

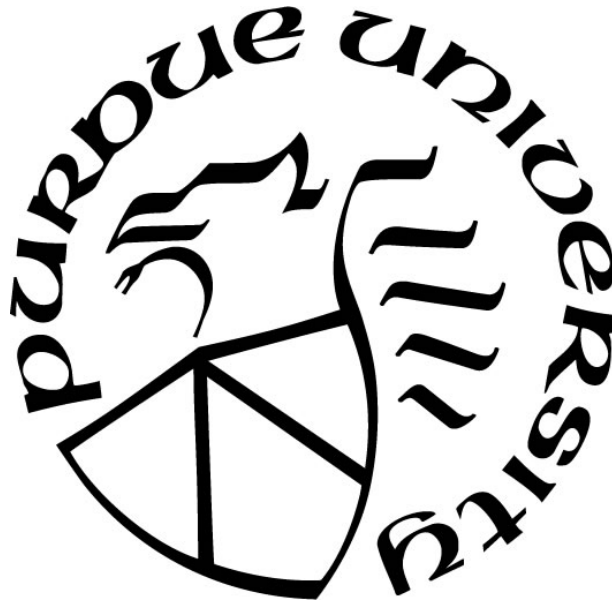
**TRANSFORMATION OF THE HYPERARID DESERT SOILS IN
AREQUIPA PERU DURING FOUR DECADES OF IRRIGATION
AGRICULTURE**

by
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A Thesis

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This work has been performed with the deep love I feel for Arequipa, the land of my grandparents, and dedicated especially to them, who sowed in me the love that today is reflected in this work.

El siguiente trabajo ha sido realizado gracias al enorme amor que siento por Arequipa, la tierra de mis abuelos y está dedicado especialmente a ellos, quienes cultivaron en mí el amor que hoy se ve reflejado en este trabajo.

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LIST OF ABBREVIATIONS

ANA	Agencia Nacional del Agua
AUTODEMA	Autoridad Autonoma de Majes
CEC	Cation Exchange Capacity
CIEPA	Centro de Investigación, Enseñanza y Producción Agrícola
EC	Electrical conductivity
FAO	Food and Agriculture Organization
INEI	Instituto Nacional de Estadística e Informática
MEF	Ministerio de Economía y Finanzas
MINAGRI	Ministerio de Agricultura y Riego
MINAN	Ministerio del Ambiente
MINCETUR	Ministerio de Comercio y Turismo
ONERN	Oficina Nacional de Evaluación de Recursos Naturales
SIC	Soil inorganic carbon
SOC	Soil organic carbon
SOM	Soil organic matter
UNSA	Universidad Nacional de San Agustín

ABSTRACT

The growth in the human population increases the global demand for food. However, in countries with limited arable land and abundant water, it means expanding into marginal lands or fragile ecosystems and mining non-renewable water resources to meet that demand. Converting deserts into productive agriculture heavily depends on distant water supplies and efficient irrigation methods. In Peru, nearly 32 million people rely heavily on human-made coastal irrigation agricultural hubs that rely on water from melting glaciers, snowpack, and rain transported by rivers and canals from high in the Andes. However, Peru's water resources are in a vulnerable state as climate change has shifted rainfall patterns causing glacier retreat affecting nearly the loss of one-third of the glaciers. In recent decades, an increase and expansion of irrigation projects in Peru require agriculture practices to consider environmental impacts directly. Now is the time to explore the sustainability of the desert agroecosystems and understand how different water management practices influence the supporting soil's health so decision-makers can plan for future change in water resources and any feedbacks to the productivity of the soils.

The increase in the global population, changing food and goods consumption patterns, and the expansion of irrigated agriculture has drastically increased the global demand for freshwater. In many parts of the world, there are significant spatial and temporal variations between the demand for water for irrigation and cities and its availability, leading to severe water scarcity. In some of these places, a large percentage of national populations rely on water sources like glacial melt, distant high mountain precipitation, and snowpack, which are also disappearing at an alarming rate due to a regional warming climate. In the nation of Peru, these challenges converge 65 % of Peru's 33 million people live where there is only 5% of the nation's water supply. Over the past 40 years, Peru has led some of the largest scale water management projects on earth to convert infertile coastal desert soils into irrigated agricultural land. Still, these efforts can come at a severe local cost with impacts to groundwater quality, salination of the soil, toxic concentrations of trace metals due to evaporation, and overuse of fertilizer and pesticides.

This thesis presents a study to assess how drip irrigation impacts desert soil chemistry within one of Peru's desert irrigation projects in Arequipa's southern district. We explored a chronosequence of drip irrigation in vineyards of 9-, 16- and 35- years. Results showed that both soil carbon and salinity accumulated progressively over time but that spatial accumulation patterns

were influenced by proximity to the irrigation drip line. By 35 years, salinity levels exceeded what would be tolerances for most crops. Trace metals, such as Mn, Zn, and Ni, increased with time under drip irrigation and have significant relationships with Fe, present in the highest concentrations, seemingly controlling the patterns due to co-precipitation. However, no trace metals were found in quantities that would exceed Peru's limits for agricultural soils. While drip irrigation is considered a water conservation strategy and widely promoted in the region over other irrigation techniques like high water volume furrow irrigation, its use may accelerate localized negative impacts to surface soil health. These progressive changes highlight the need for effective monitoring and salinity mitigation strategies in the region. This project is part of the bilateral technical program between Purdue University and Universidad Nacional San Agustín (UNSA) called the Arequipa Nexus Institute for Food, Water, Energy, and the Environment.

CHAPTER 1. INTRODUCTION

1.1 Irrigation farming in arid environments

According to the World Atlas of Desertification, drylands are defined as tropical and temperate areas with water scarcity as characterized by seasonal climatic extremes with an aridity index (AI) less than 0.65 (Cherlet et al. 2018). While there are several ways to calculate AI, the UN defines it as the ratio of the annual precipitation to the potential evapotranspiration (Cherlet et al. 2018) and is frequently used to designate specific climate regimes and monitor drought events. The aridity classification used by the FAO (2009) divides drylands into subtypes of hyper-arid ($AI < 0.05$), arid ($0.05 \leq AI < 0.2$), semiarid ($0.2 \leq AI < 0.5$) and dry sub-humid ($0.5 \leq AI < 0.65$). However, recent works indicate that the AI is changing due to increasing CO₂ emissions and associated global warming, and consequently efforts have been made to design more accurate aridity models (Spinoni et al., 2015; Greve et al, 2019; Yang et al. 2019).

Arid lands are predominantly located in northern and southern-western Africa, southwestern and central Asia, northwestern India and Pakistan, and Australia (Lal 2004). In America, deserts are represented by the Chihuahuan desert, the Sonoran desert, the Mojave desert and the Great Basin in North America, and with the Atacama-Sechura desert and the Patagonian desert in South America. From the perspective of sustainable development, it is critical to make efficient use of resources to deliver both immediate and long-term benefits for the welfare of the people and the environment. Nowadays, however, many regions of the world are under risk of desertification and this situation is a developing hazard to the global population. Desert farming represents an opportunity to implement potentially long-term projects, if water resources are available, for enhancing crop production. Some examples of deserts transformed into agricultural lands includes but it is not limited to Australia, China, the Mediterranean Region, Jordan, India, Mexico, the Southwestern United States, Chile, and Peru (Prasad et al., 2004; Castellanos et al., 2005; Su et al., 2008; Vásquez-Rowe et al., 2017; Naber & Molle ,2017).

1.1.1 Desert Irrigation

Global demand for crops is increasing and driven by a growing population. Modern irrigation practices attempt to sustainably transform arid regions into zones of productive agriculture by compensating for the natural water deficit (Denef et al., 2008; Wu et al., 2008; Li et al., 2009; Su et al., 2010; Fallahzade & Hajabbasi, 2010; Paiva de Oliveira et al., 2013; Trost et al., 2013; Schwarz et al., 2017; Chen et al., 2018; Deng et al., 2018). In the global effort to increase food production, the demand for freshwater sources for irrigation has also dramatically increased, with about 70% of freshwater withdrawals worldwide (Sivakumar, 2011).

Effective desert farming depends on many variables but primarily upon the water supply and irrigation infrastructure system. An irrigation system consists of the natural environment and the physical structure for irrigation, and the skills required to operate such infrastructure. These considerations are part of what is known as irrigation management that aims to mobilize and use water resources to ensure that the agricultural activities are carried out without any adverse effects on the environment and health (Palacios, 1990). Unfortunately, in Latin America, the arid land's productive potential is not realized due to poor optimization and users with little experience in sustainable irrigation management.

Irrigation systems can range from traditional structures to highly engineered systems. They include, but are not limited to, surface irrigation, sprinkler irrigation, and drip irrigation. Furrow irrigation consists of small, parallel channels that carry water through the cropland, and is not the most efficient water conservation method in arid lands. However, it is accessible and inexpensive (Bjorneberg, 2013). Sprinkler irrigation supplies water to soil by spraying water through the air simulating rain to the soil surface (Bjorneberg, 2013). An advantage of sprinkler irrigation is to supplied moisture to the soil during the seedling germination period (Pasternak et al., 1985). However, a disadvantage is water loss is high due to water evaporation before reaching the soil within the sprinkled area (Abo-Ghobar, 1992). Drip irrigation consists of water application through point or line sources on the soil surface or shallow subsurface at low operating pressure. Drip irrigation can be divided into surface where the drip line is located at surface level and subsurface where the drip line is located below the soil surface (Martínez & Reca, 2014). Some disadvantages of the method are the need for consistent maintenance and monitoring to avoid mechanical or accidental damage. It also may cause salt accumulation near the plant root (Skaggs, 2001). A variation of this technique is the subsurface drip irrigation, where the entire root zone of the plant

is irrigated to avoid excessive evaporation and reduce the amount of water required below the soil surface (Wang et al., 2018).

1.1.2 Irrigation areas in Latin America

Agriculture is the largest water-use sector by far, accounting for about 70% of all water withdrawn worldwide. In general terms, Latin America and the Caribbean regions globally have the highest water availability per capita (28,000 m³) and represent the largest percent of agricultural land area (15%) of the world (Flachsbarth et al., 2015). However, the water resources are not accessible year-round and widely distributed geographically, and the arable land is often fragile and hard to access.

Latin American countries show great potential for expanding their irrigated areas to arid lands in order to strengthen local and regional economies and for enhancing food security, but in the region, the precipitation ranges vary according to the climate, and thus the total amount of water required for irrigation will also vary. In humid climates, irrigation might be necessary to avoid significant yield reduction during short drought periods; in subhumid climates, irrigation is necessary for drought periods that might occur during the crop season. While in semiarid and arid climates, crop growth may not be possible without irrigation (De Oliveira et al., 2009). Specifically, in South America, surface irrigation, i.e., furrow irrigation, is the dominant method accounting for the 95.6%; sprinklers contributed with 2.7%, and localized irrigation, i.e., drip and micro-sprinkler, account for only 1.7% of the surface irrigation (De Oliveira et al., 2009). Figure 1.1 shows the changes over time of the three Latin American countries with the most significant irrigation areas (Siebert and Döll, 2001; INEI, 2012a). Other important irrigated areas in Latin America include valleys of central Chile.

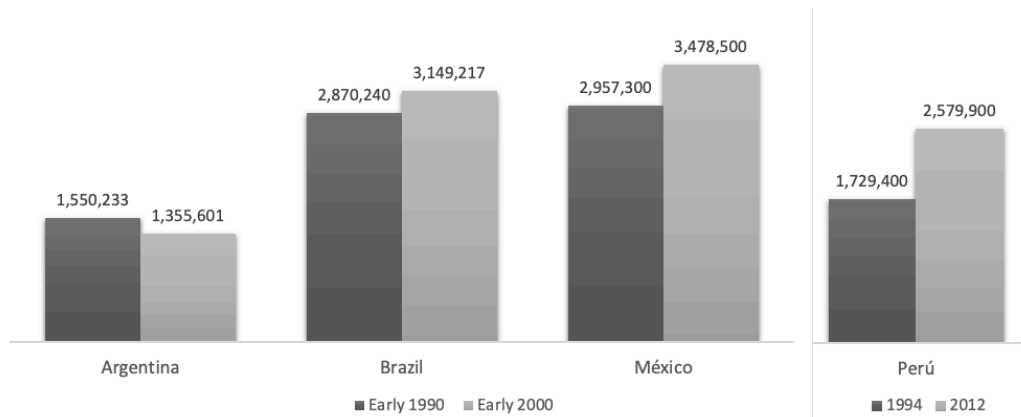


Figure 1.1. Changes in area of land under irrigation in Argentina, Brazil, Mexico and Peru. Numbers above the column indicate the irrigated areas (ha) in each country. Modified and extract from: Siebert and Döll, 2001 and IV National Census of Agriculture 2012-National Institute of Informatic and Statistic (INEI).

For the South American region, Palacios (1990) reported the following irrigation projects in Chile, the Conchi dam (1,400 ha), Rio Claro de Rengo (8,000 ha), Digua Project (65,000 ha), Coihueco dam (6,500 ha), and Convento Viejo dam (30,000 ha) and in Uruguay, the India Muerta Project (8000 ha) with several agricultural settlements such as the Bella Union, Berreta and Molinelli. According to Delgado (2013), in 1994, the World Bank listed the potential nine large irrigation system that currently are being developed: Chira-Piura (96,115 ha); Jequetepeque-Zaña (63,000 ha); Olmos (127,000 ha); Chavimochic (124,000 ha); Chinecas (51,000 ha); Majes-Sihuas (62,000 ha); Pasto Grande (9,500 ha); Tacna (18,000 ha), and the binational Puyango-Tumbes (20,000 ha in Tumbes, Peru) irrigation between Peru and Ecuador. It is expected that irrigation areas from irrigation projects in Peru to increase in total to 369 thousand hectares total between 211,500 new and 157,500 improved by 2030. The projects in Peru that seek improvements by 2030 are: Puyango-Tumbes with a total of 19,500 hectares; Alto Piura (Piura); 50,000 hectares; Chavimochic III, 111,500 ha; Olmos, 48,500 ha; Chinecas, 43,500 ha; Tambo Ccarocha-Canal Río Pisco, 68,000 ha and Majes-Siguas II with 38,500 ha (AGAP, 2016). In 2012 according to the IV National Agriculture Census, agriculture under irrigation was 36.2 % of the total agriculture surface, with Lima and La Libertad as the regions with the most superficial area under irrigation. In 2010, exports increased to 38% of the gross added value of agricultural production, up from 21% reported in 2000. With an increase in agricultural products sold in international markets, coastal regions such as Ica have found long-term sustainability problems due to water depletion (Vázquez-Rowe et al., 2017). Peru expects an imminent increase in the areas cultivated by irrigation,

requiring that particular agricultural practices be considered for the environmental impacts typical of desert agriculture.

1.1.3 Desert Irrigation in Peru

Peru has a total land area of 1,285,215 km². It is located on the west-central coast of South America, bordered by Ecuador and Colombia to the north, Chile to the south, Bolivia and Brazil to the east, and the Pacific Ocean to the west. The country is divided into three geographically distinct regions: The Coast, a narrow desert strip 3,080 km long that accounts for 11.7% of Peru's territory with a population of almost 19 million inhabitants, according to the National Census of 2017. The Highlands (Andes) in the Andean Mountain Range with an area that represents 27.9% of the country's territory and contains 9.2 million inhabitants. The Amazon Jungle, the largest region occupying 60.4% of Peru's territory with 4.5 million inhabitants (INEI, 2018).

Peru's coastal area is warm and dry due to the Humboldt Current's influence and the orographic effect of the Andes mountain range on the air masses coming from the Amazon Basin. The Andean Highlands has a dry climate with cold temperatures that varies according to altitude. On the other hand, the climate is tropically hot and humid in the Amazon jungle, with high precipitation and little temperature variation throughout the year. (FAO, 2003). The coastal region has 57% of the currently irrigated land in Peru, while the Andes and Amazon region have respectively 38% and 5% of the total irrigated surface. However, not all the potential irrigated land has been put into production (ONERN, 1967; Alva, 1976; INEI, 2012a). Although Peru has three important water sources, the Pacific Basin, the Atlantic Basin, and the Titicaca Basin, the country's water is unevenly distributed. The Pacific basin has the highest deficiency of surface water with the highest water demand due to the greater concentration of population and industries activities, like mining and agriculture, compared with the other two basins. In contrast, the Atlantic basin has the most significant availability of surface water with minimum demand.

In general, irrigation systems in Peru can be divided into four main categories or types: surface, drip, sprinkler, and exudation. Surface irrigation is where water flows by gravity over the soil. Sprinkler irrigation applies water to the soil by sprinkling water onto the soil surface. Drip irrigation is the application of water through a line source at a small operating pressure in a localized way. Exudation irrigation, or surface irrigation with a porous pipe, is where water is applied continuously through a porous tube that exudes in its surface in the entire length or in part

of it. Furrow irrigation is the least water-efficient, while drip, sprinkler, and exudation are water-efficient techniques. In Peru, furrow irrigation is used in more than 1,590,500 hectares representing 88% of the country's irrigated surface, while drip and sprinkler irrigations are used in 7% and 4.8%, respectively (INEI, 2012b) (Figure 1.2). Furthermore, drip irrigation is concentrated in the coastal region; almost a million hectares of land are irrigated on the coast, and about 13.2% (from the total irrigated area) uses drip irrigation (INEI, 2012a). Crops cover an area of 1,808,302 hectares representing 70.1% of the irrigated agricultural area, while the remaining 29.9% or 771,598 hectares are fallow areas (INEI, 2012b).

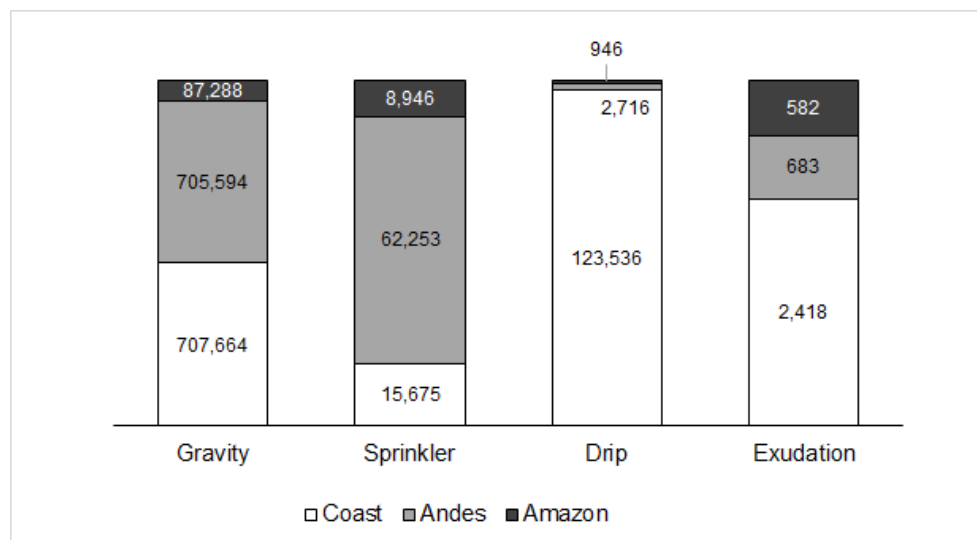


Figure 1.2. Relative contribution of water efficient irrigation systems used in the Peru. Numbers show the areas irrigated (ha). For representation purposes, furrow irrigation is not shown in this figure. Modified and extract from: IV National Census of Agriculture 2012-National Institute of Informatic and Statistic (INEI).

1.1.3.1 Evolution of irrigation in Peru

The idea of extracting water from the rivers that drain the Andes to irrigate the arid coast was already used by the native inhabitants of Peru's coast (Nordt et al., 2004). Before 900 BC, practices were based on floodwater farming in marshlands along the valley floors, and they were supplemented progressively by the construction of elaborate gravity-fed irrigation systems. It was relatively simple to divert water from the east side of the mountains (Park, 1983). Pre-Hispanic irrigation was strongly developed by ancient civilizations on the North coast of Peru. These ancient irrigation systems have been extensively studied and documented (Willey, 1953; Kus, 1974; Farrington, 1974; Farrington & Park, 1978; Nordt et al., 2004; Hayashida, 2006; Huckleberry et

al., 2012; Goodbred et al., 2020). Agriculture has been practiced for more than 5,000 years on the northern coast of Peru. Peruvian ancient civilization methods of water distribution included aqueducts and irrigation canal systems. In the Andes, terraces were built to take advantage of the mountain slopes to crop and counteract erosion. The engineering of terrace agriculture reached its peak with pre-Hispanic cultures of Huarpa, Wari, and Inca (Goodman-Elgar, 2008; Londoño, 2008; Londoño et al. 2017; Castro et al. 2019). In Southern Peru, terrace agriculture has been practiced for more than 15 centuries in the Colca Valley. This ancient soil management has dramatically altered the properties of the Mollisols in the area. After the Spanish conquest, cultivation ceased on most terraces; some remnants terraces are currently used for agriculture or were renovated in recent years (Londoño et al., 2017).

Cultivation systems in the Andes were developed before the Inca empire by 8,000-5,000 B.P.; crops such as peppers, beans, lucuma, quinoa, cañihua, and potato were domesticated. Maize cultivation dates from 6,000 B.P. along the Peruvian coasts and from 2,900-2,000 B.P. in the Central Andes. (Halloy et al., 2005). The Terraces were designed to take advantage of the slopes more efficiently due to the stepped design, which leveled the terrain by sections and expanded the total cultivable area. Terraces of the Colca Valley encompass more than 14,000 hectares of fields with evidence dated from 2,250 and 2,750 B.P. For irrigation, Peruvian terraces used complex webs of water channels from the mountains or springs (Treacy, 1987; Inbar & Llerena, 2000). These agricultural systems are also present in other regions of the world, such as Mediterranean landscapes (Bevan and Conolly, 2011).

Large irrigation projects started with ancient pre-Hispanic cultures. The Chimú and Inca empire built public administrative centers that helped establish stable management of the irrigation systems (Hayashida, 2006). In the 1950s, modern large irrigation projects started to take shape along the Peruvian coast with public and private investment (FAO, 2000). According to the Fourth National Agricultural Census of 2012 (INEI, 2012a), as a result of these large-scale projects over the previous 50 years, the irrigated area has increased by 133 percent (Figure 1.3). Also, the water used for irrigation has seen an increase of approximately 6,000 km³ in the last 50 years (Table 1.1).

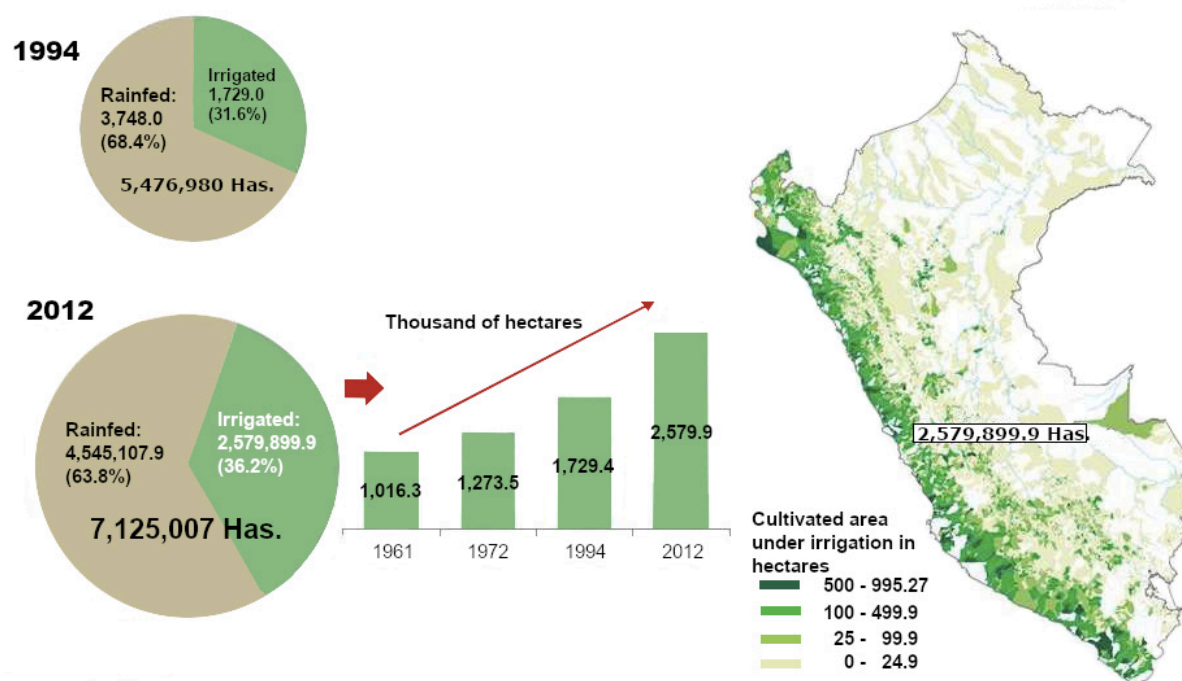


Figure 1.3. Diagram of the increase of type of irrigation techniques from 1994 to 2012 and map of cultivated area on census units under irrigation in hectares in Peru. Extracted and modified from: report of IV National Agriculture Census (INEI 2012)

Table 1.1. Variation of water demand by agriculture irrigation through time by agriculture irrigation in the Peruvian coast from 1964 to 2015. Source: Project “Integrated management of water resources in ten basins- PGIRH” (Proyecto “Gestión integrada de los recursos hídricos en diez cuencas- PGIRH”)-ANA 2017

Year	Water used for irrigation (km ³)
1964	8,000
1969	9,000
1976	9,700
1984	11,300
2004	14,000
2012	14,051
2015	14,400

Typical irrigation systems in Peru generally use large volumes of water compared to water used in cities and industry. Therefore, there is a high competition for water resources. Improved

water management practices in agriculture can lead to important benefits in terms of water availability for expanded agricultural activity and society at large, which could reduce conflict. New technologies for efficient water management in medium to large irrigation schemes such as remote sensing may allow an efficient monitoring of crop water requirements over extended areas and make information readily available to decision makers.

1.1.4 Importance of arid agricultural economics in Peru

Trade can be a fundamental ally in developing countries to combat food security and achieve environmental efficiency. Flachsbarth et al. (2015) indicate that the global agricultural market share of Latin America and the Caribbean doubled between 1980 to 2010, from 9.5% to 8.1%, respectively. Peru is a diverse country due to the climatic, natural, and cultural variations of its regions. It has rich deposits of copper, gold, silver, lead, zinc, natural gas, petroleum, and urea. Before the COVID-19 outbreak, Peru had achieved significant macroeconomic performance advances, with a very dynamic Gross Domestic Product growth rate (USD 6,941.2 per capita; WBG, 2019). The country's main economic activities include agriculture, fishery, mining, the exploitation of petroleum and gas, and the manufacturing of goods, most notably textiles (INEI, 2018). Peru has several Free Trade Agreements with the United States, China, Thailand, the European Union, South Korea, Canada, Costa Rica, Chile, Honduras, Mexico, Venezuela, Panama, Singapore, Cuba, Japan, and the European Free the Trade Association. The traditional and nontraditional main exports include gold, copper, petroleum oil, natural gas, zinc, lead, iron, fishmeal, quinoa, grapes, asparagus, mangoes, cacao, berries, and coffee (MINCETUR, 2019b).

Agriculture Sectors in Peru Supported by Irrigation

Peru is a country that exports many of its raw and produced materials. According to the decree supreme N° 076-92-EF of the Ministry of Economic and Finance (MEF), exportations are divided into traditional and nontraditional (BCR, 2011). Traditional exports are the products that have been historically exported, and their value represents most of the country's exportations. Subsequently, nontraditional exports are exports of the new or non-typical products; usually, the exportation is minimum. Agricultural products classified as traditional exports are called "rest of

agricultural," which consists of coca leaves and derivatives, coffee, sugar, molasses, wool, fresh leather, and chancaca (raw, unrefined sugar from sugarcane).

Most agricultural exportation is considered nontraditional export. The top 10 crops produced for exportation are asparagus, organic banana, avocado, artichoke, mango, cranberry, grape, tangerine, onion, garlic, and pomegranate (MINCETUR, 2019b). In 2018, nontraditional fresh produce exports grew 8%, for a total increase of 24% per year over the last decade. The United States is the main destination for fresh agricultural produce, with 32% of the total exports, followed by the Netherlands (15%), Spain (6%), the United Kingdom (5%), and Ecuador (4%). The January 2019 trade report of the directorate-general for research and studies on Foreign Trade of the Ministry of Commerce listed grape as the nontraditional crop with the highest exportation of 1.9% of the national exports followed by blueberries with 1.8%; avocado, 1.8%; asparagus, 1.2%; mango, 0.8%; cacao, 0.6%; and citrus, 0.5%, respectively (MINCETUR, 2019a).

Viticulture is one of the principal economic activities in the Peruvian coast. As of 2017, Peru was the 21st largest producer of grapes globally and third in Latin America, following Chile, ninth place globally, and Argentina, 10th place globally. However, Peru holds an eighth place on global fresh table grape exports with Chile in the first place (MINAGRI, 2019). According to the General Directorate for Monitoring and Evaluation of Policies (Dirección General de Seguimiento y Evaluación de Políticas - MINAGRI), grape production value increased exponentially in the last 20 years from 152.6 to 909.6 million soles (Peruvian currency). Grape production in Peru can be divided into two areas: northern and southern. The northern production zone is in the La Libertad region, while the southern zone comprises the following regions: Lima, Ica, Arequipa, Moquegua, and Tacna (MINAGRI, 2008). Ica is the region with the highest area cultivated with grapes, while Arequipa ranks third largest with 9 percent of total agricultural land cultivated to grapes. However, Arequipa is the region with the highest yield of total grape production (MINAGRI, 2008). Grapes from La Joya are mainly used for producing wine (Zhang, 2012). One advantage of Peru's grape production is that Peru can produce grapes year-round. It provides a unique opportunity for exportation during the northern hemisphere winter, especially when the grape season goes from May to December.

Peru is geopolitically divided into 24 regions and one constitutional province. The Arequipa region is in southwestern Peru. It consists of 63,345 km², divided into eight provinces: Arequipa, Camaná, Caravelí, Castilla, Caylloma, Condesuyos, Islay, and La Unión. Arequipa city

is the region's capital and is the second-largest city in Peru (INEI, 2015). A total of 1,965,269.61 ha of the Arequipa region are classified as areas with potential for agricultural activities. From that area, 7.5% corresponds to agricultural lands, 76.9% to grasslands, 7.5% to the forest, and 8.1% to other uses (GRAG, 2019). From the agricultural lands of the Arequipa region (37,834 ha), 33,186 ha require irrigation and 4,648 ha depend on rainfall. The irrigation systems used are gravity (90.40%), drip irrigation (7.20%), sprinkler irrigation (2.40%), and exudation (0.03%). This data corresponds to the year 2012 and is found in GRAG (2019). The main economic activities of the Arequipa region are agriculture, fishing, and mining, with a remarkable garlic production of 73.9% of the national production, followed by onion production, 59.3%; alfalfa, 43.8%; squash, 24.0%; quinoa, 21.2% and artichoke, 21.2% (INEI, 2015). Arequipa exports for year 2019 included 3,770,069 kg of garlic, 3,773,077 kg of pomegranate, 2,439,85 kg of grapes and 1,221,748 kg of avocado (GRAG, 2019).

Description of Arequipa Region: Climate, Soils and Geography

Arequipa is one of the 24 regions in which Peru is divided. It is located in the southwestern part of Peru, bordered with Ica and Ayacucho regions to the north, Apurímac, Cusco, and Puno region to the east, the Moquegua region to the south, and the Pacific Ocean to the west. Arequipa geography is rugged with volcanic activity crossed from north to south by derivations of the Andes' Western Cordillera. The Arequipa Region can be physiographically divided into the Coastal Cordillera at the west flank of the Andes Mountains (coast) and the Highlands (Andes). Altitude ranges from sea level up to 6,398 meters above sea level. The climate in the region closely depends on the altitude: along the coast it is warm and cloudy with temperatures between 12°C to 29 °C and in the Andes Highlands, it is dry and varies from warm to intensely cold during the daytime. The average temperature in the highlands is 14°C with frequent presence of "heladas", ice and hail during winter. Also, precipitation is in the form of small drizzles from 0 to 50 mm along the coast and ranges from 100 to 900 mm in the highlands (BCR, 2012). Along the coast, its arid desert regions are divided into four types; hyperarid, arid, and semi-arid (Figure 1.4). The predominant landscape is known as "planicie" of relatively flat terrain with a 0-4% slope with an alluvial, colluvial, eolian, colluvial-alluvial, and marine sedimentary structures.

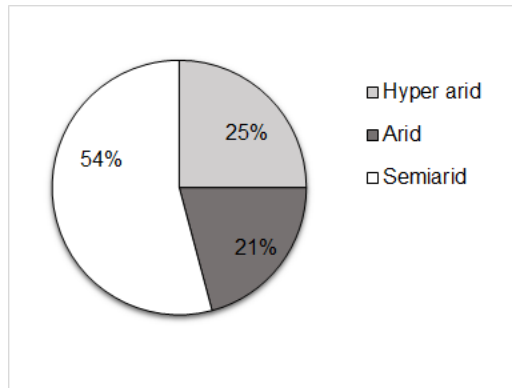


Figure 1.4. Distribution of Peru's arid lands (data from Le Hou  rou 1996)

Arequipa's soils, as all soils in general, can be classified and described using a hierarchy classification system known as Soil Taxonomy. Soils that share the same physical and chemical properties, mineralogy, and formation processes are classified in the same Series - the base category of the United States Department of Agriculture (USDA) national soil classification system. A soil series is described and assigned a name, usually after the place where it was first described or where it can be found the most. In 1985, a Peruvian Supreme Decree N  033-85-AG established the basis of soil survey regulations in Peru with uniform sets of guidelines and technical procedures. Due to the consolidation of governmental administrative offices, a necessity arose to upgrade the regulations in 2009. Until 2009, the Peru government encouraged, but not mandated, the use of the USDA Soil Taxonomy (MINAGRI, 2009) or any other similar system for soil survey. However, the use of Soil Taxonomy was made mandatory for official reports under the current regulation of soil survey as established by the Supreme Decree N  013-2010-AG (MINAGRI, 2010). The soil survey regulation will be updated every 25 years. Also, the government established "Clasificaci  n de Tierras por su Capacidad de Uso Mayor" a system that classified land according to a given aptitude for the sustainable use of optimal and permanent productivity under an established management system (ARMA, 2016). Chapter 2 of this thesis provides a detailed description of the soil classification of the sites investigated in this study. In brief, there are a total of six soil orders in Arequipa region, and the most predominant is Aridisol, with 42% of the region territory.

Arequipa's rugged geography of deserts and inter-Andean valleys only makes it possible for agriculture to be carried out in a small area of the region. Only 6.8% of the region's territory can be cultivated naturally to annual and permanent crops, without significant landcover and

hydrological modification, due to climatic and edaphological conditions (ARMA, 2016). As of 2012, there were 127,890 ha under irrigation in the Region of Arequipa, representing 6.5% of Arequipa's land area (INEI, 2012c). Given temperature constraints, cultivated agriculture in the region is difficult above 3,500 m.a.s.l. However, warm and stable temperatures along the coast make it possible to produce crops all year round, which is an advantage for export production. Another advantage of the Arequipa coast is their plain relief, which is ideal for cultivating large areas using mechanized systems. The warm climate, the low relief topography, and the altitude make the desert the only environment where agriculture can be expanded if irrigation is available. Arequipa's agriculture coastal areas require high investment in water resource infrastructure. Prior to the advent of desert irrigation in Arequipa 46% of all cultivated land was in the coastal valleys; by 1996, 85% of the region's cultivatable land is from both valleys and irrigated desert (Obando, 1996). According to the IV National Agricultural Census (INEI, 2012b), 55% of the land along Peru's coast can still be transformed into agriculture.

Pampas de Majes and Majes-Siguas Irrigation Project

Arequipa is home to one of Peru's main irrigation projects. The Majes-Siguas project is near the coast and spans the pampas de Majes and Siguas (Figure 1.5). The region approved for irrigation is 104 km west of Arequipa city and bounded by the Siguas River in the south and Majes River in the north. It has a width of 45 km and an average altitude of 1,400 m (16° 10' and 16° 29' S; 72° 14' and 72° 24' E). The Majes-Siguas irrigation project was originally conceived in 1960s as a two-stage project: Majes and Siguas (ONERN, 1975). The original soil survey for the irrigation project, performed by Electroconsult-ELC, identified 23,000 ha suitable for agriculture in Majes (ONERN, 1975). The project was divided into two stages: the first was named Majes-Siguas I or "Majes Irrigation" with approximately 16,000 ha currently in irrigation (AUTODEMA, 2017). The second phase was named Majes-Siguas II or "Siguas Irrigation" with an additional 38,500 ha in Siguas and 7,000 ha in Majes for a total of 45,500 ha. The project started in 1971 with the first stage, but the first settlers migrated to the area in 1983. The Majes-Siguas II project is set up to begin sometime in 2020. The two stages targeted different types and scales of agriculture. The first stage was designed for helping the small family farm in Majes, while the second part was designed exclusively for intensive agroindustry dedicated to exportation activity.

Water for the project was first supplied from the Conderoma reservoir in 1983. The reservoir, supplied by the Colca River, holds a million cubic meters of water (Maos, 1985).



Figure 1.5. Location of Majes-Siguas Irrigation project diagram. Modified and extracted from Executive Summary- Municipality of the Majes district, Majes, Arequipa, Peru (Resumen Ejecutivo- Municipalidad de Distrital Majes, Arequipa, Perú)

Changes to the nature and quality of desert soils under irrigation

The conversion of desert soils to agricultural soils entails a change in the soils' original physical characteristics (Shang et al., 2019). Agricultural practices, including irrigation, assist the conversion of desert soils by increasing soil organic matter, soil moisture, microbial communities, and aggregates formation (Vieira Guimaraes et al., 2013; Ghosh et al., 2016; Li et al., 2019; Nayak et al., 2019). Because the initial conditions are not favorable for agriculture, due to salts, crusts, and a lack of supporting soil organic matter, farmers must adopt land management to improve soil conditions. Irrigated agriculture has the capacity to increase organic matter input from plant tissue both above and below ground (Ogle et al., 2005; Li et al., 2006; Li et al., 2009; Torst et al., 2013). Additionally, if the appropriate clay mineralogy and fine textures are available, soil nutrients can effectively accumulate and improve soil properties. Such conditions are desired to improve the predominantly sandy soil's quality to attain increased soil aggregate structure, cation exchange

capacity, and water holding capacity (Chai et al., 2019). Soil quality describes the chemical and physical conditions of the soil, and it helps in the decision making of more sustainable agriculture practices. Additionally, increased soil moisture and soil organic matter enhances microbial growth and diversity-supporting plant growth (Shang et al., 2019). Irrigation, however, can also present adverse effects in soils. Salinization, caused by evaporation of irrigation water, reduces soil microbial activity, alters osmotic pressure in plants, and decrease soil organic matter quality (Chen et al., 2017; Nunes et al., 2007). Farmers need to consider the positive and negative effects of irrigation on their soil. For example, the farmers in the Majes region choose crops such as alfalfa to bring benefits to soil quality, such as increased organic matter, the formation of soil aggregates, and leaching of preexisting salts during the spray irrigation needed to maintain the alfalfa (Sainju & Lenssen, 2011; Stensrud, 2016a; Zapana, 2018).

1.2 Soil Quality in Arid Environments:

Soil health and soil quality are terms used to help farmers evaluate soil conditions for suitability to agriculture. Soil quality is defined by the soil's functions to sustain biological productivity and maintain environmental quality (Doran & Parkin, 1994), while soil health defines the soil broadly as a living ecosystem and its ability to provide a provisional or ecosystem service (Bünemann et al., 2018). The main difference between both terms is the complexity of measuring soil health in contrast with the soil quality; therefore, soil quality is frequently used by land managers (Bünemann et al., 2018). Agricultural management practices influence soil quality. For example, irrigation can improve soil quality by increasing above and belowground biomass (Chen et al. 2018), which enhances soil organic carbon. The increase of soil organic carbon (SOC) under such systems has mainly been attributed to the input of plant residues, root biomass, and associated microbial residues (Yang et al., 2013; Yost, 2019). Soil organic matter development in a barren desert or other hyperarid soils is a critical variable in consideration of the evolution of soil quality and soil health in such systems, where a good quality soil will contain high organic carbon concentrations (Bünemann et al., 2018). In an arid ecosystem, physical and chemical factors often limit land quality, mainly soil texture, high salt content, and rugged topography. Naturally, soils in arid environments often have low organic content due to low plant input and low levels of soil microbial processes, but agricultural practices on desert soils can change that dramatically (Sainju & Lenssen, 2011). Agriculture can also have negative impacts by producing soil damage as

desertification and salinization become problems in an arid environment. Therefore, soil quality changes with cultivation practices help farmers develop sustainable agriculture practices in arid regions.

1.3 Water dynamics in desert irrigation

Agricultural lands in arid and semiarid environments are susceptible to salinity due to high evapotranspiration (ET) rates and the scarcity of water needed to leach the salts out the root zone (Singh et al., 2015; Villalobos et al., 2016). Salinization is the accumulation of soluble salts, mainly Na, Cl, and B in the soils caused by saline irrigation water, imperfect drainage conditions, uncontrolled irrigation, dry climate, and seawater intrusion in coastal areas (Villalobos et al., 2016; Okur & Orçen, 2020). Additionally, the high salt concentration in irrigated land might originate from the weathering of the parent material. Soil salinization is one of the main problems in arid and semiarid regions, and it affects nearly 1.1 billion ha in the world - nearly one-third of the irrigated land (Singh, 2018; Batistao et al., 2020). Arid soils often have high salt and sodium contents; therefore, soluble salts need to be removed from the root zone by leaching to avoid damage in plants and decrease in productivity (Nunes et al., 2017; Phogat et al., 2020; Merchán et al., 2020). Subsequent salinization from irrigation lowers soil quality by causing soil degradation and affects crop productivity by limit crop growth and reduces yield (Singh, 2018). Furthermore, soil salt content affects soil structure development, limits soil horizon differentiation, and have low organic content due to the reduced soil microbial function (Batistao et al., 2020).

Salts can accumulate in the soil profile and be removed by percolating water to dissolve the salts and mobilize them into the subsoil (Singh, 2018; Merchán et al., 2020). Salinization toxicity occurs when the plant absorbs and accumulates harmful ion species in high concentrations causing damage to crop (Villalobos et al., 2016; Singh, 2018). The effect of salinity in soils depends on the ion composition of soil salinity and the developmental stage of the plants (Zheng et al., 2009; Villalobos et al., 2016). Soil salinity, a measurement used to assess salinization, can be assessed as soil electric conductivity (EC) (dS/m) where most plants grow best when EC is below the threshold of 4 dS/m (Villalobos et al., 2016; Jahany & Rezapour, 2020). As early as 1970, agricultural reports identified that approximately 300,000 ha of cultivated land in Peru's Coastal Valleys were affected by high salinity, but it was not until 2012 that information about this problem was made widely available to land practitioners (FAO–ITPS, 2015). In 2009, the

country's water problem was addressed by the Peruvian government, emphasizing the threat of climate change, the urban population's growth, and mining activities (Stensrud, 2016a).

Additional negative implications of desert irrigation in the Majes area include slope instability. Lacroix et al. (2020) studied the impact of irrigation-based land-use change over 40 years (1978–2018) using satellite imagery and concluded that irrigation for desert farming might cause landslides, especially in sites with pronounced elevation differences in the deeply incised valley walls. The use of crops that require less water and therefore produce less water infiltration can help mitigate the environmental problem, but this is not always economically feasible and raises concerns about irrigation development.

1.4 Soil organic matter accumulation in Arid Environments

SOM originates from a variety of sources, such as dead or decaying plant and animal tissues and microbial residues (Contrufo et al., 2015; Liang et al., 2019). Three factors can contribute to the stabilization of organic carbon (Sollins et al., 1996; Creamer et al., 2011): a) chemical protection, b) physical protection and c) inherent structural resistance to degradation or recalcitrance. Chemical protection occurs when organic carbon is preserved by association with silt and clay particles through ionic bonding or via Van der Waals interactions especially with aluminum-silicates and iron hydroxides; on organic surfaces, organic carbon may sorb and become protected and persist in soil. Physical protection refers to the existence of physical barriers between organic carbon and soil pores or aggregates that delays or restricts microbial accessibility. Recalcitrance occurs when the molecular structure of SOM includes thermodynamically stable structures such as aromatic structures that are difficult to use as energy sources by microbial communities (Six et al., 1998; Cotrufo et al., 2015). However, most recent work (Marschner et al., 2008; Creamer et al., 2011) suggests that the turnover rate of SOC is controlled by the physicochemical protection rather than its molecular structure alone. Recently, microbial contribution to SOM has been included in conceptual models that describe the accumulation of organic nutrients in the soil, such as the soil continuum model (Lehmann & Kleber, 2015) that considers plant and animal litter as a continuous SOM input in continuous decomposition (Marín-Spiotta et al., 2014). Microbial residues also contribute to the soil carbon stock through mineralization or incorporation into soil aggregates (Cotrufo et al., 2013; Shang et al., 2019). This view is supported by the microbial carbon pump (MCP) framework that aims to understand the

role and resilience of microorganisms in the production of recalcitrant soil organic carbon (SOC) and C storage (Liang et al., 2017).

Worldwide, Pal et al. (2015) suggested that 684 Pg of SOC are contained in the uppermost superficial layer of the soil (from 0-30 cm), which is of agricultural importance. Arid lands store approximately 46% of the global carbon share, and from this amount, 78% corresponds to inorganic carbon in arid and semiarid environments (Pal et al., 2015; UN 2010-2020). A common feature of such ecosystems is the existence of islands of fertility that represents the accumulation of nutrients in the surface soil beneath woody plant canopies, so it is evident that nutrients are not evenly distributed (Austin et al., 2004). However, most of the C stored in arid lands is dominated by large concentrations of soil inorganic carbon (SIC) such as calcite and aragonite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and siderite (FeCO_3), probably to depletion overtime of the SOC pool in the surface layer because of wind and water erosion processes (Lal, 2009). In arid lands, soil moisture is expected to be the primary control on nutrient turnover, which is, in turn, controlled by rainfall events or by irrigation water input (Xie & Steinberger, 2001; Kurc and Small, 2007). Nitrogen (N) is also another limiting factor for plant nutrition and productivity, and for the C cycling (Peri et al., 2019) and so temperature and nitrogen (N) content can both alter the rate of SOC sequestration (Feng et al., 2002; Liang & Balser, 2012).

Valdivia-Silva et al. (2012) evaluated the distribution and deposition of organic and inorganic forms of carbon within an arid and semiarid region of Arequipa that are designated for irrigate agriculture, finding the lowest levels in the desert area of Pampas La Joya. In uncultivated hyperarid regions of northern Chile, Valdivia-Silva et al. (2012) found SOC (2 - 50 $\mu\text{g C/g-soil}$) to be much lower than soil inorganic carbon (SIC) (200-1,500 $\mu\text{g C/g-soil}$). In nearby arid and semiarid areas, SOC was present in higher amounts and directly related to humidity transects (120 – 465 $\mu\text{g C/g-soil}$), whereas SIC ranged from 73 -3,600 $\mu\text{g C/g-soil}$ and from 2,700-to 10,000 $\mu\text{g C/g-soil}$ in the top 0–10 cm, respectively. Agricultural management of such hyperarid or arid lands may alter the accumulation patterns of SOC and SIC at depth as a result of irrigation, which, ideally, can improve the interaction between soil microorganisms, organic residues, and plant roots to create more stable SOM (Jobbágy & Jackson, 2000). However, the agricultural intensification may also lead to the depletion of SOM and the pollution of ground and water bodies due to excessive agrochemicals and salt leachates (Rozemeijer & Broers, 2007; Agnelli et al., 2014; Burges et al., 2015).

The increase of soil organic matter in desert agricultural systems with time has been reported in the literature, and many common practices in dryland systems could be appropriate for use in hyperarid land management. For example, to study carbon accumulation, cover cropping experiments have been proposed to enhance nutrient cycling, especially in hot environments (Ashworth et al., 2020). In vineyard systems, a primary focus of this thesis work, an increase of the SOC in the top-soil, was achieved using organic-mulch or bluegrass (Goulet et al., 2004) or the incorporation of plant residues in grass-covered vineyards (Ruiz-Colmenero et al., 2013). Seddaiu et al. (2013) reported that tillage and grass-cover after 20 years also caused an increase in the SOC content in vineyard soils in a semi-arid Mediterranean environment.

In Peru, an additional negative aspect of desert irrigation is the potential for the accumulation of heavy metals from primary minerals, pesticides, contaminated irrigation water, and regional mining residues or dust (Lynch, 2012; Dunlap, 2019). With increase organic matter accumulation and crop root activity, there could be a strong interaction between SOM and heavy metals that concentrates metals in ag systems. Soil organic matter has large sorption and chelation capacity for metals, which influences metal speciation, transport, and bioavailability (Sauvé et al., 2000; Yin et al., 2002; Fest et al., 2008; Matijevic et al., 2014; Rahman et al., 2018; He et al. 2019). The affinity of metals to organic matter varies depending on the metal; for example, Pb and Cu are metals with relatively high affinity, while Ni will show a weak affinity (Fest et al., 2008; Rahman et al., 2018). Soil physical and chemical properties such as soil pH, cation exchange capacity (CEC), and metal transportation are affected by the interactions between organic matter and metals (Vieira Guimaraes et al., 2013; Ramseh et al., 2019) and, in turn, influence prevention of microbial decomposition of carbon pools (Quenea et al., 2009). Therefore, soils with higher organic carbon will have higher concentrations of heavy metals.

1.5 Project Goals:

There are few studies about the influence of agricultural practices on the content and dynamics of organic carbon and trace metals in perennial cropping systems in the hyper-arid region of coastal Peru to the best of our knowledge. Therefore, the goal of this thesis research was to obtain a better understanding of the impact of drip irrigation on the accumulation of organic carbon and trace elements, as well as those properties that influence the health of the soil, such as salinity, under one perennial crop, i.e., vineyards. Additionally, a chronosequence approach was taken to explore

the time the vineyards were exposed to drip irrigation in order to explore the evolution of soil over time.

The study site of this work is in the “Centro de Investigación y Enseñanza de Producción Agrícola (CIEPA)”, operated by the Universidad Nacional de San Agustín in the Majes irrigation region of Arequipa, Peru. At this site, vineyard plots of different ages of exposure to drip irrigation (35, 16, and 9 years) were investigated to explore how irrigation intensity and carbon input control SOC accumulation, metal associations, and soil chemical properties like salinity and pH. Vineyards systems provide the opportunity to study long terms effects of drip irrigation in a specific, fixed location, of both the rhizosphere of perennial crops under the drip lines and between the rows. It creates a unique opportunity for a chronosequence approach that can be extrapolated to other perennial systems in the region. In this work, the following hypotheses were tested: 1) Organic carbon accumulation is directly proportional to the vineyard age and time in irrigation; 2) spatial patterns of SOC accumulation are controlled by proximity to the drip lines; 3) trace element, and heavy metal, accumulation may be alternatively controlled by the degree of past flushing (application of furrow irrigation in initial land preparation to remove salts) or years under drip irrigation, which would permit salt accumulation near the drip line.

CHAPTER 2. STUDY SITE AND AREQUIPA REGIONAL SOILS

2.1 Arequipa's Soils and Climate

The Arequipa region has been geomorphologically influenced by tectonic activity related to compression, faulting, and uplift following the Andes orogeny. Other geomorphological forces that have influenced the region are volcanic activity, rainfall rate, marine and glacial sedimentation, and wind velocity and erosion processes (ARMA, 2016). Some of the major climatic and geologic events that emplaced the major soil parent materials are listed in Table 2.1.

The Arequipa region soil survey of 2016 identified six soil orders in Arequipa: Andisols, Aridisols, Entisols, Histosols, Mollisols, and Inceptisols (ARMA, 2016). In the coastal hyperarid region of Arequipa, soils are dominated by Aridisols and contain substantial amounts of CaCO_3 (ARMA, 2016). They contain subsurface horizons in which clays, calcium carbonate, silica, salts, and/or gypsum have accumulated. Andisols are soils derived from volcanic ash and characterized by highly variable soil organic matter content that, in some cases, can reach up to 33.1% and good soil physical properties (ARMA, 2016). Entisols are soils of recent origin with no genetic horizons other than possibly an A horizon in this region. Histosols are soils composed mainly of organic soil materials, approximately (20-30 wt % C), and are predominantly found in the perennially wet areas in the Andean uplands. Mollisols are formed under grassland ecosystems and are characterized by a thick, dark surface horizon. Inceptisols show minimal horizon development (Shoji et al., 1993; Soil Survey Staff, 2014). Aridisols, Andisols, and Entisols represent 41.9%, 30.2%, and 12.9% of the region, respectively (ARMA, 2016). In general, Arequipa soils are shallow, with low organic matter content and low cation exchange capacity. Additionally, the amount of assimilable potassium (K) is high, with phosphorus (P) content fluctuating from low to moderate concentrations (ARMA, 2016).

Soils in the Arequipa region are commonly also classified according to the agricultural practices and vegetation coverage. The total amount of land that supports agricultural activities comprises 4.3% of the region's total area, but faces problems such as extreme weather, poor soil quality, high salinity, and requires permanent irrigation to be productive. In contrast, those soils that are not suitable for agriculture (46.3%) are used for recreational activities or have been designated protected areas. The remaining areas include diverse soil categories. According to the

vegetal coverage, agricultural croplands represent 6.8% of the region's total surface and bare lands, 35.3%. The remaining coverage percent represent other coverage types, including urban areas, forests, and water sources (ARMA, 2016).

The Peruvian legislation (D.S.N 017-2009-AG) also officially requires soil series to be classified according to the primary land use as "consociations" or edaphic units. Under this consideration, Arequipa region soils are classified into 38 edaphic units (Table 2.1) with most of the land area comprised of the Vitor, Misahuana Mauras, Confital, Solamina, and Josefita consociations (ARMA, 2016). The Vitor edaphic unit's parent material is of alluvial origin and represents 25.2% of the land surface in Arequipa. The soil surface is frequently stony without vegetal cover, shallow with a depth of less than 25 cm, low organic matter content, good to excessive natural drainage, and pH ranging from 5.1 to 7.8. The Misahuana Maura consociation represents 9.7% of Arequipa's surface area, whose parent material was developed during the superior Barroso Event (Table 2.1). It has a relatively deep soil formation, not calcareous, with variable amounts of organic matter, moderate to excessive drainage, and vegetation cover dominated by grass and shrubs. The Confital consociation's parent material was developed during Tacaza and Inferior Barroso Event; it represents 8.3% of Arequipa's surface area and generally contains a high amount of organic matter. It has good drainage, with cover vegetation of the high Andean pastures. The Solimana consociation's parent material is a product of the superior Moquegua Formation; it represents about 9% of Arequipa's surface area and has good drainage and dominant grass vegetation. The Josefita consociation is an alluvial deposit that represents 6.8% of Arequipa. It has a moderate to excessive drainage and dry shrub vegetation and cacti (ARMA, 2016).

Table 2.1. Major edaphic units in Arequipa (Source: ARMA, 2016)

Edaphic Unit	Geologic Period and system	Age (Million years from the present)	Geologic stratified unit	Soil Subgroup	Area (ha)
Vitor	Neogene Miocene	5.3 to 23	Sillapaca Event	Typic Haplocambids	1,592,542.29
Misahuana Mauras	Neogene Pliocene	2.6 to 5.3	Superior Barroso Event	Typic Haplustands	615,649.04
Solimana	Paleogene oligocene	23 to 33.9	Superior Moquegua Formation	Typic Ustorthents	572,124.64
Confital	Paleogene eoceno	33.9 to 56	Tacaza Event	Typic Hapludands	527,025.03
	Neogene pliocene	2.6 to 5.3	Inferior Barroso Event		
Josefita	Paleogene oligocene	23 to 33.9	Superior Moquegua Formation	Lithic Haplocambis	430,797.40

2.2 Soils and Climate in Majes-Siguas Irrigation area

The Majes-Siguas irrigation region is in a super arid subtropical desert that extends along the Peruvian coast with altitude ranging from 950 to 1,750 meters above sea level (m.a.s.l.). The region spans 2,138 km² (Chapter 1, Figure 1.5). The annual average temperature ranges between 18°C and 20°C, with an annual total average precipitation ranging from 50 mm to 120 mm (Marquina, 2012). Three different sub-climatic zones have been identified in the Majes Irrigation area (Marquina, 2012): subtropical desiccated desert (75%), subtropical super arid desert (20.1%), and warm temperate arid desert (4.5%).

Soils in the Majes-Siguas Irrigation region developed in alluvial Pleistocene conglomerates with alluvial, alluvial pyroclastic, or alluvial mixed origin covered in places by a layer of recent wind depositions and colluvial material (ONERN, 1974; Marquina, 2012). It constitutes part of a coastal plain that ascends smoothly from the Coastal Cordillera to the Western Andean Flanks. It is characterized by a high percentage of sand, sandy loam, and coarse material transported from the Andes (ONER, 1974; MINAM, 1975). Due to poor development and prevalence of the parent

material's original mineral conditions, coarse fragments, pebbles, and rocks, the soils of Majes are considered young with a lack of development classified as either Entisols or Aridisols. According to the soil survey 2012 report (Marquina, 2012), they have minimum horizon development with either cambic or salic horizons. Majes is characterized by stratified soils with a high content of fine to medium gravel, sub-rounded to rounded fragments that increase with depth (ARMA, 2016). Soils have good natural drainage, medium to low fertility, slightly to moderate alkalinity (7.4 - 8.4 pH), low organic matter content (0 - 1.5 %), low levels of phosphorus (0 -3 ppm), and high concentration of potassium (>177 ppm) (Marquina, 2012).

Majes irrigation soils have been classified by two official expeditions, which has generated discrepancies in the number of orders. The study of the pampas of Majes and Sigvas (MINAM, 1975) identified 16 soil series: Pampa Alta, Terraza, Pumicita, Desierto, Coladera, Vitor, Majes, Boza, Cauce, Yesosa, Borde Quebrada, Alto Sigvas, Santa Rita, Gonzales, Pampa Alta Sigvas and Complejo Desierto-Cauce. A later study, Marquina (2012), identified 17 soil series with a difference from the early report, such as the designation of two new series: Pampa alta (superficial: depth of 15 cm) and Cauce irrigado, and the replacement of Pumacita series with the Ruta Quilca series. The dominant soil series is the Majes soil series that comprises an area of 22,872 ha (Marquina, 2012).

2.3 Study site: Centro de Investigación y Enseñanza de Producción Agrícola (CIEPA)

The research for this thesis took place at the Centro de Investigación y Enseñanza de Producción Agrícola (CIEPA); the agricultural research station of the College of Agriculture of Universidad Nacional de San Agustín (UNSA). It is located approximately 104 km west from the city of Arequipa in section B of the Majes District, Caylloma province (-16° 19' 29.5", -72° 12' 60"; lat,lon WGS84). It comprises a total area of 101.93 ha (Figure 2.1). CIEPA was established in 1983 by Autoridad Autonomía de Majes (AUTODEMA). It was transferred to UNSA in two stages, in 1995 and in the early 2000s. Since 2017, CIEPA management has consisted of a full-time field manager. Before that year, a professor from the College of Agriculture was regularly selected as a part-time manager. However, this situation, along with a limited budget, caused management issues, such as the lack of written records of water use and land practices.

2.3.1 History of CIEPA's Land and Water Management

CIEPA is divided into several experimental plots (Figure 2.1) that can be used for academic research. Crops farmed include alfalfa (*Medicago sativa* L.), citrus fruits (*Citrus* sp.), chili (*Capsicum* sp.), and maize (*Zea mays* L.). However, 15% of CIEPA's land is used for viticulture activities, and the research station produces and sells wine and pisco, a kind of Peruvian brandy. Seven varieties of grapes (*Vitis vinifera* L.) are grown in CIEPA, cv. Italia, Borgogna, Thompson, Alphonse Lavallée, Negra Criolla, Flamel, and Moscatel, including table grapes, wine grapes, and pisco grapes.

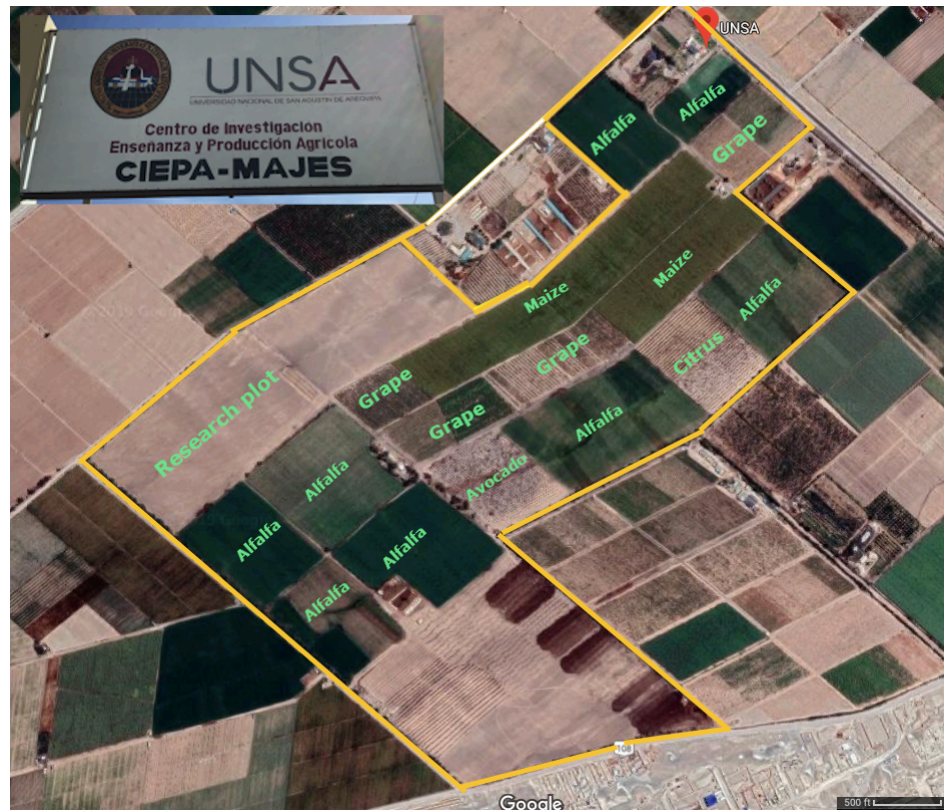


Figure 2.1. Crop distribution (2018) of the Centro de Investigación, Enseñanza y Producción Agrícola (CIEPA). Modified from Google Maps screenshot with approximate scale

While no written history of the management of CIEPA appears to exist, interviews of current and past land managers of CIEPA, including the current field manager (Eng. Julio Cesar Flores), former professors managers (Eng. Luis Zegarra, Eng. Lazaro Anculle), and a long term field engineer (Eng. Eloy Medina) were used to reconstruct the history of water and land use. A special focus was given to the land's vineyard section, which is also the vineyards plots of this

thesis's focus. Specifically, these plots (Figure 2.1) represent three out of the seven grape varieties grown at CIEPA: Borgogna grape, Negra Criolla grape, and Alphonse Lavallée grape. Borgogna grape is used to produce wine, while Negra Criolla is one of the varieties most frequently used in pisco production in Peru (Cacho et al., 2013). The Alphonse Lavallée variety is a French table grape (Aubert & Chalo, 2018).

One of the most important land practices that control the field's productivity is the type and extent of irrigation. Each of the three fields has a different history of water and land management that could impart distinct soil chemical characteristics. Based on the timeline of land use retrieved from the interviews, we can separate the three fields into the length of time the fields have been in irrigation, either with high volume furrow irrigation or low volume drip irrigation (Figure 2.2). Current CIEPA land management includes water to remove soil salt content, subsoiling, plowing with stone removal, and leveling the land. As is done commonly across the region (Stensrud, 2016a, 2016b) since the time of the settlers who introduced alfalfa to the area, the transformation of CIEPA desert land into agricultural land started with the use of alfalfa crops under sprinkler or furrow irrigation for at least five years to leach the high salt concentrations from the shallow soil (personal communication, Eng Julio Flores). Also, according to data collected by personal communication, the electrical conductivity of CIEPA soil ranged from 30 to 40 dS/m, before any land management; therefore, alfalfa is used to improve the soil conductivity (ideally to 3 to 4 dS/m) (Personal Communication, Eng. Eloy Medina; ONERN, 1975) by fixing nitrogen, reducing soil compaction and salt removal. However, it remains unclear when the use of alfalfa was first established as a salt flushing crop at CIEPA. Based on these criteria, Borgogna grape plot corresponds to the high flush plot because it was irrigated for 27 years in a combination of furrow and sprinkler before installation of the drip irrigation system. The Negra Criolla plot is classified as a medium flush plot, with five years of sprinkler irrigation before the use of drip irrigation and the Lavallée plot corresponds to the low flush, with no prior flushing irrigation management. Landsat satellite images (from 1984 to 2015) on vegetation coverage (Appendix A) corroborate the information about the expansion and evolution of CIEPA obtained from the land manager interviews. It can be observed (Appendix A) that agricultural expansion happened in patches, without any apparent order. Also, how crop diversification happened is unclear due to constant changes in the use of the field.

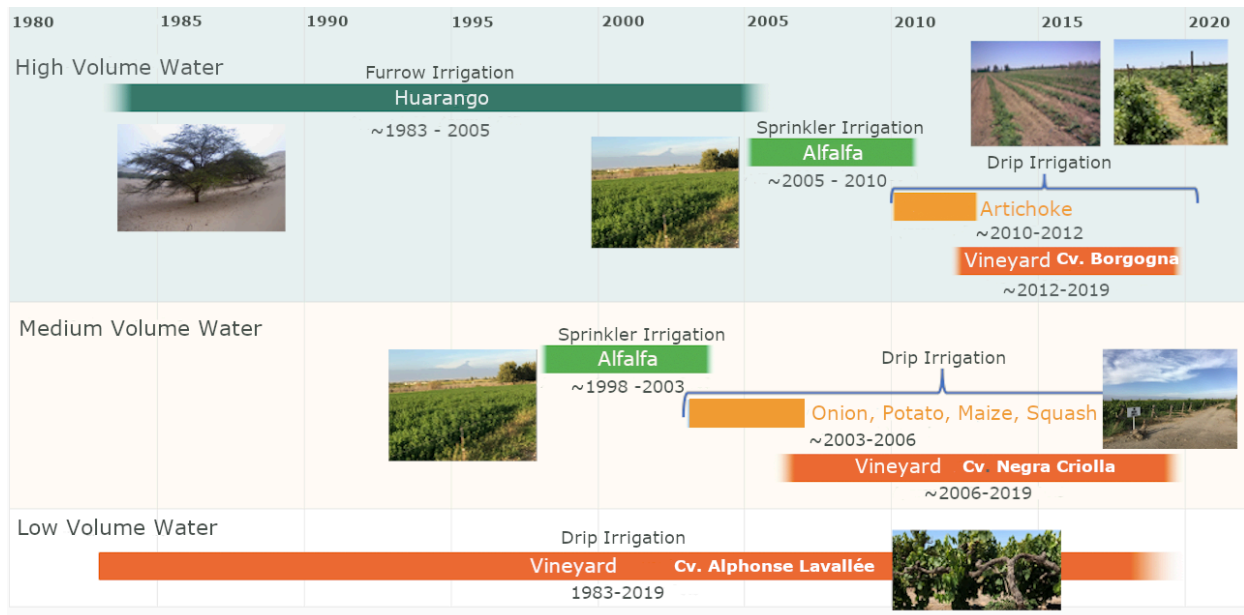


Figure 2.2. Timeline, based on interviews with current and past CIEPA managers, of land of Borgoña, Negra Criolla and Alphonse Lavallée vine plots arranged by water management: high flush, medium flush and low flush, respectively in the CIEPA, Majes Irrigation.

The plot corresponding to the Borgogna grape (high volume water) has been in grape cultivation since 2012. However, in 1983, when AUTODEMA managed CIEPA, the plot was planted with huarango, a mesquite family tree, as part of a research project to find the best colonizing tree species for the region. The hurango (*Prosopis pallida* (Humb. & Bonpl. ex Willd.) Kunth) plot was irrigated once a week by furrow irrigation. In 2005 the CIEPA managers finished the experiment and cut down the huarango trees. Alfalfa was then grown for approximately five years to improve the soil quality. This crop was irrigated using sprinkler irrigation at that time. From 2010, the plot was leased to a private company interested in artichoke production. Artichoke (*Cynara scolymus* L.) was grown for two years, with drip irrigation before the Borgogna grape was planted using the same drip irrigation in the plot.

The Negra Criolla (medium volume water) plot has been used for grape production since 2006; however, initially, this plot was uncultivated and bare for roughly 15 years until 1998, when alfalfa was planted and kept for five years, using sprinkler irrigation. From approximately 2003 to 2006, onion (*Allium cepa* L.), potato (*Solanum tuberosum* L.), maize, and squash (*Cucurbita maxima*) were cultivated using drip irrigation. Spacing between the irrigation lines changed according to the crop at that time. Briefly, for onion, the spacing was 30 cm; for potato, it was 1

m; for maize, it was 1.5 m, and for squash, it was 6 m. The vine Negra Criolla was planted in 2006, keeping the same irrigation system but with spacing between irrigation lines of 3 m. In 2017 a new drip irrigation system was installed, but the spacing between the drippers changed from 75 cm to 20 cm apart while maintaining the 3 m distance between the drip lines.

The Alphonse Lavallée (low volume water) grape plot was planted in 1983 when AUTODEMA still managed CIEPA. According to our information sources, the land did not receive previous management or work before planting the vines, except for removing rocks, coarse fragments, and leveling of the land. These plots only received drip irrigation from the time of their planting with no furrow and sprinkler irrigation flushing of salt. The Alphonse Lavallée vines were planted directly into the furrow, filled with cow manure and covered with soil. Alphonse Lavallée was the only plot to receive manure.

After planting the vines in each of the vineyards, only weed control was conducted as routine management twice a year: at the beginning of the season, when the herbicide is applied to the field, and in the grape midseason when weeds are removed by hand. Litter from weeds and pruned leaves are separated from the vineyard and burnt. Common weeds in CIEPA vineyards are grasses, *Amaranthus sp.*, *Chenopodium sps.*, and *Malva sp.* A tractor prunes the roots from approximate 25 to 30 cm from the plants and a fungicide is applied to the roots. According to the field manager, it allows the plant to generate new roots and hence reduce soil compaction. Until 2019, Alphonse Lavallée vines were the only plantation that did not follow this practice due to issues with plant morphology and intricate growing. Regarding the application of fertilizers, the application will depend on the plants' needs and is supplied via irrigation.

The collaborative work between CIEPA management and the Arequipa Nexus Institute aims to strengthen the research activity of UNSA, and specifically, to improve the production of wine and pisco. Future plans for the research station include remodeling the infrastructure, including new areas, to enhance research activities.

CHAPTER 3. INFLUENCE OF WATER MANAGEMENT AND SOIL PROPERTIES ON SOIL CARBON ACCUMULATION IN VINEYARDS AT CIEPA-UNSA

3.1 Introduction

3.1.1 Agricultural soils in arid environments

As demand for food has grown globally, governments and farmers are under pressure to expand farming into marginal lands, including deserts. Regardless of the adverse and extreme climate conditions, natural desert soils have been converted to agricultural land using extensive irrigation. In arid ecosystems, soil physical and chemical factors often limit land quality, such as sandy soil texture, salt content, and rugged topography. Naturally, soils in arid environments have low organic content due to low plant input, low moisture, and minimal soil microbial processes. However, agriculture practices on desert soils can dramatically increase soil organic content and achieve very productive soils (Sainju & Lenssen, 2011).

3.1.2 Soil Carbon serves as a metric of soil quality

Arid environments typically have low carbon biomass input and lower turnover rates of input carbon, limiting the production of SOC (Lal et al., 2004; Chen et al., 2018). Irrigation water stimulates the production of both aboveground belowground plant and microbial biomass, increasing SOC production (Su et al. 2010; Yang et al. 2013; Castellano et al., 2015; Chen et al. 2018). The accumulation of soil organic carbon (SOC) is one of the key parameters vital for soil health and crop productivity because it is the key component in the production of soil organic matter (SOM), which is typically composed of 58% of soil organic carbon (Bayer et al., 2002; Haynes, 2005). One factor contributing to the stabilization of organic carbon is the physical protection, or physical barriers to microbial decomposition, afforded by soil aggregates (Sollins et al., 1996; Creamer et al., 2011). Soil aggregation directly promotes SOM stability and is essential for long-term sequestration of organic matter and mineral fertilization in sandy soils (Six et al., 2000; Simansky et al., 2019).

3.1.3 Negative impacts of agricultural management in arid lands

Arid regions often have high salt concentrations in the soil, influencing other physical properties such as aggregation and structure (Zheng et al., 2009). Additionally, according to Yuan et al. (2007), salinity suppresses soil microbial growth and activity in arid environments decreasing soil organic matter decomposition. Salinization is one critical environmental problem, and it is caused by the accumulation of soluble salts in the topsoil (Villalobos et al., 2017; Okur & Orçen, 2020). High soil electrical conductivity (EC) (contributed by salts of Cl, Na, Ca, and Mg) may indicate a condition of salinization (Levi et al., 2020) caused by water management such as irrigation. The agricultural system affects soil's electrical conductivity (EC) with irrigated soils having higher EC than soils maintained as rain-fed because of high evapotranspiration. According to Merchán et al. (2020) and Phogat et al. (2020), sustainable irrigated agriculture requires leaching salts from the soil root zone to avoid plant deleterious effects and decreased crop production. Soil salinity depends on different events like type of irrigation, root water uptake, and soil's evapotranspiration (Li et al., 2014). EC is a factor used to assess soil degradation due to prolonged irrigation (Nunes et al., 2007).

To ameliorate some of the negative impacts of soil salinization, agricultural producers can use different irrigation strategies. The first consideration may be to implement drip irrigation, a strategy widely used in desert areas. Studies on drip irrigation by Zheng et al. (2009) and Guan et al. (2013) did not find any additional salinization created by drip irrigation. Furthermore, the irrigation water quality might have an impact on salinization. Chen et al. (2010) found that poor water quality can cause "secondary salinization" and progressively decrease yield. Calcium carbonates concentrations can increase with saline irrigation water as salts are deposited on soil surface; however, it is reported that long-term irrigation results in a significant decrease in soil salinity (Fallahzade & Hajabbasi, 2010; Singh, 2015). Furthermore, irrigation can have a beneficial impact on soil quality. According to Zang et al. (20017), irrigated desert soils presented a favorable trend on soil physical properties compared with uncultivated sand land.

3.1.4 Managing for soil carbon accumulation benefits in desert irrigated systems

In desert systems under irrigation, soil organic carbon increases with time (Wu et al., 2008; Li et al., 2009; Trost et al., 2013; Dong et al., 2018; Chen Y. et al., 2018; Chenu et al., 2019; Xu

et al. 2020). For example, Li et al. (2009) found an increase of soil organic carbon after ten years of cultivation, and Su et al. (2010) reported an increase of 6.4 times of soil organic carbon after 40 years of farming. Trost et al. (2013) analyzed 22 different studies on the effect of irrigation of SOC. After 20 years of desert reclamation, SOC contents increased significantly and reached a maximum of 50 years (Li et al., 2019). The mechanism behind the high SOC of irrigated soils is the increased biomass production as compared to the native desert system.

Specifically, vineyard systems, a primary focus of this thesis work, an increase of the SOC in the topsoil, can be achieved using organic-mulch or bluegrass (Goulet et al., 2004) or the incorporation of plant residues in grass-covered vineyards (Ruiz-Colmenero et al., 2013). Seddaiu et al., (2013) reported that vineyard soil can be specifically managed for SOC accumulation using cover crops in semiarid Mediterranean environment in keeping with a variety of semiarid and arid region management practices to enhance SOC (Lal, 2004; Alidoust et al., 2018).

3.2 Methodology

3.2.1 Soil Sampling

Study area

Details of the experimental design are presented in detail in Chapter 2 of this thesis. In summary, the UNSA's agriculture research station "Centro de Investigación y Enseñanza de Producción Agrícola" (CIEPA) has a total area of 101.9 ha and is in Majes District, Caylloma province (-16° 19' 29.5", -72° 12' 60" WGS84). Crops cultivated at CIEPA include alfalfa (*Medicago sativa*), citrus, chili (*Capsicum*), maize (*Zea mays*), and vines (*Vitis vinifera*). The long-term goal of the research station and collaboration with the Arequipa Nexus Institute (<https://www.purdue.edu/discoverypark/arequipa-nexus/en/index.php>) is to improve the production of wine and Pisco.

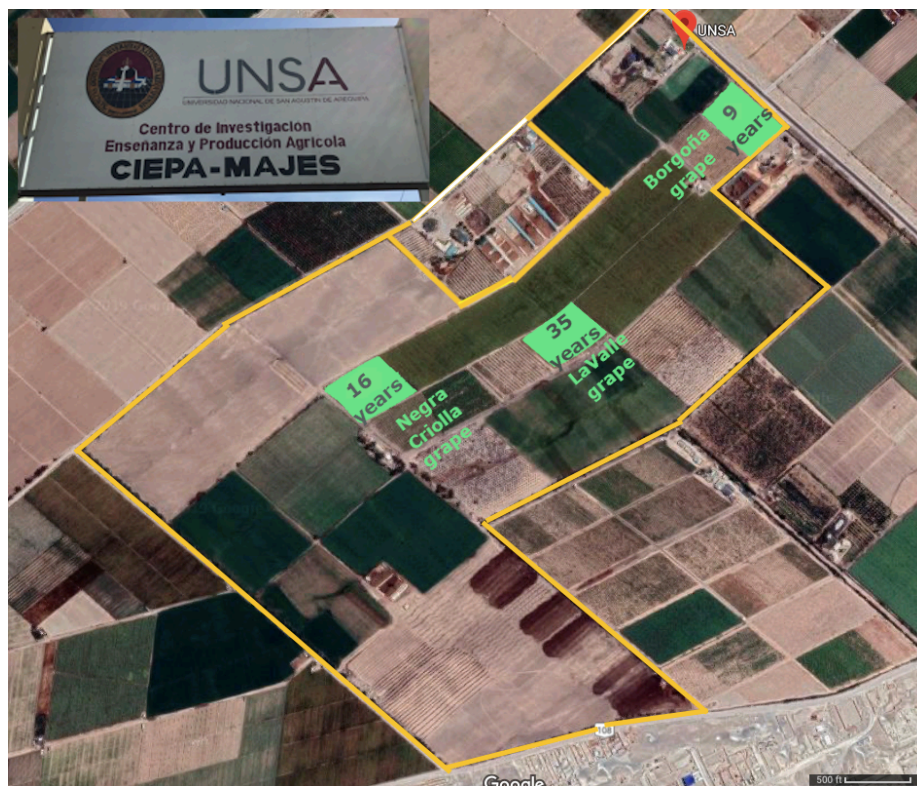


Figure 3.1. Vineyard's location in CIEPA's. Modified from Google's maps screenshot.

Seven different varieties of grapes are grown at CIEPA for direct consumption, wine, and pisco production. Three vineyards, currently under drip irrigation, were selected because they encompass a wide range of ages, from the oldest to the youngest vineyard in CIEPA. The grape varieties and installation of drip irrigation differ from plot to plot: cv. Borgogna, cv. Negra Criolla and cv. Alphonse Lavallée were 9, 16, and 35 years under drip irrigation, respectively (Figure 3.1). Also, the times under drip irrigation are consistent with the vineyard age. Furthermore, each vineyard had a different land management history. For example, the 9- and 35-years plots under drip irrigation were converted to agriculture around the same time, and alfalfa was planted in the 9- and 16- years plot (more details chapter 2).

With the use of a bucket auger, soil samples were collected in two positions: “under drip line” about 20 cm from the drip irrigation line and “between drip lines” approximately 1.5 m from the drip irrigation line. In the 9, 16, and 35 years vineyards, 10, 18, and 18 sampling points, respectively, were outlined and soils were sampled from under and between driplines in a series of transects in the vineyards. Each sample is a composite of three subsamples, forming a line with

one sample in the middle and two samples at each side at 2 meters from the center (Figure 3.2). A total of 90 samples were collected in the three plots from approximately 0 to 20 cm depth.

The soil samples were sieved to 2 mm using a stainless-steel sieve in the field, and approximately 1 kg was bagged, transported, and air-dried in the chemistry laboratory at UNSA. Samples were shipped from UNSA, Arequipa, Peru to Purdue University and transferred to an APHIS quarantine approved facility at the Purdue University Soil Biogeochemistry Laboratory. Before the samples were analyzed, they were removed from quarantine after autoclaving them at 121° C for 30 minutes with a pressure of up to 17 psi for subsequent analysis (STERIS AMSCO 250LS sterilizer).

CIEPA currently has two types of irrigation: sprinkler and drip. Sprinkler irrigation is only used in alfalfa cultivation, and all other crops use drip irrigation. CIEPA has a modern irrigation system, recently installed in June 2018, responsible for distributing and in-line filtering irrigation water. Water is supplied daily according to the crop development at the maximum allowed watering period of 4 hours per day. In the vineyards, drip irrigation lines are on each side of the vines with 20 cm apart and 1.5 m between vines along each row (Figure 3.2). Weeds are managed twice per growing cycle: the first the weed is pulled chemical, and the second time is manually removed.

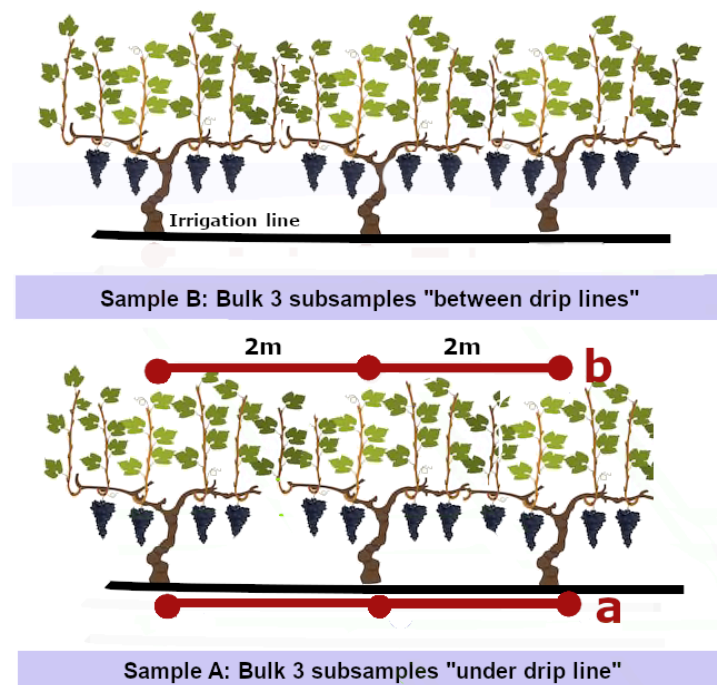


Figure 3.2. Soil sample position scheme in vineyards on CIEPA-UNSA, Majes, Arequipa.

3.2.2 Soil chemical properties

For total carbon and stable carbon isotopic analysis, vineyards samples were ground with a ball mill (MM2000 Retsch, Haan, Germany) and 30 mg were weighed into tin capsules for analysis on a Sercon Ltd. GSL flash combustion elemental analyzer (EA) interfaced to a Sercon 2022 Ltd. isotope ratio mass spectrometer (IRMS) (Sercon Ltd., Crew, UK). For organic carbon analysis, carbonates were removed using the acid fumigation method developed by Harris et al. (2001). For this procedure, 30 mg of ground sample was weighed into silver capsules and placed on a Teflon microwell tray. Each sample was moistened to soil field capacity with 50 μ l of deionized water and placed in a desiccator with a petri dish on the base containing 45 ml of 37% HCl and a beaker of 20 ml with water. The samples were left in the desiccator to fumigate for at least six hours. After the fumigation, the samples were dried in an oven at 60 °C overnight, then wrapped on aluminum foil to avoid sample loss due to air movement. Silver capsules can become brittle after fumigation; therefore, they were carefully closed and tightly double wrapped with tin capsules for EA-IRMS analysis (Sercon Ltd., Crew, UK).

Soil electrical conductivity (EC) and pH values were analyzed in the laboratory of Dr. Juan Lopa at the Chemistry Department at UNSA. Electrical conductivity was determined by measuring 25 grams of air-dry soil sample into a 50 ml beaker and mixed with 25 ml of distilled water. The soil pH was determined using the same soil sample and 1:1 ratio on H₂O and 1:2 ratio on CaCl₂. For electrical conductivity, the meter was calibrated using a solution of 0.01 N KCl. For both measurements, the content was stirred for 1 minute, at intervals of 10 minutes over a 30 minutes period (USDA Soil Survey Staff, 2014 b). After 30 minutes, the pH or EC meter was immersed at 2.5 cm below the aqueous solution's surface to obtain a reading (Oakton PC 700 Benchtop pH meter).

Soil samples were analyzed by dry combustion for total nitrogen content (%) using a LECO TruMac CNS Macro Analyzer with an autosampler (St. Joseph, MI) at the USDA Agricultural Research Service National Soil Erosion Research Laboratory (USDA-ARS NSERL). One gram of air-dried samples was weighed directly into ceramic boats, placed in the autosampler, and loaded into the furnace. The furnace regulates at a temperature of 1,100 to 1,450 °C. Reference standards of EDTA and blanks were spread within the analysis runs every 20 samples.

3.3 Statistical Analysis

Two-way Analysis-of-Variance (ANOVA) analysis was used to test the effects of time under drip irrigation and row position with respect to the irrigation drip line on soil carbon accumulation among the three vineyards. Row position (i.e., distinguishing in the row/under the drip line from in between the drip lines) and years under drip irrigation (i.e., 9, 16, and 35 years) were the two factors analyzed. Prior to statistical analysis, data were examined for normality with the Shapiro-Wilk test and the Levené test for the variance. Total carbon, organic carbon, and pH data were normalized/transformed by taking the natural log, and electrical conductivity was transformed using a square root transformation. Least squares means for multiple comparisons was used as a post-hoc test for significance between treatments. For nonparametric normalizations, the Kruskal-Wallis test was used to analyze significance due to the unbalanced nature of the sample's points. Dunn's multiple comparison test and Games-Howell post-hoc were used for comparison ages and row and their interaction, respectively. A 95 % confidence interval was used to establish significance between treatments. Untransformed data was used to make the graphs. Statistical software R (R Core Team) package Agricole was used for significance between the treatments. Relationships between soil physical and chemical properties were correlated using Kendall's rank.

3.4 Results

3.4.1 Soil carbon accumulation

Our results indicate that total soil carbon accumulated differently depending upon position with respect to the drip line. The interaction between the time under drip irrigation and the row position is significant (ANOVA, $F = 7.52$, $p < 0.01$). Soil carbon accumulation differed significantly between the 9- and 35-years irrigation vineyards in the “between the drip lines” position (Figure 3.3). The average total carbon concentration increases from $5.24 \pm 1.73 \text{ mg g}^{-1}$ on the 9-year plot to $9.14 \pm 2.71 \text{ mg g}^{-1}$ on the 35- years “under the drip line”. There was no interaction of time under drip irrigation and sample position.

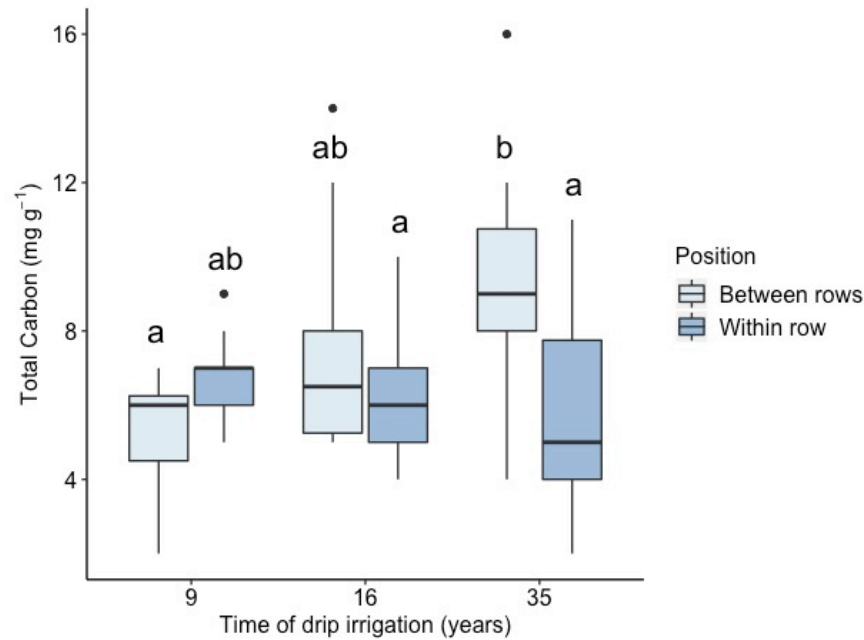


Figure 3.3. Soil total carbon concentration (mg g^{-1}) accumulation in three vineyards under drip irrigation for different times with respect to drip line and row position in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Solid dots are outliers. Significant differences for position are represented by lower case letters at $\alpha=0.05$ (Least mean square, $p<0.001$)

Soil organic carbon concentration increased similarly to total carbon concentrations (Figure 3.4). The interaction between time under drip irrigation and row position is significant (ANOVA, $F=7.06$, $p<0.01$). Soil organic carbon concentrations in the 35-year plot was significantly higher than the 9-year field for between the drip lines. Time under drip irrigation did have a significant interaction with position. Organic carbon increased from $4.89 \pm 1.46 \text{ mg g}^{-1}$ on the 9-years under the drip irrigation line and $7.94 \pm 2.34 \text{ mg g}^{-1}$ on the 35-years under the drip irrigation line. The highest concentration of organic carbon is the vineyard under the drip irrigation for 35 years. Furthermore, inorganic carbon concentrations are not significantly different between the three vineyards, nor among under the drip lines and between drip lines samples (Kruskal-Wallis, $p=0.3072$).

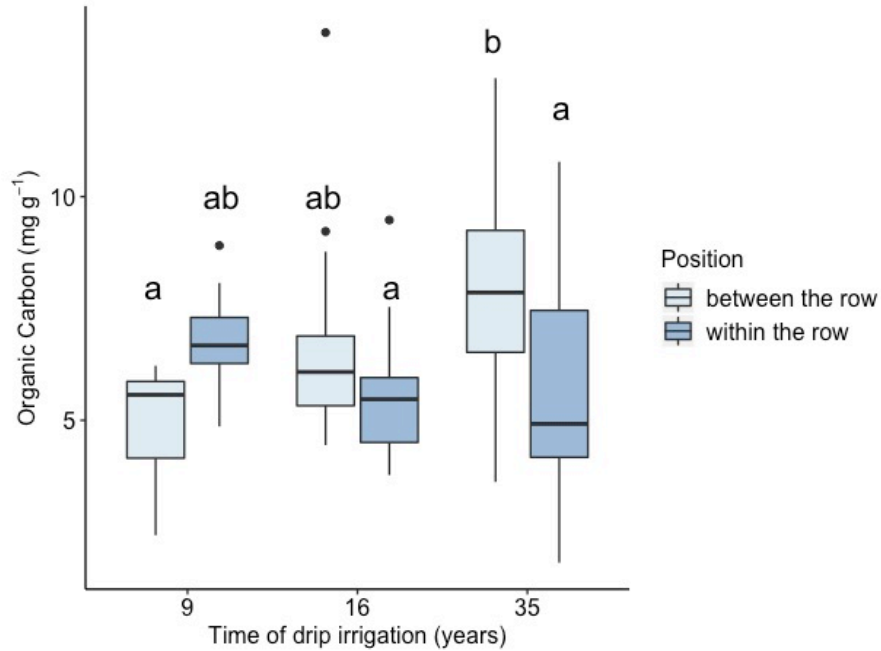


Figure 3.4. Soil organic carbon concentration (mg g^{-1}) in three vineyards under drip irrigation (under and between rows) for different times in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Solid dots represent outliers. Significant differences for position are represented by lower case letters at $\alpha=0.05$ (Least mean square, $p<0.001$)

3.4.2 Soil physical and chemical properties

pH values ranged from 7.23 to 8.27 in the vineyard under 9-years of drip irrigation; from 6.80 to 7.90 in the vineyard under 16 years of drip irrigation and from 6.88 to 8.07 in the vineyard under 35-years of drip irrigation. Mean values of soil pH for 9-, 16-, and 35- year vineyards were 7.55, 7.25 and 7.69, respectively (Figure 3.5). The 9-and 35-years had a significantly higher pH than the 16-years under the drip irrigation line. There was no interaction of time under drip irrigation and sample position.

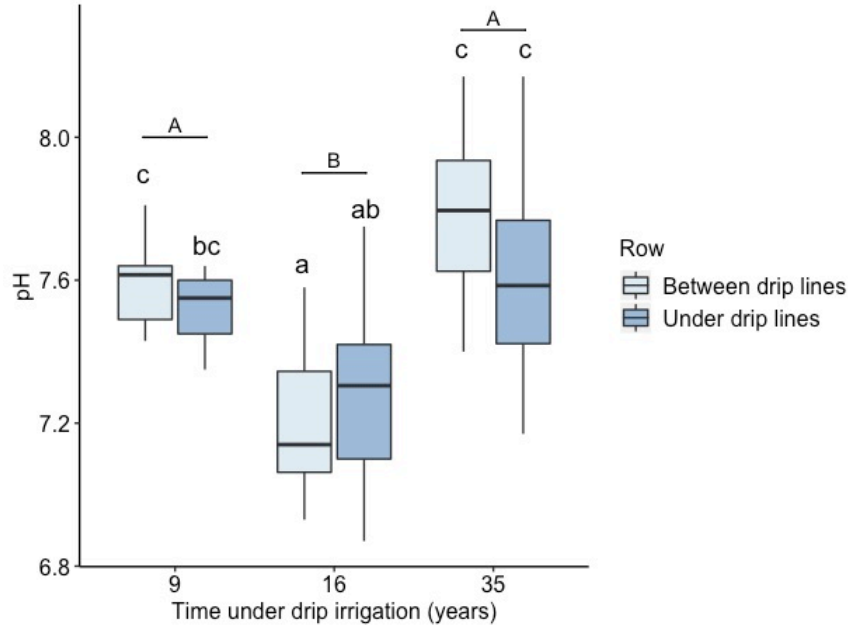


Figure 3.5. Changes of soil pH values in three vineyards under drip irrigation for different times with respect to drip line and row position in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters at alpha and differences across time are represented by capital letter; 0.05 (Least mean square, $p < 0.001$).

The soil electrical conductivity (EC) was significantly impacted by sample position and vineyard age, and their interaction (ANOVA, $F = 23.192$, $p < 0.01$; $F = 25.33$, $p < 0.01$; $F = 3.295$, $p = 0.042$, respectively). EC increased over time regardless of the row position. Samples “between drip lines” had higher EC values (e.g. salt concentrations) than “under drip line”. Soil electrical conductivity values ranges from 0.67 to 24 dS/m across the three different plots with lowest in the row in the 9-year and the highest in between the row on the 35-year plot (Figure 3.6).

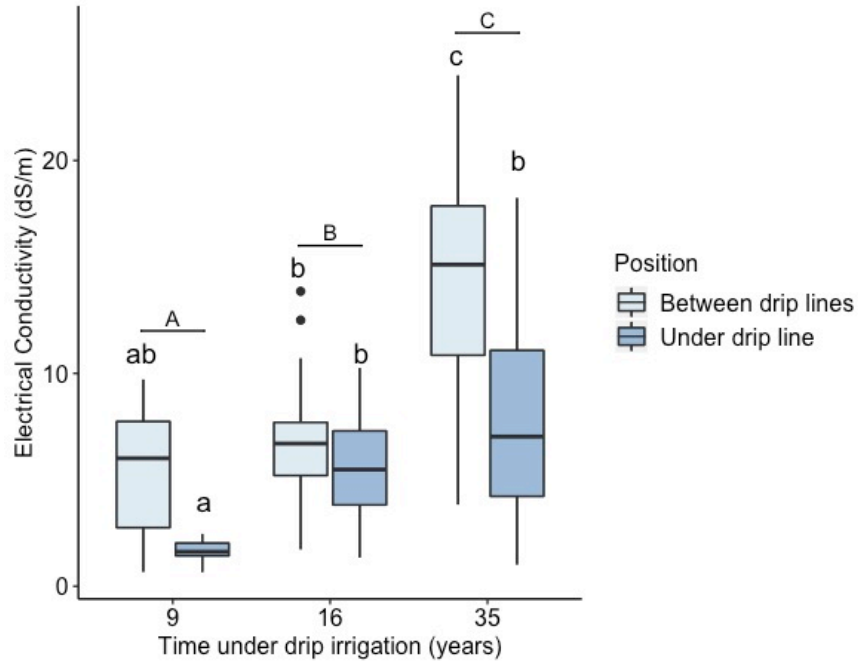


Figure 3.6. Soil electrical conductivity (dS/m) values of the 0 -20 depth in three vineyards under drip irrigation for different times regarding its row position in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Solid dots represent outliers. Significant differences for position are represented by lower case letters and differences across time are represented by capital letter at alpha;0.05 (Least mean square, $p < 0.001$).

3.5 Discussion

3.5.1 Time under drip irrigation affects carbon accumulation

Time is the main factor for soil carbon accumulation in desert irrigated agriculture. The results herein show a significant increase in soil total carbon and soil organic carbon accumulation in the position between the drip lines. Our results are consistent with those reported by Li et al. (2009), where SOC had significantly increased after 20 years of irrigation agriculture. Wu et al. (2008) and Su et al. (2010) both found that at least 50 years under irrigation were necessary to reach soil structure and increase carbon in the soil necessary for desirable fertility. The relationship between pH and soil organic carbon has been explored extensively in the literature; according to Dogan et al. (2019) and Zhang et al. (2020), soil organic carbon concentration increases with low pH because pH will depress microbial activity during the decomposition of soil organic matter. In the present system, 25 years under drip irrigation corresponded to the highest organic carbon but also the highest pH, so in this case, time in irrigation, the length of organic matter input may be the controlling factor.

It is unknown if the crops planted and water management previous to the installation of drip irrigation influenced soil organic carbon accumulation in the three vineyards. Alfalfa was a common crop before vines at CIEPA, and it was planted for approximately five years before drip irrigation to improve soil conditions by building carbon storage and increasing soil nitrogen (Chapter 2). Several studies have investigated using leguminous crops such as alfalfa to increase soil organic carbon (Su et al., 2007; Fallahzade & Hajabbasi, 2010; Sainju & Lenssen, 2011; Giongo et al., 2020). Zhang et al. (2020) showed that such legume species perform better in improving the soil on arid areas than non-leguminous crops, particularly for soil organic content. Two of the three vineyards, 9- and 16- years old, were planted to alfalfa before the vineyard was established, but it is inconclusive that management plays a role in carbon accumulation.

3.5.2 Effects of proximity to irrigation on soil carbon accumulation

The proximity of soil to the drip irrigation line affects carbon accumulation. There is a lack of soil organic carbon studies regarding the effect of sample position from the drip line in an arid environment. According to our results, “between the drip lines” position was where the most significant carbon accumulation occurred. The largest area of a vineyard agroecosystem is inter-row space (Brunori et al., 2016). Inter-row spaces, however, have low vegetation coverage, except for occasional weeds unless a cover crop is intentionally used. Nonetheless, in arid environments, irrigation increases soil microbiota activity and SOM decomposition (Chen Y. et al., 2018). That may be the deciding factor for the control on proximity to the drip line. Therefore, soil organic carbon will likely be preserved and protected between the row position due to the lack of soil microbial activity and disturbance.

Our results were not consistent with our hypothesis that soil organic carbon would accumulate preferentially under the drip line. The accumulation of SOC in between the drip lines in CIEPA could be influence by the management of organic residues and weeds. For example, it could be possible that not all weed’s roots may be pulled off during manual removal, or plant wastes from weed removal and vine pruning could be place in between the drip lines for prolonged periods. As result, there may have been more organic matter additions between the drip lines than under the drip lines. Several studies have had a focus on overall irrigation effects in an increase of soil organic matter input but yielded variable findings (Ogle et al., 2005; Li et al., 2006; Li et al., 2009; Trost et al., 2013; Dong et al., 2018). Li et al. (2019) found that the amount of above-ground

biomass influenced soil organic carbon stocks at 0-20 cm. Nunes et al. (2007) demonstrated that in irrigated soils, organic matter degradation rates were linked to an increase in soil microbial activity. In the CIEPA system, salt concentrations may also have simultaneously suppressed organic matter decay in between the drip lines position, which would be consistent with known effects of salinity microbial activity suppression and lower SOM decomposition rates (Yuan et al., 2007). Many factors, however, are simultaneously at play in such systems as Li et al. (2009) found that soil microbial activity, carbon storage, and carbon accumulation were higher in moist oasis subsoil than adjoining desert soils – which ultimately may be related to plant biomass input.

3.6 Conclusion:

Position and time under drip irrigation influenced in the increase of soil organic carbon accumulation at CIEPA-UNSA. After 35-years under drip irrigation, soil organic carbon was significantly increased in the between the drip lines position. The arid environment seems to protect and decrease soil organic matter decomposition away from the irrigation drip. The arid climate and high evapotranspiration will decrease carbon decomposition rates between the rows. In contrast, in the under the drip line position, the row position irrigation enhances the microbial activity due to high moisture. Also, the irrigation proximity and management practices such as pruning and weeding will impact soil organic carbon accumulation by disturbing the soil.

CHAPTER 4. TRACE ELEMENT AND HEAVY METAL INTERACTIONS WITH SANDY IRRIGATED SOILS

4.1 Introduction

4.1.1 Importance of trace elements and metals in agriculture

Nine elements (Si, O, Al, Fe, Ti, Ca, Mg, Na, and K) constitute most of the soil's mineral fraction; the remaining elements are known as "trace elements" because they occur at a concentration of less than one percent (Davies, 1997). The primary source of trace elements is the parent rock or sediment material that the soil formed from; however, they can also come from atmospheric deposition, contamination, and anthropogenic sources like irrigation, fertilizer, and industrial activities (Sun et al., 2013). Trace elements also constitute an important part of agrochemicals; due to the intensive use, they can bioaccumulate in plants, and they can accumulate in agricultural soils (Kabata-Pendias & Szteke, 2015). Tracing elements can be classified in an agricultural context depending on plant physiological needs into macronutrients and micronutrients. Primary macronutrients are nitrogen (N), phosphorus (P), and potassium (K), while secondary macronutrients include calcium (Ca), magnesium (Mg), and sulfur (S). Micronutrients are important for the plant in trace amounts, and include boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn). A potential negative aspect of desert irrigation is the potential to accumulate trace elements in toxic concentrations due to evaporative concentration (Lynch, 2012; Dunlap, 2019).

Trace elements, and in particular, some heavy metals, in excessive concentrations can be toxic to human health and can persist and accumulate in plant and animal tissues, jeopardizing animals and human health (Balkhair & Ashraf, 2016) where specific toxicity levels vary by metal and physiology (Kabata-Pendias, 2010). Significant environmental contamination can occur due to human-caused accumulation of heavy metals, predominately lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), copper (Cu), zinc (Zn), mercury (Hg), and nickel (Ni) (Beigi et al., 2008; Wuana & Okieimen, 2011). Pb affects the gastrointestinal tract, kidneys, and nervous systems, and accumulation in the body can lead to poisoning or even death (Wuana & Okieimen, 2011). Cadmium (Cd), arsenic (As), and chromium (Cr) are considered carcinogens. Cadmium mainly impacts the respiratory system, renal health, bone health, and cancer (Waalkes, 2000; Fu & Wang,

2011). Chromium (IV) is known for causing allergic dermatitis, carcinogenic effects such as lung cancer in humans (Swaroop et al., 2019). Arsenic (As) produces adverse health harm in different physiological systems, including cancer, cardiovascular and neurological diseases, and diabetes (Sun et al., 2013; Zhou et al., 2018). Copper in high doses affects the gastrointestinal system (Wuana & Okieimen, 2011). Zinc can cause stomach cramps and irritation, vomiting, nausea, anemia, or even death (Plum et al., 2010). Nickel mainly affects the pulmonary system and causes allergic reactions (Fu & Wang, 2011; Grandjean, 1983).

Metal mobility in soil and soil water depends on a variety of edaphic (i.e., pH, EC, clay content and type, SOC content) and metal (i.e., redox, ionization potential) physicochemical properties (Kabata-Pendias, 2010). Soil organic matter has significant sorption and chelation capacity for metals, and so it influences metal speciation, transport, and bioavailability (Sauvé et al., 2000; Yin et al., 2002; Fest et al., 2007; Matijevic et al., 2014; Rahman et al., 2018; He et al., 2019). The mobility of SOM can determine the heavy metal availability because metals are commonly adsorbed into the organic fraction of the soil (Lair et al., 2007). Additionally, metal affinity to SOM varies depending on the metal; for example, Pb and Cu are metals with relatively high affinity. In contrast, other metals like Ni will show a weak affinity because of charge density, hydration layers, and redox chemistry (Fest et al., 2007; Rahman et al., 2018). Overall, metal speciation and export from the zone of input is controlled by soil physical and chemicals properties such as soil pH and cation exchange capacity (CEC), as these state variables control the chemical nature and quantity of organic matter and metal interactions (Vieira Guimaraes et al., 2013; Ramseh et al., 2019). Changes in soil salinity have also been an important factor in metal mobility (Acosta et al., 2011).

4.1.2 Trace element and heavy metal accumulation in irrigated vineyards

Analysis of trace metals in soil can provide an important insight into the impacts and suitability of agriculture and irrigation water management (Nicholson et al., 2003; Teng et al., 2010; Sun et al., 2013; Cai et al., 2015). Often, there is a shortlist of metals that are most frequently studied based on environmental impacts to human and ecosystem health as well as nutrient requirements for plants. Copper (Cu) accumulation and bioavailability in vineyards soils has been heavily studied due to its historical use to treat fungal diseases (Chaignon et al., 2003; Pietrzak et al., 2004; Chopin et al., 2008; Wightwick et al., 2013; Zhu et al., 2017; Miotto et al., 2017). Most

Cu from agrochemicals enters the soil and attaches to SOM and since SOM may preferentially accumulate under the irrigation line where root tissue is Cu also will persist there (Ruyters et al., 2013; Duplay et al. 2014; Antoniadis & Golia, 2015; Komàrek et al. 2008, 2010). Besides Cu, fungicides can contribute to the accumulation of other heavy metals because they usually present impurities of other elements such as Cd, Cr, Ni, Pb, and Zn (Thomas et al., 2012).

Other heavy metals that are an environmental concern in the vineyards are Zn, Cd, Cr, Pb, and Ni (Vystavna et al., 2014; Duplay et al., 2014; Zhu et al., 2017; Beygi et al., 2018; Mirzaei et al., 2019). Elevated Zn in the soil can either be from a natural or anthropogenic activity and is closely related to Cu (Kabata-Pendias, 2010; Beone et al., 2018). High Zn concentrations can be linked to the direct addition of mineral Zn fertilizer and fungicides (Bai et al., 2014; Kelepertzis et al., 2018). Even though Zn is naturally important as a key constituent of many enzymes, proteins, and other biochemical pathways (Alloway, 2009), Zn can compromise cell membrane permeability at high concentrations (Tiecher et al., 2016; Dhaliwal et al., 2019). In comparison to Cu, Zn has a lower affinity for organic matter and is absorbed by Fe-oxides (Tiecher et al., 2016). Both Ni and Cd are often contaminations from parent material in mineral-rich zones (Kelepertzis et al., 2018). Ni is another essential micronutrient with a significant role in nitrogen assimilation where soil deficiencies lead to retarded plant growth and where excessive levels negatively impact leaf soluble sugars as a response to the impact on plant carbohydrate metabolism (Brown et al., 1987; Nie et al., 2015; Shahzad et al., 2018). Cadmium is an extremely poisonous element not essential for plant growth and human development. Cd is also a trace element that accumulates due to the usage of chemical fertilizer, sludge application, sewage irrigation, and atmospheric deposition (Zhu et al., 2017; Qin et al., 2020). Cd causes growth inhabitation and reduced photosynthetic activity at toxic levels (Gallego et al., 2012; Nazar et al., 2012).

Boron has naturally high concentrations in volcanic and coastal soils, and it often in high concentrations in ground and surface water of such systems (Landi et al., 2019; Hugo & Iquiapaza, 2020). Boron is an element of concern in arid and semi-arid environments as irrigation water is one of the most important sources where B accumulates in surface horizons due to the high evaporation rates (Kot, 2015; Landi et al., 2019). Furthermore, in volcanic areas like Arequipa, B levels are naturally high and often exceed Peruvian environmental standards (Masson, 1973), with soil values 5 to 20 times higher than recommended. Boron is essential for normal plant growth because of its association with maintaining cell wall structure and membrane function and

supporting metabolic activities (Bell, 1997; Kot, 2015; García-Sánchez et al., 2020). However, B does present toxicity for plants (Kot, 2001; Landi et al., 2019), particularly in systems influenced by marine evaporites, irrigation inputs, or surface mining, causing inhibition of growth because of cell wall damage and direct impact to photosynthetic activity (Nable et al., 1997; Reid et al., 2004).

Like many regions under irrigation in Arequipa's desert, the CIEPA station has been in cultivation for over 30 years under different forms of irrigation (See Chapter 2). CIEPA provides an excellent opportunity to assess how trace elements and heavy metals are partitioned across vineyard soils, which will provide crucial environmental knowledge for the region's perennial crops.

4.2 Methodology

4.2.1 Soil sampling and sample preparation

Study area

Details of the experimental design are presented in detail in Chapter 2 of this thesis. In brief, the "Centro de Investigación y Enseñanza de Producción Agrícola" (CIEPA) is the agriculture research station at the Universidad Nacional de San Agustín (UNSA) in Majes District, Caylloma province ($-16^{\circ} 19' 29.5''$, $-72^{\circ} 12' 60''$ WGS84). It has a total area of 101.9 ha. Crops cultivated at CIEPA include alfalfa (*Medicago sativa*), citrus, chili (*Capsicum*), maize (*Zea mays*), and grapes (*Vitis vinifera*). Three different vineyard plots under drip irrigation for 9, 16, and 35 years at the time of sampling (2019) were selected to establish a chronosequence approach to assess the distribution of trace elements and heavy metals over time. Each vineyard had a different type of grape: cv. Borgogna (9 years under drip irrigation), cv. Alphonse Lavallée (35 years under drip irrigation), and cv. Negra Criolla (16 years under drip irrigation).

The soil sampling protocol is described in detail in Chapter 2 of this thesis. In brief, soil was collected proximal to the drip irrigation line as well as in the middle of the inter-row (Chapter 3, Figure 3.1). At each point, a total of three subsamples, one sample in the center, and two samples 2 meters apart from the sides were collected from 0 to 20 cm depth using a bucket auger. The samples were mixed and homogenized into a composite sample in the field, then sieved through a 2 mm stainless steel sieve and approximately 1 kg was bagged, transported, and air-dried at UNSA. For this study, a total of 90 samples were collected using a sampling grid shown in Figure 3.2,

Chapter 3. To follow USDA APHIS rules, the samples were quarantined upon arrival at Purdue and then autoclaved at 121°C for 30 minutes before their further analysis.

4.2.2 Chemical analysis

Soil pH, EC, organic and total soil carbon were measured on all samples using the methods described in Section 3.2.2. Ch 3. Trace element concentrations in the soil were determined by acid-microwave digestion with subsequent analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES). Briefly, one gram of soil was transferred to a 50-ml Teflon Xpress Digestion Vessel and then 12 ml of aqua regia, $\text{HNO}_3 + \text{HCl}$ (1:3 v/v), was added to the reaction vessels for an overnight pre-digestion within a fume hood (US EPA method 3050). Vessels were placed equally distributed in the Microwave Accelerated Reaction System, Model MARS (CEM Corporation, NC, USA). The microwave power program was set to max 1600 W, power 75%, ramp temperature to 160 °C for 10 minutes, held for 15 minutes, and with a cooldown time of 5 minutes. At the conclusion of the heating program the samples were placed in a fume hood to cool down for one hour. Samples were filtered with glass funnels through Whatman N 42 ashless filter paper into a 50 ml volumetric flask. Digestion vessels were rinsed three times with 1% HNO_3 , and residue left behind was discarded. Finally, all filtered solutions were diluted and brought to 50 ml with 1% HNO_3 for later metal analysis by an inductively coupled plasma optical emission spectroscopy (ICP-OES). Samples were digested in batches of 20 with 16 samples, two blanks, and one reference standard soils (SRM 2711a). Quality control of the chemical analysis was performed by digestion and analysis of the standard soil SRM 2711a (Montana II), as well as multiple element standard solutions, and a blank solution using the same acid mixtures, digestion procedure, and dilutions. A total of 14 blanks and reference materials were included for analysis. It is important to note that the quartz-sand rich soils from the CIEPA samples had significantly more residue remaining in the vessel compared with an almost clean vessel of the standard soils. This proved problematic as it did not allow a determination of extraction completeness (discussed later).

The protocol for ICP-OES, including specific wavelengths and standard mixtures, are described by (Cancappa et al, in prep). Briefly, digested solution samples were analysed for trace elements using a standard mix matrix of 38 elements with concentration ranges from 2 ppb to 1000 ppb. An internal standard of 10 ppm yttrium (Y) was spiked into all samples and standard mixes.

For simple dilution, digested samples were diluted (1:33.33) by weight using 2% (v/v) HNO₃. The dilution procedure was the following: 0.5g of Y internal standard, 1.5g of digested sample solution were brought to a final weight of 50 g with 2% HNO₃. For the second dilution, the digested sample was diluted (1:10000) by weight in 2% (v/v) HNO₃. Trace metals concentrations were quantified using iCAP7400 ICP-OES (Thermo Fisher Scientific, Loughborough, UK).

Details of detection limits, the limit of quantitation (LOQ), and coefficient of recovery (RC) are provided in Appendix Table C.1. A subset of metals was chosen for attention in this thesis based on their potential as environmental pollutants in vineyards and included Cd, Cu, Pb, Ni, and Zn (Beygi et al., 2008). The full suite of elements measured with this method in Appendix C.1.

4.3 Statistical analysis

Two-way ANOVA was used to test the trace elements concentration in soils under different time of drip irrigation and proximity to the irrigation line where time (i.e. 9, 16, 35 y) under drip irrigation and row position (i.e. within the drip line and between the drip line row) were two factors. To achieve normality, before the analysis, B, Mn and Fe were transformed by the natural log, Cr, Co and Ba concentrations didn't need transformation, and Cd, Cu, Mg, Zn, and Ni concentration were nonparametric. For posthoc testing, Tukey HSD was used for ANOVA test and Dunn test for Kruskal-Wallis rank-sum test. Kendall correlation was for nonparametric distributions run between trace elements and the physical-chemical properties of the soil. All calculation used R statistical analysis, Agricole package.

4.4 Results

A total of 30 elements were analysed in the soil, but not all elements are reported in this thesis after careful quality assessment and checks (See Appendix C, Table C.1). The micro acid digestion standard reference soil (SRM 2711a) certified yield recovery ranged from 0.5–257.45 % among the quantified elements. Trace elements with acceptable recovery of more than 50% according to the reference standard included: Ba, Fe, and V. However, the concentration of Al, As, Ca, Cu, K, Mn, P, Pb, Sb and Zn were above the calibration curve or higher than 100% recovery (See Appendix C, Table C.1). Overall, the trace metals in SRM 2711a with a coefficient variance under 20% and above limit of detection were As, Ba, Cd, Co, Cr, Fe, Mg, Mn, P, Pb, Sb, Sr, Ti,

and V (See Appendix C, Table C.1). Of all the trace elements analyzed only significant differences were observed for B, Ba, Cu, Mg, Mn, Ni and Zn that will be discussed in the following paragraphs.

4.4.1 Trace element concentration with time in irrigation and row position:

Cu concentrations ranged from 22.2– 37.5 mg kg⁻¹ in the 9-year irrigation plot, from 11.7 – 33.4 mg kg⁻¹ in the 16-year plot, and from 14.0- 48.9 mg kg⁻¹ in the 35-year plot. Mean Cu concentrations for 9- , 16- and 35-year plots were 29.4 mg kg⁻¹, 19 mg kg⁻¹ and 27.3 mg kg⁻¹, respectively. There was a significant difference in soil Cu concentrations between the 16-year plot and both the 9- and 35- year plot (Kruskal-Wallis, $p<0.001$); however, row position was not significant in soil Cu accumulation (Figure 4.1). There was a significant difference between 16- and 35-years Cu concentration (Dun test, $p<0.001$). Cu concentrations ranged from 22.2 – 37.5 mg kg⁻¹ in the 9-year plot, from 11.7 – 33.4 mg kg⁻¹ in the 16-year plot and from 14.0- 48.9 mg kg⁻¹ in the 35-year plot. Cu concentrations for 9- , 16- and 35-year plots were 29.4 mg kg⁻¹, 19 mg kg⁻¹ and 27.3 mg kg⁻¹, respectively. The highest Cu concentration was in 35-year plot, while the lowest concentration was the 16-year plot. There was a significant effect of time under irrigation on soil total Cu concentrations (Kruskal-Wallis, $p<0.001$); however, row position was not significant in soil Cu accumulation (Figure 4.1). There was a significant difference between 16- and 35-years Cu concentration (Dun test, $p<0.001$).

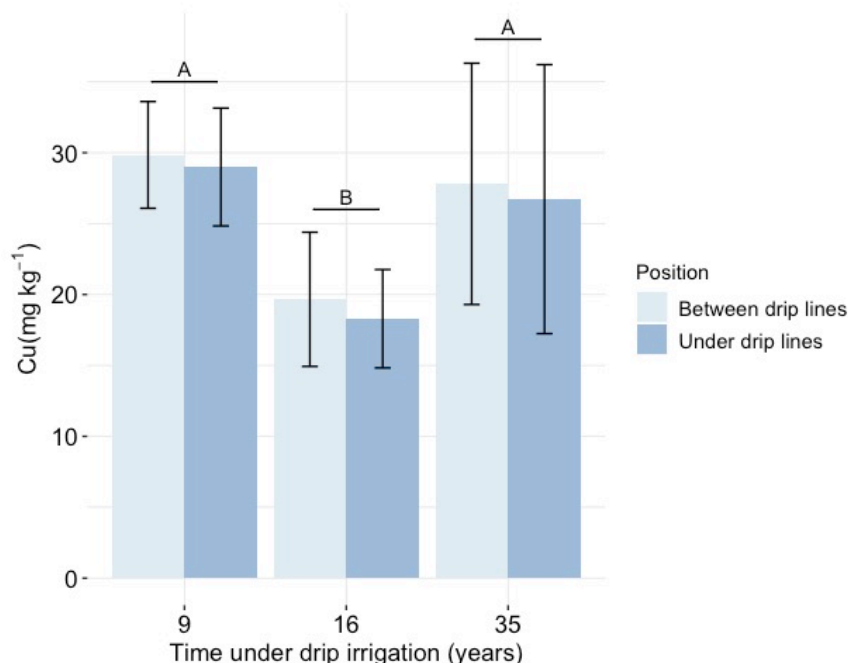


Figure 4.1. Concentration of Cu (mg kg⁻¹) in vineyards soil plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha 0.05 (Kruskal-Wallis $p < 0.01$, Dunn test, $p < 0.001$)

Zn concentrations ranged from 26.8 – 55 mg kg⁻¹ in the plots in 9-years in irrigation, from 15.4 – 51.1 mg kg⁻¹ under 16-year drip irrigation, and from 27.2- 74.4 mg kg⁻¹ under 35-year drip irrigation. Mean Zinc concentrations for 9-years, 16-years, and 35-years in irrigation was 37.4 mg kg⁻¹, 34.8 mg kg⁻¹, and 48.2 mg kg⁻¹, respectively. The highest concentration was in the 35-years old vineyard, while the lowest concentration was in the 16-years old which were significantly different. Overall, time under drip irrigation influenced zinc (Zn) concentration in the vineyard soil at CIEPA; however, row position was not significant in soil Zn accumulation (Tukey's HSD test, $p < 0.001$) (Figure 4.2).

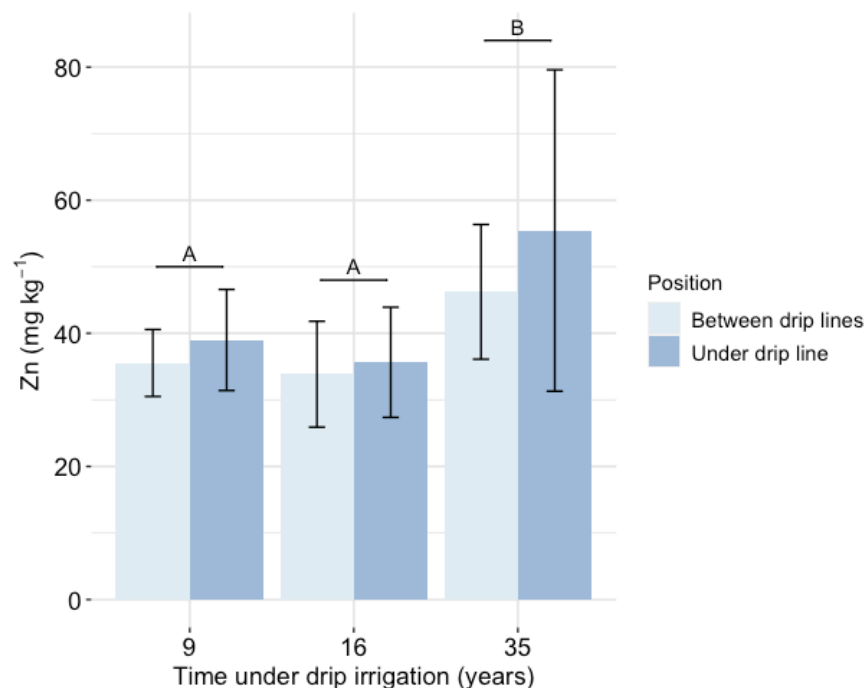


Figure 4.2. Concentration of Zn (mg kg⁻¹) in vineyards soil plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha 0.05 (Tukey's HSD test, $p < 0.001$).

Ni concentrations ranged from 8.0 – 10.6 mg kg⁻¹ in vineyards under 9-years irrigation, from 6.5 – 18.6 mg kg⁻¹ in the 16-year irrigation, and from 7.7 – 17 mg kg⁻¹ under 35-years irrigation. Mean Ni concentrations for 9-years, 16-years, and 35-years irrigation were 9.2 mg kg⁻¹, 10 mg kg⁻¹, and 11 mg kg⁻¹, respectively. The highest and lowest concentrations were with under 16-years drip irrigation. For position, under the drip line position significant influence the concentration of Ni; however, between the drip lines position was not significant in soil Ni accumulation (Kruskal-Wallis, $p = 0.33$) (Figure 4.3). Overall, cultivation time under drip irrigation and the position under drip line significant influenced soil Ni concentrations. The difference in the concentration of Ni between 9 - and 35-years old was significantly different (Dunn test, $p < 0.001$) (Figure 4.3).

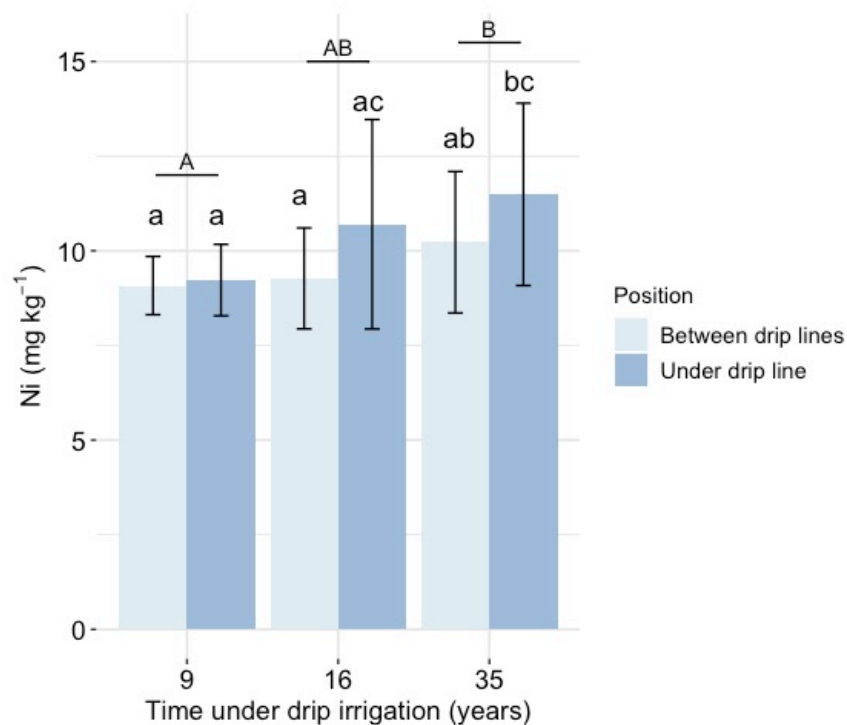


Figure 4.3. Concentration of Ni (mg kg^{-1}) in vineyards soil plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha 0.05 (Kruskal-Wallis $p < 0.01$, Dun test, $p < 0.05$).

Mn concentrations ranged from $246.6 - 329.8 \text{ mg kg}^{-1}$ in vines under 9-years drip irrigation, from $269.4 - 380.9 \text{ mg kg}^{-1}$ in vines under 16-years drip irrigation, and from $278.2 - 380.3 \text{ mg kg}^{-1}$ in vines under 35-years drip irrigation. Mean Mn concentrations for 9-years, 16-years and 35-years old under drip irrigation were 286.2 mg kg^{-1} , 316.1 mg kg^{-1} and 325.9 mg kg^{-1} . The highest concentration was for the vineyard under 35-years drip irrigation, while the lowest concentration was the 9-years. Proximity to the drip irrigation significantly influenced Mn's concentrations, where both position concentrations increased with time. Overall, time under drip irrigation and position significant influenced manganese (Mn) concentrations in the vineyard soils at CIEPA (ANOVA, $p < 0.001$, $p < 0.01$) (Figure 4.4).

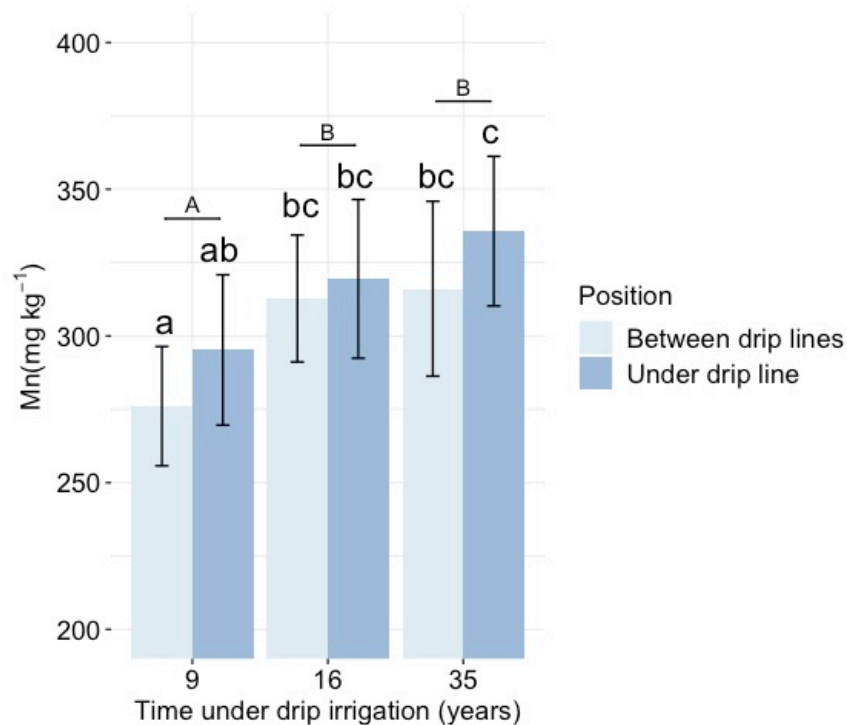


Figure 4.4. Concentration of Mn (mg kg^{-1}) in soil in three different vineyards under drip irrigation for 9, 16 and 35 years in CIEPA-UNSA, Majes irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha 0.05 (Tukey's HSD test, $p < 0.001$).

Boron concentrations ranged from 44.9 - 64.5 mg kg^{-1} in vines under 9-years drip irrigation, from 27.9 - 74.3 mg kg^{-1} in vines under 16-years drip irrigation, and from 38.5 - 93.3 mg kg^{-1} in vines under 35-years drip irrigation. Mean B concentrations for 9-years, 16-years and 35-years under drip was 54.6 mg kg^{-1} , 50.6 mg kg^{-1} and 61.3 mg kg^{-1} . The highest concentration was for the vineyard under 35-years drip irrigation, while the lowest concentration was the 16-years under drip irrigation. Overall, time under drip irrigation influenced Boron (B) concentrations in the vineyard soils at CIEPA; however, row position was not significant in soil B accumulation (Figure 4.5). The difference between 16- and 35-years old was significantly different (Tukey's HSD test, $p < 0.001$).

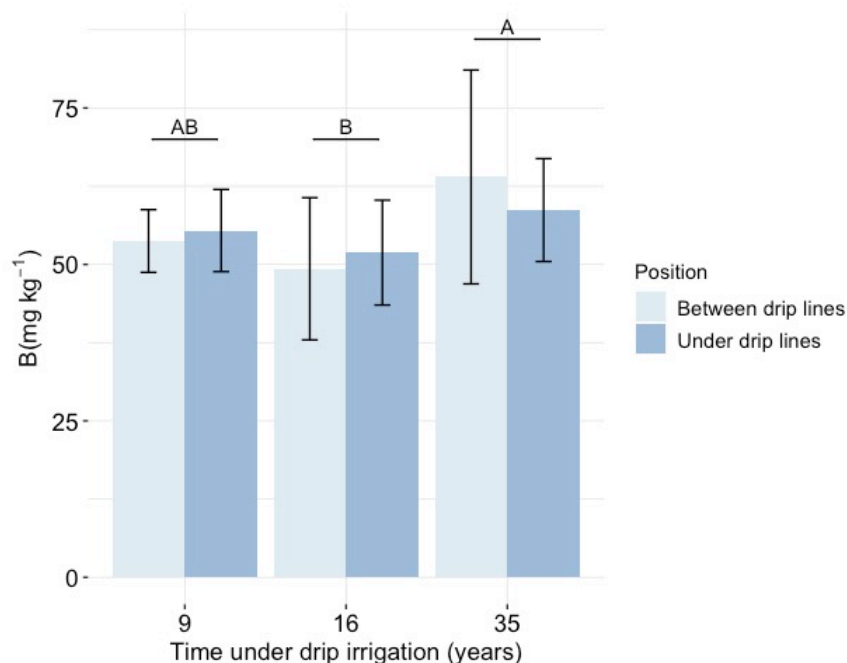


Figure 4.5. Concentration of B (mg kg⁻¹) in vineyard soil plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha;0.05 (Tukey's HSD test, p<0.001).

Barium concentrations ranged from 87.6 – 144.9 mg kg⁻¹ in vines under 9-years drip irrigation, from 81.7 - 139.1 mg kg⁻¹ in vines under 16-years drip irrigation, and from 72.2 – 128.5 mg kg⁻¹ in vines under 35-years drip irrigation. Mean Ba soil concentration in vines under 9-years drip irrigation, 16-years, and 35-years was 115 mg kg⁻¹, 102 mg kg⁻¹, and 96.3 mg kg⁻¹, respectively. Unlike the other trace elements, the highest concentration was for the vineyard under 9-years under drip irrigation, while the lowest concentration was in the 32-years under drip irrigation. Overall, time under drip irrigation and position influenced barium (Ba) concentrations in the vineyard soils at CIEPA (ANOVA, p<0.001) (Figure 4.6.).

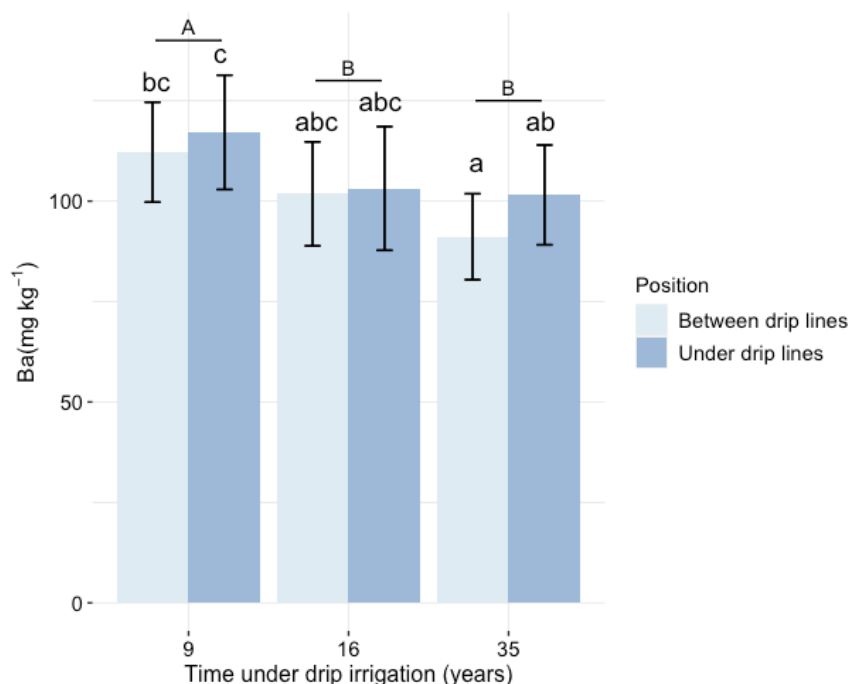


Figure 4.6. Concentration of Ba (mg kg^{-1}) in soil of three different vineyards under 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes, Arequipa. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha 0.05 (Tukey's HSD, $p < 0.001$).

4.5 Relationships between trace metals and soil physical and chemical properties

Soil organic carbon showed significant weak correlations with B ($r=0.21$, $p<0.01$), Cu ($r=0.21$, $p<0.01$), Fe ($r=0.17$, $p<0.05$) and Zn ($r=0.21$, $p<0.01$) while soil pH was slightly correlated with B ($r=0.25$, $p<0.001$), Cu ($r=0.28$, $p<0.001$) and Zn ($r=0.27$, $p<0.001$). Soil electrical conductivity was weakly correlated with Ba, B, and Mg. Our results show that B ($r=0.19$, $p<0.01$) and Mg ($r=0.22$, $p<0.01$) have a slightly positive correlation with electrical conductivity; while, Ba has a negative correlation ($r=-0.20$, $p<0.01$). Boron and zinc were the only elements that correlated with the three soil properties. Trace elements have significant correlation between one another. Fe and B are the elements that significant correlates with the all the other elements (Appendix Table C.5). However, Mn, Ni and Cr had a strong positive correlation with Fe (Figures 4.7, 4.8 and 4.9). Moderate correlations found between B/Cu ($r=0.417$), B/Ni ($r=0.458$), B/Mn ($r=0.376$), B/Cr ($r=0.465$), B/Zn ($r=0.54$) (Figure 4.10), and B/Fe ($r=0.458$). Cr has a significant strong correlation with Ni ($r=0.683$) (Figure 4.11), and Mn ($r=0.622$) (Figure 4.12). Cobalt is a trace element that significantly correlates with the exception of Mg. The strongest correlations for

Co were Co/Mn ($r=0.622$, Figure 4.13), Co/Ni ($r=0.527$, Figure 4.14), Co/Fe ($r=0.556$, Figure 4.15), Co/B ($r=0.559$, Figure 4.16), and Co/Cr ($r=0.577$, Figure 4.17). Furthermore, Ni is the element with highest correlation with Zn ($r=0.469$), Fe ($r=0.509$) (Figure 4.9), Mn ($r=0.517$) (Figure 4.18), and Cr ($r=0.683$) (Figure 4.11).

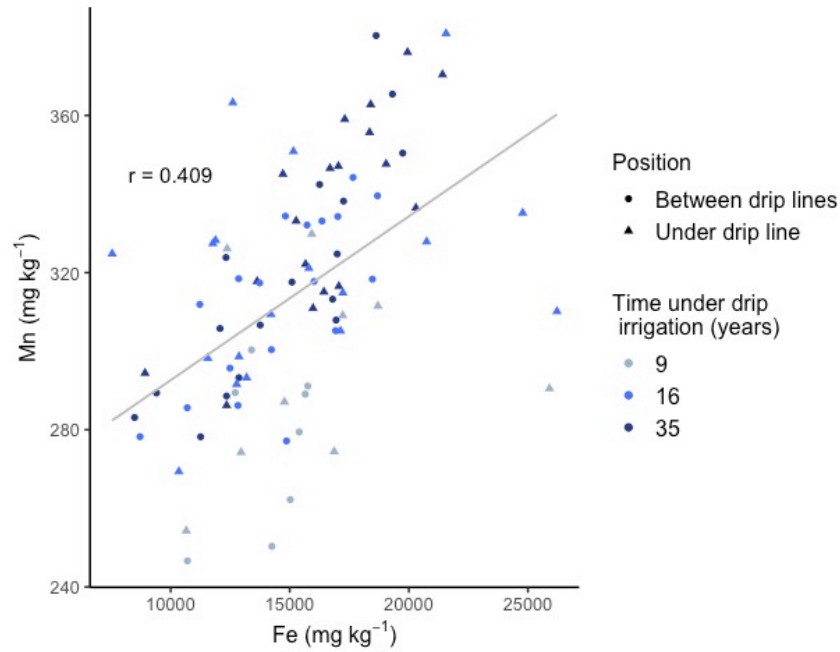


Figure 4.7. Significant positive correlation between soil iron (Fe) and manganese (Mn) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa. (Kendall, $p<0.001$, $r=0.409$).

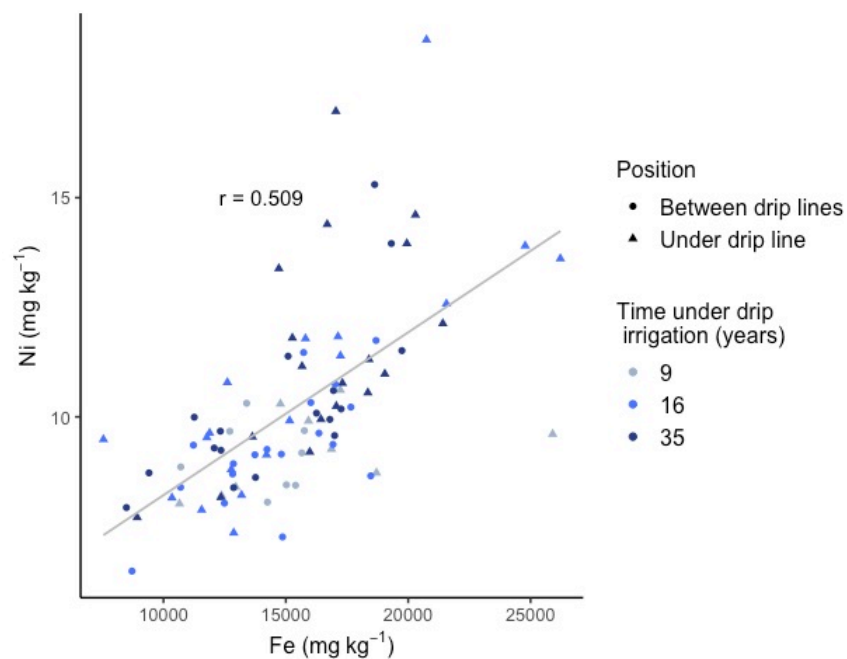


Figure 4.8. Significant positive correlation between soil iron (Fe) and nickel (Ni) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa. (Kendall, $p < 0.001$, $r = 0.509$).

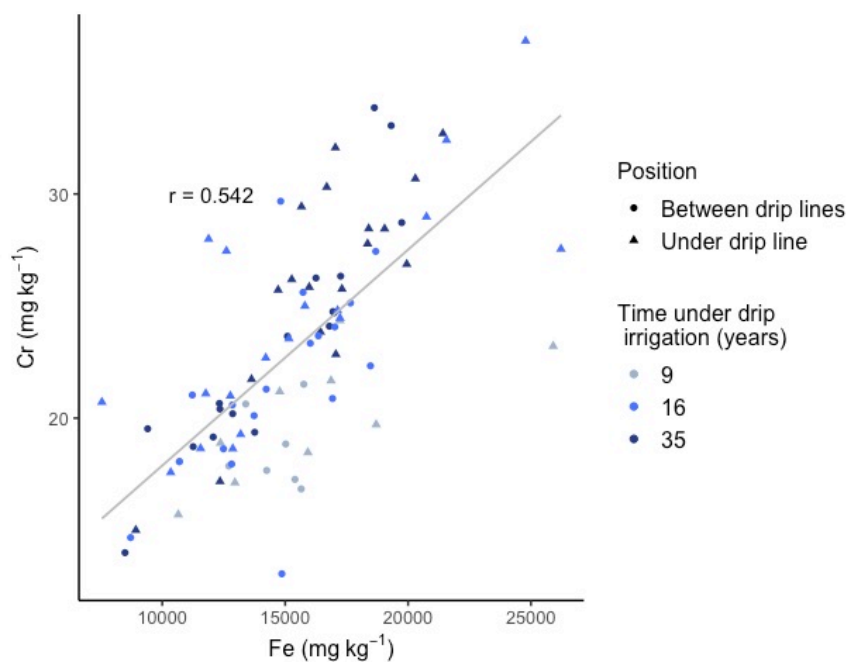


Figure 4.9. Significant positive correlation between soil chromium (Cr) and iron (Fe) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa. (Kendall, $p < 0.001$, $r = 0.542$).

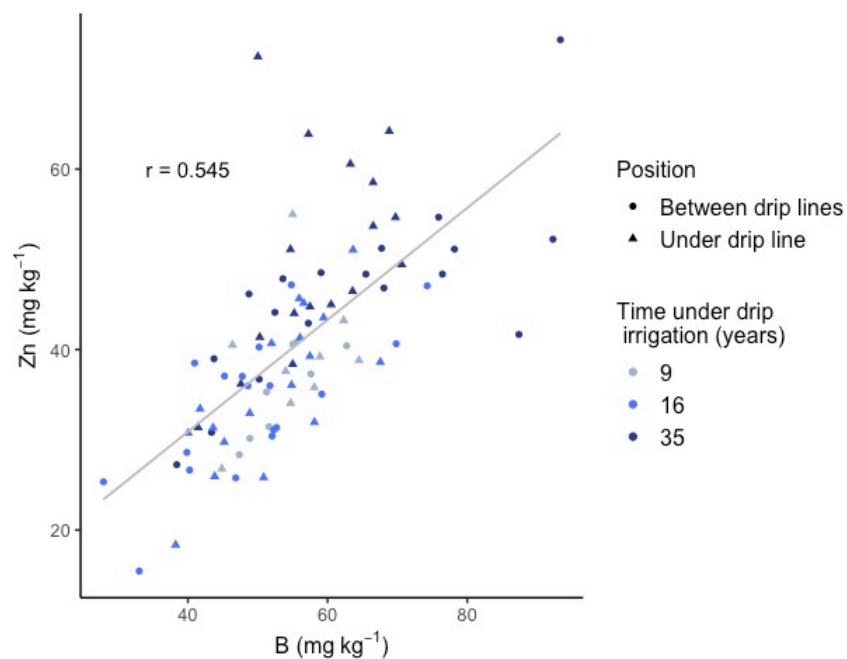


Figure 4.10. Significant positive correlation between soil boron (B) and zinc (Zn) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.545$).

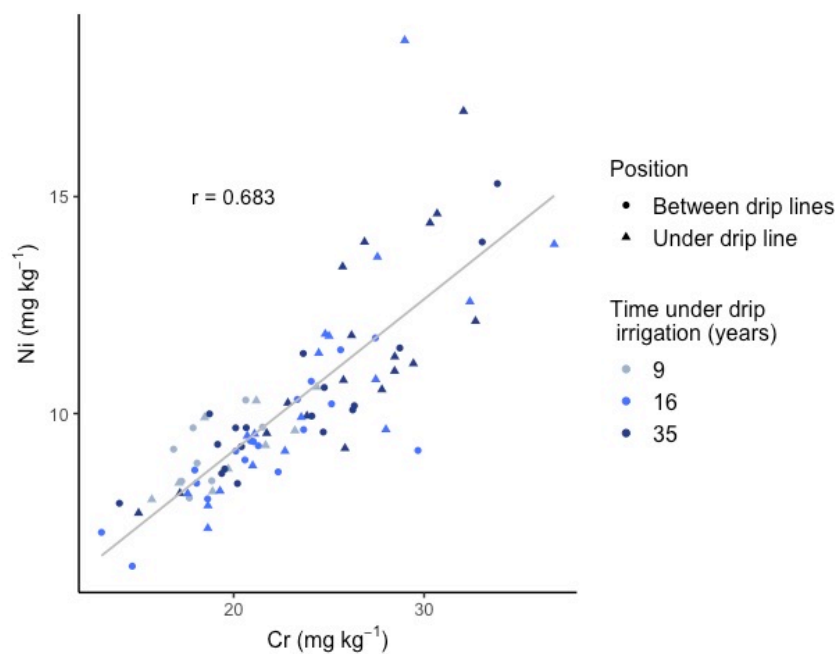


Figure 4.11. Significant positive correlation between soil chromium (Cr) and nickel (Ni) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa. (Kendall, $p < 0.001$, $r = 0.683$).

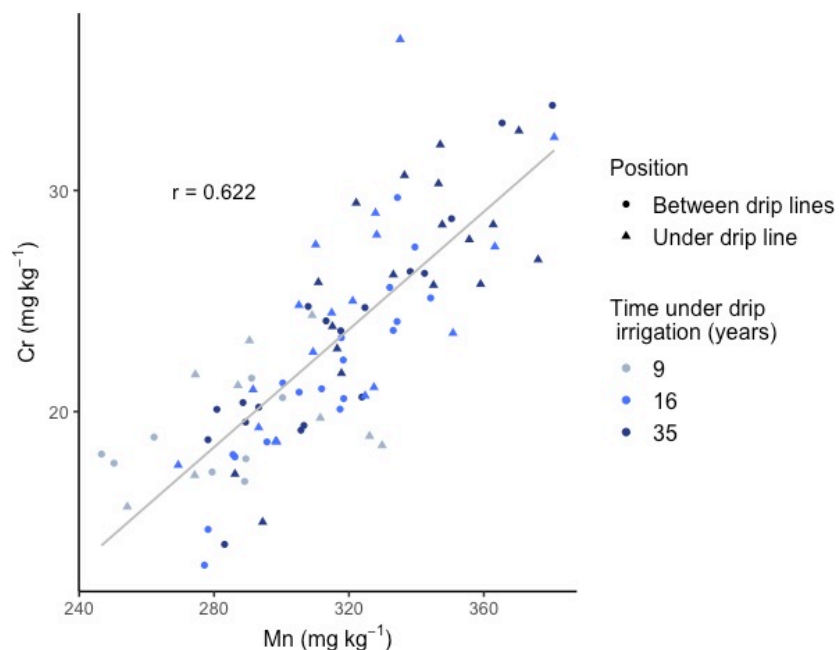


Figure 4.12. Significant positive correlation between soil chromium (Cr) and Manganese (Mn) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.622$).

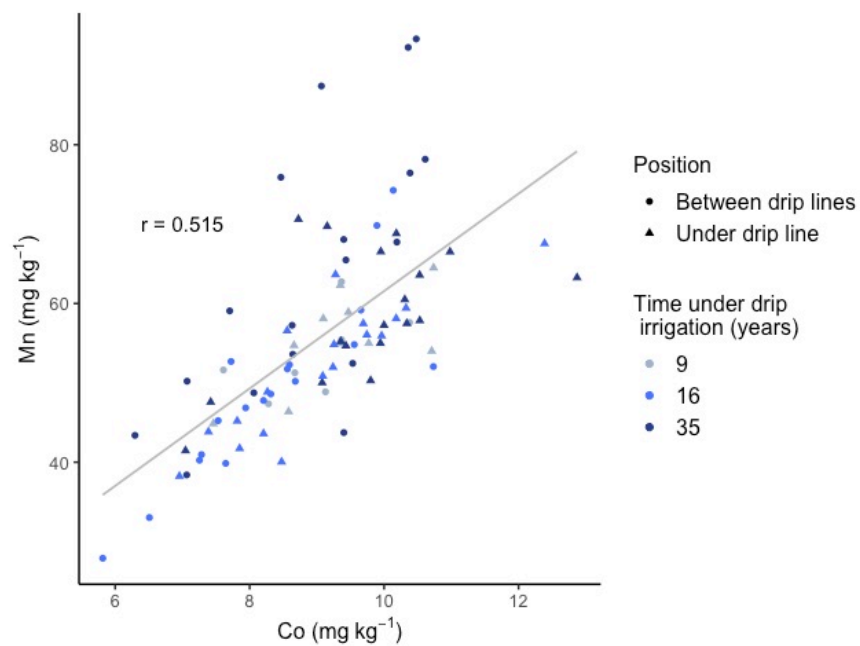


Figure 4.13. Significant positive correlation between soil cobalt (Co) and manganese (Mn) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.622$).

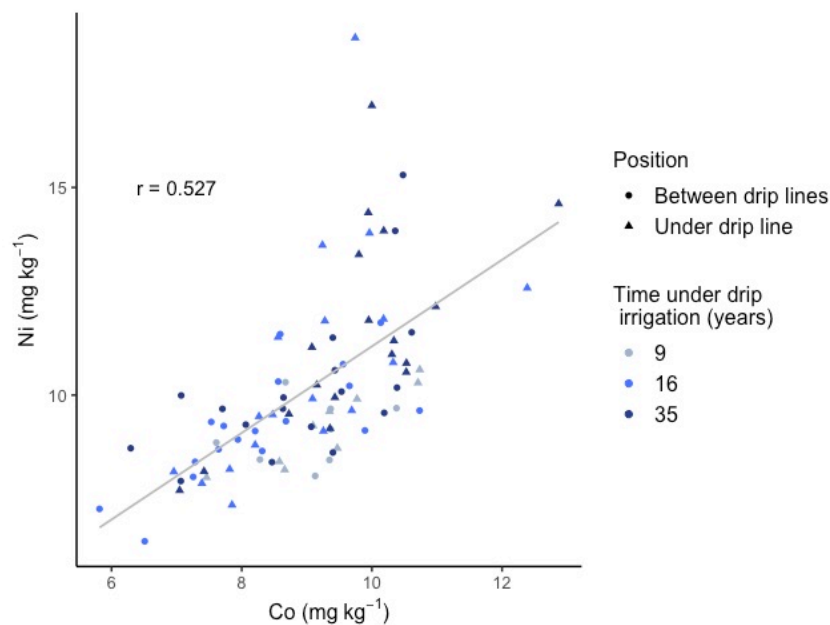


Figure 4.14. Significant positive correlation between soil cobalt (Co) and nickel (Ni) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.527$).

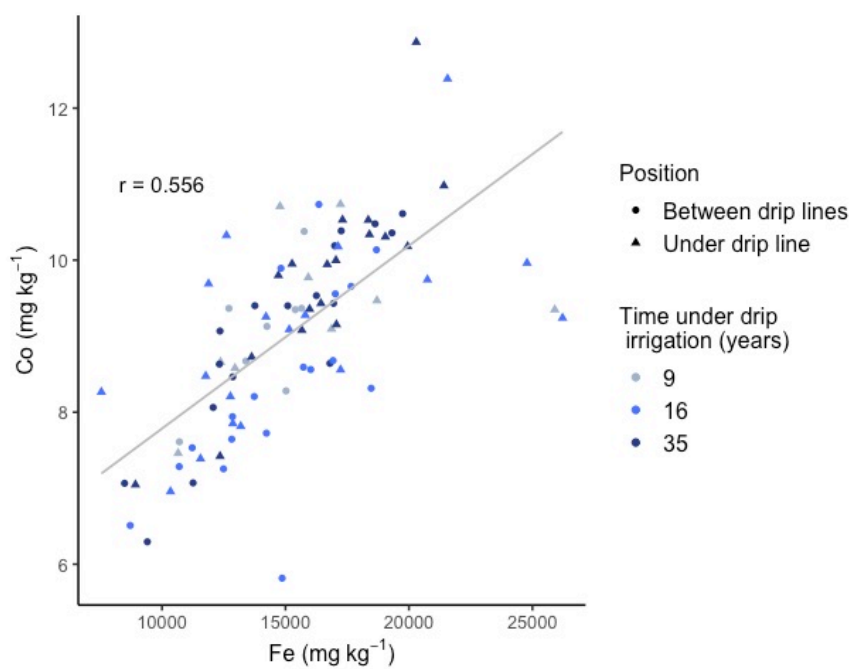


Figure 4.15. Significant positive correlation between soil cobalt (Co) and iron (Fe) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.556$).

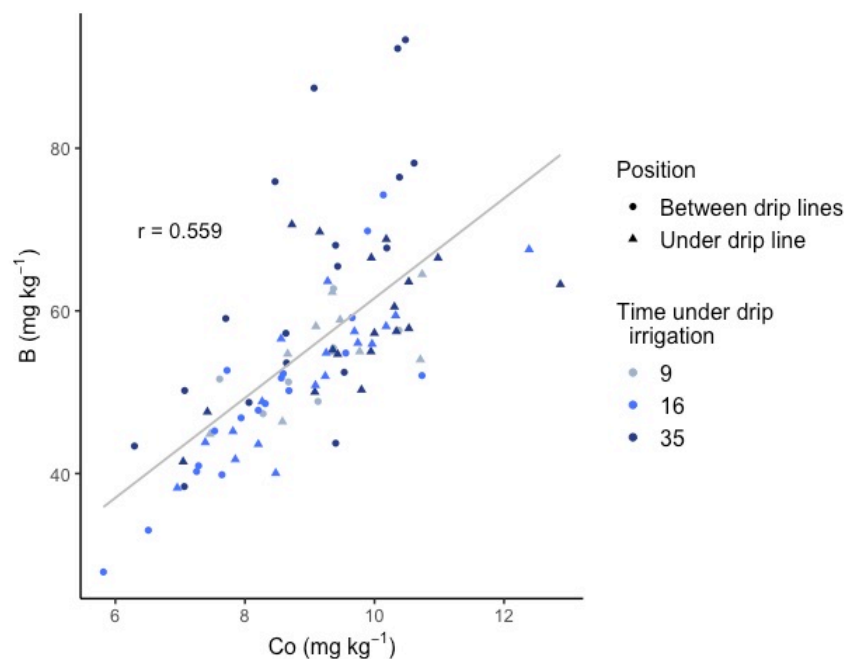


Figure 4.16. Significant positive correlation between soil cobalt (Co) and boron (B) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.559$).

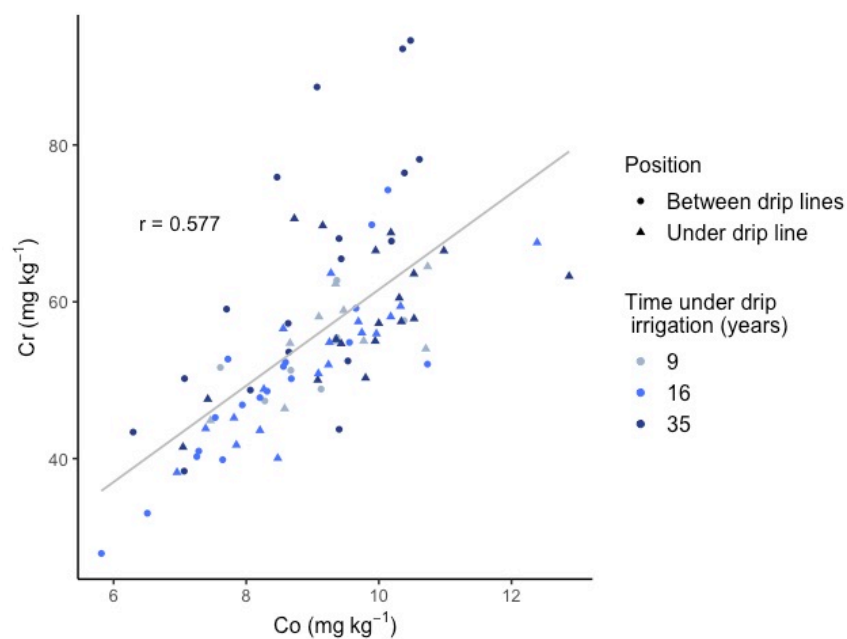


Figure 4.17. Significant positive correlation between soil cobalt (Co) and chromium (Cr) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.577$).

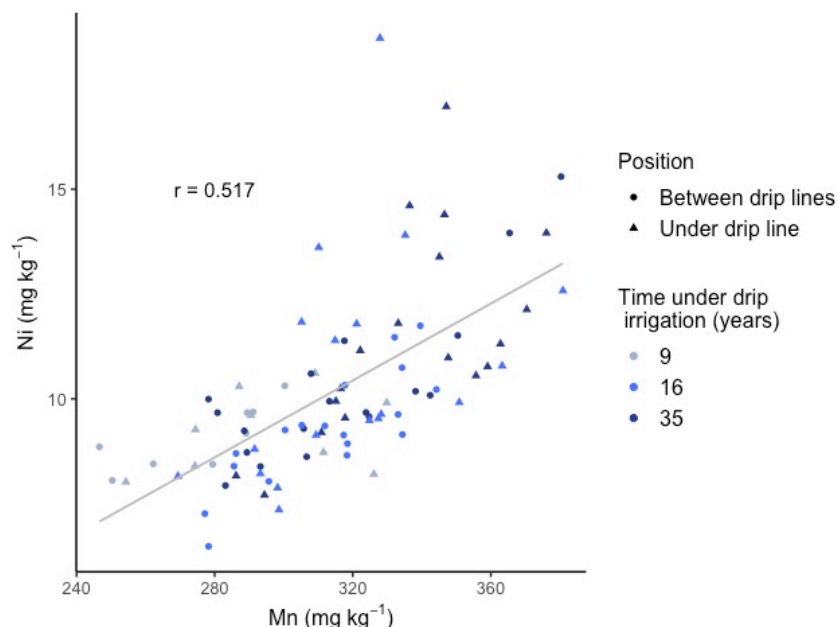


Figure 4.18. Significant positive correlation between soil nickel (Ni) and manganese (Mn) concentrations in drip irrigated vineyards in CIEPA-UNSA, Majes, Arequipa (Kendall, $p < 0.001$, $r = 0.517$).

4.6 A Note on Analytical Problems Encountered During Digestion

This thesis aimed to assess the accumulation of specific trace elements of vineyards soils in agriculture in this arid environment Cd, Pb, Cu, Ni, and Zn which are some of the most critical environmental metal pollutants in vineyards (Beygi et al., 2008). Unexpected analytical problems were encountered when assessing the metal contents for As, Pb, and Cd and, unfortunately, these elements could not be reported with confidence. While the standard SRM 2711a is commonly used to analyze heavy metal concentrations in soils, the standard analysis results in this study exhibited significant variation from the unknown samples. The texture of the soil standard, a silt loam, imparted a significant difference in percent recovery from the coarse sandy loams of CIEPA. After digestion, CIEPA samples exhibited substantial residues remaining compared with SRM 2711a. Also, as the dilutions were optimized to quantify metals in our CIEPA samples, they did not allow for detection of all the metals of interest in the standard sample. A standard with similar composition and texture as the samples would need to be used to assess the percent recovery and complete quality assurance and control. For a complete understanding of metal accumulation, future research might include a complete digestion with hydrofluoric acid or X-ray fluorescence (XRF) analysis for total trace elements concentrations.

4.7 Discussion

4.7.1 Trace Metals Accumulation at CIEPA controlled by water and crop management.

Peru's current soil environmental quality standards were established in 2017 by the Supreme Decree N 011-2017-MINAM. The standards are specific for different land uses; agriculture soil standards are provided in Appendix C (Table C.5). Only a few trace elements have been established with permissible national limits which are the following: As, total Ba, Cd, total Cr, Cr (IV), Hg and Pb. In the current study, the concentration of Ba, Cr and Cd were below the permissible national limits for agriculture. This study demonstrates, with the appropriate caveat about analytical issues related to percent recovery, that heavy metals concentrations are below the government's agroecosystems soil quality concentrations.

Overall, the Cu concentrations of CIEPA are quite low averaging 24.3 mg kg^{-1} when compared to other developed viticulture regions in France (232 mg kg^{-1} , Chopin et al. 2008), Spain (range $157\text{--}434 \text{ mg kg}^{-1}$, Fernandez et al., 2008), Brazil ($40\text{--}250 \text{ mg kg}^{-1}$, Correa et al., 2010), China ($18.4\text{--}188.4 \text{ mg kg}^{-1}$, Sun et al., 2018), Australia (249 mg kg^{-1} , Pietrzak et al., 2004), Greece ($331\text{--}291 \text{ mg kg}^{-1}$, Kelepertzis et al., 2017), Germany ($43\text{--}142 \text{ mg kg}^{-1}$, Mackie et al., 2013) and Iran ($46.63\text{--}44.11 \text{ mg kg}^{-1}$, Beygi et al., 2019). The low values at CIEPA could be due to the relatively short time the system has been active, less than 35 years, compared to mature viticulture regions around the world. At CIEPA, Ni appears to accumulate in the soil controlled by the total time under drip irrigation (Figure 4.3). Several vineyard studies have found an increase of Cu concentration in soil with time (Preston et al., 2016; Rusjan et al., 2007; Komárek et al., 2008). At CIEPA, row position did not significantly influence Cu concentration in contrast to similar studies (e.g. Pietrzak et al., 2004) that found a significant decrease between rows of approximately four-fold in vineyards of 30 years and two-fold in vineyards older than 90 years.

We observed a significant increase in Zn concentrations after 16 years under drip irrigation. According to CIEPA's written records (Personal communication, Julio Flores Caesar – CIEPA Manager), Zn is used in two ways in the vineyards: directly applied to the leaves as foliar fertilizer and is compound of a desalinator (Saltrad) used to manage salt content in soils. However, the row position does not influence Zn concentrations. In CIEPA, Zn concentration levels were lower (mean value 41.76 mg kg^{-1}) than compared to other viticulture regions in China ($107.17 \text{ mg kg}^{-1}$, Zhu et al., 2017; 150 mg kg^{-1} , Dong et al., 2008), France (318 mg kg^{-1} , Chopin et al., 2018), Brazil ($29.1\text{--}161.8 \text{ mg kg}^{-1}$, Preston et al., 2016), Spain ($44\text{--}90 \text{ mg kg}^{-1}$, Ramos et al., 2006; $60\text{--}149$

mg kg⁻¹, Fernández-Calviño et al., 2012), Brazil (29.1-161.8 mg kg⁻¹, Preston et al., 2016), and Iran (95 mg kg⁻¹ Beygi et al., 2018). Cu and Zn concentration are important nutrients at low concentrations but toxic on high concentrations (Antoniadis et al., 2015).

High correlations between trace metals can suggest the origin from a same source (geogenic or anthropogenic) where significant correlations higher than 0.5 strongly suggest the same source. Our results showed a weak positive correlation between Cu and Zn ($p < 0.01$, $r = 0.35$) consistent with other agriculture systems showing these elements increasing with time in cultivation (Preston et al., 2016). The strong covariation is in line with previous studies that have found evidence that Cu and Zn can originate from the same anthropogenic source in vineyards (Komárek et al., 2010; Kelepertzis et al., 2018; Milicevic et al., 2018). Zn has been applied in several fertilizer products; while Cu is only used in one product (ORGABIOL) in CIEPA. This agrees with previous findings of Zn impurities found in Cu fungicides and the Zn enriched produced by intensive use of fertilizers (Thomas et al., 2012; Bai et al., 2014; Kelepertzis et al., 2018). The use of Cu-based fungicides CIEPA is documented, but it lacks records for quantities and its frequencies. Therefore, it could be possible that Cu and Zn concentration might have different sources or be transported from local fields as dust.

Nickel and Mn both increased with time under drip irrigation at CIEPA. Our results showed that the position (under the drip line and between the drip lines) does only influence the content of Ni in the soil. Our results agree with those found by Preston et al. (2016), where Ni concentration increase after five years of agriculture. Nickel in soils can be strongly dependent on the parent material in mineral rich systems, and it can be high in soils of arid and semi-arid regions (Beygi et al., 2018). Overall, total concentration of Ni under drip irrigation at CIEPA's was lower when compared to other systems for example Iran (35-45.5 mg kg⁻¹, Beygi et al., 2018) and Greece (54.2 – 262 mg kg⁻¹, Kelepertzis et al., 2018). At CIEPA, Ni had a strong correlation with Fe ($p < 0.001$, $r = 0.5088$) (Figure 4.10) which could indicate Ni is co-precipitated with iron hydroxyoxides derived from irrigation water. Mn exhibited one of the clearest signals of increase with time in drip irrigation. According to CIEPA's manager, Mn is used as a foliar fertilizer (Personal communication) and so its concentration profile can be attributed to vineyards land management. Manganese also strongly correlates with Ni and Fe. Ni and Mn concentrations are influenced by irrigation time, but they might have different sources depending on the origins of Ni and Mn. Fe, Ni, and Mn can be geogenic elements, but further analysis is needed to identify if any other source

exists. Both Mn and Fe are sensitive to redox reactions, and organic matter accretion in the soil surface will adsorb Mn and Fe fractions (Sakar et al., 2004; Dhaliwal et al., 2019). Mn concentrations in CIEPA soils are higher (mean 314.37 mg kg⁻¹) than those found in surface soils in vineyards from Brazil 112.6 – 145.2 mg kg⁻¹ (Preston et al., 2016) mg kg⁻¹ but lower than the concentrations found in a calcareous vineyards in Greece (481-3,489 mg kg⁻¹, Kelepertzis et al., 2018).

Besides the trace metals discussed, the results at CIEPA showed significant change in barium (Ba) and boron (B) concentrations with time under drip irrigation. Ba was the only metal showing a consistent drop in concentration with time under drip irrigation suggesting it was progressively leached from the system or taken up by the plants (Cappuyns et al., 2018). Ba concentrations (range from 72.2 – 114.9 mg kg⁻¹) at CIEPA are similar to those identified in a nearby desert site near La Joya, Arequipa which ranged from 102 – 175.1 mg kg⁻¹ (Rodriguez Almonte, 2016). Boron concentrations increased with total irrigation time which differed from time under drip irrigation (Figure 4.5). Boron tends to concentrate in the arid irrigated surface horizons due to the high evaporation rates and irrigation inputs (Kot, 2015). When comparing our results with the nearby desert of La Joya, Arequipa, the B concentrations at CIEPA (mean 55.7 mg kg⁻¹) were lower than La Joya (ranged 97.5 – 124.1 mg kg⁻¹) (Rodriguez, 2016). Overall, the soil in the Majes pampas have a wide range in concentration from 0 to 200 ppm (Masson, 1973).

Furthermore, B and Fe are the trace elements that best correlated with the other trace elements. The highest correlation is between Cr and Ni; therefore, it could be implied that Cr and Ni share the same source origin. Co is the only element that correlates higher than 0.5 with other 5 elements. Fe and Mn oxides have strong affinity for Co and Cr (Kabata-Pendias & Szteke, 2015). Therefore, further research on trace elements is needed to determine the origin or source of trace elements in CIEPA's soils.

4.7.2 Soil carbon accumulation and pH have nascent control on trace distribution at CIEPA

Soil organic matter content in combination with soil pH, which determine the speciation of metals and surface charge of organics and clays, can be the principal factors in controlling the mobility of trace metals in aerobic soils (Miottoo et al., 2017). Soil pH at CIEPA ranged from 6.80 to 8.27 and SOC ranged from 0.18 to 1.37 mg g⁻¹ (Table B.1). Our results showed that Cu weakly

positively correlates with SOC ($p < 0.01$, $r = 0.20$). This result is consistent with previous results by Tiecher et al. (2016) and Beygi et al. (2008) on Cu having a high affinity for organic matter. Cu also showed a weak positive correlation with the concentrations of Fe; ($p < 0.05$, $r = 0.15$); therefore, Cu could have an affinity by adsorption by SOM and Fe-hydroxide. Previous work demonstrates that Cu is strongly immobilized by soil organic matter, Fe- and Mn-hydroxide, and the highest concentration is usually found in the upper layer of the soil profile (Komárek et al., 2010; Duplay et al., 2004). The pH values higher than 7.5 cause mobility of organic matter in the soil which influences Cu's mobility (Komárek et al., 2010; Duplay et al., 2004). The increase in pH reduces bioavailability of Cu because the speciation of Cu changes when it complexes to dissociated organic acids (Mackie et al., 2012). At CIEPA, Cu has a weak relationship with both soil pH ($r = 0.28$, $p < 0.001$) and SOC ($r = 0.21$, $p < 0.01$).

Zn has a weak correlation with Mn ($r = 0.36$), Fe ($r = 0.38$), and organic carbon ($r = 0.21$), indicating Zn has a similar affinity for adsorption among organic matter and Fe- and Mn-hydroxide. This is consistent with studies that show Zn is strongly associated with the soil iron oxides (Tiecher et al. 2016). Moreover, Cu and Zn can compete for the same adsorption sites. Our results showed a correlation between Cu and Fe ($r = 0.15$, $p < 0.05$) and soil organic carbon ($r = 0.17$, $p < 0.05$), but not with Mn. Our findings showed that Zn and Fe significantly correlate with SOC agrees with those of Dogan et al. (2019), and Dhaliwal et al. (2019) who found significant relationships between Zn, Fe and Mn with SOM. Also, Zn and Fe results showed a significant correlation with pH as found by Bravo et al. (2017) who found soil availability of Zn, Fe and Mn depend of pH. In contrast to the studies, SOC and soil pH does not influence Mn concentration in CIEPA's soil.

Preston et al. 2016 found a positive correlation between organic matter and nickel in the layer from 0-20 cm in 5 to 30 years vineyard soils from Brazil but our results did not find a similar significant correlation. We hypothesize that the differences between the results could be rooted in the methodology of metal extraction from soil as Preston et al. used a total soil extraction with an acid solution ($\text{H}_2\text{O}:\text{HF}:\text{HClO}_4:\text{HNO}_3$, 2:2:1:1) while our study only acid digested values from aqua regia extraction, i.e., Preston et al quantified total metal concentration rather than metal availability.

Boron has a weak correlation with SOC ($r = 0.21$, $p < 0.01$) and pH ($r = 0.25$, $p < 0.001$). This is consistent with studies found that soil pH influences B adsorption (Chen et al., 2009; Saltali et al., 2005; Steiner & Lana, 2013). Steiner & Lana (2013) found that pH in the range between 4.6 and 7.4 influences the increase of boron adsorption. Also, Yermiyahu et al. (2001) and Sarkar et

al. (2004) found that SOM is the soil property that mainly controls the concentration of available B. Overall, soil's B is controlled by time under drip irrigation at CIEPA.

4.8 Conclusion

This research aimed to quantify the concentration of trace elements in irrigated desert agriculture, in response to time under drip irrigation and position between or under the drip line. Based on the analysis, time under drip significantly impacted metal accumulation, while irrigation position is irrelevant for metal accumulation. This contrasted with the influence of position in the accumulation of overall salts (Chapter 3). Also, it can be concluded that soil physical-chemical properties such as soil electrical conductivity and soil organic carbon accumulation and the time under drip irrigation influence the accumulation of the different trace elements but to difference extents. This research fits into the body of literature that assesses the impact of irrigation on desert soils, particularly the time under drip irrigation.

A contrast between the actual accumulation of trace elements with the natural concentrations will help understand how irrigated agriculture is affecting the soil geochemistry and sustainability of these agricultural ecosystems. Incorporating the irrigation water analysis as a source function will help understand if any trace elements are sourced specifically by water. The results present also suggest no significant contamination problem by a particular trace metal in the vineyard, although future work will need to assess bioavailability to crops.

CHAPTER 5. CONCLUSIONS

5.1 Summary

This research aimed to assess the changes produced by irrigated agriculture in desert soil in arid environments in the newly developed desert agroecosystems of Arequipa, Peru. Peru's increase in food demand and desire to expand agricultural markets necessitated expansion into coastal deserts which radically transformed the natural landscape into an intensively managed anthropogenic one. The thesis's goal was to have a better understanding of the impact of long-term drip irrigation desert soil state variables like organic carbon, pH, electrical conductivity, and trace elements. A chronosequence of vineyards at CIEPA were chosen as they represent stable placement of irrigation lines in one location and represent potentially similar responses from all classes of perennial crops common to the region. We tested the following assumptions: 1) Organic carbon accumulation is directly proportional to the vineyard age and years in irrigation; 2) the position of the drip lines controls spatial patterns of SOC accumulation; 3) Trace element, and heavy metal, accumulation may be alternatively controlled by the degree of flushing (application of furrow irrigation in initial land preparation to remove salts) or years under drip irrigation which would permit salt (as measured by electrical conductivity) accumulation near the drip line.

It is vital to understand the past to address the future successfully. Site history is an essential tool to understand and assess future problems caused by damaging land management practices. After regarding the site history, we identified a common management pattern used to condition the desert soil for agriculture. The use of alfalfa with sprinkler irrigation helped increase nitrogen levels, improve soil structure, and decrease the salt content; therefore, soils were improved before the for-profit production began. This same process is used to treat sites that have accumulated too much salt and limit plant growth.

This research encountered several limitations during development of the thesis. One of the most significant research limitations is poor record keeping related to management history and the extensive effort through interviews required to reconstruct decades of land management. This effort uncovered a wide variety of management history between the three vineyards plots chosen for this study. For example, two of the plots, termed the 9- and 35- year in drip irrigation plot, actually were converted into agriculture in the same year (1983), but the irrigation system was

completed differently, with the 9- years old vineyard using more sprinkler and furrow irrigation than the 35- year old vineyard. A consistent management pattern was developed over time, but the first attempts were more experimental and did not follow the same trend that would make for an ideal chronosequence approach. Variation in the correlations obtained herein may be the result of this irregular management.

Soil carbon accumulation is one of the most important indicators of soil health (Bünemann et al., 2018). I found that soil carbon accumulation increases over time in irrigated arid soil, and it is influenced by position from the point of drip irrigation. However, the time under drip irrigation had a higher influence on soil carbon than row position. Another important indicator of soil health is soil salinity. As our result showed agriculture in arid regions will have salt concentration increase with the time under irrigation. Therefore, the goal of agricultural managers in arid environments is to increase soil organic matter to improve soil properties such as water retention, nutrient releases, soil structure, and microbial cycling.

Besides organic carbon and overall salinity, time under drip irrigation also affects the trace elements contents in soil however, the proximity to the drip line did not have a significant impact on the accumulation pattern of trace metals. A strong positive correlation between different trace elements can suggest they originated from the same source or have a common mechanism of concentration like co-precipitation. Most trace elements at CIEPA significant correlated with iron and manganese suggesting that these two elements have either a common geogenic origin from the mafic igneous rock or they are associated with authigenic iron and manganese oxide precipitates. Further analysis is needed to address the difference between natural and anthropogenic sources.

This thesis shows that irrigation systems in the Majes region have substantially and predictably, for some properties, impacted the original soil. Desert irrigation practices are proposed to increase in the Arequipa region with the construction of the Majes-Siguas II project and it is vital to understand these new anthropogenic activities impact the land to avoid future impairment in soil and to maximize agricultural productivity. Incorrect management practices can cause more harm than benefits, especially in a fragile ecosystem like the desert. Human intervention has impacted soil chemistry; however, it is up to land management to determine if the soil changes produced by the impact of agriculture are beneficial and positive.

5.2 Future work

This study highlights the impacts of irrigated agriculture in transformed desert soils in arid environments. Over time, the effects of irrigation on soil properties were assessed with implications on soil carbon, solution chemistry, and specific trace element accumulation. A comprehensive geochemistry assessment of the soils of the area is needed to assess the changing system. The Majes project provides an invaluable opportunity to study the changes in desert soils and sampling the different sections of Majes of different ages of irrigation over the last 40 years could provide a chronosequence approach that will provide valuable information for soil conservation to decision makers. Furthermore, the study on the whole pampas of Majes can be used as reference case for the different irrigations project along the Peruvian coastal region.

The identification of SOC source and the proportion of particulate and mineral-bound carbon would be crucial to help the improvement of the vulnerability of the new SOC to land use and climate change. A management strategy that works to promote more mineral-bound C would make for higher quality SOC that is more stable and less vulnerable to management changes (Bünemann et al., 2018).

Metal speciation in soils is a critical aspect of assessing the potential hazards these soils pose to humans and other aspects of the ecosystem. A more in-depth approach to assess metal accumulation could include the soil infiltration rates and patterns and the water input during a growing season. Also, the irrigation water chemistry assessment over a growing season can help determine if any of the trace elements in the irrigation water are accumulating in the soil. This thesis only measured the total digested amounts of trace elements in the soil; however, it is essential to find the metal speciation in the soil since the harm level range of the metal changes from species to species. For example, some species are innocuous for health like Cr (III), and others can be harmful like Cr (IV).

APPENDIX A. AREAL IMAGERY OF THE EVOLUTION OF CIEPA'S LAND MANAGEMENT SINCE 1984 TO 2015

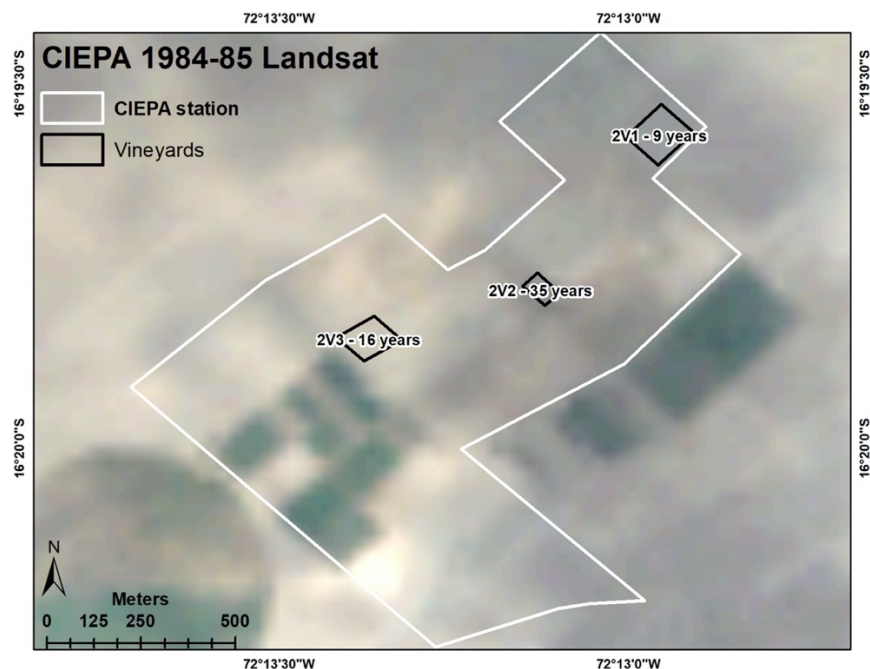


Figure A.1. CIEPA's Landsat image from 1985 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

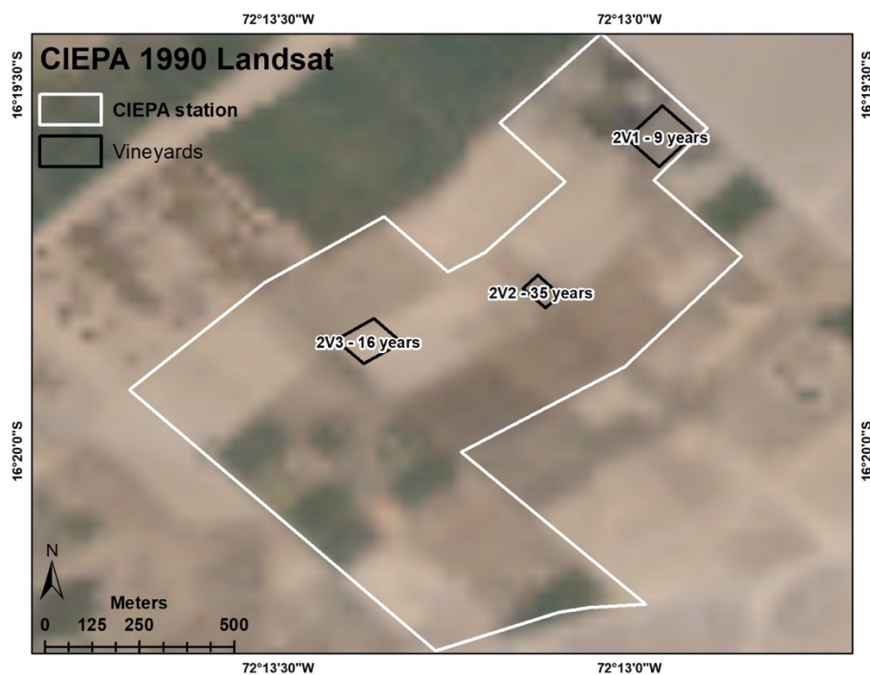


Figure A.2. CIEPA's Landsat image from 1990 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

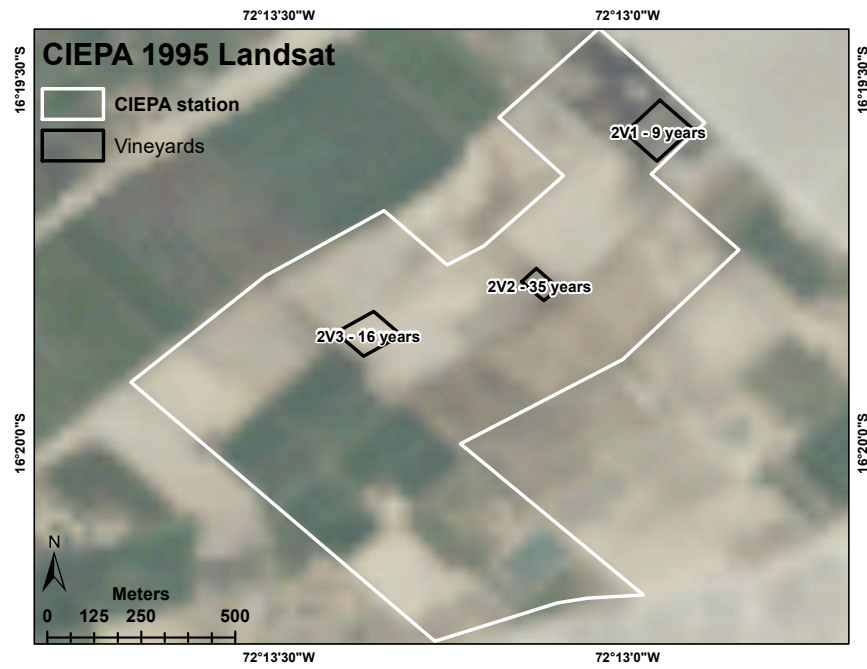


Figure A.3. CIEPA's Landsat image from 1995 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

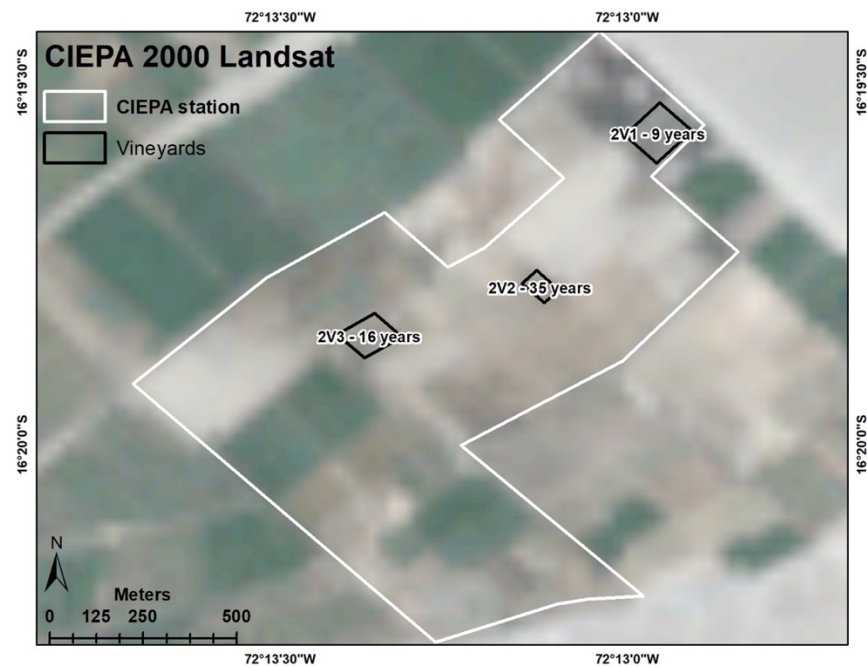


Figure A.4. CIEPA's Landsat image from 2000 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

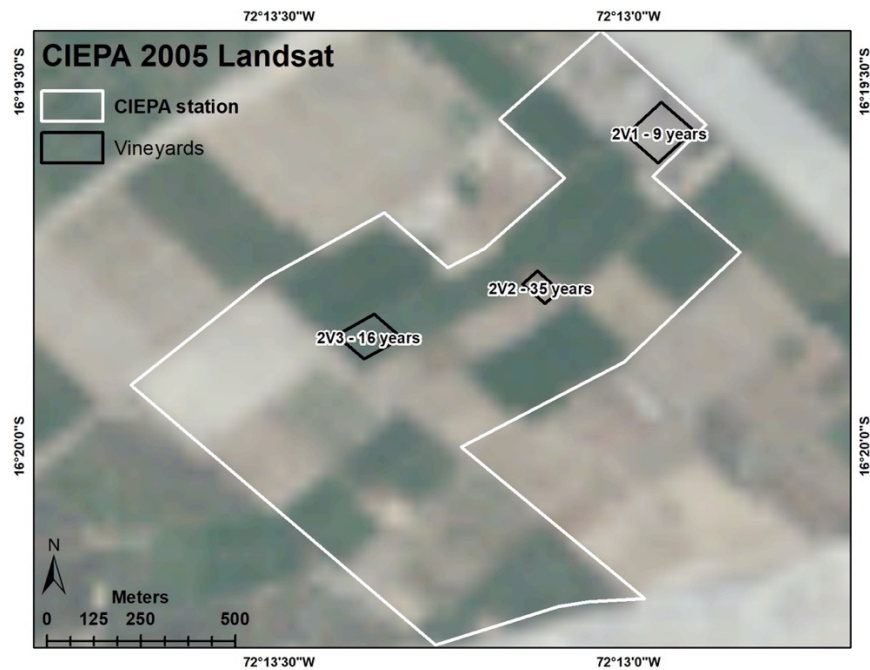


Figure A.5. CIEPA's Landsat image from 2005 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

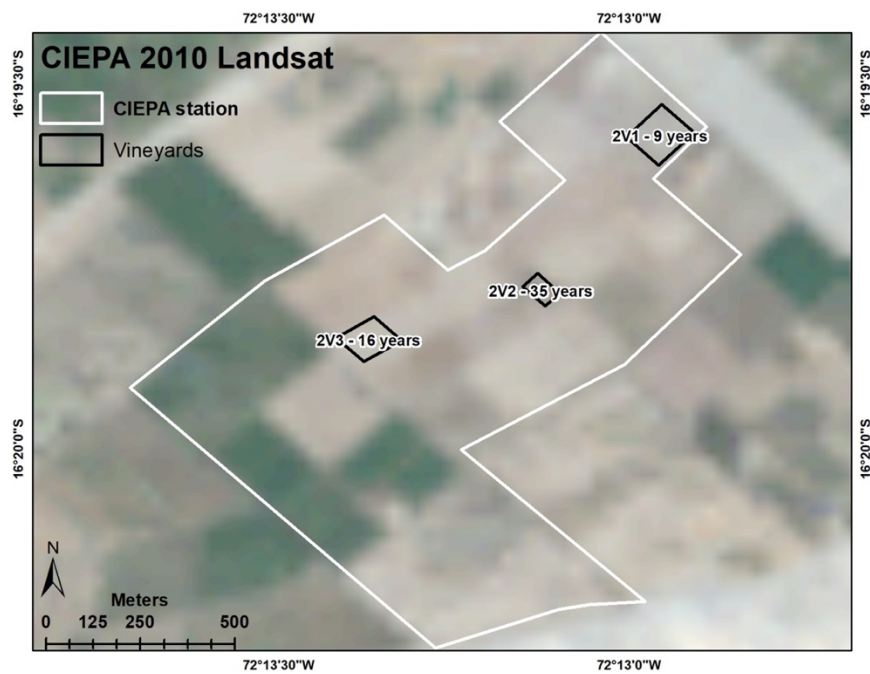


Figure A.6. CIEPA's Landsat image from 2010 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

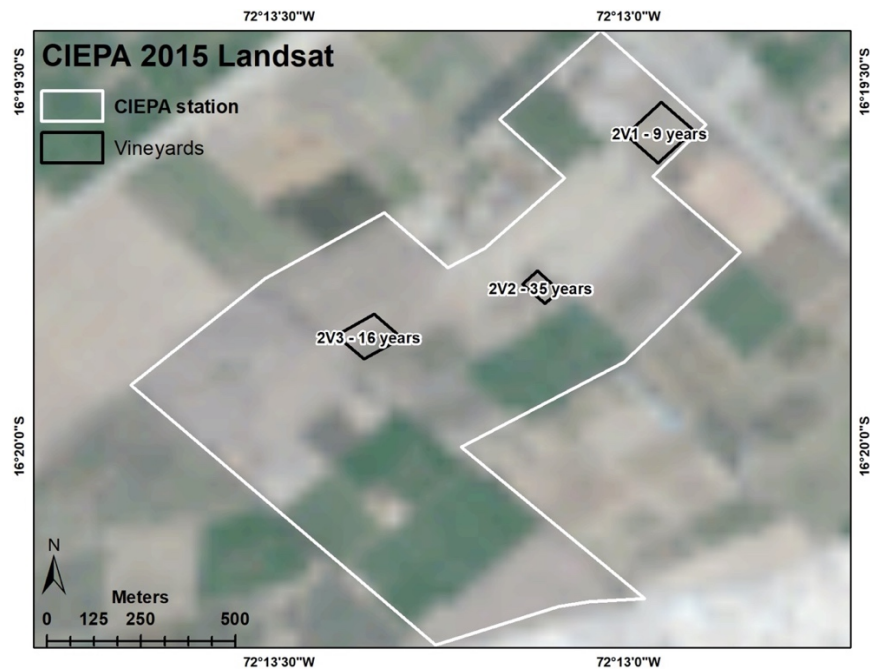


Figure A.7. CIEPA's Landsat image from 2015 with the location of the three sampling vineyards plots.
(credits: Dr. Zach Brecheisen)

APPENDIX B. SOIL CHEMICAL CHARACTERISTICS OF CIEPA SOILS

B.1. Soil chemical characteristics of CIEPA soils

Table B. 1. Maximum and minimum soil (0—20 cm) chemical properties at CIEPA

	Total Carbon (mg g⁻¹)	Organic Carbon (mg g⁻¹)	Inorganic Carbon (mg g⁻¹)	pH	Electrical Conductivity (dS/m)
Min	0.20	0.18	0	6.80	0.67
Max	1.58	1.40	0.60	8.27	24.00

Table B. 2. Statistical analysis performed for soil geochemical properties at CIEPA

Soil geochemical property	Parametric	Normal Transformation	Statistical analysis	Posthoc Analysis
Total carbon (mg g ⁻¹)	Parametric	Log	Two-way ANOVA	Least means square
Organic carbon (mg g ⁻¹)	Parametric	Log	Two-way ANOVA	Least means square
Inorganic carbon (mg g ⁻¹)	Non-parametric	-	Kruskal- Wallis Test	Dunn
pH	Parametric	Log	Two-way ANOVA	Least means square
Electrical conductivity (dS/m)	Parametric	Square root	Two-way ANOVA	Least means square

Table B. 3. CIEPA's soil (0-20 cm) chemical properties including total carbon (mg g^{-1}), organic carbon (mg g^{-1}), inorganic (mg g^{-1}), pH and electrical conductivity (dS/m) regarding row position.

Position	Time in Drip Irrigation	Total Carbon (mg g^{-1})	Organic Carbon (mg g^{-1})	pH	Electrical Conductivity (dS/m)
Under the drip line	9	0.69	0.67	7.7	1.64
	16	0.60	0.55	7.4	5.79
	35	0.60	0.56	7.6	7.64
Between the drip lines	9	0.52	0.49	7.5	5.57
	16	0.74	0.66	7.2	7.04
	35	0.91	0.79	7.7	14.23

B.2. Inorganic carbon concentration in vineyards 0-20 cm:

No significant variation of inorganic carbon. High presence of carbonates values on the 16- and 35-years old plot where there have not been sprinkler irrigation or high flush. Inorganic carbon has not significantly accumulated in the soil.

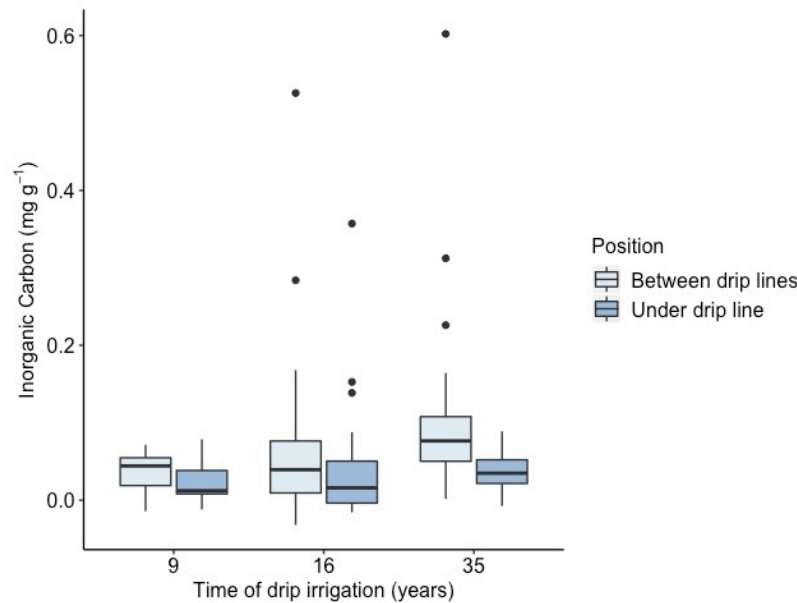


Figure B. 1. Soil inorganic carbon concentration (mg g^{-1}) accumulation in three different vineyards of 9, 16 and 35 years under drip irrigation regarding between and in the row position on CIEPA-UNSA, Majes Irrigation, Arequipa. Solid dots represent outliers. There is no significant accumulation of inorganic carbon.

B.3. Stable Carbon Isotopes

Stable carbon isotopes values were measured by the EA-IRMS on total carbon and organic carbon. The $\delta^{13}\text{C}$ values lower for organic carbon than total carbon with mean $\delta^{13}\text{C}$ values for organic carbon of $-25.7 \pm 0.3 \text{ ‰}$, $-23.7 \pm 0.6 \text{ ‰}$ and $-23.8 \pm 1.1 \text{ ‰}$ while for total carbon of $-24.4 \pm 1.1 \text{ ‰}$, $-22.1 \pm 2.6 \text{ ‰}$ and $-22.2 \pm 1.9 \text{ ‰}$ for 9, 16 and 35 years old, respectively (Figure B.2. and Figure B.3). The 9 years old plot had the most depleted carbon isotopic.

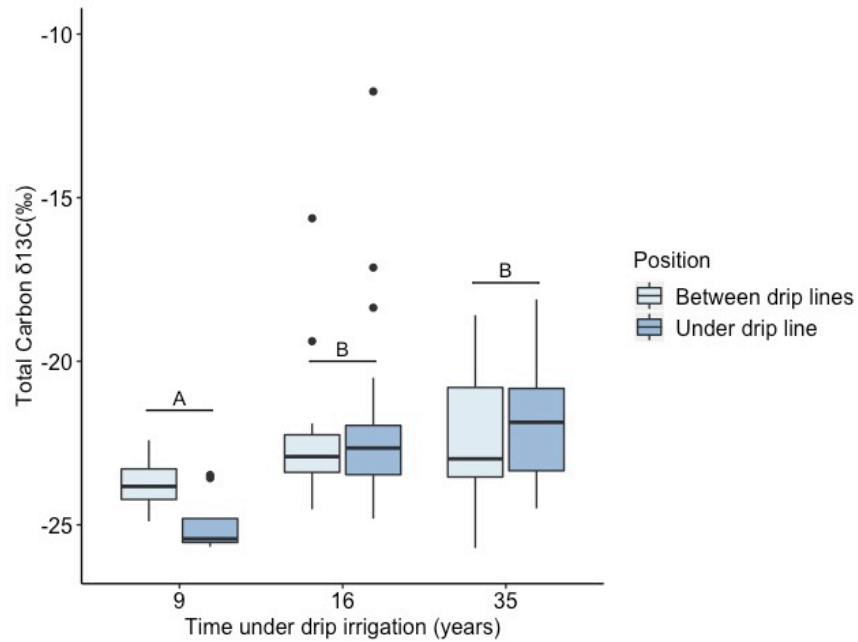


Figure B. 2. $\delta^{13}\text{C}$ values for Total carbon (‰) in depth of 0 -20 cm in 9-, 16- and 35- years old vineyards under irrigation in CIEPA-UNSA in Majes Irrigation, Arequipa. Solid dots represent outlier values. Significant differences across time are represented by capital letters at alpha 0.05 (Tukey's HSD, $p < 0.001$)

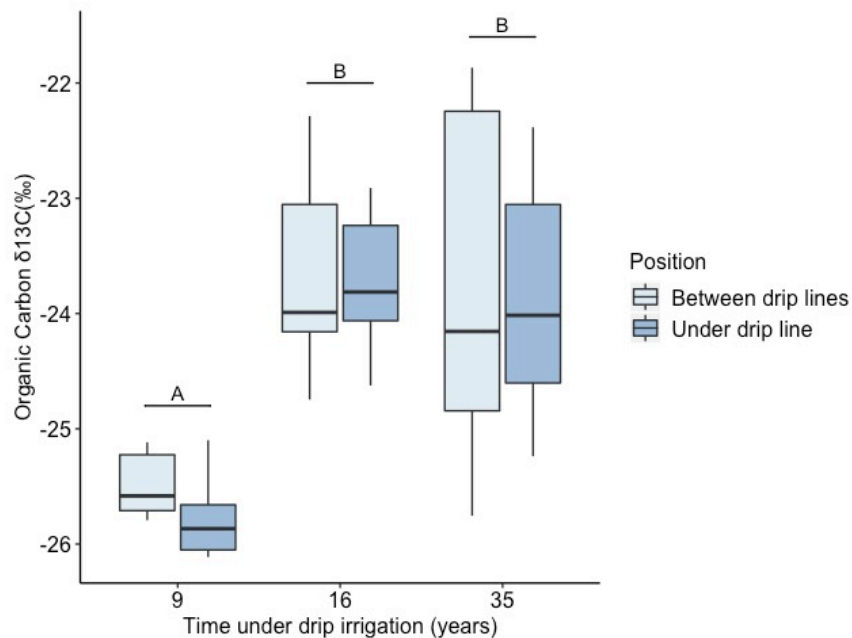


Figure B. 3. $\delta^{13}\text{C}$ values for organic carbon (‰) in depth of 0 -20 cm in 9-, 16- and 35- years old vineyards under irrigation in CIEPA-UNSA in Majes Irrigation, Arequipa. Significant differences across time are represented by capital letter alpha 0.05 (Tukey's HSD, $p < 0.001$)

B.3. Correlation between soil chemical properties and carbon accumulation:

It was evaluated the correlation between carbon accumulation and electrical conductivity between three different vineyards. The relationship between total carbon (Kendall, $r=0.2257$, $p=0.001$), organic carbon (Kendall, $r=0.1547$, $p=0.031$) and inorganic carbon (Kendall, $r=0.2785$, $p<0.01$) with soil electrical conductivity was significant (Figure B.4, B.5, and B.6).

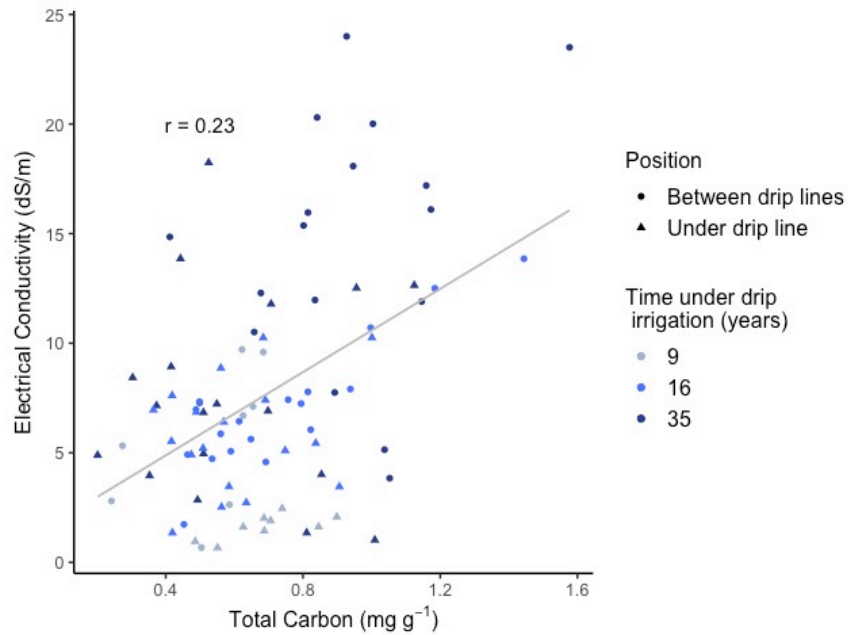


Figure B. 4. Change of soil electrical conductivity as function of soil total carbon concentration on three different vineyards under drip irrigation for 9, 16 and 35 years regarding its row position on CIEPA-UNSA, Majes irrigation, Arequipa. (Kendall, $r=0.2257$, $p=0.001$)

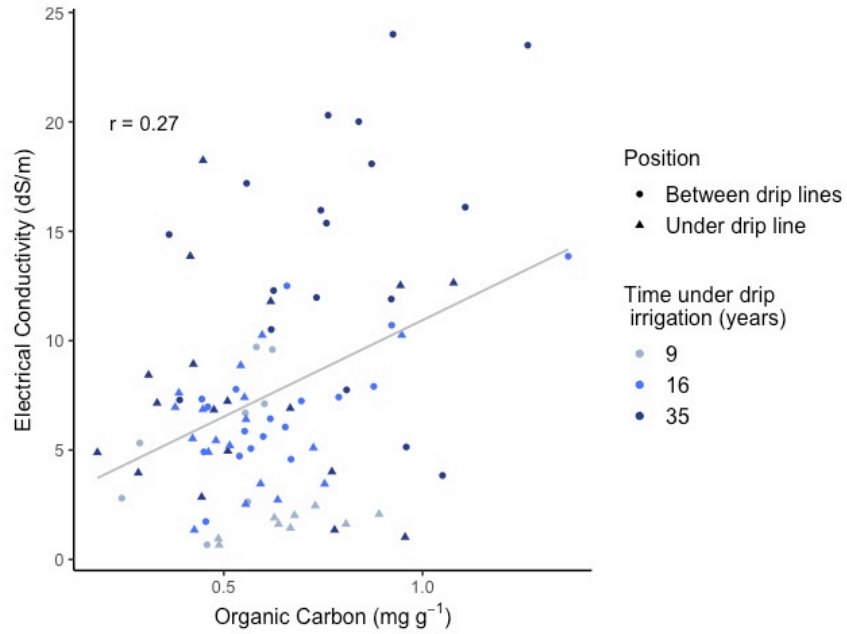


Figure B. 5. Change of soil electrical conductivity as a function of soil organic carbon concentration on three different vineyards under drip irrigation for 9, 16 and 35 years regarding its row position on CIEPA-UNSA, Majes irrigation, Arequipa. (Kendall, $r = 0.15$, $p = 0.031$)

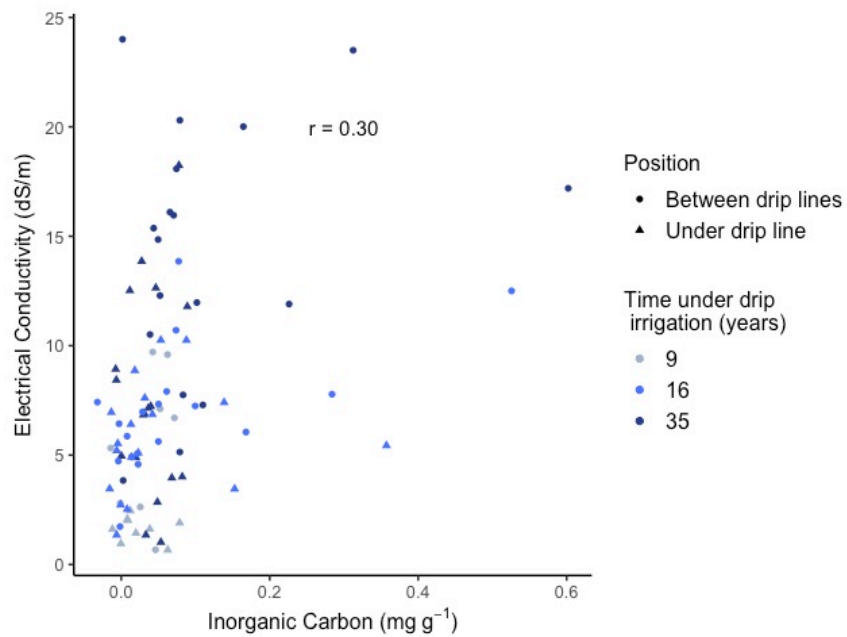


Figure B. 6. Change of soil electrical conductivity as function of soil inorganic carbon concentration in three vineyards under drip irrigation for 9, 16 and 35 years, respectively, and its row position on CIEPA-UNSA, Majes Irrigation, Arequipa (Kendall, $r = 0.278$, $p < 0.01$).

APPENDIX C TRACE ELEMENTS CONCENTRATIONS IN CIEPA'S SOILS

C.1. Parameters of metal analysis:

Metal analysis was done by the ICP-OES in the Jafvert lab at Civil Engineer at Purdue University. A total of 30 metals were analyzed which include metals beyond the interest of this thesis. The comprehensive list of the analyzed metals: Al, As, Au, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mg, Mo, P, Pb, Pd, Pt, Sc, Se, Si, Sr, Sb, Sn, Ti, V, Zn and Zr. In the following table are the specific instrument measurement parameters: instrument detection limit (IDL) (ppb), Limit of quantification (LOQ) (ppb), coefficient of variance, and percent recovery of the standard (%). Limit of detection (LOD) and Limit of quantification (LOQ) were based on the results of many blank tests. The coefficient of variance ranged from 3.44 (As) to 109.45 (Mo).

The soil standard NIST 2711 (National Institute of Standards and Technology) did not have concentrations for the following elements, Li, Er, Pd, Pt Au, Se, Ge, Mo, Sn, and W, and elements above the calibration curve Al, Ca, Cu, Fe, K, Mg, Se, Pt, Au and Zn. Data from the ICP-OES is not reported for values lower than the 90% accuracy. CRM provides metrological traceability, and it can ensure reliable measurements for users. For this thesis, the certified reference material for the detection of trace elements in soil was SRM 2711 or Montana II Soil Moderately Elevated Trace Element Concentrations which is highly contaminated soil. The certified reference did not have similar characteristics to the sample soils the difference where observed when the samples left more weight residues than the sample after acid digestion. A better soil reference for our study would be the CRM 142 light sandy soil with similar carbon and nitrogen percent of our samples. The similarities between the sample and the certified reference will give accurate results.

Table C.1. ICP-OES measurement parameters for soil metal analysis: instrument detection limit (IDL) (ppb), limit of quantification (LOQ) (ppb) and certified standard concentrations (mg kg⁻¹) with percent recovery (%) and coefficient variance (%) obtained for SRM 2711a.

Trace Element	IDL (ppb)	LOQ (ppb)	Certified Standard concentrations (mg kg ⁻¹)	Standard Percent Recovery (%)	Standard Coefficient variance (%)
Au	2.19	7.29	-	-	-
Al	0.26	0.85	67,200	Above CR	-
As	1.97	6.57	107	1195.72*	3.44
B	1.09	3.62	-	-	-
Ba	0.05	0.17	730	59.29	8.09
Ca	6.90	22.99	24,200	Above CR	-
Cd	0.10	0.34	54.1	17.58	4.39
Co	0.24	0.79	9.89	47.14	6.13
Cr	0.26	0.86	52.3	25.40	18.37
Cu	0.61	2.04	140	Above CR	-
Fe	0.52	1.73	28,200	67.85	11.64
Ge	1.73	5.78	-	-	-
Gd	0.75	2.51	-	-	-
K	0.94	3.14	25,300	Above CR	-
Li	0.05	0.15	-	-	-
Lu	0.13	0.45	-	-	-
Mg	0.20	0.68	10,700	32.37	25.75
Mn	0.18	0.59	675	233.20	4.41
Mo	0.54	1.80	-	-	-
Nd	1.74	5.80	-	-	-
Ni	0.45	1.49	21.7	19.59	29.24
P	2.21	7.36	842	116.88	7.23
Pb	1.55	5.20	1,400	257.45	13.78
Pd	0.85	2.82	-	-	-
Pt	0.90	3.00	-	-	-
Sc	0.15	0.50	-	-	-
Si	2.69	8.96	314,000	0.50	22.02
Sb	2.33	7.77	23.8	242.03	5.66
Sn	0.87	2.89	-	-	-
Sr	0.08	0.27	242	25.19	5.18
Ti	0.30	1.01	3,170	24.52	5.39
V	0.60	2.00	80.7	51.04	4.22
W	4.07	13.57	-	-	-
Yb	0.14	0.47	-	-	-
Zn	0.24	0.81	414	Above CR	-
Zr	0.45	1.50	-	-	-

Note: Above CR: Value above calibration curve, high interference for As

C.2. Trace element concentration of vineyard:

Table C.2. Summary of statistical analysis of trace elements concentrations (mg kg⁻¹) on the CIEPA (UNSA, Majes, Arequipa) vineyards with 9-, 16- and 35- years in drip irrigation.

Time under drip irrigation (years)	Metals	Mean (mg kg ⁻¹)	Min (mg kg ⁻¹)	Max (mg kg ⁻¹)	Standard Deviation	Coefficient Variance (%)
9	B	54.6	44.9	64.5	5.8	10.6
	Ba	114.8	87.6	144.9	13.3	11.5
	Cd	0.6	0.6	0.6	NA	NA
	Cu	29.4	22.2	37.5	3.9	13.2
	Ni	9.2	8.0	10.6	0.8	9.2
	Zn	37.4	26.8	55	6.6	17.6
	Mn	286.2	246.6	329.8	24.6	8.6
	Cr	19.4	15.7	24.4	2.4	12.4
	Co	9.2	7.5	10.7	0.9	9.8
	Fe	15,192.4	10,654.2	25,902.5	3,528.9	23.2
	Mg	2,571.4	1,590	4,845.7	725.9	28.2
16	B	50.6	27.9	74.3	9.9	19.6
	Ba	102.5	81.7	139.1	14.0	13.7
	Cd	0.7	0.6	0.7	0.0	3.1
	Cu	19	11.7	33.4	4.2	21.9
	Ni	10	6.5	18.6	2.3	22.6
	Zn	34.8	15.4	51.1	8.1	23.2
	Mn	316.1	269.4	380.9	24.4	7.7
	Cr	23	13.1	36.8	4.9	21.2
	Co	8.7	5.8	12.4	1.3	14.9
	Fe	15,019.3	7,545.8	26,217.9	4,035.9	26.9
	Mg	4,700.5	2,586.2	11,213.4	1,953.7	41.6
35	B	61.3	38.4	93.3	13.5	22
	Ba	96.3	72.2	128.5	12.6	13.1
	Cd	0.6	0.6	0.7	0.0	6.7
	Cu	27.3	14.0	48.9	8.9	32.6
	Ni	10.9	7.7	17	2.2	20.4
	Zn	48.2	27.2	74.4	10.7	22.2
	Mn	325.9	278.2	380.3	29.1	8.9
	Cr	24.7	14	33.9	5.1	20.6
	Co	9.3	6.3	12.9	1.3	14
	Fe	15,659.0	8,485.3	21,414.4	3,308.1	21.1
	Mg	3,410.0	1,590	6,744.9	1,222.6	35.9

Table C.3. Trace elements concentrations (mg kg^{-1}) concentration in vineyards soils in CIEPA, (UNSA, Majes, Peru).

Metals	Parametric	Transformation	Statistical Analysis	Post-hoc
B	Parametric	Log	Two-way ANOVA	Tukey's HSD
Ba	Parametric	None	Two-way ANOVA	Tukey's HSD
Cd	Nonparametric	-	Kruskal-Wallis test	-
Cu	Nonparametric	-	Kruskal-Wallis test	Dunn test
Ni	Nonparametric	-	Kruskal-Wallis test	Dunn test
Zn	Nonparametric	Log	Two-way ANOVA	Tukey's HSD
Mn	Parametric	Log	Two-way ANOVA	Tukey's HSD
Cr	Parametric	None	Two-way ANOVA	Tukey's HSD
Co	Parametric	None	Two-way ANOVA	Tukey's HSD
Fe	Parametric	Log	Two-way ANOVA	-
Mg	Nonparametric	-	Kruskal-Wallis test	Dunn test

Table C.4. Trace elements concentrations (mg kg^{-1}) concentration in vineyards soils in CIEPA, (UNSA, Majes, Peru).

Metals	Mean value (mg kg^{-1})	Minimum concentration (mg kg^{-1})	Maximum concentration (mg kg^{-1})	Standard deviation	Coefficient Variance (%)
B	55.7	27.9	93.3	11.9	21.4
Ba	102.4	72.2	114.9	14.8	14.4
Cd	0.7	0.6	0.7	0.0	6.4
Cu	24.3	11.7	49	7.8	32.2
Ni	10.2	6.5	18.6	2.1	20.9
Zn	41.8	15.2	142.1	15.2	36.5
Mn	314.4	246.6	380.9	29.9	9.5
Cr	23	13.1	36.8	5	21.5
Co	9.0	5.8	12.9	9.2	1.3
Fe	15,307.2	7,545.8	26,217.9	3,634.1	23.7
Mg	3,771.8	1,590	11,213.4	1,701	45.1

C.3. Environmental standards for agricultural soils

Peru's law established the concentrations of different compounds according to the land use. The following table C.5. shows the concentrations for inorganic compounds for agricultural soils. The concentrations found at CIEPA are below the threshold of the quality levels.

Table C.5. Peru's soil environmental quality standards for inorganic elements in agricultural soils.

Element	Allowed concentrations (mg kg⁻¹)
Arsenic	50
Total Barium	750
Cadmium	1.4
Total Chromium	-
Chromium IV	0.4
Mercury	6.6
Lead	70

C.4. Metal analysis for Cr, Co, Fe and Mg:

Cultivation time under drip irrigation and row position influenced soil chromium (Cr) concentrations (ANOVA, $p < 0.001$) (Figure C.1). All the different vineyards exhibited significant differences in Cr concentrations (Tukey HSD, $p < 0.001$) (Figure C.1). Cr concentrations ranged from 15.7 – 24.4 mg kg⁻¹ in the 9-years old, from 13.1 – 36.8 mg kg⁻¹ in the 16-years old and from 14 – 33.9 mg kg⁻¹ in the 35-years old. Chromium concentrations for 9-years, 16-years and 35-years old was 19.4 mg kg⁻¹, 23 mg kg⁻¹ and 24.7 mg kg⁻¹, respectively. The highest concentration was in 35-years old while the lowest concentration was in the 9-years old.

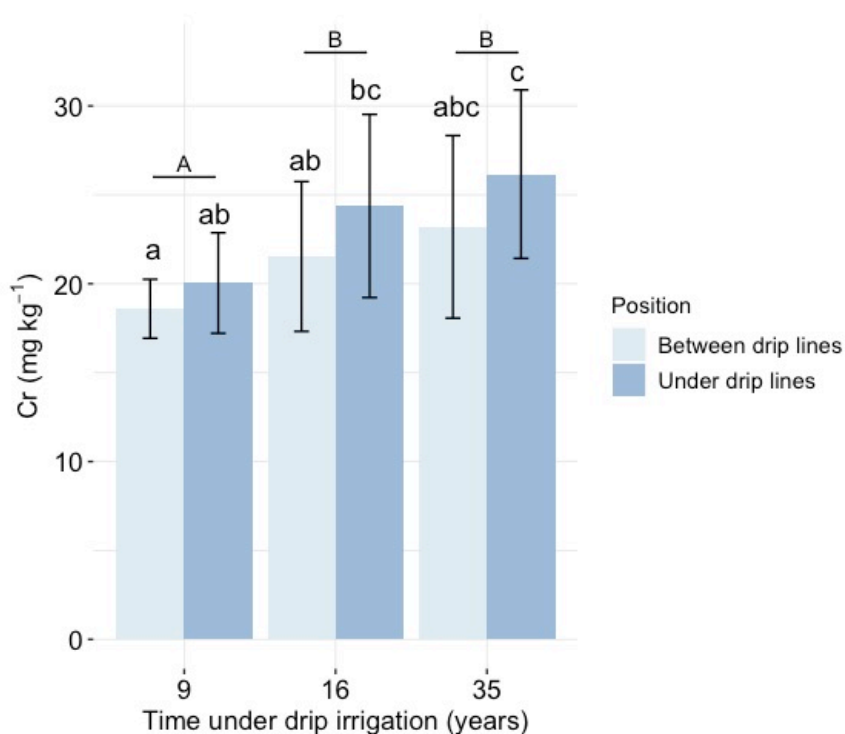


Figure C.1. Concentration of chromium (mg kg⁻¹) in soil (0 -20 cm) in vineyards plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters and differences across time are represented by capital letters at alpha 0.05. (Tukey HSD, $p < 0.05$)

Row position influenced soil cobalt (Co) concentrations with significant difference between “between” the drip lines of the 16- years old and “under” the drip line position of the 35-years. (ANOVA, $p < 0.001$) (Figure C.2). Co concentrations ranged from 7.5– 10.7 mg kg⁻¹ in the 9-years old, from 5.8 – 12.4 mg kg⁻¹ in the 16-years old and from 6.3 – 12.9 mg kg⁻¹ in the 35-

years old. Cobalt concentrations for 9-years, 16-years and 35-years old was 9.2 mg kg⁻¹, 8.7 mg kg⁻¹ and 9.3 mg kg⁻¹, respectively. The highest concentration was in 35-years old while the lowest concentration was in the 16-years old.

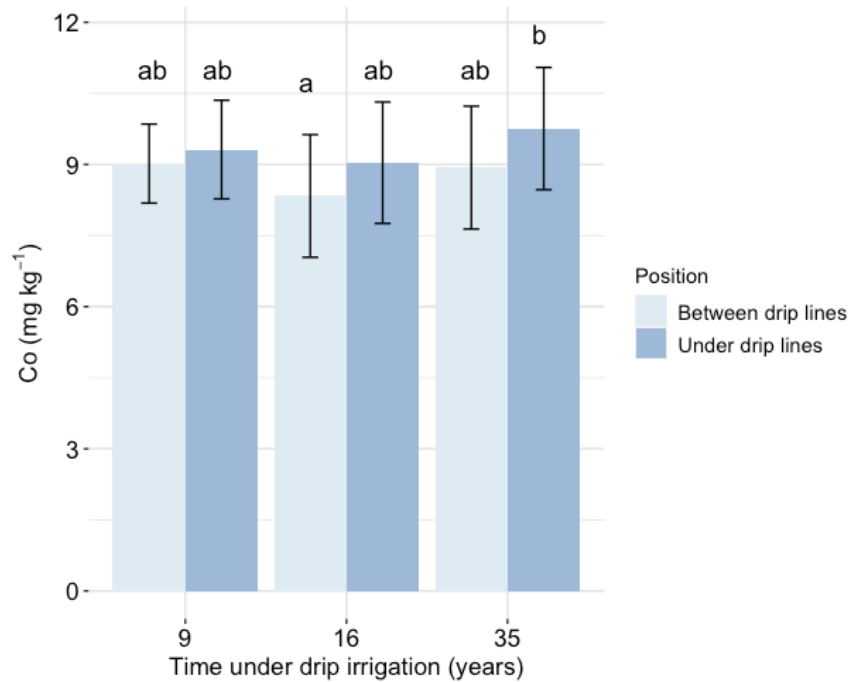


Figure C.2. Concentration of cobalt (mg kg⁻¹) in soil (0 -20 cm) in vineyards plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences for position are represented by lower case letters (Tukey HSD, p<0.05).

Time under drip irrigation and position did not significant influence Iron (Fe) concentrations were no significant (ANOVA,) (Figure C.3). Fe concentrations ranged from 10.7 – 25.9 g kg⁻¹ in the 9-years old, from 7.5 – 26.2 g kg⁻¹ in the 16-years old and from 8.5 – 21.4 g kg⁻¹ in the 35-years old. Iron concentrations for 9-years, 16-years and 35-years old was 15.2 g kg⁻¹, 15 g kg⁻¹ and 15.7 g kg⁻¹, respectively. Both the highest concentration and lowest concentration of Fe were in 16-years old.

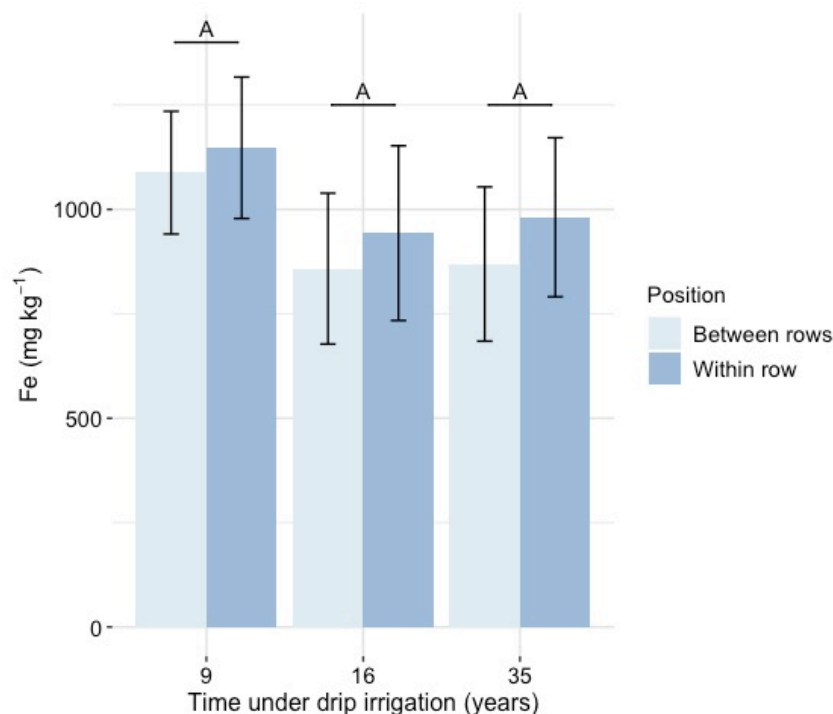


Figure C.3. Concentration of iron (g kg^{-1}) in soil (0 -20 cm) in vineyards plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Treatments with the same letter are not significantly different. Significant differences across time are represented by capital letters at alpha 0.05 (ANOVA).

Cultivation time under drip irrigation influenced soil magnesium (Mg) concentrations (Kruskal-Wallis, $p < 0.001$) (Figure C.4). All the different vineyards exhibited significant differences in Mg concentrations (Dunn test, $p < 0.001$) (Figure C.4). Mg concentrations ranged from 1.6 – 4.9 g kg^{-1} in the 9-years old, from 2.6 – 11.2 g kg^{-1} in the 16-years old and from 2 – 6.7 g kg^{-1} in the 35-years old. Magnesium concentrations for 9-years, 16-years and 35-years old was 2.6 g kg^{-1} , 4.7 g kg^{-1} and 3.4 g kg^{-1} , respectively. The highest concentration was in 16-years old while the lowest concentration was in the 35-years old.

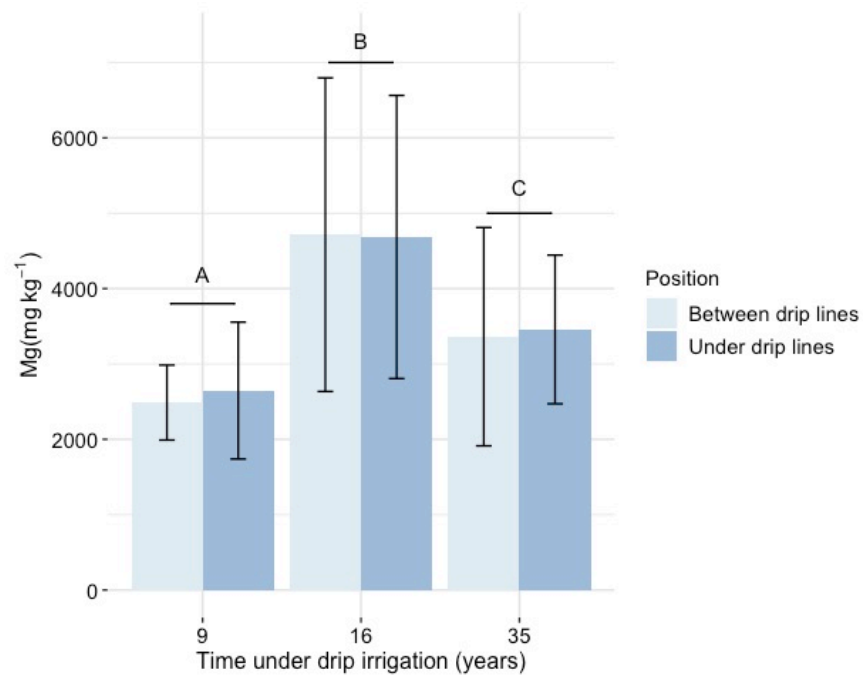


Figure C.4. Concentration of magnesium (mg kg⁻¹) in soil (0 -20 cm) in vineyards plots of 9, 16 and 35 years under drip irrigation in CIEPA-UNSA, Majes Irrigation, Arequipa. Significant differences across time are represented by capital letters at alpha 0.05 (Dun test, $p < 0.05$).

Table C.5. Kendall's matrix correlation between trace metals (mg kg⁻¹) in CIEPA's vineyard soils.

	B	Ba	Cu	Ni	Zn	Mn	Cr	Co	Fe	Mg
B	1	0.220**	0.417***	0.458	0.545***	0.376***	0.465***	0.559***	0.458***	0.183*
Ba	0.220**	1	0.172*	0.171*	0.111	0.157*	0.113	0.228***	0.183*	0.120
Cu	0.417***	0.172*	1	0.134	0.358***	-0.004	0.0117	0.219**	0.154*	-0.102
Ni	0.458	0.171*	0.134	1	0.469***	0.517***	0.683***	0.527***	0.509***	0.265* [^]
Zn	0.545***	0.111	0.358***	0.469***	1	0.361***	0.414***	0.428***	0.385***	0.146*
Mn	0.376***	0.157*	-0.004	0.517***	0.361***	1	0.622***	0.515***	0.409***	0.246* [^]
Cr	0.465***	0.113	0.0117	0.683***	0.414***	0.622***	1	0.577***	0.542***	0.297* [^]
Co	0.559***	0.228***	0.219**	0.527***	0.428***	0.515***	0.577***	1	0.556***	0.105
Fe	0.458***	0.183*	0.154*	0.509***	0.385***	0.409***	0.542***	0.556***	1	0.268* [^]
Mg	0.183*	0.120	-0.102	0.265* [^]	0.146*	0.246* [^]	0.297***	0.105	0.268* [^]	1

p<0.05 *, p<0.01 **, p<0.001 ***

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