Terroir 4, and extend further into the lower half of the study area into Terroir 3, where vineyard soils have the lowest Al_2O_3 content among the four terroirs. Although the soils are derived primarily from glacial materials, the high TiO_2, MgO, and Fe_2O_3 compositions in the vineyard soils from Terroirs 3 and 4 are indicative of the influence of basalt, and result from ferromagnesian minerals such as pyroxene, amphibole, and biotite from mafic igneous rocks like the basalt cobblestone gravels and the weathered basalt bedrock that characterize these areas.

The total concentrations of trace elements in the vineyard soils show the most variability for V (94-241 ppm), Zr (201-341 ppm), and Ba (531-684 ppm). The compositions indicate the highest mean concentrations of Ni and Cr in Terroir 2 soils, Zr, Ce, and Ba in Terroir 3 soils, and V, Zn, and Sr in Terroir 4 soils. In general, the trace element compositions of Terroir 1 and 2 soils are similar to the granite and Touchet data from Meinert and Busacca (2000), while the trace element compositions of Terroir 3 and 4 soils are more comparable to the Meinert and Busacca (2000) basalt chemical composition data. The mineralogy and chemistry data indicate that the soils of the study vineyards have preserved a signal of the inherited geochemical fingerprint of parent materials despite transformations resulting from weathering and pedogenesis factors, which can alter the inherited geochemistry and the resulting concentrations of plant-available nutritive elements, emphasizing the dynamic relationship between geology and biology.

For example, Figure 4-5b illustrates a decreasing shift in K_2O composition from the rock end members to the vineyard soil samples, demonstrating the effects of soil weathering and pedogenesis processes, which result in the partitioning of K_2O from parent material to the bulk soil and subsequently in the distribution of the bulk soil K_2O between the soil potassium form used in mineral-forming structures (potassium-bearing minerals such as biotite, muscovite, orthoclase, and microcline) and the soil potassium in the form of ionized solution, exchangeable, and nonexchangeable (fixed). Specifically, across the four terroirs, mean bulk soil K_2O concentrations are lower in Terroirs 3 and 4; however, a higher percentage of soil potassium is distributed in ionized solution form (plant available) in these soils. This is indicative of distinct sinks for potassium in soil-formed minerals, which differ unsystematically for the soils of the four terroirs.

The soils of Terroirs 1 and 2, which developed from various glacially-derived parent materials, including loess, silty loess over calcareous lacustrine, and glacio-fluvial deposits representing the granitic end member influence on the soils, have higher mean bulk soil K_2O concentrations and a lower percentage of soil potassium distributed in ionized solution form, thus having a lower fraction of potassium available to the vines. This is the result of potentially more sinks for potassium in soil-formed minerals in these soils, such as solid state transformations of muscovite to vermiculite, which occur during weak chemical weathering conditions, as noted in the mineralogy of these soils.

Conversely, soils of Terroirs 3 and 4, which developed from loess mixed with colluvium from basalt and mixed, very gravelly alluvium representing the basaltic end member influence on the soils, have lower mean bulk soil K_2O concentrations and a higher fraction of potassium available to the vines as a result of potentially fewer sinks for potassium in the chemical weathering products, such as alteration of muscovite or vermiculite to a smectite-group clay (montmorillonite), which is corroborated by the mineralogy of these soils.

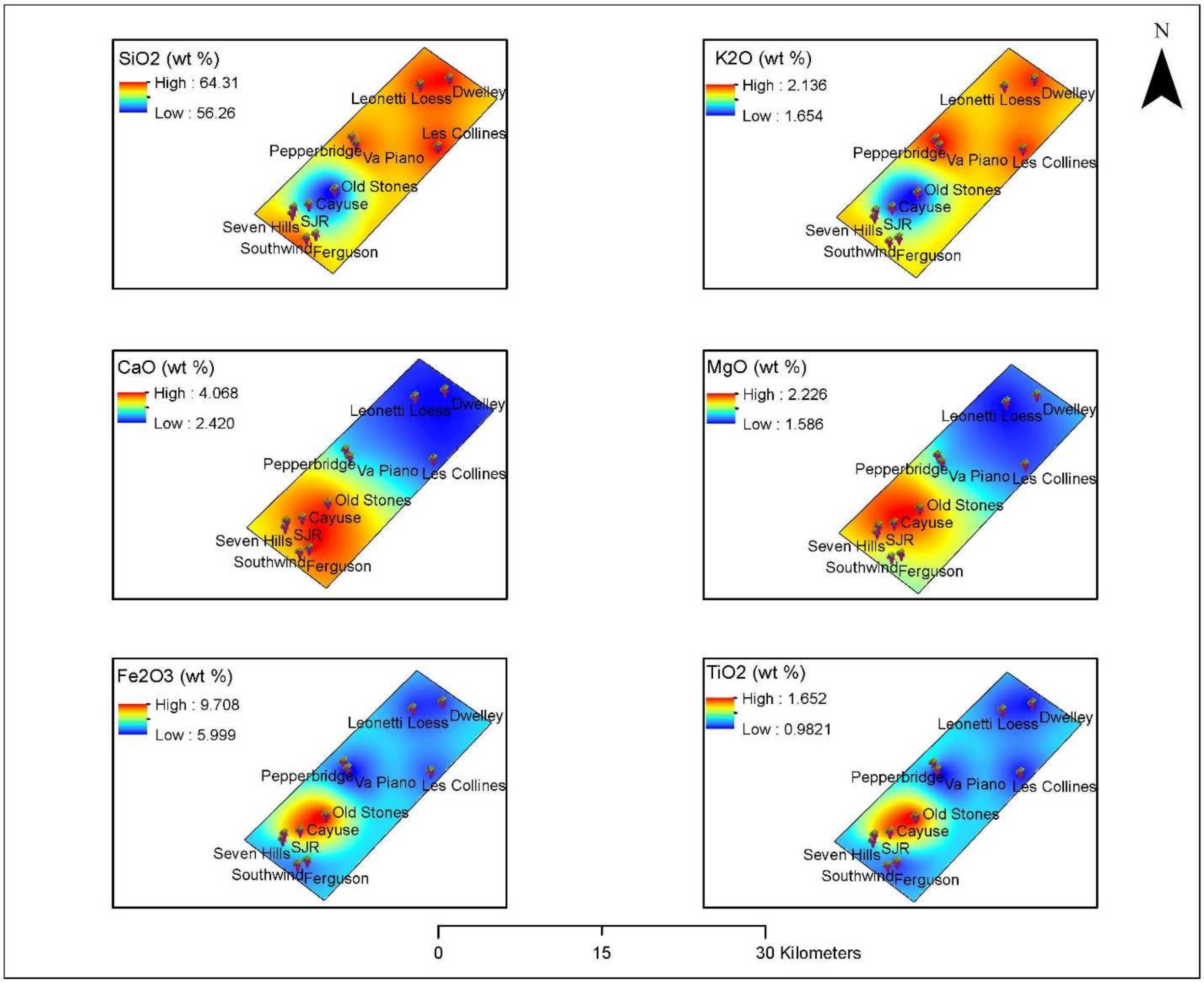


Figure 4-6. Map showing the spatial distribution of selected major elements, reflecting the variety of parent materials in which the soils formed.

4.5.2.3 Soil Nutrient Chemistry

The plant-available essential elements are necessary for the completion of the plant life cycle, and must be dissolved in an ionized water solution to allow absorption into the metabolism of the vines. In addition to the geochemical contribution of parent materials and various pedogenesis factors, the plant available soil chemistry depends on soil parameters such as texture, organic matter content, pH, and microbe activity, and can be indicative of the individual vineyard's fertilization practices. Soil OM, CEC, and pH, along with concentrations of plant-available macronutrients (potassium, calcium, magnesium, phosphorus, and sulfur), and micronutrients (boron, manganese, and zinc), which are essential elements necessary for completion of the plant life cycle are presented in Table 4-1 and Figure 4-7. All these elements have important roles in the metabolic functions of vines and require minimum levels

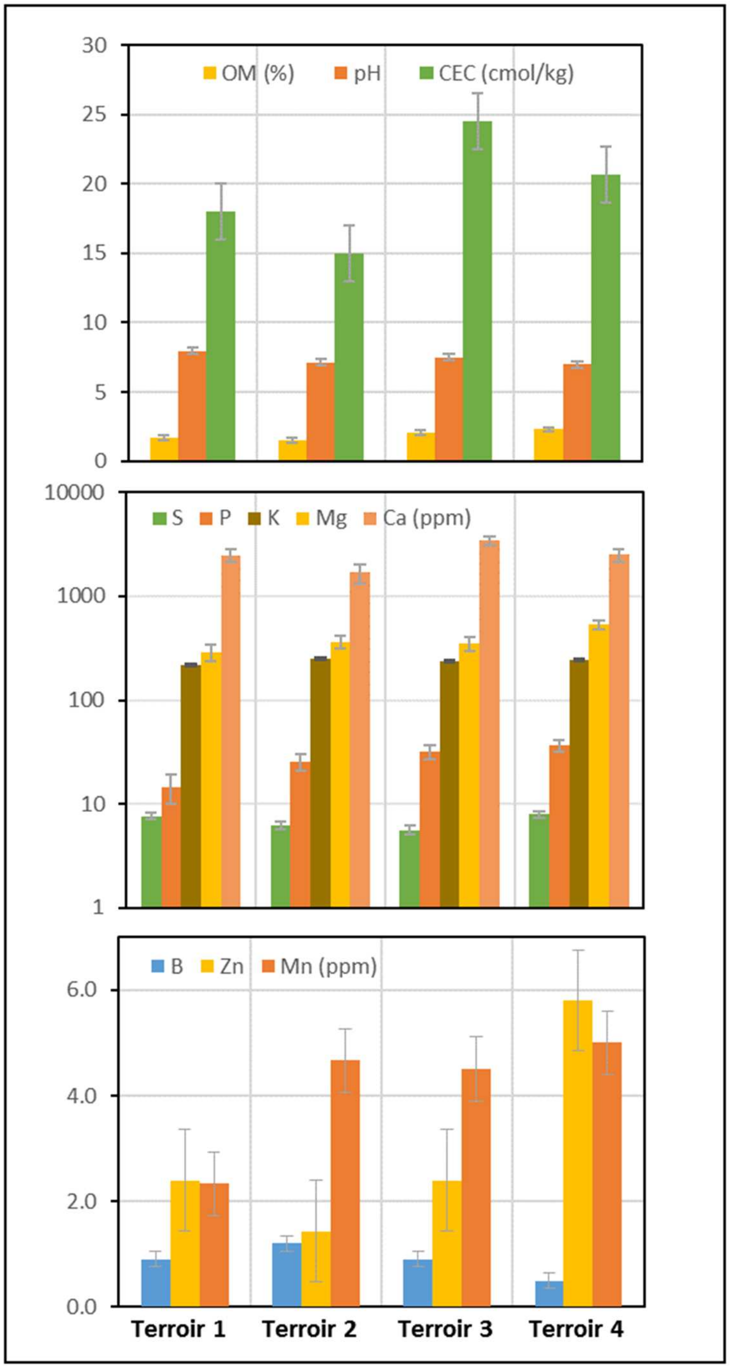


Figure 4-7. Graphs depicting the concentrations of plant-available macronutrients (K, Ca, Mg, P, and S depicted on a log scale) and micronutrients (B, Mn, and Zn) along with OM, CEC, and pH in the vineyard soils for each terroir.

maintained. The physical and chemical characteristics of the vineyard soils such as the texture, pH, percent OM, and CEC affect the nutrient pool, availability, adsorption, and retention potential. For example, fine textured, clayey soils can reduce the availability of potassium to vines, whereas coarse textured, sandy soils are prone to leaching and can drain nutrients from soils (Lambert et al. 2008). The textures of the vineyard soil samples, consisting of silt loams in Terroirs 1 and 2, and very stony/cobbly loams in Terroirs 3 and 4, are primarily dominated by silt sized grains (76.6% average silt content), providing a good balance between drainage and water holding capacity. The pH values of the vineyard soil samples, ranging from 6.5 to 8.5 pH units, indicate mostly neutral conditions with some slightly acidic, slightly alkaline, and strongly alkaline conditions, which provide good nutrient availability and balance for the health of the vines. Mean pH values indicate neutral conditions for the vineyard soils from Terroir 2 and Terroir 4, and moderately and slightly alkaline conditions for the soils from Terroir 1 and Terroir 3. Soils rich in OM are generally high in available nutrients, as decomposition of OM adds nutrients to soil and improves water holding capacity, while CEC affects the ability of soil to hold positively charged nutrients for plant uptake. Mean OM percentages and CEC measurements, ranging from 1.5 – 2.3 % and 15 – 24.5 cmol/kg, respectively, are representative of appropriate ranges for vineyard soils, with the highest mean OM and CEC values corresponding to the soil samples collected from the vineyards located in Terroir 3 and Terroir 4.

The concentrations of plant-available macronutrients potassium (191 – 276 ppm), calcium (1,359 – 4,940 ppm), magnesium (208 – 564 ppm), phosphorus (12 – 55 ppm), and sulfur (3.5 – 11.5 ppm), and micronutrients boron (0.4 – 1.8 ppm), manganese (1 – 7 ppm), and zinc (1.2 – 8.1 ppm) indicate wide ranges across the vineyard soils. Overall, the nutrient concentrations of the vineyard soil samples are largely within the ranges specified by Moyer et al. (2014), as pre-plant soil fertility guidelines for establishing productive vineyards; however, when assessing the nutrient requirements of established vineyards, analyzing vine tissue samples in conjunction with soil samples is critical in determining vine nutrient status and identifying potential deficiencies (Moyer et al. 2014). Generally, the plant-available soil chemistry shows the most variability for phosphorus, potassium, calcium, and magnesium, with the highest phosphorus and calcium corresponding to vineyards located in Terroir 3 and 4, and the highest potassium and magnesium corresponding to vineyards located in Terroir 2 and 4.

4.5.3 Grape Phenolic Panel Analysis

Grape phenolic compounds are present in the grape seeds and skins, and during maturation, the concentrations of seed and skin phenolics shift as a result of their physiological roles in these two different plant tissues (i.e., seed phenolics decrease while skin phenolics increase). Overall increases in the concentrations of total phenolics are associated with grape maturity and ripeness, which are monitored for harvest planning. Increases in sugar content (i.e., °Brix) occur during grape maturation as a result of sugar transfer from the leaves to the grapes and during the final stages of grape development as a result of grape dehydration. As phenolic compounds are the source of color, flavor, and mouth-feel in wines, phenolic ripeness, which is an indicator of physiological ripeness, is a more reliable indicator than the traditional sugar content (°Brix) measurements in evaluating grape ripeness (Bisson 2001; Hellman 2004; Ferrer-Gallego et al. 2012).

The grape phenolic analytical results, including concentrations of quercetin glycosides, total anthocyanins, polymeric anthocyanins, tannin, catechin, and °Brix, along with the catechin/tannin and polymeric anthocyanins/tannin indices are presented in Table 4-3 and Figure 4-8. Quercetin glycosides are flavonols produced in the grape skins in response to sun exposure, and their increasing concentrations over the growing season can be used as indicators of sunlight available to the developing grapes. Quercetin has a color-enhancing role and participates in co-pigmentation reactions with anthocyanins supporting the color stability of wines (Teixeira et al. 2013). Anthocyanins and tannins are vital grape quality elements influencing the color and taste of red wines. Anthocyanins are the primary phenolic compounds responsible for the color of red wines; and tannins, which are found in the grape skins and seeds, are responsible for the astringency of wines and for the pigmented polymers they form with anthocyanins, which provide stable pigments for long-term color stability of wines (Cortell et al. 2007; Kennedy et al. 2007).

The accumulation of anthocyanins in grapes is light and temperature dependent (Bergqvist et al. 2001; Cortell et al. 2007), starting at veraison and reaching a maximum in the latest phases of fruit maturation (Teixeira et al. 2013). Total anthocyanins include all monomeric and polymeric anthocyanins. The formation of polymeric anthocyanins, which are pigment complexes that develop through the chemical binding of anthocyanins and tannin, advances progressively during ripening (Kennedy 2008; Teixeira et al. 2013). The polymeric anthocyanins/tannin ratio increases as a result of anthocyanin-tannin polymerization and can be utilized as an indicator of tannin modifications and phenolic ripening. Tannins are naturally found in grape skins and seeds and have a great influence on the body and astringency of red wines. Total extractable tannin includes both skin and seed tannin, and during ripening, the skin tannin concentrations remain relatively stable or increase slightly, whereas the seed tannin concentrations decrease while becoming incorporated into the grape seed coat over time. Tannin maturation results in gradually reduced extractability, which is associated with perceived softening and ripening of tannins. Similarly, catechins, which are found primarily in the grape seeds, impart a bitterness and potential astringency to wines, and have a structural role in the formation of the grape seed coat. As catechin becomes incorporated into the seed coat, its concentration decreases as grapes ripen and can be utilized as an indicator of seed maturity and ripeness. As the seed phenolics catechin and tannin become incorporated into the seed coat, they are consequently more difficult to extract, resulting in decreasing concentrations of extractable catechin and tannin over time. The ratio of catechin (found only in seeds) to total tannin (found in seeds and skins) concentrations can be used to assess grape ripening, separately from the total tannin variations, as the catechin/tannin ratio reflects the decline of seed phenolic contributions to the total extractable phenolics during grape maturation.

The mean phenolic concentrations associated with each of the four terroirs are presented in Table 4-3. An analysis of variance reveals no statistically significant differences ($p > 0.05$) in the phenolic data among the four terroirs, given the small sample size for this regional scale study; and although only subtle differences are discerned, overall the most variability in mean grape phenolic concentrations is noted for total anthocyanins (1152 – 1551 mg/L), tannin (633 – 862 mg/L), and quercetin glycosides (99 – 131 mg/L).

TABLE 4-3 - Grape Phenolic Profile Analysis

Terroir	Vineyard	Brix (degrees)	Catechin (mg/L)	Quercetin Glycosides (mg/L)	Tannin (mg/L)	Polymeric Anthocyanins (mg/L)	Total Anthocyanins (mg/L)	Catechin/ Tannin Index	Polymeric Anthocyanins/ Tannin Index
1	Pepperbridge	29.6	16	106	1101	41	1606	0.015	0.037
	Seven Hills	29.1	28	111	593	34	1694	0.047	0.057
	Va Piano	27.1	17	80	671	26	1136	0.025	0.039
2	Les Collines	30	20	189	1176	37	1840	0.017	0.031
	Leonetti Loess	31.8	15	131	950	40	1774	0.016	0.042
	Dwelley	27.8	13	50	392	21	1009	0.033	0.054
3	Ferguson	27.5	8	176	950	49	1497	0.008	0.052
	Southwind	29	14	74	773	39	1605	0.018	0.05
4	Cayuse	30.1	27	144	648	47	1120	0.042	0.073
	SJR	28.7	28	107	676	48	1275	0.041	0.071
	Old Stones	27.9	23	143	574	48	1060	0.04	0.084
Terroir 1	Mean ± SD	28.6 ± 1.32	20 ± 6.66	99 ± 16.6	788 ± 274	34 ± 7.51	1479 ± 300	0.029 ± 0.016	0.044 ± 0.011
Terroir 2	Mean ± SD	29.9 ± 2.00	16 ± 3.61	123 ± 69.8	839 ± 404	33 ± 10.2	1541 ± 462	0.022 ± 0.010	0.042 ± 0.012
Terroir 3	Mean ± SD	28.3 ± 1.06	11 ± 4.24	125 ± 72.1	862 ± 125	44 ± 7.07	1551 ± 76.4	0.013 ± 0.007	0.051 ± 0.001
Terroir 4	Mean ± SD	28.9 ± 1.11	26 ± 2.65	131 ± 21.1	633 ± 52.7	48 ± 0.577	1152 ± 111	0.041 ± 0.001	0.076 ± 0.007

In the context of these minor variations, generally, the higher mean concentrations of grape phenolic compounds correspond to the vineyards of Terroir 3 and Terroir 4, and the higher mean °Brix value corresponds to the vineyards of Terroir 2. Specifically, the grapes of Terroir 3 have higher mean total anthocyanin (1551 mg/L) and tannin (861.5 mg/L) along with lower catechin (11 mg/L) concentrations and catechin/tannin index (0.041); and the vineyards of Terroir 3 (Ferguson and South Wind) are characterized by thin loess over weathered basalt and correspond to the highest mean elevations potentially benefiting from more solar radiation and enhanced ripening. Similarly, the low catechin/tannin ratio is indicative of increased seed maturity and tannin development, reaching a higher level of ripening as a result of decreasing extractable catechin and increasing extractable skin tannin over time. The grapes of Terroir 4 have higher mean concentrations of quercetin glycosides (131 mg/L) and polymeric anthocyanins (48 mg/L) along with a higher polymeric anthocyanins/tannin index (0.076). The vineyards of Terroir 4 (Cayuse, SJR, and Old Stones) are characterized by basalt cobblestone river gravels, which absorb and retain solar energy during the day increasing soil temperatures and radiate the retained heat after sunset. This temperature cycling enhances grape ripening and may contribute to a reduced risk of spring and fall freezes. Quercetin glycosides are indicative of sunlight available to the grapes and contribute to color stability in wine along with polymeric anthocyanins, which increase progressively during ripening. The polymeric anthocyanins/tannin ratio is an indicator of tannin modifications, as it increases with anthocyanin-tannin polymerization, which starts as red grapes ripen. The grapes of Terroir 2 have the highest mean °Brix value of 29.9, and the vineyards of Terroir 2 (Les Collines, Leonetti Loess, Dwelley) are characterized by thick loess overlying basalt bedrock. °Brix values provide an estimated concentration of the dissolved sugar, representing the degree of ripeness for grapes (in terms of sugar level) at harvest, and can generally be used to predict potential alcohol percentage in wines using an average conversion rate of fermenting sugar into alcohol. Typically, the vineyards of Terroir 2 generally have the highest number of GDDs in the valley.

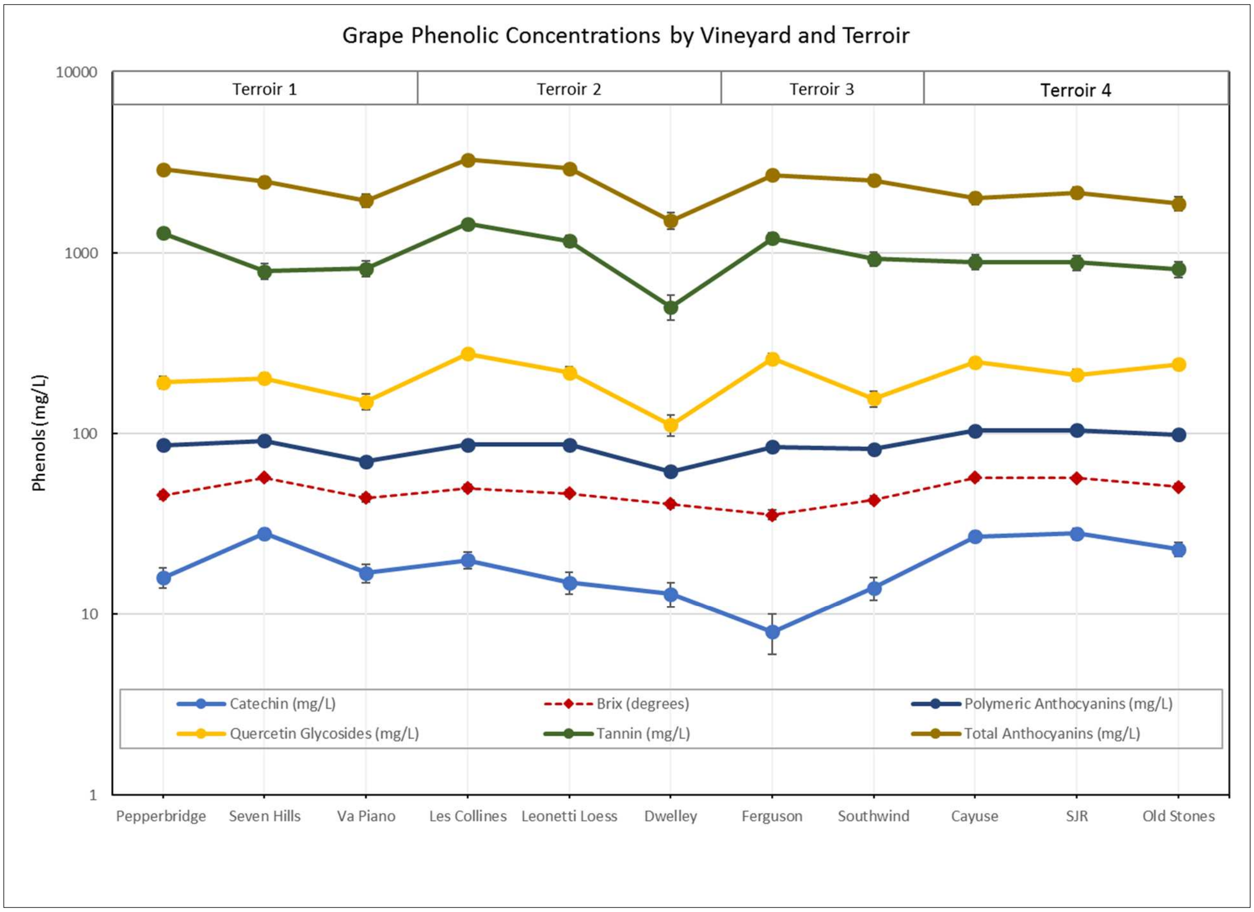


Figure 4-8. Graph depicting the concentrations grape phenolic compounds (quercetin glycosides, total anthocyanins, polymeric anthocyanins, tannin, catechin) and °Brix in grapes by vineyard and terroir.

Overall, the minor variations discerned among the four terroirs indicate that higher mean concentrations of grape phenolic compounds are associated with Terroir 3 and Terroir 4, and a higher mean °Brix value with Terroir 2; however, the results of this regional scale study indicate that generally, the soil variability observed among the four terroirs in the Walla Walla Valley AVA does not impart a major control on the magnitude of phenolic variation for the phenolic compounds analyzed. Other organic flavor compounds, such as rotundone (linked to the pepper flavor in Syrah), which has been shown to be spatially related to variability in vineyard characteristics (Bramley et al, 2017), or other grape-derived flavor and aroma compounds, may have different concentrations in the four terroirs.

4.6 Conclusions

Grape phenolic compounds are sensitive indicators of differences between vineyards and variations in grape and wine quality, and are directly related various terroir factors, including the vineyard soils, which affect the phenolic composition of grapes through variations in the availability of water and nutrients. Water and nutrient availability is, in turn, a function of soil properties including parent material, mineralogy, texture, rooting depth, drainage, chemistry, fertility, and water holding capacity. Although the distinct differences among the four terroirs, represented by the 11 study vineyards of the Walla Walla Valley AVA, are apparent in terms of soil characteristics, the phenolic concentrations of the Syrah grapes collected during the 2014 harvest reveal no statistically significant differences with only subtle variations among the four terroirs. However, considering these minor variations, overall, higher grape phenolic concentrations are associated with coarser-textured, well to somewhat excessively drained, limited depth, and reduced AWC soils; these physical soil characteristics promote mild water deficit enhancing phenolic concentrations in grapes. From a geological perspective, the bulk soil chemistry of the study vineyards is indicative of variation corresponding to the diversity of parent materials from which the soils formed. Although weathering and pedogenesis factors can alter the inherited geochemical background of parent materials, the soils of the study vineyards have preserved a signal of this fingerprint. Notably, the vineyard soils with elevated Fe_2O_3 and MgO content, resulting from the weathering of ferromagnesian minerals in mafic igneous rocks like the basalt cobblestone gravels and the weathered basalt bedrock that characterize them, highlight the basalt influence and are generally associated with higher grape phenolic concentrations. Consistent with the soil chemistry, the mineralogy of the vineyard soils reflects minerals typical of glacially-derived materials, with mafic minerals biotite and amphibole predominantly present in the vineyard soils demonstrating the influence of basalt. From a plant physiology perspective, soil fertility indicators are generally within suitable ranges for all vineyard soils, with the highest plant-available calcium, phosphorus, and zinc corresponding to the vineyard soils representing the basalt effect.

In this regional scale reconnaissance study, many observations support the hypothesis that physical soil properties are fundamental variables in geologic studies of terroir because of their role in water and nutrient availability affecting grape phenolic composition; additionally, the geochemical influence from parent material on the vineyard soil is demonstrated to be a contributing factor and variable that warrants evaluation. However, overall, the variation in soil properties among the four distinctive terroirs in the Walla Walla Valley AVA does not correspond to significant variability in the concentrations of grape phenolic compounds at this scale; although the observed subtle differences in grape phenolic concentrations among the four terroirs appear to indicate a potential connection between higher grape phenolic concentrations and soils exhibiting the influence of basalt.

The results of this study indicate that mesoscale studies and large scale characterizations can be limited by the microscale variability of soil properties, given their geospatial diversity and sharp spatial variations that can be observed at the vineyard level. Thus, taking into consideration the heterogeneity of soils and the degree of variability in soil properties, broader scale, regional characterizations may obscure microscale variability and become ambiguous, while studies at the vineyard level with discernable variability at the local scale may provide precision in the assessment of the relationships and controls of soil properties on grape sensory and chemical properties. Nonetheless, regardless of its undefined scale, soil is the foundation of the grapevine, and the controls of its properties are essential terroir factors to be considered when evaluating grape phenolic concentrations, which are vital for harvest timing, wine making decisions, and ultimately wine quality.

Further studies should take into consideration a larger sample size for a more robust mesoscale (regional) characterization to determine if statistically significant differences can be observed in the phenolic content of the grapes at this scale; along with toposcale (vineyard) studies that consider variations in vine age, clone, and rootstock; as well as viticultural practices, such as pruning habit, irrigation, canopy vigor control measures, fertilization, and spraying patterns.

References

André, F., van Leeuwen, C., Saussez, S., Van Durmen, R., Bogaert, P., Moghadas, D., de Rességuier, L., Delvaux, B., Vereecken, H., and Lambot, S., 2012. High-resolution imaging of a vineyard in south of France using ground-penetrating radar, electromagnetic induction and electrical resistivity tomography: Journal of Applied Geophysics, v. 78, p. 113–122, http://dx.doi.org/10.1016/j.jappgeo.2011.08.002.

Anesi A, Stocchero M, Dal Santo S, Commisso M, Zenoni S, Ceoldo S, Tornielli GB, Siebert TE, Herderich M, Pezzotti M, Guzzo F., 2015. Towards a scientific interpretation of the terroir concept: plasticity of the grape berry metabolome. BMC Plant Biol. 15:191.

Arnason, B., 1969. Equilibrium constant for the fractionation of deuterium between ice and water. J. Phys. Chem., 73(10), 3491- 3494.

Attig, J.W., Bricknell, M., Carson, E.C., Clayton, L., Johnson, M.D., Mickelson, D.M., and Syverson, K.M., 2011. Glaciation of Wisconsin [fourth edition]: Wisconsin Geological and Natural History Survey, Educational Series, v. 36, p. 4.

Barbour, M.M., Andrews, T.J., and Farquhar, G.D., 2001. Correlations Between Oxygen Isotope Ratios of Wood Constituents of Quercus and Pinus Samples from Around the World, Aust. J. Plant Physiol., 28, 335 – 348.

Bergqvist, J., Dokoozlian, N. and Ebisuda, N., 2001. Sunlight exposure and temperature effects on berry growth and composition of Cabernet Sauvignon and Grenache in the Central San Joaquin Valley of California. Am. J. Enol. Vitic., 52, 1-7.

Bisson, L. F., 2001. Department of Enology & Viticulture, UC Davis, Practical Winery & Vineyard Jul/Aug, 32.

Bowen, P.A., Bogdanoff, C.P., Estergaard, B.F., Marsh, S.G., Usher, K.B., Smith, C.A.S., and Frank, G., 2005. Geology and Wine 10. Use of geographic information system technology to assess viticulture performance in the Okanagan and Similkameen valleys, British Columbia: Geoscience Canada, v. 32, p. 161–176.

Bramley R.G.V., Ouzman J. and Boss P.K., 2011. Variation in vine vigour, grape yield and vineyard soils and topography as indicators of variation in the chemical composition of grapes, wine and wine sensory attributes. Aust. J. Grape Wine Res., 17(2), 217-229.

Bramley R.G.V., Siebert, T.E., Herderich, M.J., and Krstic, M.P., 2017. Patterns of within-vineyard spatial variation in the ‘pepper’ compound rotundone are temporally stable from year to year. Aust. J. Grape Wine Res., 23(1), 42-47.

Brooks, J. R., Barnard, H. R., Coulombe, R. & McDonnell, J. J., 2009. Ecohydrologic separation of water between trees and streams in a Mediterranean climate. Nature Geosci. 3, 100–104.

Brooks J., 2015. Water, bound and mobile. Science 349(6244): 138–139

Brunel, J.P., Walker, G.R., Kennett-Smith, A.K., 1995. Field validation of isotopic procedures for determining sources of water used by plants in a semi-arid environment. Journal of Hydrology 167, 351–368.

Buhay, W.M., Edwards, T.W.D., 1995. Climate in southwestern Ontario, Canada, between AD 1610 and 1885 inferred from oxygen and hydrogen isotopic measurements of wood cellulose from trees in different hydrologic settings. Quat. Res. 44, 438–446.

Buol, S. W., Southard, R. J., Graham, R. C., and McDaniel, P. A., 2003. Soil genesis and classification 5th ed 494 Ames, IA Iowa State Press 494.

Carson, R.J, and Pogue, K.R., 1996. Flood basalts and glacier floods: Roadside geology of parts of Walla Walla, Franklin, and Columbia Counties, Washington: Washington Department of Natural Resources Division of Geology and Earth Resources, Information Circular no. 90, 47p.

Chapman, N., Miller, A. J., Lindsey, K., and Whalley, W. R., 2012. Roots, water, and nutrient acquisition: let's get physical. Trends in Plant Sci. 17, 701–710.

Chaves, M.M., Zarrouk, O., Francisco, R., Costa, J.M., Santos, T., Regalado, A.P., Rodrigues, M.L., and Lopes, C.M., 2010. Grapevine under deficit irrigation: Hints from physiological and molecular data. Annals of Botany 105, 661-676.

Chone, X., Van Leeuwen, C., Chery, P., Ribereau-Gayon, P., 2001. Terroir influence on water status and nitrogen status of non-irrigated Cabernet sauvignon (Vitis vinifera). Vegetative development, must and wine composition (Example of a Medoc Top Estate Vineyard, Saint Julien Area, Bordeaux, 1997). S. Afr. J. Enol. Vitic. 22(1), 8-15.

Clark I., 2015. Groundwater Geochemistry and Isotopes. CRC Press, Taylor and Francis Group: Boca Raton, FL. Available at: www.crcpress.com

Clayton, L., and Attig, J.W., 1997. Pleistocene geology of Dane County, Wisconsin: Wisconsin Geological and Natural History Survey Bulletin, v. 95, p. 64.

Cohen, S.D. and Kennedy, J.A., 2010. Plant metabolism and the environment: Implications for managing phenolics. Crit. Rev. Food Sci. Nutr. 50, 620–643.

Cortell, J. M.; Halbleib, M.; Gallagher, A. V.; Righetti, T.; Kennedy, J. A., 2005. Influence of vine vigor on grape (Vitis Vinifera L. cv. Pinot noir) and wine proanthocyanidins. J. Agric. Food Chem. 53, 5798-5808.

Cortell, J. M. and Kennedy, J. A., 2006. Effect of shading on accumulation of flavonoid compounds in Vitis Vinifera L. Pinot noir fruit and extraction in a model system. J. Agric. Food Chem. 54, 8510-8520.

Cortell, J.M., Halbleib, M., Gallagher, A.V., Righetti, T.L. and Kennedy, J.A., 2007. Influence of vine vigor on grape (Vitis vinifera L. cv. Pinot noir) anthocyanins. 1. Anthocyanin concentration and composition in fruit. J. Agric. Food Chem. 55, 6575–6584.

Coombe B.G., 2004. Grapevine growth stages - The modified E-L system. In: Dry PR Coombe BG, eds. Viticulture 1 - Resources, 2 edn. Adelaide, Australia: Winetitles, 152–153.

Craig, H. and Horn, B., 1968. Relationships deuterium, oxygen-18 and chlorinity in the formation of sea ice. Trans. Am. Geophys. Union, 49:216-217.

Dami, I., Bordelon, B., Ferree, D.C., Brown, M., Ellis, M.A., Williams, R.N., and Doohan, D., 2005. Midwest grape production guide: Ohio State University Extension, Bulletin 919, Columbus, OH, 155 p.

Dawson T.E. and Ehleringer J.R., 1991. Streamside trees that do not use stream water, Nature 350:335–37.

Dawson, T.E., 1993. Water sources of plants as determined from xylem water isotopic composition: perspective on plant competition, distribution, and water relations. In: Ehleringer, J.R., Hall, A.E., Farquhar, G.D. (Eds.), Stable Isotopes and Plant Carbon–Water Relations. Academic Press, San Diego, pp. 465–496.

Dawson, T. E., Mambelli, St., Plamboeck, A. H., Templer, P. H., Tu, K. P., 2002. Stable isotopes in plant ecology, Annual Review of Ecological Systems 33, 507 – 559.

De Andres-de Prado R, Yuste-Rojas M, Sort X, Andres-Lacueva C, Torres M, Lamuela-Raventos RM., 2007. Effect of soil type on wines produced from Vitis vinifera L. cv. Grenache in commercial vineyards. J Agric Food Chem. 55(3):779–86.

Deloire, A., Carbonneau, A., Wang, Z.P., and Ojeda, H., 2004. Vine and water a short review. Journal International Des Sciences De La Vigne Et Du Vin. 38(1): 1–13.

Deluc, L.G., Quilici, D.R., Decendit, A., Grimplet, J., Wheatley, M.D., Schlauch, K.A., Merillon J.M., Cushman, J.C., and Cramer, G.R., 2009. Water deficit alters differentially metabolic pathways affecting important flavor and quality traits in grape berries of Cabernet Sauvignon and Chardonnay. BMC Genomics 10, 212.

Di Majo D., La Guardia M., Giammanco S, La Neve L., Giammanco M., 2008. The antioxidant capacity of red wine in relationship with its polyphenolic constituents. Food Chem 111:45–49.

Ehleringer, J. R. and Osmond, C.B., 1989. Stable isotopes, p. 281-300. In R. W. Pearcy, J. R. Ehleringer, H. A. Mooney, and P. W. Rundel (eds.), Plant Physiolog-ical Ecology Field Methods and Instrumentation. Chapman and Hall Ltd., London.

Ehleringer, J.R. and Dawson, T.E., 1992. Water uptake by plants: perspective from stable isotope composition. Plant Cell and Environment 15, 1073–1082.

Ferrer-Gallego, R., Hernández-Hierro, J.M., Rivas-Gonzalo, J.C., and Escribano-Bailón, M.T., 2012. Influence of climatic conditions on the phenolic composition of Vitis vinifera L. cv. Graciano Analytica Chimica Acta, 732, pp. 73–77.

Gat, J.R., 1996. Oxygen and Hydrogen Isotopes in the Hydrologic Cycle, 1996. Annu. Rev. Earth Planet. Sci. 1996. 24:225–62

Gat J., 2005. In Isotope Hydrology: A Study of the Water Cycle, Gat J (ed). Imperial College Press: 57 Shelton Street, Covent Garden, London.

Gladstones, J., 1992. Viticulture and Environment. 1. Winetitles, Adelaide.

Goldammer, T., 2015. Grape Grower's Handbook. Apex Publishers: Centreville, Virginia.

Goldsmith, G.R., Muñoz-Villers, L.E., Holwerda, F., McDonnell, J.J., Asbjornsen, H., and Dawson, T.E., 2011. Stable isotopes reveal linkages among ecohydrological processes in a seasonally dry tropical montane cloud forest. Ecohydrology 5:779–790.

Gómez-Míguez M.J., Gómez-Míguez M., Vicario I.M., Heredia F.J., 2007. Assessment of colour and aroma in white wines vinifications: Effects of grape maturity and soil type. Journal of food engineering 79:758–764.

GPO Electronic Code of Federal Regulations, 2015, Approved American Viticultural Areas: 9.146 Lake Wisconsin: Electronic Code of Federal Regulations, U.S. Government Publishing Office, Washington, DC. Accessed 05/10/2015.

Haynes, S.J., 1999. Concept of terroir and the role of geology. Geoscience Canada, 26: 190-194.

Haynes, S.J., 2000. Geology and Wine 2. A geological foundation for terroirs and potential sub-appellations of Niagara Peninsula wines, Ontario, Canada: Geoscience Canada, v. 27, p. 67–87.

Hewlett, J. and Hibbert, A. 1966. Factors affecting the response of small watershed to precipitation in humid areas. In International Symposium on Forest Hidrology Pergamon Press: Oxford & New York; 275–279. Available at: http://coweeta.ecology.uga.edu/publications/851.pdf

Hubbard, S., Lunt, I., Grote K., and Rubin, Y. 2003. Vineyard soil water content: mapping small scale variability using ground penetrating radar, in Macqueen, R.W., and Meinert, L.D., eds., Fine Wine and Terroir--The Geoscience Perspective: Geoscience Canada Reprint Series 9, Geological Association of Canada, p. 193-202.

Imre, S.P., and Mauk, J.L., 2009. Geology and Wine 12. New Zealand Terroir: Geoscience Canada, v. 36, p. 145–159.

Imre, S.P., and Mauk, J.L., 2011. Geophysics and wine in New Zealand, in Dar, I.A., ed., Earth and Environmental Sciences: InTech, online access: http://cdn.intechweb.org/pdfs/24548.pdf.

Imre, S.P., Kilmartin, P.A., Rutan, T., Mauk, J.L. and Nicolau, L., 2012. Influence of soil geochemistry on the chemical and aroma profiles of Pinot noir wines. J. Food Agric. Environ. 10, 280–288.

Jackson, P.C., Meinzer, F.C., Bustamante, M., Goldstein, G., Franco, A., Rundel, P.W., Caldas, L., Igler, E., Causin, F., 1999. Partitioning of soil water among tree species in a Brazilian Cerrado ecosystem. Tree Physiol 19:717–724.

Jones, G.V. and Davis, R.E., 2000. Climate influences on grapevine phenology, grape composition, and wine production and quality for Bordeaux, France. American Journal of Enology and Viticulture 51: 249–261.

Jordan, T.D., Pool, R.M., Zabadal, T.J., and Tompkins, J.P., 1981. Cultural practices for commercial vineyards: New York State College of Agriculture and Life Sciences, A statutory college of the State University, at Cornell University, Miscellaneous Bulletin 111, 70 p.

Kennedy, J.A., Matthews, M.A. and Waterhouse, A.L., 2002. Effect of maturity and vine water status on grape skin and wine flavonoids. Am. J. Enol. Vitic., 53, 268-274.

Kennedy J.A., Saucier C., and Glories Y., 2006. Grape and wine phenolics: History and perspective. Am. J. Enol. Vitic. 3:20–21.

Kennedy, J.A., 2008. Grape and wine phenolics: Observations and recent findings. Cien.Inv. Agr. 35(2):107-120.

Koundouras, S., Marinos, V., Gkoulioti, A., Kotseridis, Y. and van Leeuwen, C., 2006. Influence of vineyard location and vine water status on fruit maturation of nonirrigated cv. Agiorgitiko (Vitis vinifera L.). Effects on wine phenolic and aroma components. J. Agric. Food Chem. 54, 5077–5086.

Lambert, J.-J., Anderson, M.A., and Wolpert, J.A., 2008. Vineyard nutrient needs vary with rootstocks and soils: California Agriculture, v. 62, p. 202–207, http://dx.doi.org/10.3733/ca.v062n04p202.

Lehmann, M. and Siegenthaler, U., 1991. Equilibrium oxygen and hydrogen isotope fractionation between ice and water, J. Glaciol., 37, 23–26.

Martínez-Lüscher J., Kizildeniz T., Vučetić V., Dai Z., Luedeling E., van Leeuwen C., Gomès E., Pascual I., Irigoyen J.J., Morales F., and Delrot S., 2016. Sensitivity of Grapevine Phenology to Water Availability, Temperature and CO2 Concentration. Front. Environ. Sci. 4:48.

McDonnell J., 2014. The two water worlds hypothesis: ecohydrological separation of water between streams and trees? Wiley Interdisciplinary Reviews: Water 1(4): 323–329.

McGovern, P. E., Glusker, D. L., Exner, L. J., and Voigt, M. M., 1996. Neolithic resinated wine. Nature 381:480-481.

Meinert, L.D., and Busacca, A.J., 2000. Geology and Wine 3. Terroirs of the Walla Walla Valley appellation, southeastern Washington State, USA: Geoscience Canada, v. 27, p. 149–171.

Meinert, L.D., and Busacca, A.J., 2002. Geology and Wine 6. Terroir of the Red Mountain appellation, central Washington State, U.S.A.: Geoscience Canada, v. 29, p. 149–168.

Meinert, L.D., and Curtin, T., 2005. Terroir of the Finger Lakes of New York (Abstract): The Colorado College, Extended Abstracts, 18th Keck Symposium, Colorado Springs, p. 34–40.

Meinzer, F.C., Andrade, J.L., Goldstein, G., Holbrook, N.M., Cavelier, J., and Wright, S.J., 1999. Partitioning of soil water among canopy trees in a seasonally dry tropical forest. Oecologia 121:293–301.

Mickelson, D.M., Knox, J.C., and Clayton, L., 1982. Glaciation of the Driftless Area: An evaluation of the evidence, in Knox, J.C., Clayton, L., and Mickelson, D.M., eds., Quaternary history of the Driftless Area: Wisconsin Geological and Natural History Survey Field Trip Guidebook, v. 5, p. 155–169.

Mickelson, D.M., 2007. Landscapes of Dane County: Wisconsin Geological and Natural History Survey Educational Series v. 43, p. 36; map (07-6).

Moreno-Gutiérrez, C., Dawson, T., Nicolás, E., and Querejeta, J., 2012. Isotopes reveal contrasting water use strategies among coexisting plant species in a Mediterranean ecosystem. New Phytol 196:489–496.

Morlat, R., and Bodin, F., 2006. Characterization of viticultural terroirs using a simple field model based on soil depth – II. Validation of the grape yield and berry quality in the Anjou vineyard (France). Plant and Soil 281:55-69.

Moulton, G. A., King, J., Washington State University., and Washington State Library, 2005. Growing wine grapes in maritime Western Washington. Pullman, Wash.: Washington State University, Extension.

Moyer, M.M., Peters, R.T., and Hamman, R., 2013. Irrigation Basics for Eastern Washington Vineyards. WSU Extension Publication #EM061e. Washington State University.

Moyer, M., Moulton, G., and Henick-Kling, T., 2014. Growing winegrapes in maritime western Washington: Washington State University Extension, EM068E, 29 p.

National Oceanic and Atmospheric Administration, 2015. Storm data and unusual weather phenomena with late reports and corrections, May 2015, Volume 57, No.5.

O'Neil, J. R., 1968. Hydrogen and oxygen isotope fractionation between ice and water. J . Phys. Chcm.,72(10), 3683- 3684.

Philips, F., 2010. Hydrology: soil-water bypass. Nat Geosci 2010, 3:77–78.

Pinney, T., 1989. A history of wine in America: From the beginnings to prohibition: University of California Press, Berkeley, CA, p. 269–285.

Pogue, K., 2009. Folds, floods, and fine wine: Geologic influences on the terroir of the Columbia basin, in O'Connor, J., Dorsey, R., and Madin, I., eds., Volcanoes to Vineyards: Geologic Field Trips through the dynamic landscape of the Pacific Northwest: Geological Society of America Field Guide 15, p. 1–17.

Posey, C. and Smith, A., 1957. The equilibrium distribution of light and heavy waters in a freezing mixture, J. Am. Chem. Soc., 79,555- 557.

Prichard, T.L., Hanson, B., Schwankl, L., Verdegaal, P., and Smith, R., 2004. Deficit irrigation of quality winegrapes using micro-irrigation techniques. University of California Cooperative Extension, Department of Land, Air, Water Resources, University of California, Davis.

Roden, J. S., Lin, G., and Ehleringer, J. R., 2000. A Mechanistic Model for The Interpretation of Hydrogen and Oxygen Isotope Ratios in Tree-Ring Cellulose, Geochim. Cosmochim. Acta, 64, 21 35.

Scarlett N.J., Bramley, R.G.V., Siebert, T.E., 2014. Within-vineyard variation in the ‘pepper’ compound rotundone is spatially structured and related to variation in the land underlying the vineyard. Aust J Grape Wine Res., 20(2):214–22

Shange, L.P. and Conradie, W.J., 2012. Effects of soil parent material and climate on the performance of Vitis vinifera L. cvs. Sauvignon blanc and Cabernet Sauvignon-Part I. Soil analysis, soil water status, root system characteristics, leaf water potential, cane mass and yield. Afr J Enol Vitic 33, 161.

Smart, D.R., Schwass, E., Lakso, A., and Morano, L., 2006. Grapevine Rooting Patterns: A Comprehensive Analysis and a Review: Am J Enol Vitic. 57: 89-104.

Smart, D. R., Cosby Hess, S., Plant, R., Feihn, O., Heymann, H., and Ebeler, S., 2014. Geospatial variation of grapevine water status, soil water availability, grape composition and sensory characteristics in a spatially heterogeneous premium wine grape vineyard. SOIL Discuss., 1, 1013-1072.

Stiles, C.A., and Stensvold, K.A., 2008. Loess contribution to soils forming on dolostone in the Driftless Area of Wisconsin: Soil Science Society of America Journal, v. 72, p. 650–659, http://dx.doi.org/10.2136/sssaj2007.0112.

Swinchatt, J., 2012. Finger Lakes a new-found source of great intrigue: The world of fine wine, v. 38, p. 60–66.

Syverson, K.M., and Colgan, P.M., 2004. The Quaternary of Wisconsin: A review of stratigraphy and glaciation history, in Ehlers, J., ed., The glacial stratigraphy of the northern U.S.: Elsevier, p. 289–305.

Taylor, V.F., Longerich, H.P., and Greenough, J.D., 2002. Geology and Wine 5. Provenance of Okanagan Valley wines, British Columbia, using trace elements: Promise and limitations: Geoscience Canada, v. 29, p. 110–120.

Teixeira, A., Eiras-Dias, J., Castellarin, S.D., Gerós, H., 2013. Berry Phenolics of Grapevine under Challenging Environments. Int. J. Mol. Sci. 14, 18711-18739.

Tramontini S., van Leeuwen C., Domec J.C., Destrac-Irvine A., Basteau C., 2013. Impact of soil texture and water availability on the hydraulic control of plant and grape-berry development. Plant and soil 368: 215–230.

Tuck, B., and Gartner, W., 2014. Vineyards and wineries of Wisconsin: A status and economic contribution report: Regents of the University of Minnesota, Extension Center for Community Vitality, 51 p.

Ubalde, J.M., Sort, X., Zayas, A. and Poch, R.M., 2010. Effects of soil and climatic conditions on grape ripening and wine quality of Cabernet Sauvignon. J. Wine Res. 21, 1–17.

USDA. United States Department of Agriculture Natural Resources Conservation Service, Web Soil Survey data, http://websoilsurvey.nrcs.usda.gov/. Accessed 03/29/2015 and 10/13/2015.

Van Leeuwen, C., Friant, Ph., Chone, X., Tre Goat, O., Koundouras, S., and Dubourdieu, D., 2004. Influence of climate, soil and cultivar on terroir, American Journal of Enology and Viticulture, 55, 207– 217.

Van Leeuwen, C., Trégoat, O., Choné, X., Bois, B., Pernet, D. and Gaudillère, J.-P., 2009. Vine water status is a key factor in grape ripening and vintage quality for red Bordeaux wine. How can it be assessed for vineyard management purposes? Journal International des Sciences de la Vigne et du Vin, 43(3) 121–134.

Van Leeuwen, C., 2010. Terroir: the effect of the physical environment on vine growth, grape ripening and wine sensory attributes: In Managing Wine Quality, Volume 1: Viticulture and wine quality, Ed. Andrew Reynolds, p. 273-315.

Wample, R.L. and Smithyman, R., 2002. Regulated deficit irrigation as a water management strategy in Vitis vinifera production. In: Deficit Irrigation Practices. Water reports Publication 22, FAO, Rome, pp. 89-100.

Washington State Wine, http://www.washingtonwine.org

Wershaw, R. L., Friedman, I., Heller, S. J., and Frank, P. A., 1966. Hydrogen isotopic fractionation of water passing through trees, Advances in organic geochemistry, International series of monographs on earth sciences, edited by: Hobson, G. D., Speers, G. C., and Inderson, D. E., 32, Pergamon Press, New York, USA, 55–67.

West, A.G., Patrickson, S.J., and Ehleringer, J.R., 2006. Water extraction time for plant and soil materials used in stable isotope analysis. Rapid Commun Mass Spectrom 20:1317–1321.

Weston, R.E., 1955. Hydrogen isotope fractionation between ice and water. Geochim. Cosmochim. Acta, 8:281-284.

Whalley, W.R., Ober, E.S., and Jenkins, M., 2013. Measurement of the matric potential of soil water in the rhizosphere. J Exp Bot 64 (13): 3951-3963

White, M.A., Whalen, P., and Jones, G.V., 2009. Land and Wine, Nature Geoscience, 2: 82-84.

White, Robert E., 2009. Understanding Vineyard Soils. Oxford University Press, 230 p.

Wilson, J.E., 1998. Terroir: The role of geology, climate and culture in the making of French wines: University of California Press, 336 p.

Winkler, A.J., J.A. Cook, W.M. Kliewer, and L.A. Lider, 1974. General Viticulture: University of California Press, Berkley, CA, p. 287-337.

Zimmermann U, Ehhalt D, Munnich K. 1967. Soil-Water movement and evapotranspiration: changes in the isotopic composition of the water. In Conference on Isotopes in Hydrology Vienna 567–585.

Curriculum Vitae

SNEJANA KARAKIS
University of Wisconsin-Milwaukee
Department of Geosciences

EDUCATION

University of Wisconsin-Milwaukee, Milwaukee, WI

2017 **PhD: Geosciences,** Advisor: Dr. Barry Cameron

Dissertation: Terroir Studies in Wisconsin and Washington American Viticultural Areas

2004 **MS: Geosciences**, Advisor: Dr. Barry Cameron

Thesis: Degassing Study of Subglacial Volcanoes in the Tuya Region of Northern British Columbia Using Water Content and Hydrogen Isotope Analyses.

2002 **BS: Geology/Geophysics**

POSITIONS

- Teaching Assistant	University of Wisconsin-Milwaukee (9/2012 – 12/2016)
- Lecturer	University of Wisconsin-Milwaukee (1/2012 - 5/2012)
- Adjunct Faculty	Carroll University, Waukesha, Wisconsin (5/2011 - 12/2011)
- Geologist	AECOM (7/2004 – 8/2012)
- Geologist	Ramboll Environ US Corporation (8/2012 – present)

RESEARCH GRANTS, SCHOLARSHIPS, AND AWARDS

2012-2016 Chancellor's Graduate Student Award (4 awards)
2012-2014 UWM Graduate School Graduate Student Travel Award (2 awards)
2012 Geosciences Department Conference Travel Award
2013-2014 UWM Geosciences Graduate Student Research Award (2 awards)

2014-2016 L. Joseph Lukowicz Memorial Scholarship (2 awards)
2014-2015 Wisconsin Geological Society Research Grant (2 awards)
2014 Geological Society of America Graduate Research Grant
2015-2016 Nelson Cherkauer Lasca Legacy Scholarship (2 awards)
2016 Dr. Katherine Greacon Nelson Memorial Scholarship

PUBLICATIONS

Karakis, S., Cameron, B., & Kean, W. (2016). Geology and Wine 14. Terroir of Historic Wollersheim Winery, Lake Wisconsin American Viticultural Area. Geoscience Canada, 43(4), 265-282. doi:http://dx.doi.org/10.12789/geocanj.2016.43.107

Karakis, S., Gulbranson, E, & Cameron, B. Insight into Grapevine Source Water Acquisition During Key Phenological Stages Using Stable Isotope Analysis. Submitted to Australian Journal of Grape and Wine Research (April 2017).

CONFERENCE PROCEEDINGS/ABSTRACTS

S. Karakis, B.I. Cameron, and K. Pogue (2016), Effects of Vineyard Soil Properties on Phenolic Compounds in Syrah Grapes from the Walla Walla Valley AVA, Washington, Proceedings Vol. 1 Session 4 Part 1 pg. 210-215, presented at XIth International Terroir Congress, Willamette Valley, Oregon, July 10-14.

S. Karakis (2014), Terroir of Historic Wollersheim Winery, Lake Wisconsin AVA, Prairie du Sac, Wisconsin, Abstract Vol. 46 No. 187-7 presented at 2014 Geological Society of America Annual Meeting, Vancouver, BC, Canada, October 19-22.

B.I. Cameron, **S. Karakis**, and B.S. Ketter, (2014), An Emerging Wine Region in Nova Scotia, Canada: Terroir Trials and Tribulations, Proceedings Vol. 1 Session 3, presented at Xth International Terroir Congress, Tokaj and Eger, Hungary, July 7-10.

B.I. Cameron, B.S. Ketter, and **S. Karakis**, An Emerging Wine Region in Nova Scotia, Canada: Terroir Trials and Tribulations, Abstract H53F-1590 presented at 2012 Fall Meeting AGU, San Francisco, California, 3-7 Dec., 2012

B.I. Cameron, S. Boscov **(Karakis)**, A.H. Peterson, and K. Roggensack, Degassing of Subglacial Volcanoes in British Columbia and Iceland Revealed by Hydrogen Isotopic Analyses, Geological Association of Canada meeting, Halifax, Nova Scotia, Abstracts Volume 30, p. 23-24, 2005.

B.I. Cameron, K. Roggensack, S. Boscov **(Karakis)**, and A.H. Peterson, What's it Tuya: Ice Thickness Determined From H_2O Contents Measured in Glasses From Subglacial Volcanoes in British Columbia and Iceland, EOS Transaction, American Geophysical Union, v. 85 (52), Fall Meeting Suppl., Abstract V12B-04 (Invited), 2005.

B.I. Cameron and S. Boscov-Parfitt (**Karakis**), Degassing at basaltic tuyas in northern British Columbia: Insights from the hydrogen isotopic composition of glasses and whole rocks, EOS Transactions, American Geophysical Union, vol. 84 (46), Fall Meeting Suppl., Abstract V42B-0367, 2003.

T.A. Baxter, S. Boscov-Parfitt (**Karakis**), H.S. Bretzmann, P.J. Schmitz, A.I. Shultis, T.W Temme, M.J. Lahr, K.A. Sverdrup, and V.S. Cronin, Detailed Gravity Profile Across the Waukesha Fault, SE Wisconsin, GSA Abstracts with Programs, Vol. 34, No. 2, p. A-81, 2002.