The relationship between agricultural practices and selected heavy metals in vineyards of the Cape Winelands, Western Cape.

by

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THE RELATIONSHIP BETWEEN AGRICULTURAL PRACTICES AND SELECTED HEAVY METALS IN VINEYARDS OF THE CAPE WINELANDS, WESTERN CAPE

Declaration

I, Amanda Mahlungulu, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed Date

Dedication

- My late dad; Madoda Mahlungulu; all your sleepless nights and relentless efforts to give me better opportunities have finally paid off. Thank you for always putting my needs before yours. Qhubeka ulale ngoxolo Dlamini omhle, Zizi, Jama ka Sjadu. I wish I could have shared this part of my life with you but it’s all in God’s hands, I know you’re with me every step.

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Abstract

Heavy metal toxicity is a major threat to the health of both humans and ecosystems. Toxic levels of heavy metals in food crops, such as grapes, can have devastating effects on plant health and the market value of the produce. Two important factors that may influence the prevalence of heavy metals in grapevines are seasonal change and farming practices. The objectives of this study were (i) to conduct a detailed pioneer screening of heavy metal levels in soils and grapevine leaf tissues in selected wine farms and (ii) to study the influence of season and farming on heavy metal levels in soils and grapevine leaf tissues. Soil and grapevine leaf samples were collected from demarcated areas in selected vineyards in the Cape Winelands region of South Africa. The sampling was conducted in winter and summer from the same sites. The soil and the leaf samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS) techniques. The pooled data from the farms practicing conventional or organic farming showed that seasonal variation had no significant effect (DF =1, 22; $P > 0.05$) on the heavy metal contents in the soil. When soil data from winter and summer months were compared separately or pooled, the influence of agricultural practice was well-pronounced in As (DF =1, 22 or 46; $P < 0.05$) and Cu (DF = 1, 22 or 46; $P <0.05$). The agricultural practice greatly influenced (DF = 1, 22; $P< 0.05$) Cu, As, Cr, and Hg uptake, with little effect on Ni, Co, Cd, and Hg leaf contents. Generally, the heavy metals studied (Cr, Co, Ni, Zn, As, Cd, Hg, and Pb) were substantially below the maximum permitted levels in plant and soil samples, per the recommendations of the WHO and Er indices, respectively. However, moderate contamination of the soils was recorded for Cr, Ni, Zn and Pb. Remarkably, Cu levels in organic vineyard soils were significantly higher than in conventional vineyards. Furthermore, based on the Igeo index, Cu occurred at moderate to heavy contamination levels.

Keywords: seasonal variations in heavy metals; plant health; ICP-MS; crop cultivation

Chapter one

1.1 introduction

Heavy metals are widespread in the environment. Natural and anthropogenic activities are responsible for the build-up of dangerous levels of heavy metals. Heavy metal toxicity is a major threat to human health. Hu *et al*. (2013) suggested that one of the most important natural resources for human survival is soil, which is also an important part of an ecosystem. The emissions of heavy metals from the rapidly expanding industrial areas, mining tails, leaded gasoline and paint, fertilizers, animal manure, wastewater irrigation, and pesticides may contaminate the soil (Raymond *et al.,* 2011), leading to many environmental problems (Zeng *et al*., 2018). Plants take up heavy metals through the root system. Exposing grapevine to high levels of heavy metals may negatively affect plant maturation, berry formation and the final composition of wine. Many factors affect the prevalence of heavy metals in grapevines (Tariba, 2011). According to Alves et al. (2016), one of the main sources of heavy metals like lead, chromium, arsenic, zinc, cadmium, copper and nickel in the soil is agricultural practices. Heavy metals accumulation in food crops including grapes can have devasting effects on plant heath and market value of the produce (Onakpa *et al.,* 2018). The Cape Winelands is among the most important agriculture-producing regions in South Africa. It contributes approximately 26 223 million Rands to the annual GDP of South Africa (Cape Winelands district, 2010). It is a world-renowned wine-producing region; hence, it is of utmost importance to study the heavy metal occurrence in grape vines of the Cape Winelands. It is important to understand the ecological factors and farming practices that influence the prevalence and accumulation heavy metals in grapevines. The Cape Winelands region is an excellent model to study the ecological dynamics of heavy metals. The Cape Winelands include Stellenbosch, Franschhoek, Constantia, Paarl and Worcester (Waverley Hills organic wine and olive estate, Org De Rac, Springfield estate, Nidita, Meerlust and La Bri).

1.2 Thesis outline

Data on heavy metals in many agro ecosystems are scanty, consequently early detection of risks is hindered making the management of heavy metals difficult. During this study, the relationship between agricultural practices and occurrence of heavy metals in the Western Cape vineyards was investigated. The study collected baseline data on the occurrence of some heavy metals and provided insights on ecological factors that influence heavy metal accumulation in vineyards.

1.3 Objectives

Objective one: Investigate the relationship between farming approaches (organic, polycultures and conventional) and heavy metal presence in the soil and tissues of *Vitis vinifera*.

Objective two: Investigate the relationship between location and heavy metal accumulation.

Objective three: Investigate the relationship between season and heavy metal accumulation.

1.4 Hypothesis

Hypothesis one: farming approach influences heavy metals accumulation in grapevines of the Cape Winelands. Hypothesis

Hypothesis two: location influences heavy metals accumulation in grapevines of the Cape Winelands Hypothesis

Hypothesis three: season influences heavy metals accumulation in grapevines of the Cape Winelands.

1.5 Rationale and significance of study.

Agricultural activities can result in long-term damage of soils (Razanakoto *et al.,* 2021). Agricultural activities have been found to be one of the major contributors in the environmental heavy metal pollution (Omwoma *et al.,* 2010; Nyairo *et al.,* 2015). Soil is a major sink for the heavy metals released into the environment; heavy metals may enter surface and ground water and taken up by crop plants in toxic amounts (Javid *et al.,* 2018). The accumulation of heavy metals in crops is a concern because of their nonbiodegradable nature; they may cause health problems to both animals and humans even if consumed in small quantities (Huang *et al*., 2014). Physical and chemical processes (leaching and oxidation) may be the driver behind the release of heavy metals into the soil. Crops may take up these heavy metals from water bodies and eventually affect public health through water supply and food chain (Hussain *et al.,* 2017). In the past, the African continent was considered relatively safe from heavy metals (Rajeshkumar *et al.,* 2018). However, this is no longer the case due to rapid population growth and urbanization without proper planning and appropriate waste disposal facilities, excessive use of fertilizers and pesticides (Haregu *et al.,* 2017). The United Nations Centre for Human Settlement (UNCHS) observed that in African urban areas only one third of the solid wastes generated is collected and of that only 2% is recycled (UNCHS, 2001). Heavy metal pollution on the African continent has increased due to the use of leaded gasoline, fugitive dust, unselective dumping and burning of toxic wastes including nickel/cadmium-based batteries and weak pollution legislation (Nabulo *et al*., 2006;Hassaan *et al.,* 2016). With South Africa being the largest producer of gold in the world, mining is the major source of environmental pollution (Greenfield *et al.,* 2012). It is widely accepted that wine is a social beverage and moderate consumption of wine, and more especially red wine, has certain health benefits. Finding that wine from certain European countries such as Slovakia and Hungary contained high concentrations of heavy metals was, therefore, a cause for concern (Zokaei *et al.,* 2018). The same authors found a variety of metal ions at relatively high concentrations in red wine, compared to other beverages such as stout and apple juice. Heavy metals have become a public health issue that affects foodstuffs and alcoholic beverages (Sherameti *et al.,* 2015). It is imperative to determine heavy metals levels in South African grapevine.

“Chapter two

2.1 Introduction

Heavy metals are inherent elements of the earth's crust, but their geochemical cycles and biological equilibrium have been severely disrupted by indiscriminate human activity. As a result, metals accumulate in plant parts that produce secondary metabolites responsible for a specific pharmacological activity. Heavy metals such as cadmium, copper, lead, nickel, and zinc can have negative health impacts in people if they are exposed for an extended period (Sing *et al.,* 2011).

Heavy metals contamination of the environment has been steadily increasing, exposing living things to dangerous stresses. This heavy metal contamination is retarding farming efficiency and is disruptive to plant and animal health (Varsha *et al.,* 2010). Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by humans (Su *et al.,*2014). Human activities such as agriculture, industrial production and transportation have been the key drivers of heavy metal deposition. Some important heavy metals in agricultural soils include mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr) and arsenic (As), zinc (Zn), copper (Cu), nickel (Ni), stannum (Sn), vanadium (V) (Sridhara Chary *et al*., 2008; Li *et al*., 2009). There has been a great increase in contamination of heavy metals and metalloids in irrigation water, soil, and vegetables in farmlands due to anthropogenic and natural activities, such as weathering of parent materials, volcanic activity, and agricultural/industrial activities (Ali *et al*., 2019; Rai *et al.*, 2019; Spiegel, 2002), the recent global economic development also plays a major role in the increase of heavy metal contamination resulting in environmental deterioration (Han *et al*., 2002; Sayyed and Sayadi, 2011). Heavy metals are particularly problematic because of their persistence in the environment, these heavy metals are nonbiodegradable and non-thermodegradable thus excessive accumulation in a dietary form could lead to serious systemic health problems (Oliver, 1997). Despite the fact that many researchers have reported on the substantial accumulation of heavy metals in agricultural soil, there has been little research done on the distribution of heavy metals on various types of agricultural land (Atafar *et al*., 2010; Li *et al*., 2014; Xia *et al*., 2014). It is desirable to research heavy metal distribution and concentration of different agricultural land types as the soil pollution of different land-use types may have different impacts on public health (Li *et al.,* 2001).

2.2 Heavy metals in Philippi horticultural area in the Western Cape Province

Malan *et al.* (2014) conducted a study on the occurrence of heavy metals in Philippi horticultural area, analyses of Cd, Cr, Cu, Mn, Ni, Pb and Zn in the water, soil and vegetable samples were performed. The results suggested that there was a difference in 5 heavy metal concentration during winter and summer seasons; Cd and Cu concentrations were slightly higher in the winter season, while zinc concentrations were higher in the summer season. Cd concentrations in the irrigation water collected from sampling locations were found to slightly exceed the maximum permissible concentrations of 0.05 mg Cd/L. Malan *et al.* (2014) also found significantly high levels of Cu, Mn, Ni and Zc concentrations in the soils collected in the summer season. According to Saeedi et al. (2010), dust from urban areas contains high levels of trace elements. The source of these trace elements could be vehicle exhaust, sinking particles in air, house dust, soil dust, and aerosols that are carried by air and water (Popoola, 2012). Olowoyo *et al.* (2016) carried out research on the composition of trace metals in dust samples collected from selected high schools in Pretoria, South Africa and found that schools closer to the main road have higher concentrations of Zn and Pb. The authors linked the high concentrations of metals to wear and tear of tyres, lubricating oils and corrosion of galvanized vehicular parts.

2.3 Heavy metals in agricultural soils

Soils contaminated with heavy metals have become one of the major environmental problems around the world (Gratão *et al.,* 2015). Industrial expansion, mine tailing, combustion of fossil fuels, spillage of petrochemicals, disposal of high metal waste such as Batteries, atmospheric deposition and agricultural practices may be the sources of heavy metals (Khan *et al.,* 2008; Zhang *et al.,* 2010, Liu *et al.,* 2016). The agro-ecosystems are exposed to pollutants in fertilizers, biosolids, pesticides and wastewater. Agricultural soils may accumulate high levels of heavy metals, which have dire consequences for the quality and health of plants (Shamar, 2014).

2.4 Common sources of heavy metals in soils

The disposal of industrial and municipal waste, automobile emissions, mining activities and the application of fertilizers and pesticides have added to the continuous accumulation of heavy metals in the soil (Nouri *et al*., 2008; Tu *et al.,* 2000; Selene *et al.,* 2003).

2.5 Fertilizers

For plants to complete their lifecycle they need more than the macronutrients (N, P, K, S, Ca, and Mg). They also need essential micronutrients (such as Co, Cu, Fe, Mn, Mo, Ni and Zn). However, some soils are deficient in these heavy metals (Lasat, 2000), creating the need for long-term application of fertilizers, which leads to high accumulation of heavy metals in the soil (Parkpian *et al.* 2003, Huang and Jin 2008). Fertilizers is a major contributor of Cd accumulation in agricultural soils (McLaughlin *et al.* 1999). In addition, Ju *et al.* (2007) reported that over usage of manure and phosphate fertilizers increases Cd concentrations.

2.6 Pesticides

Although pesticides are desired for killing invasive weeds and crop-damaging insects, most pesticides have the ability to remain in the environment for extended periods. Ground application of pesticides could leach into the groundwater and eventually into the water supply (Wallace, 2015).

2.7 Wastewater

Most of the industrial sewage discharges used for irrigation contain heavy metals, which cause toxicity to crop plants as the soils are able to accumulate heavy metal for many years (Hussain, *et al*., 2017). Although wastewater is not a major contributor of heavy metals, long-term irrigation with wastewater eventually results in accumulation of heavy metals in the soil (Raymond and Felix, 2011).

2.8 Heavy metals and seasonal changes

In a study conducted by Mondol *et al*. (2011), it was determined than environmental changes contribute to the differences in heavy metals uptake from soils. The study also concluded that trace elements were higher during dry season compared to wet season. Ullah *et al*. (1999) suggests that this might be the result of lower pollution levels during wet season as the heavy rainfalls flush pollution into canals. A study conducted by Oluyemi *et al*. (2008) at a landfill in Nigeria showed that there were higher heavy metals in the dry season than in wet season. These claims are also backed up by Osobamiro and Adewuyi (2015) who studied three farm settlements in Ogun-State Southwest, Nigeria and found that heavy metals' concentrations were higher in the dry season than during the wet season. The study suggests that high precipitation, leaching, erosion and plant uptake may account for the reduction in heavy metal levels in rainy season observed in the results of heavy metals from the three farm settlements.

2.9 Weed absorption of heavy metals in farms.

Leafy plants are prolific accumulators of heavy metals of both essential and non-essential heavy metals. Hence, weeds have become one of the most effective and environmentally friendly ways to eradicate the effect of heavy metals in farms (Chen *et al.,* 2005). Phytoremediation has become widely accepted because it is cost effective and occurs via natural processes (Blaylock et al., 1997). Plants known as metal hyperaccumulators that can accumulate high concentration of heavy metals in their tissue and could potentially absorb heavy metals in farms (Brown *et al.,* 1994). The weeds used for phytoremediation can be safely harvested and removed from farms without the loss of topsoil and extensive excavation (Chen *et al.,* 2005).

2.10 Contamination and ecological risk assessment

Contamination indices have been used to assess the impact of human activities on the build-up of heavy metals (geo-accumulation index [I_{geo}]) and the associated ecological risk of heavy metal levels in farm (contamination factor [C_f] and ecological risks [E_r]) (Vannini *et al.*, 2021, Eijsackers *et al.*, 2020). The C_f indicates soil contamination that can be estimated as a ratio of concentration of heavy metal in the investigated soil to its reference soil background level (Hakanson, 1980), while the I_{geo} is an improved contamination index based on C_f that uses a factor of 1.5 to compensate for variation background concentration in the soil and minor anthropogenic influences (Muller, 1969). These are mathematically expressed as:

$$C_f = C_n / B_n \tag{1}$$

$$I_{geo} = \log_2[C_n / 1.5B_n] \tag{2}$$

$$E_r = T_r \times C_f \tag{3}$$

Where C_n is the measured level of each heavy metal in the investigated soil, B_n is the background level of each heavy metal, C_f is the contamination factor for each heavy metal, T_r is the toxic response factor for each pollutant, and E_r is the ecological risk index.

The background values (mg/kg) of selected heavy metals from South Africa are Cr (5.82), Cu (2.98), Cd (0.62), Zn (12), Hg (0.15), and Pb (2.99) (Herselman, 2007). The degree of metal contamination in soils as defined by Muller (1969), with seven soil quality levels ranging from 0 (uncontaminated) to 6 (extremely contaminated) is shown in table 2.1

Table 2.1: Classes of metal contamination (I_{geo}) and the ecological risk for metal pollution (E_r) (Hakanson, 1980, Muller, 1969)

I_{geo} Class	I_{geo} Value	Soil quality based on I_{geo} Value	E_r	Ecological risk of single metal
0	<0	uncontaminated	$E_r < 40$	Low risk
1	0-1	Uncontaminated to moderately contaminated	$40 \leq E_r < 80$	Moderate risk
2	1-2	Moderately contaminated	$80 \leq E_r < 160$	Considerable risk
3	2-3	Moderately contaminated to heavily contaminated	$160 \leq E_r < 320$	High risk
4	3-4	Heavily contaminated	$E_r \geq 320$	Very high risk

5	4-5	Heavily to extremely contaminated		
6	>5	Extremely contaminated		

2.11 Agricultural practices

Raina (2020) defines agricultural practices as a collection of principles applied on farms for production of better agricultural products. Land-use patterns deeply influence the soil quality therefore having a direct impact on heavy metal accumulation in the soil (Fu *et al*. 2000; Guo *et al*. 2001; Hou *et al*. 2007). Many wine producers have adopted three farming practices to maximize production which are conventional farming, sustainable farming (polyculture) and organic farming (Forbes, 2009). Organic farming- In organic wine farming, no pesticides are used. It is a holistic farming system that promotes healthy and productive biodiversity while improving soil health (Seufert *et al.,* 2017).

Polyculture farming- Adamczewska-Sowińska and Sowiński (2020) define polyculture as the cultivation of crops together in the same space at the same time. This practice slows down soil degradation processes while improving soil fertility.

Conventional farming- This practice involves the use of synthetic chemical fertilizers, pesticides, herbicides and other genetically modified organisms in crop production. Conventional farming is considered to be one of the major sources of heavy metal entering the food chain and posing risk to the environmental health (Abeywickrama and Wansapala, 2018).

2.12 The Cape Winelands

The first vines were planted in 1655 by Jan van Riebeeck (Saayman, 2009). The Cape wine lands have been booming and are now stretched from the coastal regions of the Western Cape to the Klein Karoo (Breslin, 2011) and are spread into six regions. These six regions include Coastal Region, Klein Karoo, Olifants River, Boberg Breede, River Valley, Cape South Coast (Anonymous, 2015).

Figure2.1 Geographical map of the Cape Winelands, Western Cape, South Africa (adapted from: ht.tps://.www.wine-searcher.com/m/2012/09/south-african-winemakers-call-for regionashakeup).:

2.13 Heavy metals in African soil

Heavy metal contamination is a growing concern in the developing world, the rapid economic development in Africa can cause various problems including heavy metal contamination in the environment (Akiwumi and Butler, 2008; Norman *et al*., 2007; Barsoum, 2006). Overall, while the dynamics of heavy metal pollution on the continent are similar, specific differences exist among the North, West, East and Southern regions of Africa.

2.14 North Africa

In North Africa, studies have mainly focused on coastal environments. industrial and municipal waste are the main sources of pollution in El-Mex Bay and Eastern Harbour along the Mediterranean coast in Egypt are polluted by, as several industries close to the coast discharge their effluents into the bay directly (Abdallah, 2008). Moreover, the Omoum Drain, which flows directly into El-Mex Bay contributes to Cd contamination from phosphate fertilizers carried in agricultural wastes as well as other metals including Cu and Zn carried in industrial wastes (El-Rayis and Abdallah, 2006). A concentration of Pb and Cd od up to 297.0 and 4.0 mg/kg respectively has been recorded in Nador Lagoon sediments in Morocco (Bloundi *et al.,* 2009), moreover, Cheggour *et al*. (2005) noted the contribution of agricultural (phosphate fertilisers and pesticides) and industrial waste to coastal pollution along the Atlantic Coast of Morocco.

2.15 West Africa

One of the major causes of pollution in West Africa is petroleum extraction. Crude oil is discharged to the environment by the corrosion of oil pipelines, discharges from oil industries and frequent acts of sabotage to oil facilities in the Niger Delta region of Nigeria. This contamination of the Bonny/New Calabar River Estuary in the Niger Delta by Pb, Cd, Cu, Zn, V and Cr is a direct attribution of the effluents of oil refineries (Chindah *et al*., 2004; Leopold *et al.,* 2008). In other regions, Oze et al. (2006) reported high concentrations in the Qua-Iboe river of Pb, Cd, Cr and Ni, which they attributed to effluent from crude oil processing and treatment activities. In a study conducted by Adekola and Elatta (Adekola *et al*., 2007) examining the relationship between industrial activities and pollution, found the cause of elevated levels of Zn, Fe, Cr, Cu and Mn in Asa River sediments in Nigeria to be tannery, bottling, detergent and other industries that discharge into the river. Moreover, the elevated levels of Pb and Cd during the rainy season recorded in Lagos around the Ikeja industrial estate were attributed to activities of the paint, textile, steel/metal works, pharmaceutical and other industries located in the area (Fakayode and Onianwa, 2002). Whereas, in Ghana the contamination of water in the Iture Estuary estate with Pb and Cd has been attributed to waste carried by Sorowie and Kakum rivers flowing rapidly through urbanized and industrialized central region (Fianko *et al.,* 2007). Additionally, contamination of Hg and As were recorded by Kwando (Asande *et al.,* 2007) in streams and rivers in Tarkwa, a gold mining town in Ghana.

It is common in West Africa to cultivate food crops in contaminated environments as dumpsites are used by small scale farmers to maximise yields due to the seemingly high organic contents of waste in dumpsites (Yabe *et al*., 2010). The soils used for vegetable farming at Kumasi in Ghana was reported by Odai *et al*., (2008) to contain High levels of Pb, Cd, Cu and Zn. Onions, cabbages and lettuce grown in dumpsites were found to have higher concentrations of Pb, Cd and Cu. Similarly, alarming concentrations of Pb, Cd and Cr recorded in tomatoes that grown in Challawa Riverbank in Nigeria was attributed to untreated effluents from tannery industries located in Challawa Industrial Estate (Abdullahi *et al*., 2007).

2.16 North Africa

Studies in North Africa of heavy metals have mainly focused on coastal environments (Yabe *et al*., 2010). The El-Mex Bay and Eastern Harbour along the Mediterranean coast in Egypt are mainly polluted by the municipal and industrial waste, as several industries located closely to the coast discharge their effluents directly into the bay (Abdallah, 2008). Moreover, the drain flowing into El-Mex Bay directly contributes to Cd contamination from phosphate fertilizers carried in agricultural waste (E l-Rayis *et al*., 2006). On then Tunisian side of the Mediterranean Coast, the Pb and Cd contamination of El-Me Melah Lagoon sediments has been linked to the industrial effluents (Ruiz *et al.,* 2006). The contribution of agricultural (phosphate fertilisers and pesticide) and industrial waste along the coast of Morocco was noted by Cheggour *et al*., (2005) who reported the contamination of Sebou Estuary by Cd, Ni, Zn and Cu.

2.17 East Africa

In East Africa, the Dandora solid waste dump site in Nairobi City, Kenya carries over 20000 tons of solid waste including industrial, agriculture, domestic and medical waste, this resulted in soils near the dumpsite and the Nairobi Riverbank to exceed the recommended limits of Hg and other heavy metals (Cr, Mn, Fe, Cu, Zn and Co) (UNEP, 2007). Lake Victoria has been similarly polluted by industrial and domestic waste as well as small-scale gold mining activities that use Hg around the lake (Harada *et al.,* 1999; Kishe and Machiwa, 2003). The Ugandan side of the lake was reported by Muwanga and Barifaijo (2006) to have high levels of water contamination of Pb, Cd and Ni. Similarly, in Kenya contamination of Pb, Cd and Cr has been recorded on the coast (Mireji *et al.,* 2008). The use of leaded gasoline and non-selective disposal of industrial, agricultural and domestic waste has led to heavy metal toxic pollution in several cities in East Africa. Elevated levels of Pb and Cd in vegetables have been recorded including African spinach, cowpeas, lettuce and Chinese cabbage cultivated along the Sinza river in Tanzania, which increases the exposure of the local community to toxic metals (Eslami *et al*., 2007). In a related study by Prabu (2009) in Ethiopia, levels of Cd, Cr and Zn which exceeded recommended limits were recorded in lettuce and spinach, this was directly attributed to the irrigation of vegetables with water from Akaki river which is polluted by untreated sewage and industrial effluent. In Uganda, edible vegetables including amaranthus and cauliflower that were grown in polluted roadside soils had excessive concentration of Pb and Cd and were attributed to vehicular emissions (Nabulo *et al.,* 2006).

In the past decade heavy metals have been steadily accumulating in the African environment, pollution levels in many African countries have hit their most high as levels of heavy metals continue to exceed the limit in water, soil, edible vegetables, fish and food animals (Yabe *et al.,* 2010).

2.18 Many factors are responsible for the increasing heavy metal contamination in Africa.

2.18.1 Waste management

Inadequate water and wastewater treatment, coupled with increased industrial activity, have led to increased heavy metal contamination in rivers, lakes, and other water sources in developing countries (Joseph *et al*., 2019). Regions such as Nigeria Savannah have high weathering intensity and long period of pedogenesis and so their natural soils are characterised by low heavy metal concentrations (Agbenin and Latifatu 2004).

2.18.2 Urbanization

One of the focuses of urban ecology is to study and trace the flow of pollutants in the city environment therefore understanding the interaction between anthropogenic and natural elements, such as how the accumulation of heavy metals in urban soils is affected by urbanization (Humphries, 2012). The intensity of anthropogenic activities, land use patterns, sources of pollution, and distance to emission sources were found to be the main causes of the distribution of heavy metals in urban soils as well as factors influencing it (Yuan *et al*., 2014; Lv *et al*., 2013). Soils in residential and recreational sites in cities are often reported to have high levels of cadmium (Cd), lead (Pb), zinc (Zn), and copper (Cu) (Madrid *et al*., 2002), for instance in a study conducted by Mathee *et al.* (2018), it was found that garden soils in residential areas in Johannesburg's inner city as well as close to a mine tailings facility have higher levels of As and Pb, these exceed the local and international guidelines, furthermore, Kootbodien *et al*. (2012) also found that school gardens around Johannesburg have high levels of As; whilst the Tshwane area of Pretoria showed high levels of heavy metals in areas close to high traffic density and industrial areas (Olowoyo *et al.,* 2010). Traffic and industrial emissions are identified as the main sources for the accumulation of heavy metals in urban soils (Faciu *et al*., 2012; Hamzeh *et al*., 2011; Li *et al.,* 2004).

2.18.3 Agriculture

Hani and Pariza (2011) conducted a study to evaluate heavy metal sources and their spatial distribution in agricultural fields in the south of Tehran, they found that the topsoil of agricultural lands had an increasing trend of heavy metal contamination due to the use of wastewater for irrigation, and the use of agrochemicals may play the most important role for the input of these heavy metals.

Table 2. 2: Recommended values for heavy metal concentrations in the environment.

Heavy metal	Pb	Cd	Hg	Cu	Co	Zn	Cr	Ni	Reference
Water (mg/l)	0.01	0.003	0.001	2		3	0.05	0.07	world Health Organization (WHO), 1994.
Sediments (µg/g)	20	0.3		45	19	95	90	68	Foerstner and Wittman, 1979.

Soils (mg/kg)	150	5		100	50	500	250	100	FAO and SRIC, 2004
Vegetables mg/kg)	0.3	0.2		40		60	0.2		FAO and WHO, 2003
Fish (mg/kg)	0.2	0.05	0.5						European Commission, 2005
Cattle offal (mg/kg)	0.5	0.5							European Commission, 2001

2.19 Health effects of heavy metals in humans

In the past decades there has been a rapid increase in environmental pollution caused by heavy metals, these metals can be toxic even at very low concentrations because they are non-biodegradable and have a long biological half-life (Djahed *et al.,* 2018). There are various pathways in which heavy metals can enter the human body such as inhalation of dust, dermal contact with soil, consumption of food crops grown in contaminated soils and ingestion of soil (Zheng *et al.,* 2020). Contaminated irrigation water is a major cause of metal contamination in soil and crops, heavy metal contamination will be high in the edible parts of a growing plant irrigated with wastewater (Arora *et al*., 2008). In other words, the main route of human exposure to heavy metals is the transfer of heavy metals from the soil to the plant which leads to subsequent consumption of these plants by humans (Bi *et al.,* 2018). the heavy metal extent of absorption from the environment through consumption of plants depends on parameters such as soil type, irrigation water quality, climate, irrigation period and the nature of the plant product (Ghasemidehkordi *et al.,* 2018; Maleki *et al*., 2014).

2.20 Common heavy metals

The most common heavy metals to occur naturally in the environment are lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), Mercury (Hg), zinc (Zn) and copper (Cu) (Masindi and Muedi, 2018).

2.20.1 Lead (Pb)

Lead is a natural occurring element, but it is often released by artificial sources into the environment. It is often used as an additive in gasoline and paint, ceramics, crystals and leaded pipes (Paz-Alberto *et al*., 2007). In the past, the addition of lead in agricultural herbicides/pesticides has been significant with lead concentrations in some orchard soils reaching 10 kg Pb per year (Merry *et al.,* 1983). However, these practices have been largely stopped. The use of sewage sludge in agricultural soils may also significantly add to the amount of lead in the soil, atmospheric deposition of lead derived from combustion of gasoline containing lead additives can also have an input to lead in agricultural soil (Alloway, 2012). Although soil ingestion and dust can be important contributors of lead consumption, the main exposure occurs through the food chain (EFSA, 2012). Nervous system and brain impairment can be caused by even relatively low exposure to lead, especially those of children–and elevated blood pressure, chronic kidney disease and probably cancer can be also caused by lead, even at relatively low blood lead levels (Abadin *et al,* 2007; IARC, 2006).

2.20.2. Cadmium (Cd)

The addition of manures/fertilisers, urban composts and industrial sludges are the cause of cadmium occurrence in the soil, atmospheric cadmium is the result of the production of iron and steel, mining and smelting of nonferrous metals, combustion of fossil fuels and waste incineration. Phosphate based fertilizers have a high cadmium concentration, this is due to its presence as an impurity in all phosphate rocks. There is a wide variation in countries and regions within countries in contribution of the atmosphere, sludge, fertilisers/manures to the total cadmium addition to soils (Jensen and Bro-Rasmussen, 1992; McLaughlin *et al.,* 1996). The cadmium deposition is minimal in regions that are less industrialised (Taylor, 1997).

2.20.3 Arsenic (As)

Arsenic is widely distributed into the nature in form of either metalloids or chemical compounds, it remains a human health concern as exposure to As and its compounds causes an elevated risk for developing several cancers, most notably skin cancer and cancers of the liver, lung, bladder (IARC, 2012). According to WHO the maximum admissible concentration of As in drinking water is 10 μg/L in developed countries; it however varies from that of developing countries where As is more widespread, the WHO guideline value is 50 μg/L due to the lack of facilities to analyse smaller concentrations (Edition, F, 2011). High levels of arsenic occur naturally in some sedimentary rocks and in geothermally active areas (Asati *et al*., 2016). Historically, the widespread use of As compounds as herbicides, insecticides and defoliants for agricultural production are the principal cause of elevated As concentration in soil. As is also widely used as a poultry and swine feed additive therefore manures are a significant source of soil As whereas fossil-fuel combustion, phosphate fertilizers and municipal sewage sludge are relatively minor sources of As (Alloway, 2012). Depending on the location and pollution source plants may accumulate extremely large amounts of As (Kabata-Pendias, 2011).

2.20.4 Nickel (Ni)

Nickel is generally distributed uniformly in nature and is found in animals, plants and soil, it typically accumulates at the soil surface from agricultural and industrial activity depositions. There may be a major problem presented by Ni In lands near towns, industrial areas, or even in agricultural land receiving wastes such as sewage sludge, Ni may present a major problem, this metal however does not seem to cause major concern outside urban area but may do so in future as a result of the decrease in soil pH which is a consequence of reduced use of soil liming in agriculture and increased acid rain (Beckno, 1984; Scott-Fordsmand, 1997; Murugadoss *et al*., 2017). Ni is released into the atmosphere through anthropogenetic activities such as industrial production and fossil fuel consumption as well and also through natural activities. Humans can be exposed to Ni through food ingestion, inhalation, water and percutaneous absorption (IARC, 2012; Squadrone *et al.,* 2016). EU and USA have set the permissible limits of soil on which sewage sludge can be applied (30– 75 and 210 mg/kg), respectively (Mahmood and Malik, 2014; Radojevic and Bashkin 2006).

2.20.5 Chromium (Cr)

The use of chromium in various anthropogenic activities results in soil and groundwater contamination, this is a worldwide problem that scientists have studied for decades and is still a current issue. This metal is present in all environmental compartments (water, air and soil), at different concentrations (Kimbrough *et al.*, 1999). Cr is considered by industries to be one of the most important pollutants in the environment (Nriagu, 1988), moreover it is rated amongst 14 most harmful substances to living organisms (USEPA 2000). Exposure of humans to Cr or some of this compound occurs through inhalation, ingestion and dermal contact. This metal can have both positive and negative effects to animal and human health depending on the dose, exposure time and its oxidation state (WHO, 2000). The absorption of Cr does not occur through specific mechanisms in plants because this metal is not an essential element for them. The accumulation of Cr inside the plant depends on the plant species, the oxidation state of the metallic ions, and its concentration in the growth medium (Srivastava *et al*., 1998).

2.20.6 Mercury (Hg)

Mercury is a naturally occurring element in the environment, there has been an increase of fossil fuels combined with long-range, atmospheric transport in soils and sediments by 3 to 10 times during the post-industrial era (UNEP, 2019). Most Hg forms are highly toxic to highly exposed humans but can seriously and adversely affect the central nervous system even at low exposure (Nance *et al*., 2012). Foetuses and young children are at greater health risk than adults (Holmes,2009). The transformation of inorganic Hg to methyl-Hg, a species more prone to bio-accumulate in organisms is of major concern (USGS, 2000). Hg is released from many sources by means of various natural processes, these include ubiquitous weathering of Hg-containing rocks in the Earth's crust, geothermal activity, or Hg emitted during episodic events such as volcanic eruptions (UNEP, 2019), anthropogenetic activities like), coal combustion, production of non-ferrous metals (including copper, lead, zinc, aluminium and large-scale gold production), cement production, and disposal of wastes containing Hg are also huge contributors to Hg soil contamination (UNEP, 2019; Mason *et al.,* 2012); other sources of Hg such as discarded thermometers, batteries and fluorescent lamp also need to be taken into consideration. In agriculture Hg pollution originates from pesticides, fertilizers, sewage sludge and irrigation water (Hseu *et al*., 2010).

2.20.7 Zinc (Zn)

Zinc is found everywhere in the environment, it is an important micronutrient and catalyses, contributes to protein structure and regulates gene expression (Trumbo *et al*., 2001). Although the adverse effects of Zn deficiency have been recognised it can be toxic when exposure exceeds physiological needs (Solomons and Ruz, 1998). Excessive exposure to zinc can cause acute gastrointestinal effects, headaches and impaired immune function (Meyers *et al*., 2006). Zn is a component of tyres which they release as they wear (Doss et *al.,* 1995). Although vascular plants require Zn as an essential element, it is phytotoxic and can reduce soil fertility and crop yield at high concentrations (Alloway *et al.,* 1990).

2.20.8 Copper (Cu)

Copper is an essential micronutrient for plants that is a component of several electron transport enzymes and acts as a catalyst for the redox reactions in mitochondria and chloroplasts (Marschner, 2011). However, concentrations above optimum levels also induce toxicity at tissue (Fernandes and Henriques, 1991), furthermore, the alteration in the photosynthetic and respiratory processes, enzyme activity, DNA and membrane integrity can be induced by excess leaf copper, all of which could lead to growth inhibition (Alaoui-Sossé *et al.,* 2004).

2.21 Management strategies

2.21.1 Plants

Plants have been used as a way to stabilise and remove metals from soil and water. There have been demonstrations of plants effectively cleaning contaminated soil and water (Wenzel *et al.,* 1999). The general term used for using plants to remove pollutants of the soil such as heavy metals, solvents, pesticides, crude oil, etc, is phytoremediation. In phytoremediation, to evaluate the role of plants in remediation of metalliferous soil; the accumulation and distribution of heavy metals in plant tissue are important aspects (Friedland, 1989). Phytoremediation is most desirable because it is both environmentally friendly and cost-effective. Hyperaccumulator is a term used for plants with exceptional metal-accumulating capacity (Cho-Ruk *et al.,* 2006), the unique and selective uptake capabilities of plant root systems, together with the translocation, bioaccumulation and contaminant biodegradation abilities of the entire plant body is what makes phytoremediation most effective (Paz-Alberto and Sigua, 2013). Bioavailable fraction is considered to be the faction of heavy metals which can be readily mobilized in the soil and taken up by plant roots. The extent to which a chemical can be absorbed by living organisms and reach the systemic circulation is defined as “bioavailability”, therefore, there is no correspondence between total metal concentration and metal bioavailability (Kelley *et al.* 2002).

2.21.2 Effective policy

Environmental policies are thought to aid in the attainment of environmental sustainability in a given economy. As a result, a number of previous researches have looked into the dynamic effects of environmental protection policies on the ecosystem in order to better understand how enforcing policies might spur environmental progress. Most of these researches, on the other hand, have linked environmental restrictions to CO_2 emissions-related environmental problems (Taylor *et al.* 2012). Environmental policies, for example, according to Wang and Shen (2016), increase environmental quality in China by promoting the establishment of clean Chinese industries. Similarly, Hashmi and Alam (2019) discovered that environmental legislation in OECD countries lowered CO_2 emissions. Furthermore, the authors asserted that imposing environmental levies can be useful in lowering CO_2 emissions. Environmental laws, according to Liu et al. (2018), can be successful in reducing energy consumption-induced CO_2 emissions. Several studies, on the other hand, have demonstrated the ineffectiveness of environmental regulations un promoting environmental betterment. Wolde-Rufael and Weldemeskel (2020) showed that CO_2 emissions had an inverted U-shaped connection with the stringency of environmental legislation in a recent study on BRICS, Indonesia, and Turkey. According to the authors, establishing environmental legislation may not be beneficial in enhancing environmental quality at first. A steady increase in the rigor of environmental rules, on the other hand, is eventually advantageous in reducing environmental degradation.

Metal deposition in the soil is mostly permanent, and if concentration levels are surpassed, it can cause environmental problems. The goal of long-term heavy metal management in agroecosystems is to ensure that the soil continues to serve its responsibilities in agricultural production, environmental processes like element cycle, and as a habitat for a variety of creatures (Asgari *et al*.,2015). Substance flow analysis using heavy-metal balances can be used to track metal flow trends. A preventive method based on anticipating future soil contents using (dynamic)heavy-metal balances is thus promising in terms of sustainability. To calculate heavy metal balances and expose, the repercussions of heavy metal flows within the described system, a consistent approach is required. Quantification of flows, data display, and balancing interpretation in the context of sustainability are all part of this method (Zhang, 2015).

2.21.3 Awareness

Unreasonable agricultural production methods, such as the excessive application of chemical fertilizers and pesticides and the abuse of feed additives in farming, will cause heavy metal pollution (Lu, 2019). It's critical to understand the mechanisms that cause heavy metal contamination in agricultural output and to take focused steps to address them. Farmers' awareness of heavy metal pollution and willingness to regulate heavy metal pollution is influenced by information provided by natural science (Wang *et al*., 2015). Empirical research has revealed a link between farmers' understanding of the environmental elements of heavy metal pollution and their readiness to treat it. Their willingness to treat heavy metal contamination and eagerness for participating in fallow treatment increases as their environmental awareness increases (Xie *et al.,* 2017).

Chapter three

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Levels of Heavy Metals in Grapevine Soil and Leaf Samples in Response to Seasonal Change and Farming Practice in the Cape Winelands

3.1 Introduction

Natural and anthropogenic activities are responsible for the build-up of dangerous levels of heavy metals. Many factors affect the prevalence of heavy metals in grapevines (Alagic *et al*., 2015). According to Alagic *et al.* (2016), one of the primary sources of heavy metals such as lead, chromium, arsenic, zinc, cadmium, copper, and nickel in the soil is agricultural practices. The emissions of heavy metals from the rapidly expanding industrial areas, mining tails, leaded gasoline and paint, fertilizers, animal manure, wastewater irrigation, and pesticides may contaminate the soil (Wuana et al., 2011; Mahan *et al*., 2016; Wang *et al.,* 2017) leading to many environmental problems. Heavy metal toxicity is a major threat to the health of both humans and ecosystems; their accumulation in food crops, including grapes, can have devastating effects on plant health and the market value of the produce (Alagic *et al.,* 2016; Onakpa *et al.,* 2018). Briffa *et al*. (2020) reviewed the toxicological effects of heavy metals on humans, including oxidative stress, liver damage, fever, pneumonia, asthma, brain damage, death, and DNA damage. Soils contaminated with heavy metals have become one of the major environmental problems around the world (Li *et al.,* 2019). Industrial expansion, mine tailing, combustion of fossil fuels, spillage of petrochemicals, disposal of high metal waste (e.g. batteries and metal scraps), atmospheric deposition and agricultural practices may be the sources of heavy metals (Wang *et al.*, 2017; Bora *et al*., 2015; Probayar *et al.,* 2021). The agroecosystems are exposed to pollutants in fertilizers, biosolids, pesticides and wastewater. Some farmers mix soil and sewage sludge, which may contain heavy metals (Briffa *et al.,* 2020). A recent study on the level of atmospheric concentrations of commonly used pesticides successfully quantified carbaryl, chlorpyrifos, terbuthylazine, s-metolachlor, diazinon, tebuconazole, atrazine, simazine, malathion, and metazachlor in three agricultural regions (Grabouw, Hex River Valley and Piketberg) of the Western Cape, South Africa, and the concentrations were generally higher in summer and during the spraying season (Fernandes, 2021). Commonly used fungicides in vineyards, such as the Bordeaux mixture ($Ca(OH)_2$ + $CuSO_4$) and Mancozeb ($C_4H_6MnN_2S_4$)-based products, are important sources of Cu and Zn contamination, respectively. Phosphate fertilizers often contain Cd, Hg and Pb impurities (Brunetto *et al.,* 2017). Agricultural soils may accumulate high levels of heavy metals, which has dire consequences for the quality and health of plants (Liang *et al.,* 2015). While it is helpful to regularly monitor the levels of heavy metals in agricultural soils, it is even more crucial to study the drivers of heavy metals in soils to achieve efficient and durable management of heavy metals.

Mondol *et al.,* (2011) determined that environmental changes contribute to the differences in heavy metal uptake from soils. They also concluded that trace elements were higher during the dry season compared to the wet season. Ullah *et al.,* (1999) suggest that this might result from lower pollution levels during the wet season as heavy rainfalls flush pollution into canals. A study by Oluyemi *et al.* (2008) at a landfill in Nigeria showed that heavy metals were higher in the dry season than in the wet season. These claims are backed up by Osobamiro and Adewuyi (2015), who studied three farm settlements in Ogun-State Southwest, Nigeria and found that heavy metals concentrations were higher in the dry season than during the wet season. The study suggests that high precipitation, leaching, erosion and plant uptake may account for the reduction in heavy metal levels in the rainy season observed in the results of heavy metals from the three farm settlements.

Land-use patterns, including agricultural practices, profoundly influence soil quality, directly impacting heavy metal accumulation in the soil (Fu *et al*., 2000; Fu *et al.,* 2001; Raiesi *et al.,* 2017). Many wine producers have adopted three farming practices to maximise production: conventional farming, polyculture, and organic farming (Forbes *et al.,* 2009) . In organic wine farming, no pesticides are used. It is a holistic farming system that promotes healthy and productive biodiversity while improving soil health (Seufert *et al.,* 2017). Polyculture farming is the cultivation of different crops in the same space at the same time (Adamczewska-Sowińska and Sowinski, 2020). This practice slows down the soil degradation processes while improving soil fertility. Conventional farming involves using synthetic chemical fertilizers, pesticides, herbicides, and other genetically modified organisms in crop production. Conventional farming is one of the primary sources of heavy metals entering the food chain and posing a risk to environmental health (Shennan *et al.,* 2017).

The Cape Winelands is among the most important agriculture-producing regions in South Africa. It contributes approximately 26 223 million Rands to the annual GDP of South Africa (CWD, 2021). It is a world-renowned wine-producing region; hence, it is of utmost importance to study the heavy metal occurrence in grapevines of the Cape Winelands. It is essential to understand how ecological factors, especially the season and farming practices, influence the prevalence and accumulation of heavy metals in grapevines. The Cape Winelands region is an excellent model for studying the ecological dynamics of heavy metals. The Cape Winelands include Stellenbosch, Franschhoek, Constantia, Paarl, and Worcester.

The objectives of this study were (i) to conduct a detailed pioneer screening of heavy metal levels in soils and grapevine leaf tissues in selected wine farms and (ii) to study the influence of season and farming on heavy metal levels in soils and grapevine leaf tissues. This study revealed that farming practice influenced heavy metal contamination, especially Cu - its levels in organic vineyard soils were significantly higher than in conventional vineyards. However, generally, the eight of the nine heavy metals studied (Cr, Co, Ni, Zn, As, Cd, Hg, and Pb) were substantially below the maximum permitted levels in plant and soil samples.

3.2 Materials and Methods

3.2.1 Experimental design

Soil samples and grapevine leaves were collected from demarcated areas in selected vineyards in the Cape Winelands region of South Africa. The sampling was conducted in winter and summer from the same sites. A deliberate effort was made to ensure that vineyards with different cultivation practices (organic, conventional, and mixed cropping) were selected for this study.

3.2.2 Site characteristics

Six vineyards (sites) located in different regions of the Western Cape were selected for this study: Stellenbosch (A), Eikenbosch (B), Franschhoek (C), Wolseley (D), Robertson (E) and Piketberg (F) (Figure 1). Soils were obtained from vineyards with different cultivation approaches – organic (semi to 100% organic), conventional, and polyculture.

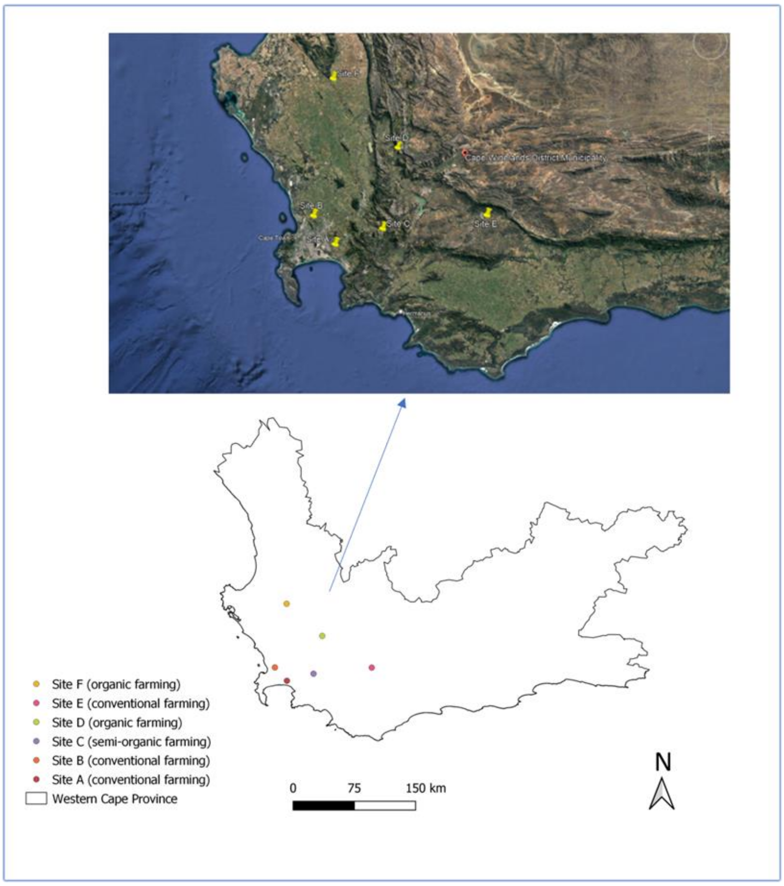

Figure 3.1. A map of the sampled vineyard sites in the Cape Winelands region; the map was created using (QGIS and Google Earth software)

3.2.3 Soil and leaf sampling

At each vineyard, four sampling points 200 m apart were randomly selected, and the sampling points were in the middle of the vineyard's location for the points. From each sampling point, one kilogram of soil samples was collected after removing surface debris using a garden spade at a depth of 15 – 20 cm. The soil samples were placed in separate paper bags. Fresh leaf material (100 g) from randomly selected plants on sampling points that were 200 m was placed in a paper bag. A total of

48 soil and 48 leaf samples were collected from six vineyards in the Western Cape, South Africa. The sampling sites were geo-referenced (Table 1). The collection of samples from the same sampling points was carried out in two seasons (summer and winter). The soil and the leaf samples were analysed at the ICP-MS & amp; XRF Laboratory, Stellenbosch University. Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for elemental trace analysis and is recommended for ultra-trace metals due to its increased sensitivity (Amman, 2007; Constaheiro *et al.*, 2020).

Table 3.1 The coordinates of sampled vineyards in the Cape Winelands, location, sampled grapevine cultivars and farming practices.

Coordinates	Site	Town	Grapevine cultivars sampled	Farming practice
Y = -34.0170461 X =18.7550072	A*	Stellenbosch	Cabernet sauvignon and Cabernet franc	Conventional
Y =-33.8347509 X =18.591131	B*	Eikenbosch	Sauvignon blanc and Cabernet franc	Conventional
Y = -33.9205238 X = 19.1186237	C*	Franschhoek	Merlot and Cabernet sauvignon	Sem-organic
Y= -33.4056598 X =19.2374146	D	Wolseley	Shiraz, Sèmillon, Merlot and Sauvignon blanc	Organic (certified)

Y = -33.836914 X =19.9131483	E*	Robertson	Chardonnay, Sauvignon and Sauvignon blanc	Conventional
Y = -32.96663 X =18.75134	F	Piketberg	Cabernet sauvignon, Cabernet sauvignon, Merlot and Shiraz	Organic (certified)

*Evidence of polyculture farming observed

3.2.4 Sample preparation and analysis

Samples were air-dried and sieved (2 mm sieve) before tests. Concentrations (units: µg kg^{-1} or mg kg^{-1}) of major, minor and trace elements of (ICP-AES and ICP-MS): Cr, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg combined were determined as described by Berg *et al*. (2018)with slight modifications. Portions of about 0.5 g (dry weight of plant samples) and 0.1 g (soil samples) will be digested with 8 ml nitric oxide at 150 °C for 6-8 hours. After cooling to room temperature, the samples were filtered, and demineralized water was added to a total volume of 50 ml. Calibration standards for ICP-MS analysis were prepared from multi-element stock solutions (Spec- troscan, Teknolab As, N-1440 Drsbak). The ICP-MS instrument was calibrated with standard solutions of 50 and 250 ng ml^{-1}. For the major elements, an additional standard of 1000 ng ml^{-1} was used. All calibration standards and blanks were matched with the nitric acid concentration of the samples. The Certified Reference Material 1573 a (tomato leaves) was used to validate the analytical methods for determining the botanical materials' major, minor, and trace elements. Accuracy and precision for the soil samples were achieved by using internal quality control standards (WQB-1). The result of digested solution in mg/L obtained from the ICP was multiplied by the dilution factor in the digestion process using the following formula: mg kg^{-1} = mg l^{-1} x [(Final volume ml) / (weight of sample g)]. Analyses were performed on a Plasma Quad I ICP- MS instrument. The ICP-MS was equipped with a peristaltic pump (Ismatec Reglo 100) and a Meinhard nebulizer. The permissible limits for heavy metals in edible plants that were published by the World Health Organization (WHO, 2015; FAO, 2011) and the Food and Agriculture Organization of the United Nations (FAO) will be used as standards for the comparison and classification of heavy metal levels into three categories (low, optimum and high); the levels for the individual heavy metals are as follows: 0.5 µg g^{-1} arsenic (As), 0.02 µg g^{-1} cadmium (Cd), 1.3 µg g^{-1} chromium (Cr), 0.01 µg g^{-1} cobalt (Co), 10 µg g^{-1} copper (Cu), and 0.03 µg g^{-1}.

3.3 Contamination and ecological risk assessment

Contamination indices were used to evaluate the influence of anthropogenic activities on the accumulation of heavy metals in the farms (geo-accumulation index [I_{geo}]) and the ecological risks associated with heavy metal levels (contamination factor [C_f] and ecological risks [E_r]). The following formulas was used $\mathrm{Igeo} = \log 2 \, [Cn / 1.5Bn$ (Mkhize, 2020; Vannini *et al.,* 2021).

Where C_n is the measured concentration of metal in the soil and B*n* is the background value of a metal.

The background values (mg kg^{-1}) for Cr (5.82), Cu (2.98), Cd (0.62), Zn (12), Hg (0.15), and Pb (2.99) were for South Africa(Herselman 2007), As (20) from Dutch and (Lizjen *et al.,* 2001) Co (18) was from China (Li *et al.,* 2018). To compensate for possible variations in the background values and minor anthropogenic influences, a factor of 1.5 is used (Mkhize, 2020) [6]. The degree of metal contamination in soils as defined by Muller (1969) with seven soil quality levels, ranging from 1 (uncontaminated) to 6 (extremely contaminated), was used (Table 2).

The ecological risk index of each heavy metal was determined using the method developed by Hakanson (1980) [1] (Table 2). The following equations were used (Mkhize, 2020; Hakanssan, 1980) [1, 6]: $C_f = C_n / B_n$ $E_r = T_r \times C_f$ Where T_r is the toxic response factor for each given pollutant, C_f is the contamination factor for each heavy metal, C_n is the measured level of each heavy metal in the sediment, B_n is the background level of each heavy metal, and E_r is the ecological risk index, The toxic response factors [1] are: Cr (2), Co (5), Cu (5), Cd (30), Ni (5), Zn (1), As (10), Hg (40) and Pb (5).

Table 3. 2 Classes of metal contamination, I_{geo} (Muller, 1969) and ecological risk for metal pollution, E_r, (Hakansan, 1980).

I_{geo} Class	I_{geo} Value	Soil quality based on I_{geo} Value	E_r	Ecological risk of single metal
0	<0	Uncontaminated	$E_r < 40$	Low risk
1	0-1	Uncontaminated to moderately contaminated	$40 \leq Er < 80$	Moderate risk
2	1-2	Moderately contaminated	$80 \leq E_r < 160$	Considerable risk
3	2-3	Moderately contaminated to heavily contaminated	$160 \leq Er < 320$	High risk
4	3-4	Heavily contaminated	$E_r \geq 320$	Very high risk
5	4-5	Heavily to extremely contaminated	-	-

6	>5	Extremely contaminated	-	-

3.4 Statistics analysis

Heavy metal concentrations in the soils and leaf tissues obtained during the winter and summer months from each farm were compared using a one-way analysis of variance (ANOVA). Heavy metal concentrations in the soils and leaf tissues obtained from farms with different farming practices were compared using a one-way analysis of variance (ANOVA). SPSS was used to process and analyse data.

3.5 Results

3.5.1 Heavy metals in soil samples

3.5.1.1 Levels of heavy metals in soil samples

Three of the farm sites (Sites A, B, and E) that were sampled practice conventional farming, and the other three farms practice organic farming (Sites D, E and F). Meanwhile, four farm sites had polycultures, three of which were conventional farms. The average concentrations of heavy metals in the soil samples from six study sites in Cape Winelands are given in Table 3. The mean concentration of heavy metal in soil was highest for chromium (58.738 ± 2.988 mg kg-1) and the lowest was for Hg (0.015 ± 0.0002 mg kg-1) in site F. The mean concentrations of Cd and Hg in the soil samples are generally low across all sites.

Table 3.3. Average concentrations (mg/kg) of selected heavy metals in soil samples from different sites collected in summer and winter

Sites	Heavy metal concentrations (SEM) mg kg^{-1} in soils									
	*FP	Cr	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
A***	C	42.933± 1.622	5.399± 0.964	15.568± 0.654	18.471± 2.508	27.171± 0.913	23.177± 1.917	0.019± 0.002	0.042± 0.0005	17.488 ± 0.763
B***	C	48.849± 14.948	5.673± 1.592	13.155± 3.609	9.343 ± 0.891	20.271± 2.884	29.166± 11.442	0.024± 0.004	0.030± 0.011	11.929± 1.498
C***	O^	13.505± 0.749	1.987± 0.001	4.695 ± 0.158	10.719± 1.876	35.406± 18.001	4.074 ± 1.752	0.044± 0.025	0.032± 0.0004	19.285± 3.452
D	O	34.763± 14.738	2.267± 0.835	7.931 ± 1.800	41.275± 7.365	25.167± 6.477	9.751 ± 0.126	0.027± 0.013	0.018± 0.010	7.896 ± 0.270
E***	C	23.586± 2.578	4.129 ±	11.112 ± 1.281	14.266 ± 1.101	23.690 ± 1.353	4.900 ± 0.826	0.022 ±	0.019 ±	10.376 ± 0.557

			0.087					0.0004	0.003	
F	O	58.738 ± 2.988	10.550 ± 0.7047	26.812 ± 0.369	37.687 ± 0.071	44.980 ± 1.651	6.455 ± 0.515	0.032 ± 0.005	0.015 ± 0.0002	17.550 ± 1.821
**FAO/WHO-ML		100	50	50	100	50	20	3.0	-	100

*FP=Farming practice – Conventional(c)/Organic(o)/semi-organic (^), SEM = Standard Error of Mean, **ML = Maximum level permitted in soil by [7]; *** = sites which also practised polyculture

3.5.2 Effect of seasonal variation on heavy metal deposit in the soil

The seasonal variations in some of the selected heavy metals distribution in soil samples from Cape Winelands are shown in Figure 2. The levels of Cd and Hg in all the vineyards are generally minimal. Site E recorded the lowest levels of heavy metal in the soil sample analysed. The heavy metal contents of the soil did not vary significantly (DF = 1,6; P > 0.05) between winter and summer in all the study sites. Furthermore, when data from the farms practising conventional or organic farming were pooled, the seasonal variation had no significant effect (DF =1, 22; P > 0.05) on the heavy metal contents in the soil.

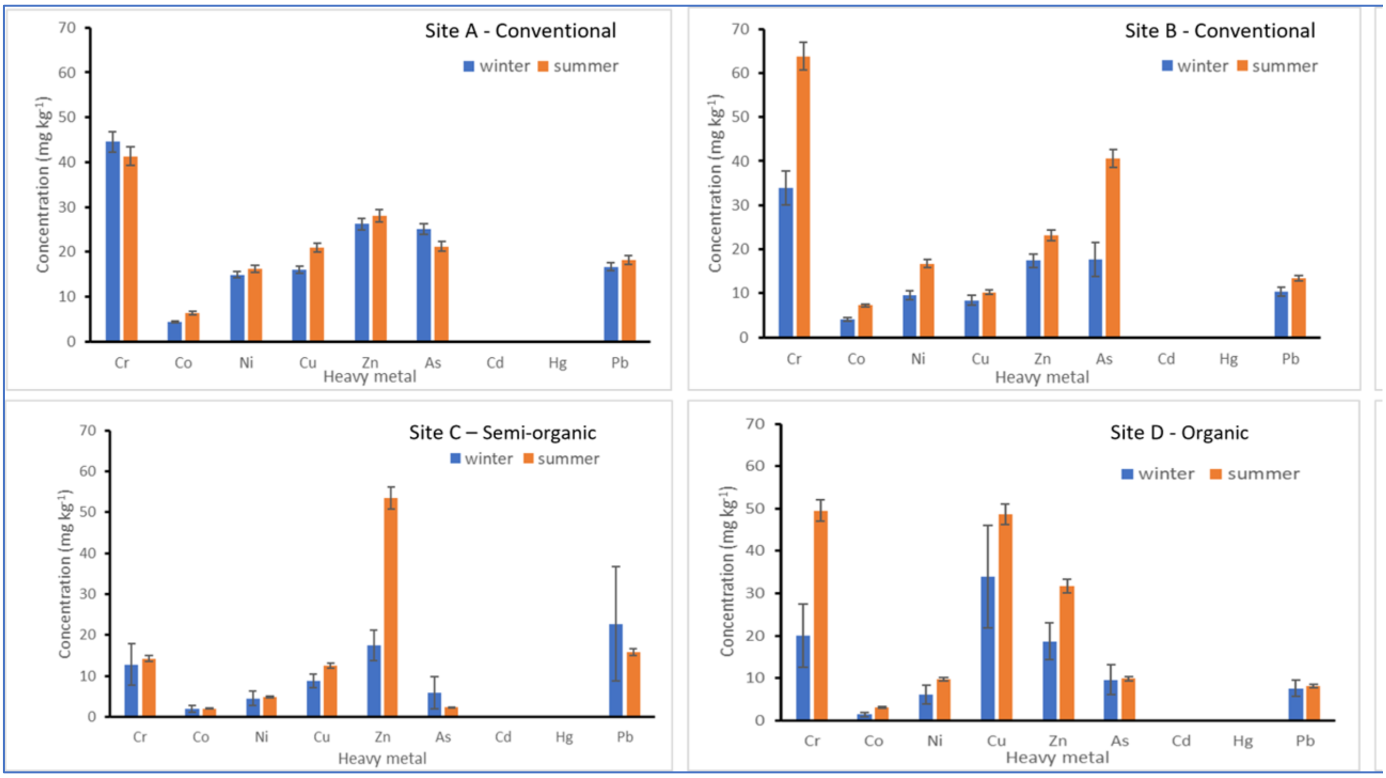

Figure 3.2. Seasonal fluctuation of heavy metal in soil samples from different grapevine sites (A, B, C, D, E and F) in the Cape Winelands.

3.5.3 Effect of agricultural practice on heavy metal deposit in the soil

The impact of agricultural practices (conventional; Sites A, B, and E) and organic (sites C, D and F) on heavy metal deposits in the soil is shown in Figure 3. When soil data from winter and summer months were compared separately or pooled, the influence of agricultural practice was well-pronounced in As (DF =1, 22 or 46; P < 0.05) and Cu (DF = 1, 22 or 46; P <0.05). There were no significant differences in the overall heavy metal deposits in soil between organic and conventional agricultural practices in both summer (DF = 1, 16; F = 0.09; P =0.76) and winter (DF =1, 16; F = 0.02; F = 0.76). The ecological risk index based on the contamination factors and background levels showed low ecological risk in the vineyards for eight of the nine heavy metals assessed — E_r was below 40, corresponding to low risk (Tables 2 and 4). Meanwhile, the geo-accumulation index (E_r < 0) indicated a low level of soil contamination for Co, As, Cd and Hg (Table 4), and neither season nor farming practice had a significant effect on the soil contamination. However, moderate contamination of the soils was recorded for Cr, Ni, Zn and Pb (Table 4). Cu I_{geo} (2.329±0.674 - 2.669±0.597) and E_r (45.068±15.234 -55.248±17.883) values in organic farms were relatively higher than Cu I_{geo}

(1.512±0.297 - 1.661±0.303) and E_r (22.249±4.043 -24.820±5.381) conventional farms suggesting moderate to heavy levels of geochemical contamination and moderate ecological risk (Table 4).

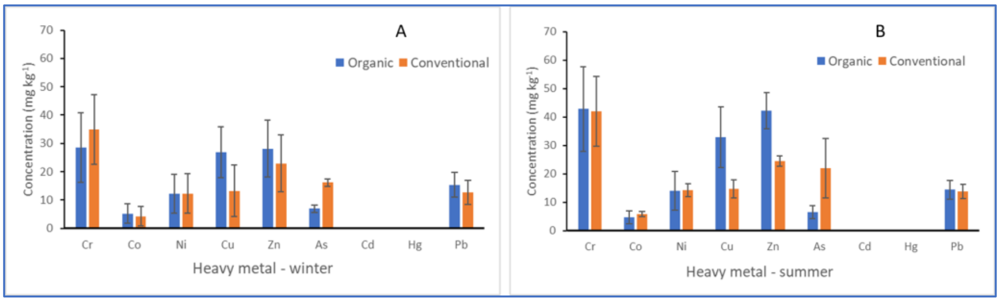

Figure 3.3. Influence of agricultural practices on heavy metal deposits in soils during winter (A) and summer (B) in vineyards in the Cape Winelands.

Table 3.4. Contamination factor (C_f), Potential ecological risk (E_r), and Geo-accumulation Index (I_{geo}) (Mean ± SE) of heavy metals occurring in soils of vineyards, calculated background levels in soils in the Cape Winelands.

Heavy metal	Season	Farming practice	C_f	E_r	I_{geo}
Cr	Winter	Conventional	5.992±0.916	11.984±1.832	1.964±0.222
		Organic	4.899±2.114	9.798±4.228	1.447±0.604

	Summer	Conventional	7.223±2.123	14.446±4.246	2.126±0.466
		Organic	7.358±2.567	14.716±5.135	2.034±0.672
Co	Winter	Conventional	0.236±0.006	1.179±0.029	-2.670±0.035
		Organic	0.285±0.190	1.424±0.951	-3.059±0.952
	Summer	Conventional	0.327±0.053	1.636±0.267	-2.239±0.256
		Organic	0.264±0.124	1.319±0.618	-2.815±0.654
Ni	Winter	Conventional	3.582±0.452	17.908±2.261	1.232±0.187
		Organic	3.571±2.020	17.853±10.100	0.804±0.779
	Summer	Conventional	4.161±0.649	20.805±3.245	1.432±0.249
		Organic	4.095±2.011	20.475±10.055	1.085±0.728

Cu	Winter	Conventional	4.449±0.809	22.249±4.043	1.512±0.297
		Organic	9.014±3.047	45.068±15.234	2.329±0.674
	Summer	Conventional	4.964±1.076	24.820±5.381	1.661±0.303
		Organic	11.049±3.576	55.248±17.883	2.669±0.597
Zn	Winter	Conventional	1.908±0.231	1.908±0.231	0.324±0.188
		Organic	2.344±0.840	2.344±0.840	0.476±0.474
	Summer	Conventional	2.044±0.149	2.044±0.149	0.439±0.102
		Organic	3.520±0.524	3.520±0.524	1.198±0.218
As	Winter	Conventional	0.809±0.282	8.091±2.822	-1.135±0.643
		Organic	0.348±0.067	3.479±0.669	-2.157±0.260

	Summer	Conventional	1.099±0.528	10.990±5.276	-0.980±0.988
		Organic	0.328±0.111	3.281±1.115	-2.432±0.640
Cd	Winter	Conventional	0.036±0.004	1.097±0.134	-5.379±0.173
		Organic	0.037±0.011	1.121±0.339	-5.451±0.414
	Summer	Conventional	0.034±0.001	1.029±0.042	-5.453±0.059
		Organic	0.073±0.020	2.179±0.617	-4.483±0.407
	Winter	Conventional	0.186±0.049	7.436±1.961	-3.105±0.357
Hg		Organic	0.122±0.046	4.865±1.837	-3.844±0.572
	Summer	Conventional	0.221±0.057	8.834±2.267	-2.890±0.456

		Organic	0.168±0.035	6.720±1.387	-3.232±0.339
Pb	Winter	Conventional	4.242±0.671	21.209±3.354	1.466±0.215
		Organic	5.139±1.460	25.693±7.301	1.639±0.463
	Summer	Conventional	4.622±0.813	23.110±4.065	1.578±0.257
		Organic	4.835±1.106	24.176±5.530	1.598±0.376

3.6 Heavy metals in plant samples

3.6.1 Levels of heavy metals in plant samples

The average concentrations of heavy metals in the plant samples from the six study sites in the Cape Winelands are provided in Table 5. The highest mean concentration of heavy metals in plant samples was for Cu (87.098 ± 19.481 mg/kg) in site D, and the lowest was for Cd (0.002 ± 0.0004 mg/kg), also in site D. There were significant (DF = 5, 18; $P < 0.05$) variations in the heavy metal contents (Cr, Cu, As, Cd, Hg and Pb) in plant leaves among the sites.

Table 3.5. Average concentrations (mg/kg) of selected heavy metals in grapevine leaf samples from different sites (vineyards) in the Cape Winelands

Sites	Heavy metal concentration (SEM) mg kg^{-1}									
	*FP	Cr	Co	Ni	Cu	Zn	As	Cd	Hg	Pb

A***	C	0.959 ± 0.057ab	0.240 ± 0.053a	0.566± 0.049a	4.230 ± 0.328a	27.906± 2.230ab	0.318 ± 0.046ab	0.007± 0.001ab	0.017± 0.002ab	0.373 ± 0.045ab
B***	C	1.335 ± 0.164a	0.269 ± 0.047a	0.574± 0.047a	4.256 ± 0.458a	23.987± 3.138ab	0.454 ± 0.102a	0.008± 0.0008ab	0.017± 0.001ab	0.619 ± 0.057a
C***	O^	0.620 ± 0.081b	0.107 ± 0.011a	0.431± 0.058a	3.957 ± 0.364a	32.289± 5.858a	0.119 ± 0.030b	0.018± 0.005a	0.018± 0.002ab	0.307 ± 0.063b
D	O	0.572 ± 0.063b	0.103 ± 0.018a	0.461± 0.069a	87.098± 19.481b	24.192± 2.730b	0.125 ± 0.022b	0.002± 0.0004b	0.020± 0.0005ab	0.295 ± 0.083b
E***	C	0.699 ± 0.069b	0.200 ± 0.044a	0.821± 0.203a	6.082 ± 0.885a	24.789± 1.437ab	0.106 ± 0.009b	0.016± 0.006ab	0.014± 0.002a	0.165 ± 0.035b
F	O	0.973 ± 0.131ab	0.298 ± 0.106aa	1.104± 0.372a	60.603± 7.971bc	16.848± 1.937ab	0.117 ± 0.021b	0.004± 0.001ab	0.023± 0.003b	0.197 ± 0.034b
**FAO/WHO-ML		1.3	50	10	10	99.4	0.0005	0.02	0.1	2

*FP=Farming practice – Conventional(c)/Organic(o)/semi-organic (^), SEM = Standard Error of Mean, **ML = Maximum level permitted in edible plants by [7]; *** = sites with evidence of polyculture farming

3.6.2 Effect of agricultural practice on heavy metal uptake by plant samples

Leaf samples from eight cultivars of grapevine plants occurring in the farms were analysed. To determine the impact of agricultural practices on heavy metals, pooled data from conventional farming sites (A, B and E) and organic (sites C, D and F) were statistically compared (Figure 4 and Table 5). The agricultural practice significantly influenced (DF = 1, 22; P< 0.05) Cu, As, Cr, and Hg uptake, with little effect on Ni, Co, Cd, and Hg. Generally, the heavy metals were substantially below the maximum permitted levels in plants.

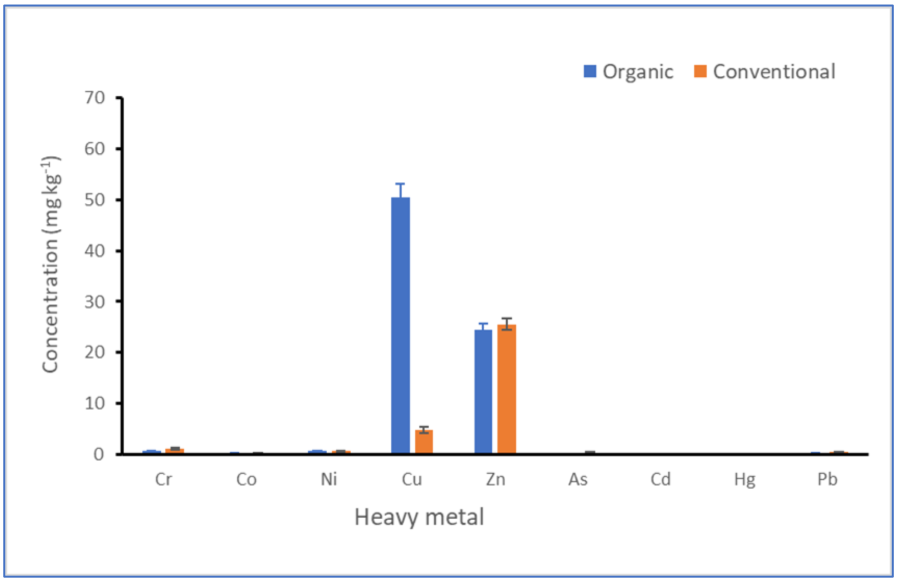

Figure 3.4. Influence of agricultural practices on heavy metal uptake by plant samples from vineyards of the Cape Winelands

Chapter four

4.1 Discussion

A key finding of this study is that heavy metal contents in soils and grape leaves are below the maximum allowed concentrations of heavy metals in the leaf samples, based on the recommendations of the WHO (2011). Furthermore, the heavy metal concentrations in the soil for eight of the nine heavy metals posed low ecological risk based on the classification of ecological risk heavy metal pollution (Hakansan, 1980). This is good news for wine consumers and the wine industry in South Africa as the Cape Winelands is the largest wine-producing region on the African continent (Meadows, 2015; Tassipoulos *et al.,* 2004). In addition, the seasonal change did not significantly influence variations in heavy metals. However, farming practices influence accumulations of As and Cu, suggesting that pesticide application is a more important factor influencing heavy metal contents in the Cape Winelands. Cu contamination levels in organic farm soils had higher I_{geo} values (2.3-2.7), which corresponded to moderately to heavily contaminated than in conventional farms. In addition to the over-dependence on agrochemicals, rapid industrialization and urbanization contribute significantly to heavy metal contamination through high use of metal, leaded gasoline, paint, and petrochemical waste disposals and atmospheric deposition (Zhang *et al*., 2010; Jordanova *et al*., 2018). Cu and As varied significantly between farms that employed organic and conventional farming practices. These two elements are contained in some well-known pesticides used in the cultivation of grapevines (Li et al.,2018). The levels of As were higher in the farms that practice conventional farming. This is expected because many insecticides used to control pests in grapevines have arsenic compounds. The application of foliar fungicides in vineyards and orchards can increase the soil concentration of heavy metals such as copper (Cu) and zinc (Zn) up to the toxicity threshold for fruit trees and cover crop (Brunetto *et al.,* 2017). However, remarkably, Cu concentrations in organic vineyards were higher than in conventional vineyards in the current study. The Cu I_{geo} and E_r values in organic farms were higher relative to the conventional farms and corresponded to moderate to heavy contamination and moderate ecological risk, respectively. Vannini et al. (2021) also reported similar findings in agricultural soils of the Valdichiana area, Tuscany, Italy; C_f and I_{geo} indices for Cu were higher than for other heavy metals, and they attributed the findings to the increased use of Cu-based products. The accumulation of Cu in soil and plant tissues could be influenced by many factors other than pesticides, such as the mineralization of organic matter, microorganisms, and minerals in the rock. It is worth noting that organic amendments such as compost and manure, which are widely used in organic farming bind with Cu more tightly than other micronutrients (Schulte and

Kelling, 2004). Previous studies have investigated the levels of heavy metals in grapefruits in Spain and China (Laczi *et al*., 2017; Ganzales-Martin, 2018).

This study showed that season did not affect the heavy metal levels. Results from previous studies suggest that heavy metal concentrations in soil, rivers, and leaves vary with the season; generally, higher heavy metal concentrations are more prevalent in the dry season than in the rainy season (Osobarmiro and Adewuyi, 2015; Raji *et al*., 2016). In a study by Okoro et al. (2017) on the concentrations of heavy metals in seawater from Cape Town harbour, South Africa, the authors reported that Sn and Cd occurred at higher levels in summer while Hg, Pb, and As were more prevalent in winter. It is worth noting that the Cape Peninsula region has a Mediterranean climate, characterised by hot and dry summers and cold and rainy winters (CSIR,2014).

Although this study only investigated the concentrations of heavy metals in vineyard soils and grapevine leaves, the results are very relevant because the use of Cu-and Zn-based pesticides in vineyards can increase the levels of these metals in wines and grapes. In the current study, the geochemical analysis showed that in addition to Cu, the heavy metals Ni, Zn, Cr, and Pb showed moderate soil contamination. In a study conducted in Sri Lanka, Prabaga et al. (2021) found that most of the accumulated metals are mainly concentrated in the leaves of the grape tree than in the fruit. A survey carried out on the west coast of Oristano province (Sardinia, Italy) revealed that cobalt occurred at a greater level than the legal limit on one vineyard, and the long-term use of copper-based fungicides in vineyards does not represent a cause of concern for the studied areas (Fabrizio and Stefania, 2012). A study that that investigated cadmium, copper, lead and zinc concentrations in wines and alcohol-containing drinks from Italy, Bulgaria and Poland revealed that these metals occurred in low concentrations; however, Cu and Zn concentrations were highest in Italian wines (Cu =0.13±0.05 mg l^{-1}; Zn =0.83±0.56 mgL^{-1}) and lowest in Polish products (Cu =0.04±0.001 mg l^{-1}; Zn =0.18±0.16 mg l^{-1}) (Formicki et al., 2012).

4.2 Conclusion

Four (Co, As, Cd, and Hg) of the nine heavy metals occurred at very low concentrations in the vineyard soils and posed low contamination and ecological risks. However, moderate contamination of the soils was recorded for Cr, Ni, Zn and Pb. Notably, Cu levels in organic vineyard soils were significantly higher than in conventional vineyards, which is surprising and requires further investigation because Cu-based pesticides are generally not used in organic farming. The season had no significant influence on heavy metal contamination. This study provides comprehensive baseline data on heavy metals in vineyard soils and grapevine leaves in the Cape Winelands. The findings of this study can be applied when adopting farming practices that promote the reduction in metals and also highlight the need for continuous monitoring of toxic metals, even in organic farming, for healthier agroecosystems.

4.3 Recommendations

Based on the findings of this study the use of phytoremediation would be recommended because In comparison to other physicochemical procedures, phytoremediation offers a number of advantages and has been shown to be a potential method for replanting heavy metal-contaminated soil and phytoremediation is most desirable because it is both environmentally friendly and cost-effective. The simplest method for phytoremediation is the application of heavy metal hyperaccumulators, however, phytoremediation with these natural hyperaccumulators still suffers from a few limitations, as it is a time-consuming process, which takes a very long time to clean-up heavy metal-contaminated soil, particularly in moderately and highly contaminated sites therefore further research and understanding is needed.

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Appendix

Data in Brief published article

Amanda Mahlungulu, Learnmore Kambizi, Enoch A. Akinpelu, Felix Nchu 2023. Chemical dataset of levels of heavy metals in vineyard soil and grapevine leaf samples from Cape Winelands, South Africa, Data in Brief, 48, 109083, https://doi.org/10.1016/j.dib.2023.109083.

“Abstract

The chemical analysis of vineyards is an essential tool for the early detection of risks, such as excessive fertilization and heavy metal and pesticide contamination in farm management. Soil and plant samples were collected in summer and winter from six different vineyards with varying agricultural practices in the Cape Winelands of Western Cape, South Africa. The samples were pretreated in a microwave using CEM MARS 6™ Microwave Digestion and Extraction System (CEM Corporation, Matthews, NC, USA). Chemical element data were obtained using an inductively coupled plasma optical emission spectrometer (ICP-OES) (ICP Expert II, Agilent Technologies 720 ICP-OES). The data will be suitable for the selection and improvement of farming practices, including the influence of seasonal variation on the elemental accumulation in farmlands.

Specifications table

Subject	Agricultural Sciences
Specific subject area	Soil science, Agronomy
Type of data	Table
How the data were acquired	The chemical dataset was obtained using an inductively coupled plasma optical emission spectrometer (ICP-OES) (ICP Expert II, Agilent Technologies 720 ICP-OES).

Data format	Raw and analyzed
Description of data collection	Soil and leaf samples were collected from six different vineyards in Cape Town in two seasons (Summer and Winter). Samples were pre-treated in a microwave using CEM MARS 6™ Microwave Digestion and Extraction System (CEM Corporation, Matthews, NC, USA).
Data source location	Institution: Cape Peninsula University of Technology City/Town/Region: Cape Town, Western Cape Country: South Africa
Data accessibility	Repository name: esango Data identification number: Direct URL to data: *e.g., https://www.data.edu.com – the URL should be working at the time of submission.* Instructions for accessing these data:
Related research article	Amanda Mahlungulu, Learnmore Kambizi, Enoch A. Akinpelu, Felix Nchu Vineyards in the Cape Winelands have acceptable levels of heavy metals – submitted.

Value of the data

- An extensive chemical analysis of plant and soil in Cape Winelands
- The chemical data can be used to determine the quality of wine produce and farming practice in the vineyard

- The dataset can be used by farmers and researchers working on soil health and sustainable farming practice
- The dataset could also be used to understand the influence of seasonal variation on metal accumulation in Winelands.

Data description

The chemical property is an important feature in soil health analysis. This data affects processes such as soil formation, nutrient cycling, pollutant fate, microbial activities and erosion, including human activity. The soil microbial activities play a major role in the processing and transformation of organic nutrients into plant accessible nutrients. Hence, soil health determines plant growth. In a study published in 2012, Tchounwou et al. found that there is little information on the toxicity of heavy metals. As a result, it is crucial to understand the molecular underpinnings of heavy metal interactions to assess health risks and control chemical combinations. Research is therefore required to better understand the molecular mechanisms and effects on public health brought on by human exposure to toxic heavy metals. According to Ali et al. (2019), environmental sciences researchers as well as graduate and undergraduate students will find the research on heavy metals to be a useful teaching resource. Such research will be helpful for a more precise and trustworthy evaluation of human and ecological risk. Chemical data of soil in different seasons with different farming approaches (organic, polycultures and conventional) are presented in Table 1 while Table 2 shows elemental data on plants in the summer season under varying farming approaches.

Experimental design, materials and methods

Experimental design

Soil samples and grapevine leaves were collected from demarcated areas in selected vineyards in the Cape Winelands region of South Africa. The sampling was done in the winter and summer months from the same sites. A deliberate effort was made to ensure that vineyards with different cultivation practices (organic, conventional and mixed cropping) were selected for this study.

Site characteristics

Soils were obtained from six vineyards with different cultivation approaches – organic farming, conventional farming, and polyculture farming in the Western Cape region of South Africa.

Soil and leaf Sampling

At each vineyard, four sampling points 200 m apart were randomly selected, and the sampling points were located in the middle of the vineyard's location for the points. From each sampling point, one kilogram of soil samples was collected after the removal of surface debris using a garden spade at a depth of 15 – 20 cm. The soil samples were placed in separate paper bags. Fresh leaf material (100 g) from randomly selected plants on sampling points that were 200 m was placed in a paper bag. A total of 48 soil and 48 leaf samples were collected from six vineyards in the Western Cape, South Africa. The sampling sites were geo-referenced. The collection of samples from the same sampling points was carried out in two seasons (summer and winter). The soil and the leaf samples were sent to ICP-MS & XRF Laboratory at Stellenbosch University for analysis, inductively coupled plasma mass spectrometry (ICP-MS) is a potent technique for elemental trace analysis and is recommended for ultratrace due to its increased sensitivity, according to Voica et al., (2012). Similar to Ganjhoui et al., (2011) who found that this method was validated in terms of accuracy and precision and provided a quick way to determine as many elements in basil powder, Castanheiro et al., (2020) found this method to be a useful approach to investigate the accumulation of atmospheric dust on leaf surfaces.

Greenhouse experiment

This experiment was conducted at the greenhouse of the Department of Horticultural

Sciences, Cape Peninsula University of Technology (CPUT), South Africa. The experiment was carried out under the following conditions: An average day temperature of 25 ± 5 ◦C and an average RH of 65 ± 5% between March and May 2022. Triticum aestivum and Secale cereale seeds were sown in 2 parts compost, 2 parts peat moss and 1 part vermiculite for 4 weeks. They were then transferred into 15 cm brown pots. 60 pots were with 2 parts river sand, 2 parts peat moss and 1 part perlite, 20 pots were treated with 80 g of AgNO3 (silver nitrate), 20 pots were treated with 80 g of $Pb(NO_3)_2$ (lead nitrate) and 20 pots were treated with 80 g of $ZnCl_2$ (zinc chloride). Of each treatment, 10 pots were that of Triticum aestivum and 10 pots were that of Secale cereale. Throughout the experiment, the plants were fertigated weekly with a hydroponic fertilizer, Nutrifeed (Starke Ayres, Cape Town, South Africa), containing 65 g/kg N, 27 g/kg P, 130 g/kg K, 70 mg/kg Ca, 20 mg/kg Cu, 1500 mg/kg Fe, 10 mg/kg Mo, 22 mg/kg Mg, 240 mg/kg Mn, 75 mg/kg S, 240 mg/kg B, and mg/kg Zn. The nutrient solution was prepared by dissolving 60 g of the fertilizer in a 60 L reservoir with tap water, and each plant was hand-fed with 500 mL every week. The experiment ran for six weeks, after which the plants were harvested and soil samples taken, then oven-dried at 25 ◦C for two days, and then ground with a Jankel and Kunkel Model A 10 mill into fine powder. They were then sent to Stellenbosch University geology lab for majors and trace analysis by inductively coupled plasma optical emission spectroscopy (ICP OES/AES).