A PRIMARY INVESTIGATION OF NUTRIENT RESIDUES ON THE SOILS OF CITRUS ORCHARDS IN GUZELYURT

A THESIS SUBMITTED TO
THE BOARD OF GRADUATE PROGRAMS
OF
MIDDLE EAST TECHNICAL UNIVERSITY, NORTHERN CYPRUS CAMPUS

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE
DEGREE OF MASTER OF SCIENCE
INTHE
SUSTAINABLE ENVIRONMENT AND ENERGY SYSTEMS PROGRAM

MAY 2013

Approval of the Board of Graduate Programs

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ABSTRACT

A PRIMARY INVESTIGATION OF NUTRIENT RESIDUES ON THE SOILS OF CITRUS ORCHARDS IN GUZELYURT

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May 2013, 93 pages

The non-point (defused) source pollution of agrochemicals on soils; surface water and ground water may be a driving force of environmental degradation and may also pose risks to human health. This thesis seeks to address concerns about environmental sustainability in agriculture systems by undertaking a first baseline study of agrichemical residues - such as nitrate, nitrite, potash, and phosphates - on the soils of citrus orchards in Guzelyurt district. The methods applied in this study are both quantitative and qualitative chemical analysis of soils samples taken at the end of the citrus farming season in April, 2012. Three classes of orchards were investigated for the concentrations of fertilizer residues in the soil of citrus in Guzelyurt. Ten orchards and 29 sample points were investigated. The orchards included inorganic orchards (receiving fertilizers),organic orchards (receiving organic manures) and an abandoned orchard (which served as a control). Soil samples were randomly collected and brought to the laboratory and analyzed by spectrophotometry and flame photometry. Following the conduct of laboratory analysis a profile of agrichemical residues in soil representing the citrus orchard soils of the Guzelyurt district was identified. Mean residue ranges were found in fertilized orchards for nitrate 15.8 to 20.50 mg/l, nitrite 0.05 mg/l, phosphate 0.15 to 0.34 mg/l and potash 0.79 to 1.49 mg/l across soil depths from 0 to 90 cm. Mean ranges for organic orchards were found to be, nitrate 7.00 to 30.55 mg/l, nitrite 0.03 to 0.05 mg/l, phosphate 0.01 to 0.15 and potash 0.64 to 1.39 mg/l across soil depths from 0 to 90 cm. These results can form the baseline measures for any future studies.

Key words: Soil, nitrate, nitrite, phosphate, potash, residues

ÖZ

GÜZELYURT'TAKİ NARENCİYE AĞAÇLARININ YETİŞTİRİLDİĞİ TOPRAKLARDAKİ GIDA ARTIKLARININ ÖN İNCELENMESİ

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Mayıs 2013, 93sayfa

Tarımsal ilaçların toprak, yeraltı ve yerüstü su kaynakları üzerindeki çıkış kaynağı fazla olan kirliliği çevresel bozulma için itici güçtür ve insan sağlığına risk teşkil etmektedir.Bu tez Güzelyurt bölgesinde narenciye bahçelerinin toprakları üzerinde çıkış kaynağı fazla nitrat, nitrik, potasyum ve fosfat kalıntılarının çevreye olası etkisinin değerlendirilmesiyle tarım sistemlerinde çevresel sürdürebilirlik hakkındaki endişelere yanıt vermeyi amaçlamaktadır. Bu araştırmada uygulanan yöntem 2012 Nisan ayında narenciye hasat sezonu sonunda toprak örneklerinin nicel ve nitel kimyasal analizidir. Üç grup meyve bahçesi, Güzelyurt narenciye toprağı üzerinde gübre kullanımından kaynaklanacak olası çevresel etkiler için incelenmiştir. İncelenen 29 farklı toprak örneği 10 narenciye bahçesinden toplanmıştır. Bu bahçeler suni gübre verilen(inorganik meyvebahçeleri), hayvan atıklarından elde edilen gübrenin verildiği (organik meyve bahçeleri) ve terk edilmiş(denetim için kullanılan) meyve bahçeleridir. Örnekler laboratuvara getirilmiş ve spektrofotometri ve alev fotometrisi yöntemleriyle analiz edilmiştir. Laboratuvar analizleri sonucunda Güzelyurt bölgesindeki narenciye ağaçlarından ötürü toprakta bir miktar tarım amaçlı kimyasalların kaldığı gözlemlenmiştir. Gübre kullanılan bahçelerin 0-90 cm derinliğinden alınan toprak örneklerinde ortalama kalıntı miktarı nitrat için 15.8 - 20.50 mg/l, nitrit 0.05mg/l, fosfat 0.15 – 0.34 mg/l, potasyum 0.79 – 1.49 mg/l arasında ölçülmüştür.Organik meyve bahçelerinin 0-90 cm derinliğinden elde edilen toprak numunelerinde ise kalıntı miktarları nitrat için 7.00 ile 30.55 mg/l, nitrik için 0.03 – 0.05 mg/l, fosfat oranı ise 0.01 – 0.15 mg/l, potasyum ise 0.64 -1.39 mg/l mertebesinde ölçülmüştür. Bu sonuçlar gelecekteki çalışmalar için temel ölçümleri oluşturabilir.

Anahtar Kelimeler: Toprak, nitrat, fosfat, potas, kalıntılar

DEDICATION

To the Great Kubam clan of Bamendankwe (Cameroon)

ACKNOWLEDGMENTS

The author wishes to express his deepest gratitude to his supervisor V. Assoc. Prof. Dr. Julian Saurin and Co-Supervisor, Dr. Begüm Tokay for guidance, advice, criticism, encouragements and insight throughout this research.

The author will also like to thank Assist. Prof. Dr. Wayne Fuller, Assist. Prof. Dr. Bertuğ Akintuğ and Prof. Dr. Kahraman Ünlü for their suggestions and comments.

I am also grateful to Assist.Prof. Dr. Ozge Ozden faculty of agricultural science and technology of European university of Lefke for establishing the initial research collaboration of this thesis with the Guzelyurt soil and water laboratory.

The technical assistance of all the members of staff of Guzelyurt soil and water laboratory, and I must also acknowledge the significant contribution of Huveyda Esen (Environment Engineer and Chief of service waste water Treatment Plant of EBI., METU. NCC.) for permission to carry out nitrate and nitrite analysis at the waste water treatment plant laboratory on campus.

I am thankful to Evren Ozdemir who did an excellent job in translating my abstract.

I will like to acknowledge the financial and moral support from members of my family (Atungsiri Daniel and Atungsiri Samuel A.) and friends and classmates.

In addition, I wish to thank the wonderful members of staff of METU NCC library for all their support and encouragement throughout the length of time I spend with them in the library as graduate assistant.

This work was financially supported by METU-NCC graduate campus research grant (BAP) decision no FEN 12 O 3.

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CHAPTER 1

INTRODUCTION

This research seeks to address concerns about environmental sustainability in agricultural systems through an assessment of the potential environmental impacts of fertilizers on soils of citrus orchards in Guzelyurt. Specifically, this thesis seeks to address concerns about environmental sustainability in agriculture systems by undertaking a first baseline study of agrichemical residues - such as nitrate, nitrite, potash, and phosphates - on the soils of citrus orchards in the Guzelyurt district. Sustainable agriculture requires a delicate balance between crop production, natural resource utilization, environmental impacts and economics. It strives to optimize productivity while maintaining economic stability, minimizing the utilization of finite natural resources and minimizing impacts on the environment (Corwin and Wagenet, 1996). Sustainability concerns in agricultural systems centers on technological developments that may be having adverse effects on environmental services and goods.

Despite great progress in agriculture productivity in the past half-century, with crops and livestock productivity strongly influenced by the increased use of fertilizers, irrigation water, agricultural machinery, pesticides, and land modifications (Pretty, 2008), it is obvious that the components of environmental ecology will depreciate over time. New approaches are required in agricultural systems that will integrate biological and ecological processes into food production while minimizing the use of non-renewable (agrochemicals) inputs that might be causing harm to the environment, producers, and consumers (Pretty, 2008).

This research therefore sets out to investigate some of the impacts of agrochemical (fertilizer) application on the soils of citrus orchards in Guzelyurt. To begin this impact assessment, the research focuses on a chemical analysis of nitrate, nitrite, phosphate, and potash soil residues from a representative sample taken from citrus orchards, conducted in spring 2012, shortly before the application of fertilizer in preparation for the subsequent farming season. In addition to this, tests were conducted to measure soils' pH, conductivity, moisture content, total organic matter, texture, and calcium carbonate in order to be able to classify the soil types. The investigations here could form the beginning of a systematic time-series data collection and therefore of a unique local longitudinal analysis (repeated measures analysis over time).

Increasing the awareness of environmental concerns in concert with human health issues that may arise from the release of agrochemical into the environment is essential in contemporary society and to incorporate environmental sustainability into agricultural systems. When these agrochemicals are introduced to the agricultural systems by any means such as spraying of plants with pesticides, application of fertilizers in their granular forms or as solvents in solution through irrigation pipes, the soil turns to act as an intermediate component of the environment where the plants absorb their nutrients from the fertilizer. In an attempt to develop sustainable agricultural land use practices and environmental protection, it is therefore essential to evaluate and monitor soil quality.

The soil is the medium from which plants obtain their nutrients and supports. In the past, farmers relied mostly on traditional subsistence agricultural systems by which little or no agrochemicals were applied to soil or on the plants. In the recent years, industrialization and green revolution has caused a shift of agricultural systems from subsistence agriculture farming to commercial agriculture system. The commercial agriculture system is the type of farming that is highly chemical intensive. The arrival of the green revolution has dramatically changed farming practice from less agro-chemically dependent to highly agro-chemically dependent crops species to produce higher yields. These agrochemicals are fertilizers, insecticides, pesticides and fungicides. Over the years it has been observed that use of agrochemicals throughout the world has steadily increased and with an increasing global population the demand continues to grow (Corwin and Wagenet, 1996) and the Turkish Republic of Northern Cyprus (TRNC) is not an exception (Serinol et al., 2008).

The Guzelyurt district in TRNC is the famous for agriculture and especially citrus fruit production that supplies the local market as well as neighbouring markets (Rural development sector program, Lefkoşa 2010). This is because of the available fresh groundwater for irrigation and fertile soils, which favour the cultivation of a variety of crop types. The quality and quantity of citrus fruits and other crops grown in this agricultural ecological environment have been enhanced with nitrogen, phosphorus and potassium fertilizers (NPK fertilizers). The Guzelyurt citrus orchards area is a typical example of an agricultural ecological environment in TRNC, where agrochemicals are used to increase production. It is supposed that the expansion of agriculture in Guzelyurt, to fertile lands has rendered the ecological environment prone to destabilization. High irrigation might also render the soil less fertile. During the irrigation process the top-most nutrients are leached to ground water resources. The leaching process and surface run off may cause soil to be less fertile, resulting to an increased need for fertilization to enhance the soil quality and crops yield. In recent years, there are increasing fears that agricultural practice driven by mostly agrochemical inputs may have a large environmental impact. This fear coupled with human health related problems is part of the ambition of this project to examine, in this one small sector of citrus production in TRNC, whether those fears are justified. Substances like nitrates, nitrite, potassium, and phosphorus have been associated with environmental issues like groundwater and surface water pollution and some human health related problems (Du et al., 2009).

Agrochemical fertilizers like nitrogen, phosphorus, and potassium mixed fertilizers (NPK fertilizers) have been observed to be the most widely used fertilizer worldwide (Heffer, 2012) and similar situation may be the case in citrus orchards in TRNC. Weathered parent rock materials and decomposed remains of once living organisms are the primary source of plants nutrients (minerals) that occurs in the form of nitrate, phosphate, and potassium. The nitrate, phosphate, and potassium in agricultural ecological environment are essential nutrients for plants (Du et al., 2009) because they aid in the formation of the plants cellular structure and other plants metabolic activities. The accumulation of these substances may result in environmental change when released in the soil in large amounts (Corwin and Wagenet, 1996). Among those, nitrate pollution has received more attention because of its potential impact on human health as well as environmental damage (Liu and Hallberg, 2002). Excessive nitrate released into agro-ecosystems has not only impacted on the quality of the components of the environment like soil quality, surface water and groundwater, but also endangered human health via the food chain (Mei et al., 2008). Nitrate ingested into the human mouth and gastrointestinal passage could be changed into nitrite and long term excessive intake might induce gastrointestinal system cancer (Wang et al., 1991). Nitrate gets into the human system from ingestion of drinking water or vegetables containing nitrate (Walker, 1975). Water nitrate pollution occurs when excessive nitrogen fertilizers are applied on the soil. This soil nitrate eventually gets to the groundwater and surface water systems through leaching and runoff, respectively (Du et al., 2009). Consequently, the nitrate together with other soil residuals that might be resulting from fertilizer application may lead to changes (contaminates) in water quality and deteriorates its quality over time (Cepuder and Shukla, 2002; Sebin et al., 2007).

Nitrogen, phosphorus and potassium are essential nutritional requirements for healthy plant growth. They occur naturally in the soil as minerals (in the form of nitrate, phosphate and potash). Soil organic matter as well as parent rock materials that are rich in any of these elements are the principal source of plants nutrimental elements. In soil where these elements are deficient, farmers might use inorganic fertilizer or organic manure to enhance the soil fertility. When these substances are introduced in the soil, they alter the soil's physical and chemical properties as well as the biological characteristics. This alteration tends to facilitate soil contamination and pollution processes.

Besides, the plants optimize their demand for these nutrients when they are available in sufficient amounts in the soils. The plants can only obtain these nutritional elements from the soil by means of their root systems. The portion of the nutrients, which does not finally enter the plants root systems, becomes soil residues that might potentially harm the environment as well as the lithosphere, biosphere, hydrosphere and atmosphere. Additionally, the TRNC soil quality might be at risk because of the soil contamination with nitrate, phosphate, and potash residues, which may be associated with excessive chemical fertilizer application.

The plant's recovery rate (that is to say, the amount of nutrients obtained from the soil within a given period) from soil that is being enriched with inorganic fertilizers remains relatively low (about 50% of N) (Shaviv and Mikkelsen, 1993). The unrecovered nutrients tend to degrade (that is to say the soil deteriorates or loses its quality and productivity because of human activity) the soil quality in the form of phosphate, potash and nitrate residues as well as heavy metal accumulation. The rate at which fertilizer pollutants degrade soil and water quality has been identified to be alarming in some parts in the world (Pimentel and Kounang, 1998). Throughout the earth, 30 to 50% is believed to be affected by NPK pollutants including erosion, fertilizers, pesticides, organic manure and sewage sludge (Pimentel and Kounang, 1998). The United State Environmental Protection Agency (USEPA) in 1990 identified agricultural nonpoint source runoff of sediments and agricultural chemicals to caused impairment of 55% of surveyed rivers and 58% of surveyed lakes to have water quality problem. The term nonpoint source is defined, in the USA, as any source of water pollution that does not meet the legal definition of “point source” in section 502(14) of Clean Water Act of the United State of America (US EPA, 2004). Recently, increase attention has been given NPK pollution of subsurface soils and water (Corwin and Wagenet 1996).

The limits issued by World Health Organization (WHO) and United States Environmental Protection Agency (EPA) of nitrate and nitrite content in drinking water is 10mg/L and 1mg/l, respectively (Du et al., 2009; Theofanis et al., 2012). These values can be used as proxy in the evaluation standard of soil residues of nitrate and nitrite because there is no standard for the evaluation soil. Phosphorus and potassium has no drinking limit because they are not associated with any health risk. However, high concentration of soil phosphorus in the form of phosphate has impact on surface water. Excessive phosphorus and nitrate in surface water will promote algae bloom, which reduces the water quality resulting to serious pollution problem to aquatic organisms, a process known as eutrophication.

In contrast, these residues have several positive effects in the microbial population in the agricultural systems (Feng et al., 2003). The residues accumulate in the surface 3 inches (approximately 7.6 cm) (Feng et al., 2003)of the soil and provide substrates and food for nitrifying and denitrifying microbes (Feng et al., 2003). However, increased residues with high carbon to nitrogen ratios slow the rate of mineralization through bacterial activity over a sustained period of time (Coleman et al., 2004). Residue accumulation might result from the decomposition of organic matter. Human influence on these organic matters through the selection of appropriate agrichemical management practices is also very important. Agronomic inputs like adding manure or fertilizers increase vegetative growth (above and below ground), thus increases soil organic matter as well as inorganic residues (Coleman et al., 2004; Feng et al., 2003).

Soils are vital for the existence of many forms of life that have evolved on our planet (Pidwirny 2006). Plants depend solely on the soils for their nutritional needs. Soils with deficiencies in plants nutrients may be supplemented with chemical fertilizers. The plants benefit from the fertilizers and some of the fertilizer may be lost into the environment resulting in soil degradation. The degradation of soils and water quality impairs the soils and water from efficient performance of their ecosystem services to mankind. These residues tend to alter the soil’s physical and chemical properties together with the soil's biological characteristics. These alterations in the soil's physicochemical properties and biological characteristics tend to facilitate soil contamination and pollution processes (Du et al., 2009).

Plants grow on the soil and depend on the soil for the extraction of their nutrients and water by means of their roots systems. Agriculture depends for its success on the exploitation of natural and human-made resources like fertilizers and other agrochemicals (Conway and Barbier, 1990). The output are products in the form of food, or fiber and their production together with that of non-agricultural goods and services, helps to secure both national economies and the livelihoods of individual household (Conway and Barbier, 1990). When the soil is considered as a vital natural resource, it can be classified in some case as a renewable resource or non-renewable resource. When the soil is considered as a non-renewable resource, there is a need for its sustenance because it is an important environmental valuable (Norton, 1992). The soil is the most important natural resource next to air and water that needs great attention for their protection from anthropogenic activities. The most harmful of these anthropogenic activities is the introduction of industrially synthesized chemicals that are released into the ecosystems in different forms (liquid, solid and gases).

1.1. The Problem Statement

Assessing the environmental impact of agrochemicals pollutants at global, regional and local scale is a key component in achieving sustainability of agriculture as well as preserving the environment. Assessment involves the determination and evaluation of changes to some constituent of the environment like soil overtime (Corwin and Wagenet, 1996). An essential factor that influences the productivity of the various ecosystems on earth is the nature of the soil. However, soil amendment with inorganic fertilizer is a common practice to boost agricultural output per cultivation seasons. Amongst others, it has been observed that the farmers in Guzelyurtin TRNC are taking advantage of agrochemical fertilizer to amend their soils' quality to increase crops output. In an attempt to address the potential environmental concern of agrochemicals in Guzelyurt, this research focused on investigating the nitrate, nitrite, phosphate and potash residues in the soil of citrus orchards that might be resulting fertilizers. Fertilization of soil is a common practice across the world but it has been identified in some parts of China (Du et al., 2009), United States (Alva et al., 2006) and European Union (EU) (Jeanrenaud, 2001) as a source of environmental concern. In addition, agrochemical fertilizer application on soils is considered to be a main source of non-point source pollution (Sharpley et al., 1998). Nonpoint source pollution generally results from land runoff, precipitation, atmospheric deposit, sewage, drainage and hydrological modification. The Clean Water Act defines point source to mean any discernible, confined and discrete conveyance including but not limited to any pipe, ditch, channel tunnel conduits, wells, discrete fissure, container, rolling stock, concentrate animal feeding operation or vessels or other floating crafts from which pollutants may be discharged. The term does not include agricultural storm water discharged or return flow water from irrigated agriculture.

Excessive application of agrochemical fertilizers and other chemicals like pesticides and herbicides are a common practice worldwide in agriculture lands (Du et al., 2009)with the aim to improve upon the agricultural output quality and quantity. However, it has been observed that the fate of these substances especially nitrate, phosphate, and potash to the environment (drinking water and foodstuff) is usually over-looked by the farmers because of inadequate information on the potential threats of those substances to the environment and human health. There has been an increase in environmental awareness concerning the agricultural sector due to the potential harmful impacts directly on human health and the ecosystem (WHO, 1972). It has been observed that citrus farmers in Guzelyurt have been applying inorganic nitrate, phosphate, and potash fertilizers as well as manure on the soils of their citrus orchards to increase the citrus production. It has been observed that one of the widely used fertilizers by the citrus farmers in TRNC is soluble mixed NPK fertilizer. This fertilizer contains 20 vol. % nitrogen (nitric nitrogen 6%, ammonium nitrogen 4% and urea nitrogen 10%), 20 vol. % water soluble phosphorus as phosphate (P_2O_5) and 20 vol. % water soluble potassium as potash (K_2O).

Across a wide range of thorough research from the available scant literature, it was observed that little or no scientific and systematic research has been documented on TRNC, on environmental concern of the agricultural sector. As a result, this research seeks to set the baseline for further research in similar area of research in an attempt to address the environmental concerns in TRNC. This research attempts to investigate the potential environmental impact of agrochemical by quantitative chemical evaluation of the levels soil residual nitrate, nitrite, phosphate, and potash that might be resulting from fertilizers. This research is the first of its kind in TRNC to quantitatively investigate the potential environmental impact of these agrochemical fertilizers on the soils of citrus orchards.

Nitrates and phosphates are common and are amongst the most harmful residues from inorganic fertilizers or organic manure that are dangerous to the environment (Jahnke, 1992; Stevenson, 1986) and as such, needs to be monitor in the environment. The movement of these nutrients on soil depends on the soil properties like texture and permeability (Darwish et al., 2011). The soils from Guzelyurt citrus orchards therefore, need to be investigated to assess the quantity of nitrate and phosphate residues that might be resulting from fertilization of the orchards with inorganic fertilizers.

1.2. Objective

This research therefore sets out to investigate the potential environmental impact of agrochemical fertilizer application on the soils of citrus orchards in Guzelyurt. To begin this impact assessment, this research will focus on a chemical analysis of nitrates, nitrite, phosphate, and potash residues on soils from a representative sample of citrus orchards, conducted in spring 2012, shortly before the application of fertilizer in preparation for the farming season. In addition to this, some tests were conducted to measure soils' pH, conductivity, moisture content, total organic matter, texture, and calcium carbonate.Altogether, this research proposes to make a baseline study of the soil residues of a set of the most commonly used agrichemicals in the Guzelyurt district citrus orchards, further studies has to be done in a similar domain.

1.3. Significance of the study

In the Turkish Republic of North Cyprus (TRNC), agriculture contributes to the economic development and as such, in 2007 the government of TRNC paid subsidies worth 94,904,772,03 TL (Serinol et al., 2008) to the agricultural sector. In 2003, agriculture alone contributed 14.5 % of TRNC GDP (Katircioglu, 2006) in TRNC. The crops grown comprised of vegetable, cereals and fruits that contributes to the GDP of TRNC. Among those the fruits and especially citrus is the most prominent because it constitutes some percentage of the country's foreign exchange, hence, the government of TRNC supports this sector with subsidies (Serinol et al., 2008). Citrus in all shapes, size and colour are very attractive, fragrant and appetizing in addition to their great nutrition values. They are one of the richest sources of vitamin C and contain a natural source of sugar. They are also rich source of mineral like calcium and magnesium, which are essential for good health (Economos and Clay, 1999).

Furthermore, citrus growers are implementing recent technologies in agricultural science to maximize production within the shortest time possible. Consequently, for the growers to get the young citrus plants to maturity, they tend to apply fertilizers on the plants systems at a very tender stage in the nurseries. This common practice of fertilization of the soils with very young trees as well as soils with older trees might be the root cause of soil quality degradation (Schoenholtz et al., 1991).

This thesis is probably the first and the only study to show the impact of fertilizers especially nitrates, nitrite, phosphates, and potash residues on the soil of citrus orchard in TRNC. The outcome of this work will serve as baseline information for further research in this domain of soil contamination and non-point source pollution. In addition, the research findings might be published in respected journals of soil science or environmental science as well. It will also be delivered to the farmers through the Guzelyurt soil and water laboratory, to the Ministry of Agriculture of TRNC and to the Government Directorate of Environment. Also, it is worth mentioning that this research is the first of its kind that has establishing research collaboration between Middle East Technical University, Northern Cyprus Campus (METU NCC) and TRNC Government Soil and Water Laboratory in Guzelyurt.

1.4. Background Study

Excessive fertilization, misuse and abuse of crop land with inorganic nitrogen, phosphorus and potassium and nitrogen, phosphorus and sulphur (NPK and NPS) fertilizers has been identified as the major environmental problem (Thompson et al., 2007b), which leads to groundwater pollution, eutrophication of rivers and lakes (Thompson et al., 2007b; Darwish et al., 2011; Angelopoulos et al., 2009). In other studies, misuse and abuse of all agrochemicals (pesticides, insecticides, herbicides) in highly productive agricultural areas constitute significant environmental concern worldwide (Thompson et al., 2007b; Daniel et al., 1998). In the United States, eutrophication resulting from nonpoint source agricultural pollution is a major environmental problem that is causing water quality degradation as well as aquatic life in such an ecosystem is threatened (US EPA 1998). This is a direct result of soil contamination of agricultural farmlands with inorganic N and P fertilizers (Robertson et al., 1997). Globally, 30-40% of earth land is believed to be affected by fertilizer pollutants (Pimentel and Kounang, 1998), yet the dependency of these resources for food availabilities is increasing considerably. For instance, between 1960 and 2000, the global N and P fertilizer usage increases from less than 2×10^7 to about 8×10^7tones (Robertson et al., 1997). The increased awareness of environmental problems associated with inorganic fertilizer usage has opened up a new era of research for soil scientist and/or environmentalist. Some research in this area focuses more on identifying the environmental risks associated with fertilizer application on the soil.

In Florida, where citrus fruits are cultivated on a commercial scale, it was observed that high rate of ground application of nitrogen fertilizer on the citrus orchards appear to contribute to salinity problems (Embleton et al., 1986) as well as pollution of groundwater with nitrate (Dasberg et al., 1984). The soil types of the orchards in Florida are sandy (Canali et al., 2012; Paramasivam and Alva, 1998) and has been confirmed to be more vulnerable to nitrate pollution problem of groundwater.

A study in Beijing shows that nitrate concentration that accumulates on the soil profile of 0-30cm was 3.8 and 1.2 times higher in vegetable and orchards, respectively, than in cropland (Du et al., 2009). This can be interpreted that nitrate recovery rate in vegetable and orchards are lower than the recovery rate in croplands in China. Excessive usage of nitrogen fertilizers on soil can also increase the risk of groundwater pollution (Du et al., 2009).

Another study of nitrate concentration in the soil solution of Danish forest reveals that soil nitrate concentration depends on a whole range of factors like soil type, tree species, and forest size (Callesen et al., 1998). For example, the nitrates residues are bound to be very little on sandy soils compared with clayey soils (Battelle, 1999). This is because the sandy soils are more vulnerable to leaching than clayey soils. Water moves rapidly through sandy soils hence, the nitrate in the soils moves along with the water in the soils through the interconnected pore spaces.

Loss of nutrients from agricultural lands through the process of leaching and surface runoff is suspected as one of the most important nonpoint source contamination (Yang et al., 2007; Su et al., 2007). This might be resulting from intensive agricultural systems and improper agricultural practices that have been considered as the main source of nitrate pollution (Ju et al., 2004; Mahvi et al., 2005; Bouwer, 2000). Excessive application of nitrogen and phosphorus fertilizer has the potential to pollute not only the soil but also the groundwater resource (Halwani et al., 1999;). The effect of prevailing cropping system and fertilization practice on nitrate contamination of the soil and groundwater continuum in Lebanon-Eastern Mediterranean was studied between 2007 to 2009 (Darwish et al., 2011). They found that in irrigation agriculture, the annual discharge of nitrogen depends on nitrogen application, plant uptake, and leaching rate. A linear regression analysis gave a significant relationship between nitrate and chloride indicating that a diffuse pollution originated mostly from complex fertilizers application on the farm land. However, over the years, there has been increasing scarcity of farm land in TRNC (Ergil, 2000) for two major reasons: salination and drought (Ergil, 2000), which has greatly decreased the suitable arable land in the island. Additionally, the TRNC soil quality might be at risk of soil contamination with NPK fertilizers application. Consequently, there is a need for similar studies in the citrus orchards in Guzelyurt. The long and lasting development of the worldwide social economic systems requires a sustainable utilization of all types of natural resources both non-renewable and renewable.

During crops cultivation process, fertilizers as well as other agrochemicals are introduced to the ecosystems. When these chemicals surpass the ecosystems carrying capacity, they tend to destabilize the proper functioning of some components of the system. Some of these chemical substances introduce to the soils are used up by the plants while others remain in the soil as residues.

Organic and inorganic fertilizer application on farmland is a worldwide practice to improve upon the quality and quantity of agricultural production to meet the growing demand of food for the ever increasing human population. The soils are the primary receiving and transmitting medium of this fertilizer, while the plants are the secondary receiving medium. As a result, the soil is exposed to the risk of being potentially contaminated. This soil contamination occurs most especially when these fertilizers are misused and abused.

The next chapter deals with the study area. This is followed by another chapter dealing with soils. The last three chapters deal with sampling and laboratory analysis of the samples, the results and conclusion.

CHAPTER 2

STUDY AREA IN TURKISH REPUBLIC OF NORTHERN CYPRUS

The island of Cyprus is situated in the eastern basin of the Mediterranean Sea. It is the biggest island in the eastern part of the Mediterranean Sea with a total surface area of 9250 km^2(Ergil, 2001). The northern part of the country is comprised of 56.7% agricultural land, 19.5% forest land, 5.0% grazing, 10.7% towns, villages, rivers and ponds and nearly 8.2% bare land (Gözen, 2008)

The Guzelyurt plain is located in the northern part of the island on latitude 35˚20′N and longitude 33˚15′E. This area is known as the western Messaoria plain. Guzelyurt (Morphou) is a district in northern Cyprus that is located on the northwest area of the island. It is bordered to the west by coastline and to the southeast by the United Nation buffer zone (green line) (Ergil, 2000). The Guzelyurt plain is the largest and historically the most productive part in the island. The red fertile alluvial soil on the coastal plain makes Guzelyurt famous for agriculture especially orchards. Underground waters in Guzelyurt are used for domestic and agricultural purposes. The aquifer containing this water reservoir is the most important and the largest aquifer in the whole Island. Its superficial area is 460 km^2 with only 275 km^2 of the total aquifer size overlapping with the plane area of this aquifer is in the north side (Ergil, 2001).

The northwest area (Lapta, Guzelyurt and Lefke) is the largest agriculture production area. The available data of 2008, reveals that approximately 177,560 tons of citrus fruits and 2,900 registered citrus farmers have been identified (Rural development sector program. Lefkoşa, 2010). North of Guzelyurt is prominent for the production of different kinds of fruits including strawberry and grapefruit. However, Guzelyurt is particularly famous for citrus production and account for around 84% of citrus produced in TRNC whereas in Lefke that is the second in production, the percentage is as low as 15 (Rural development sector program. Lefkoşa, 2010). The total surface area under citrus cultivation in Guzelyurt is 40,835 acres (16,525.34 hectares). Figure 2.1 is a map of the study area showing Guzelyurt and other locations.

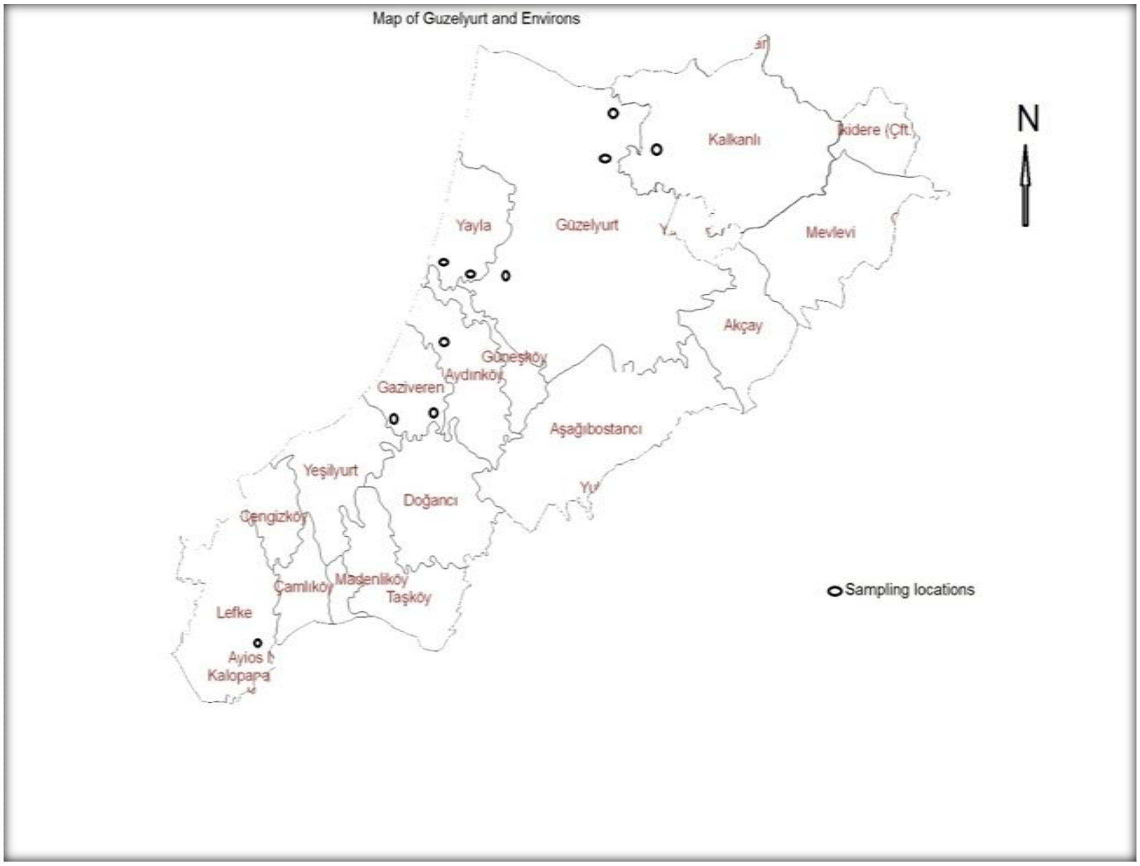


Figure 2.1 Map of the study area, which shows Guzelyurt and other locations

2.1. Climate

The climate of Cyprus is typical of the Eastern Mediterranean, which is clearly distinguished by temperature differences. The summer is hot and dry and begins in mid-May and lasts to September. Maximum temperatures during this period occasionally rise above 40˚C (Ergil 2000). Rainfall typically begins from late October and lasts to early April with an annual average of 280mm (Ergil 2000). Snow occurs on the mountain ranges above 1000m but rarely occurs at lower altitudes. Basically, most of the surface runoff occurs only during winter especially after severed rainfall. Consequently, there are no perennial streams in the study area, as well as in the in the whole island. The origin of runoff in Cyprus is from the periodic rainfall during winter and from snow melt on the Troodos Mountains that has a maximum elevation of about 2000m above sea level (Ergil 2000). When the snowmelt has dissipated after March, the flow rate of the surface runoff from the flanks of this mountain decreases considerable.

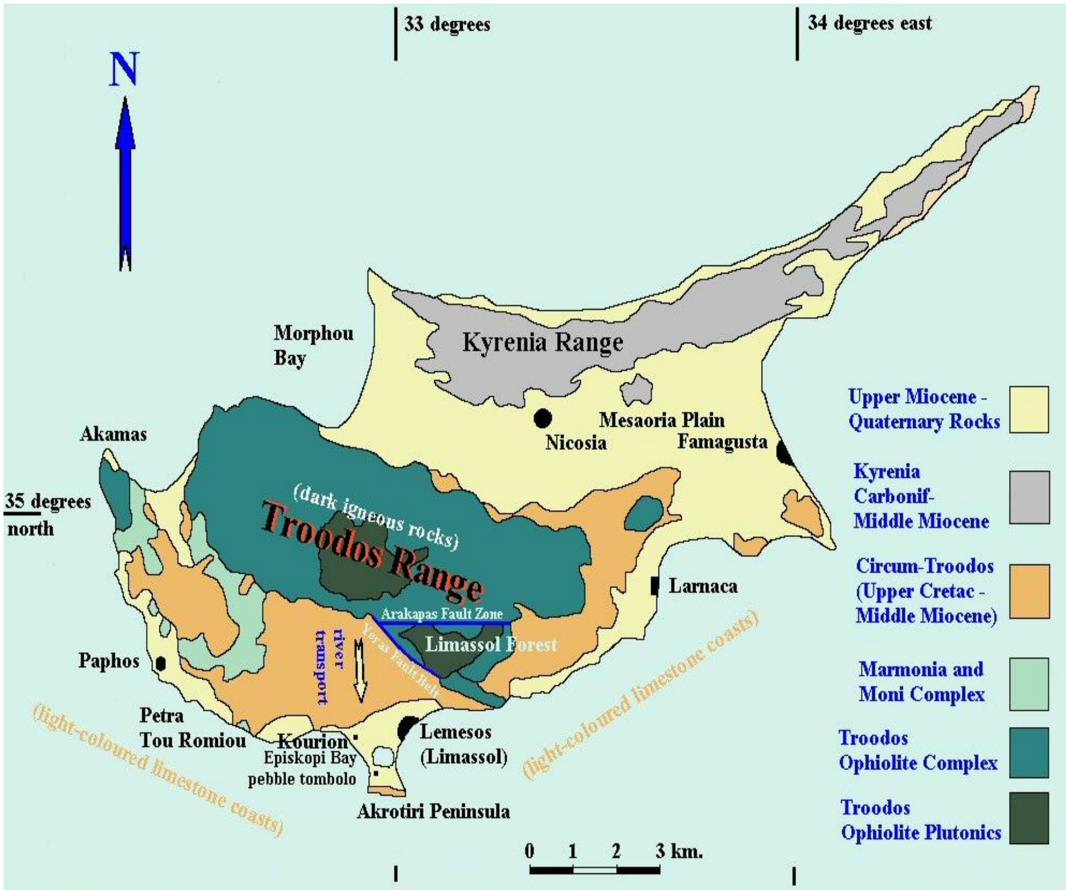
The weather conditions in Cyprus cause large variation in rainfall and rain distribution over the years. Because of these variations, there is insufficient amount of water available for domestic purposes and irrigation of agricultural lands across the Island. As a result, groundwater serves both purposes. However salt water intrusion from the sea is damaging the groundwater aquifers by increasing salinity levels and is therefore not suitable for irrigation (Ergil, 2000).

2.2. Topography

The topography of Guzelyurt is characterized by a slightly sloping coastal plain, which terminates at the Mediterranean Sea. The central part of Guzelyurt, where agricultural practices takes place, is almost flat. There are some hills, which rise from northeast to southwest of this plain. The superficial catchment area from sea level along the coast rises from 0 to 300m in the northeast part and from 0 to 400m in the southwest part of the Troodos Mountains. The study area has an average elevation of about 65m above sea level. The land surface has a gentle slope except for relatively high areas that has gradient greater than 1% (Ergil, 2000).

2.3. Geology

Cyprus is broadly divided into three geological zones: the Troodos massive to the south, the Pentadactylos or Kyrenia range to the north and the Messoaria (Guzelyurt) plain separating these two mountain ranges. The characteristic geological formation of the island can be broadly classified into two main categories, theophiolite complex and sedimentary origins (Tzortzis et al., 2004). The geology of the area enhances the understanding of the soil and their origin. The geology of Cyprus is broadly divided into the mountain ranges and the plain regions that terminate into the sea. The geologic survey of Cyprus has been used to identify parent materials of the soil. The survey reviews that about 36% of the total area of Cyprus is categorized as having slight to high calcareous soil (Hadjiparaskevas, 2005). The Figure 2.2 is a geological map of Cyprus showing the different rock types that have been transform through weathering processes to soil. The soil in Guzelyurt is as a result of mechanical, chemical and biologic weathering of the geologic formations in Cyprus.



Geological map of Cyprus, simplified and modified after Greensmith (1994), Cyprus Geological Survey and others. This map shows the relationship of the Kourion and Akrotiri pebble depositional area to the Troodos igneous source. Transport is by the Khouris River and tributaries and is seasonal. *Ian West & Joanna Bentley (c) 2007.*

Figure 2.2 Geological map of Cyprus (Southampton, 2012)

2.3.1. The Troodos range

The Troodos range is situated in the central western part of Cyprus and is composed of igneous rocks that form the ophiolite complex. They are reported to be the best-preserved and widely studied ophiolite complex in the world (Tzortzis et al., 2004). This is the highest mountain range around Mount Olympus with altitude of 1,951 m high above sea level. Torrential springs having radial arrangements frequently flow from the flanks of Troodos into the sea during the rainy season (Tzortzis et al., 2004; Robinson et al., 1983). The hard igneous rocks of this mountain are surrounded by

doom-sharp pillow lava. On the flanks of this mountain range are steep slopes, narrow valleys, and crevices together with trees creating wonderful scenery.
The Troodos Mountain is also referred to as Troodos massif in geology and composed of ophiolite complex. It occupies an overall surface area of 3,200 km^2 in the central and western parts of the Island. This mountain range is formed almost completely on the upper cretaceous (about 85 million years ago) mafic and ultramafic igneous rocks (Tzortzis et al., 2004)

2.3.2. Kyrenia Mountain range

It is mainly of limestone with an elevation of 1,024 m above sea level. A part of this mountain range known as Pentadactylos has finger like structure. The name Pentadactylos is derived from five-fingers. There are found a good number of crevices on this mountain range. Karpassia is a continuation of Pentadactylos consisting of hills, slope and valleys but lacks folds and other tectonic features.
The Pentadactylos is made of a succession of sedimentary formations. It has an age range from Permian to Middle Miocene. The oldest rocks on this mountain range consist of recrystallize limestone and dolomites in the same age range.

2.3.3. The Messoaria or Central Plain

This plain is located near Lefkosa (Nicosia) and is situated between Troodos and Kyrenia mountain ranges. It terminates to the west at Morphou bay and in the east Famagusta coastal areas. It has a low relief not exceeding 180m above sea level. The plain is composed of flysch type rocks that resulted from Troodos and Kyrenia mountain ranges. There are broad agents of transportation such as river to the low land. They are of Holocene age.

2.3.4. The Coastline

The coastline constitutes the last category in the geology of Cyprus. It mostly consists of alluvia deposits. These alluvia deposits are fertile soils which are suitable for agriculture. In TRNC, citrus orchards are observed to be relatively close to the coast.

CHAPTER 3
SOIL

3.1. Definition

Soil as defined in soil science is an independent body in nature with a unique morphology from the surface down to the parent material as expressed by the soil profile (Kim, 2005; ISO 10381–4:2003). Soils are lost particles of parent rock material as a result of biochemical weathering.

Ideally, soil is a concrete thing usually the 'dirt' on the surface of the earth. However, the word has different meanings based on the different purpose of which the soil is serving. The construction engineer and the agronomist look as at soil from a completely different point of views. Hilgard defined soil as "the more or less loose and friable material in which by means of their roots, plants may or do find a foothold and nourishment as well as other conditions of growth (Hilgard, 1907)." This is one of the many definitions, which consider soil primarily as a medium for plant production. Ramann defined soil as "the soil is the upper weathering layer of the solid earth crust." This definition is scientific in the sense that no reference is made to crop production or any other utilitarian motive (Ramann, 1928). Joffe, a representative of Russian school of soil science, objected to the Ramann formulation on the grounds that it does not distinguish between soil and loose rocks materials. According to Joffe, "the soil is a natural body, differentiated into horizons of minerals and organic constituents, usually unconsolidated, of variable depth, which differs from the parent material below in morphology, physical properties and constitution, chemical properties and composition and biological characteristics"(Joffe, 1936).

Of these definitions, it can be difficult to categorically choose any as the best. Hence, for the purpose of this research, all the definitions are suitable because they deal substantially with the soil formation process (Ramann, 1928), the function of the soil (Hilgard, 1907) as well as constituents of the soil (Joffe, 1936). The three definitions put together might give a better understanding of the word soil for the purpose of agriculture and soil science domains as, "soil is a mixture of mineral particles and organic matter, resulting from the weathering process of parent rock materials into loose and unconsolidated mineral particles having distinctive physical and chemical properties and biological characteristic." (Food and Agricultural Organization of United Nations (FAO), International Soil Reference and Information Centre (ISRIC) and International Soil Science Society(ISSS), 1998).

In short, soil is a dynamic resource that supports plants. It consists of mineral particles of different sizes (sand, silt and clay), organic matter and numerous species of living organisms. Individual soil body commonly called soil; occur side by side along other soils. This individual soil occupies very large area or volume and the smallest representative of such body of soil is known as pedon.

The soil renders numerous vital environmental, economic, social and cultural functions. These include; food and other biomass production and storage as well as filtration and transformation of water, carbon and nitrogen. Soil is also the source of many raw materials for commercial purpose. The soil degradation due to contamination, erosion, loss of organic matter, salinization and other threats has serious and long term consequences human health, natural ecosystems and the economy.

3.2. Importance

The soil impacts the global climate and air and water quality by providing functions like filtering, buffering, decomposition of organic and inorganic materials, the exchange of gases, food provision, habitats. Hence deterioration of the soil quality in any form will turn to affect the functions of the soil.

3.3. Formation

Soil forming processes are determined by climatic, biological (plants and animals) actions upon the local geologic surface materials over time under the influence of the slope of the land and human activities in a given region. Soil formation is influenced by soil formation factors, which comprise of the following: climate, organisms, parent rock material, relief and time (Brady, 1990).

The interaction of the soil forming factors initiates a series of processes that includes biologically driven accumulations and destruction of organic matters, transformation of substances, and redistribution of these substances (products of soil) like sand, clay, silts resulting to soil formation. Some soil types are made of thick layers of organic matters. These types of soils favor plant cultivation and thus better quality plants. Other soils have strong cemented horizons or acidic subsoil that inhibits rooting.

The local geologic settings of the Mediterranean islands reveal a high energy depositional environment (Tesson et al., 1999).This study shows that the surface geology of these islands is a result of marine regression sequence. The deposited materials undergo digenetic processes due to pressure and temperature differences giving rise to shale, sandstone marbles and carbonate rocks. When these rocks were exposed, weathering sets in giving rise to fertile soils of the island. In addition, the coastal parts in the island are particularly fertile because of the added advantages on sediment accumulation. For instance, Guzelyurt is located in the coastal plains and it is being fed by sediments eroded from the mountainous parts of the island.

The soils of the Guzelyurt plain have resulted from the weathering conditions of the different geologic formations in the island. The Troodos mass is highly affected by tectonic activities as a result of uplift thereby giving rise to fracture zones. These fracture zones (zones of weakness), which facilitate weathering of rocks, lead to the development of smooth, mature topography, mantled with thick covering of a diversity of soils (Robinson et al., 1983). The soils that cover the central area of the Troodos is highly alkaline whereas the soils on the slope, lower down are covered by neutral sheeted diabase (Robinson et al., 1983). On the other hand, the sedimentary rocks in the island are composed of chalk, malts, sandstone, gypsum, etc. occurs at the foot of the Troodos and undergoes weathering giving rise to the alkaline, calcium rich soils (Robinson et al., 1983).

Soils mixtures occur as alluvia deposits in Guzelyurt area. The soil is dark reddish in colour(Rural development sector program, Lefkoşa, 2010); very fertile and favours the cultivation of a whole range of crops with citrus being the most outstanding because of its economic importance (Department of Agriculture Turkish Republic of Northern Cyprus (2001–2006)). The citrus species grown in Guzelyurt are orange, mandarin, grapefruit, and lemon. Citrus orchards are grown under irrigated conditions and they are mainly located in the Guzelyurt plain. Guzelyurt is famous for agricultural activities because of the availability of fertile soil and good quality irrigation water, which promotes agriculture. In Turkish Republic of Northern Cyprus about 90% of water supply is used for irrigation purpose (Ergil, 2000).

3.4. Definition of soil quality

Soil quality refers to the capacity to which a specific kind of soil can function within natural or managed ecosystems boundaries, to sustain plants and animal production, to maintain or enhance the quality of water and air and to support human health and habitation. Changes in the capacity of soil to their function are reflected in soil properties that change in response to management or climate (United States Department of Agriculture (USDA), 2012). The soil has a great impact on the global climate, air, and water resources. The soil provides functions such as filtering, buffering, decomposition of inorganic and organic maters, exchange of gases with the atmosphere (USDA, 2012), exchange of cations and anions within the soil profile. Therefore, the soil quality is determined simply by the assessment of its physicochemical and biological properties and comparing them to the soil's inherent capacity to functions.

3.5. Soil Properties

Soil properties are very important to comprehend the nature of soil residues and the ways in which these residues moves through the soil particles. To study the potential impact of agrochemical fertilizers on soils, it is therefore necessary to understand some aspects of soil properties. The soil properties can be broadly classified as physical, chemical and biological.

3.6. Physical properties

The physical properties of the soil refer to those properties physical state of any system. In the case of soil, physical properties will deals with texture, soil structure, colour, porosity (the fraction of pore space in a soil) and permeability. In turn, these properties affect air and water movement in the soil and thus, the soil ability to function well. Mineral and soil organic matter makes up the solid fraction of soil, whereas air and water occupies the pore space of the soil. A typical agricultural soil is usually around 50% solid and 50% pore space (Brandy and Weil, 2002).

3.6.1. Texture

Soil texture is the term used in describing the different size distribution of mineral particles in the soil. Soil texture can have profound effect on many other soil properties and is considered among the most important properties. In more simplified terms, texture is the proportion of three mineral particles, sand, silt and clay in the soil (FAO, 2012). These mineral particles sizes have been used to describe the movement and behavior of nutrients in the soils. The mineral particles that make up the soil vary in size from those easily seen with the unaided eye to those below the range of a high-powered microscope. The particle sizes larger than 2 mm in diameter are considered inert (that is, the large soil particles that are above 2mm in diameter are classify as gravel which is not the point of focus in this study.) The mineral particles that are commonly found in soils, which are less than 2 mm in diameter, are broadly categorized as sand, silts and clay.

The texture is usually expressed in terms of percentage of sand, silt and clay. To avoid quoting exact percentages, 12 textural classes have been defined by United Nations Food and Agriculture Organization (FAO). Based on the size distribution of these mineral particles on the soil, they are grouped separately as separates, which can be defined to be a group of mineral particles that fit within definite size limits (diameter in millimeters). The Figure 3.1 shows the soil texture with percentage distribution of the sizes of the separates used in the United States Department of Agriculture(USDA)system of nomenclature for soil texture (USDA, 2012).

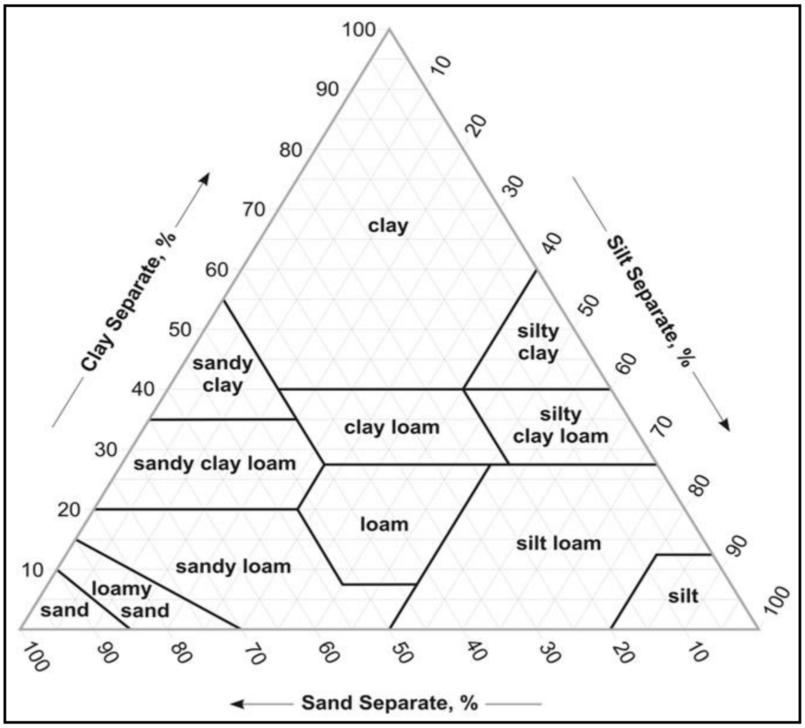


Figure 3.1 Soil texture nomenclature charts (USDA 2012 http://soils.usda.gov/technical/aids/investigations/texture/)

Texture is usually determined by calculating the relative proportion of sand, clay and silt in a given soil sample by laboratory analysis. Some laboratories measure the soil texture by measuring the saturation percentage that is related to the total soil porosity and the water holding capacity. Therefore it is a valuable characteristic for irrigation design (Berry et al., 2007). This measures the amount of saturation water by weight in saturated soil samples. Soil horizons are sometimes separated on the bases of differences in soil texture.

Soil texture is generally classified based on the FAO system. This system was adopted from the USDA system. The classification of particle sizes is shown in Table 3.1 overleaf.

Table 3.1 Particle size distribution of soil (Cartage, 2010)

Soil particle type	Soil particle sizes in diameter (mm)
Clay	<0.002
Silt	0.002-0.05
Fine sand	0.05-0.1
Medium sand	0.1-0.5
Coarse sand	0.5-1.0
Very coarse sand	1.0-2.0
Gravel	2.0-762.0
Cobbles	≥762.0

Generally, clay soil has fine texture while sandy has coarse (Berry et al., 2007). Soil texture affects soil properties that are listed below:

- drainage
- water retaining capacity
- susceptibility to erosion
- cation exchange capacity
- pH buffering capacity
- soil tilt
- saturation percentage

The saturation percentage directly related to the total soil porosity and total soil water-holding capacity and, therefore, is a valuable number to use for irrigation system design (Feng et al., 2003).

3.6.2. Structure

Soil structure can be defined as the arrangement and binding of primary particles into naturally formed secondary particles called aggregates or ‘peds’ (FAO, 2012). Aggregation of soil particle is important for increasing stability against erosion, for maintaining porosity and soil water movement and for improving fertility and carbon sequestration in the soil (Nicholas et al., 2004). Granular structure consist of loosely packed spheroidal peds that are glued together mostly by organic substances (FAO, 2012). A sandy soil may not have a definite structure because each sand grain behaves independently of all others. On the other hand, a compacted clay soil may also be called as the same because the particles of the soil are clumped together in huge massive chunks (Shobe, 2009). These are the two extreme conditions in soil structure. In between these extremes, there is granular structure of surface soil and the blocky structure of the subsoil (subsoil refers to the soils beneath the surface soil).

The soil structure may be further described in terms of the size and stability of aggregates. Structural classes are based on aggregate size, while structural grade is based on aggregate strength. The soil horizon can be differentiated on the basis of structural type, class or grade.

For soil aggregate to be formed, clay particles cohere to each other and adhere to larger particles under the conditions that prevail in most soils. Wetting and drying, freezing and thawing, rooting and animal activities and mechanical agitation are involved in rearranging of particles in soils. This whole process includes destruction of some aggregates and the bringing together of particles into new aggregate groupings. Organic materials, especially microbial cells and waste products, act to cement aggregates and thus to increase their strength. Furthermore, aggregates may be destroyed by poor tillage practices, compaction, and depletion of soil organic matter.

Good structure particularly in fine texture soils, increase total porosity because large pores occur between aggregates, allowing penetration of roots and movement of water and air.

3.6.3. Colour

The colour of any object, including soil can be determined by the unaided eyes. Generally, moist soils are darker than the dry ones. Additionally, the organic content of soils makes them darker. The surface soils are richer in organic matter relative to the subsoil hence, they are darker in colour. Reddish, yellowish and grayish hues of subsoil reflect the oxidation and hydration state or iron oxides, which are reflective of predominant aeration and drainage characteristics in subsoil. The reddish and yellowish hues are indicative of good drainage and aeration, typical for activities of aerobic organisms in the soils.

In Guzelyurt, the soil colour characterizes the origin of the soil. The soil is brownish-white confirming that the soils must have originated from calcite rich rocks. However, some parts of the study area shows reddish brown soils, it can be confirmed that these coloured soils have been transported from other sites to the study area for soil enhancement.

3.6.4. Porosity

Many important processes takes place in soil pores (the air or water filled spaces between soil particles). Soil texture and structure influence porosity by determining the size, number and interconnection of pores. Coarse size soil particles have many large (macro) pores because of loose arrangement of larger particle with one another. Fine texture show more tightly arrangement of particles and turn to have small (micro) pores. Macropores in fine-texture soils exist between aggregates. Because Fine-texture soils have both micro and macropores, they generally have greater total porosity.

The porosity of the soil can be altered by chemicals processes and water movement through their void. Long term cultivation of agricultural land turns to lower total porosity of the land because of a decrease in soil organic matter and large peds(Brandy and Weil, 2002).

3.7. Chemical properties

There are eight elements, which comprise the majority of mineral materials in the soils. Those are oxygen, silicon, aluminum, iron, calcium, magnesium, sodium and potassium. Oxygen is the most abundant in the soil in terms of weight and volume. The eight elements usually occur in crystal structures as negatively charged ions. The other seven elements are usually positively charged where aluminum is the most abundant and potassium is the least. Ions of these elements combine in different ratios to form different soil minerals. However, other elements present in the soil in small proportion relative to the major elements also exist. These categories can be called to be the minor elements.

Soils differ chemically from the parent rock materials and minerals from which they were formed. These chemical differences arise in that the soils tend to have less of the water soluble products of weathering (calcium, magnesium, potassium, and sodium). On the other hand, the water insoluble elements (aluminum and iron) are more plentiful in the soils based on the weathering conditions that thrive. Consequently, old and highly weathered soils are very rich in iron and aluminum oxides.

3.7.1. Organic matter

The organic fraction of the soil is usually less than 10% of the soil by mass. However, they have a great influence in soil chemical properties. The soil organic matter is composed mainly of carbon, hydrogen, nitrogen and oxygen and in some cases sulphur. The organic fraction of soil serves as a reservoir for plants' essential nutrients (nitrogen, phosphorus and sulphur). The organic matter increases the soil water holding and cation exchange capacity and enhances soil aggregation and structure.

3.7.2. Soil pH

Soil pH is probably the most measured soil chemical property and it is one of the most informative. pH is the negative logarithm of hydrogen ions in solution. This is an inverse or negative function in that soil pH decreases with increased acidity and increases with increased alkalinity.

Saturated soil samples with a pH value equal to 7 are known to be neutral. Those with pH values less than 7 are known to be acidic while those with pH values greater than 7 are known as alkali soils. Soil pH has profound influence on plants growth. The soil pH affects the quantity and type of micro-organisms in the soil, which influence decomposition of crops residues, manure, sludge and other organic matters. It also affects other nutrient's transformation and solubility or plants availability of plants' essential elements. For example, phosphorus is most available in slightly acidic to slightly alkaline soils while all micronutrients become sufficiently available with decreasing pH to what value except molybdenum. Aluminum, magnesium and even iron can become soluble in pH less than 5.5. In this situation, they become toxic to plants. Bacteria are mediators for the transformation mechanisms of nutrients in the soils; generally tend to be most active in slightly acidic to alkaline conditions.

3.8. Nutrient Cycle

The nutrient cycle is the nutrient flow path way within the natural environment. The Earth has a natural cycling sequence of all the limited elements that occurs in both plants and animal nutrients. Generally, the Earth functions as a closed system and therefore the potential of recycling all the substances which occur naturally are possible through biological and geological process. However, some of these substances are also synthesized and introduced into the Earth's environment. As a result, some nutrient cycles are altered and the direct impact is on the environmental values. Nitrogen and phosphorus are the important plant nutrients.

The main biochemical cycles describe the movement of nitrogen, carbon and phosphorus. These elements are cycled through the biosphere, lithosphere, hydrosphere and atmosphere. The latter three are also known as geosphere. These elements are taken up from the geosphere by the biosphere and are used for growth and reproduction. Elements can be present in the atmosphere in the form of gases, CO_2 and N_2 except phosphorus. In the hydrosphere, they occur as NO_2^- or NO_3^-, PO_4^{3-}, and CO_2. These elements can also occur as minerals in the form of carbonate, nitrates or phosphates in sedimentary or volcanic rocks.

There are 18 essential plant elements and they are classified in groups (Brandy and Weil, 1999):

a) **Major non-mineral macronutrients** (including carbon, oxygen and hydrogen): 90-95% of the dry plants weight & supplied to the plants by water absorption and photosynthesis.
b) **Primary macronutrients:** nitrogen, phosphorus and potassium
c) **Secondary macronutrients**: calcium, magnesium and sulphur
d) **Micronutrients**: copper, iron, chlorine, manganese, molybdenum, nickel, zinc.

The major factors contributing to plants nutrients and nutrient cycling are as follows:

1) The amount of nutrients available in the soil
2) The soil ability to supply the nutrients to plants
3) Environmental factors that affects nutrients availabilities and their absorption

3.8.1. Nitrogen cycle

Nitrogen is used by living organisms to form a good number of complexes like amino acid, proteins and nucleic acids. Nitrogen is one of the essential elements for plants because the plants cannot complete their life cycle without nitrogen. All living organisms require nitrogen for DNA, RNA and amino acids synthesis. Nitrogen is essential for the greening of the plant's leaves which helps in the process of photosynthesis. The greener the citrus plants, the more they will photosynthesis and produce more fruits. Deficiency of nitrogen and phosphorus in plants will results in yellowish leaves that also affect the growth of the plants (Liang et al., 2012). This paper further confirms that nitrogen deficiency in both mature and immature leaves accelerate protein degradation in the plant. Nitrogen is also a limiting factor in plant growth (i.e. sufficient soil nitrogen will favour the plants growth whereas limited amount will turn to affect the plants growth rate). Plants only have the ability to absorb nitrate and ammonium ions from the soil but not the gaseous nitrogen. Nitrogen naturally occurs in the gaseous state and occupies 73% by volume of the atmosphere. The nitrogen cycle involves the movement of nitrogen from the solid and gaseous state. This is one of the most importance cycles in the terrestrial ecosystem. Nitrogen is used by living organisms to form a good number of complexes like amino acid, proteins and nucleic acid (Pidwirny, 2006). Thus nitrate makes up a large proportion of commercial fertilizers.

Nitrogen cycle begins with the fixation of atmospheric nitrogen into nitrate in the atmosphere by lightening. These nitrates are washed by rains to the soil for further bacterial actions and plants absorb the nitrates that are consumed by animals when they eat plants.

When living organisms die, nitrogen in their tissues are decomposed by microbial organisms. This actually moves from ammonia to ammonium ions. This process is known as mineralization. In the soil, Nitrosomas bacteria convert the ammonium into nitrites. These nitrites are further converted to nitrates, which are very soluble that are used up by the plants while some are leached into the groundwater and some wash as surface runoff. Another set of bacteria known as denitrifying bacteria also convert part of nitrites to nitrates. Human activities have had significant influence on this nitrogen cycle. Nitrate can reach the soil and water resources from agricultural septic tanks, industrial effluents and animal waste. Nitrite is important for the transformation process of mixed fertilizer in the soil. This is because nitrite is an intermediate product of aerobic nitrification and anaerobic de-nitrification. In soils, where the aerobic and aerobic zones are closed to each other, the mobile nitrite is easily transformed to a more stable nitrate. Figure 3.2 overleaf shows the nitrogen cycle.

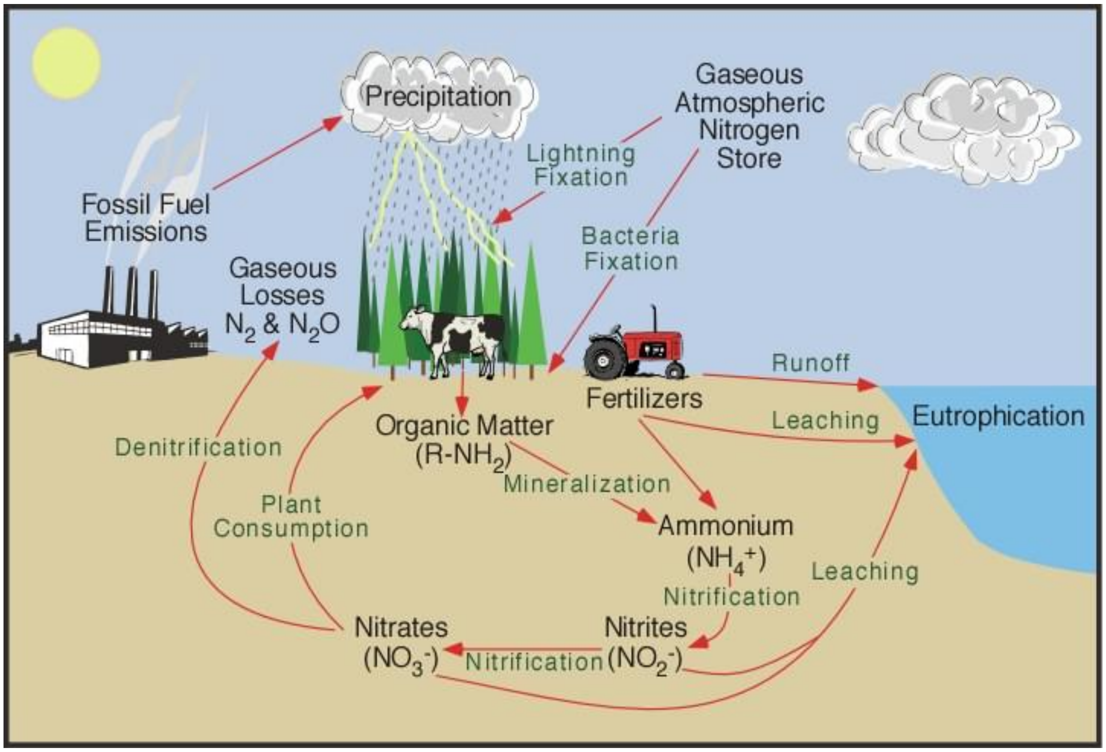


Figure 3.2 Nitrogen cycle (Pidwirny, 2006)

Almost all nitrogen found in the terrestrial ecosystem originally came from the atmosphere. The main process through which atmospheric nitrogen gets to the soil is through rainfall or lightening (Pidwirny, 2006). Human activities have greatly altered the nitrogen cycle. The application of fertilizers to crops increases rate of de-nitrification and leaches nitrate to ground water resources. The nitrogen from this source enters ground water systems and eventually flows to the streams, rivers, estuaries and lakes that might leads to eutrophication. Livestock also release large amount of nitrogen to the environment in the form of ammonia. Septic tanks also release nitrogen in the form of nitrate through seepage from sewage waste. The Haber-Bosch process of industrial nitrogen transformation to ammonia or fertilizers has altered the natural process of nitrogen cycle greatly (Crew and Peoples, 2004). These natural cycles of nitrogen transformation are through microorganisms; however the Haber-Bosch process has increased the amount of nitrogen into the environment through industrial processes.

The nitrogen fertilizer, which is a product of the Haber-Bosch process, can be substantial especially in regions that are irrigated. The deposition of such synthesized ammonia in the form of nitrogen fertilizers into the environment can cause a whole range of ecological impact (Crew and Peoples, 2004). For instance, it has been identified that, it can cause increase rate of soil acidification (Fern, 1998), change in plants community composition resulting to nitrogen favoring plants species (Wedin and Tilman, 1996), greater nitrogen fertility on the soil may result to increase fluxes of nitrogen oxide trace gases and greater sensitivity by vegetation's to drought and frost (Fangmeire et al., 1994).

3.8.2. Phosphorus cycle

Phosphorus is present in all living tissues and usually concentrates in the younger parts of plants, in the flowers and seeds. Citrus plants used phosphorus in the processes like photosynthesis and the breakdown of carbohydrate. It occurs in the form of phosphate ions (NO_3^- and NO_2^- or as HPO_4). It is an important molecule of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). It is also a component of the energy molecule adenosine triphosphate (ATP) in all living tissues. Phosphorus is also essential in bones and teeth formation. It occurs as calcium phosphate in bones and teeth.

The phosphorus cycle significantly differs from other cycles in that none of its components are directly linked to the atmosphere. Phosphorus and other phosphorus compounds only exist in the solid state at room temperature and atmospheric pressure on earth. When phosphorus is present in the atmosphere, it is usually in the form of dust particles since they do not exist as liquid or gas.

Generally, phosphorus occurs as mineral phosphate in rocks and sediments that accumulate deep in the ocean beds. When these sediments are exposed to the surface by uplift and other geologic processes over time, they together with the rocks undergo weathering and are eventually released into the soils. The plants then absorb these phosphates and use them in their cellular processes. Phosphate from the plants eventually gets to the animals when these animals directly or indirectly consumed the plants. After the death of animal and plants, decomposition takes place and the phosphates are released once more into the soil. They finally become sediments again after erosion and some are incorporated in the rocks as minerals. The Figure 3.3 below shows the phosphate cycle.

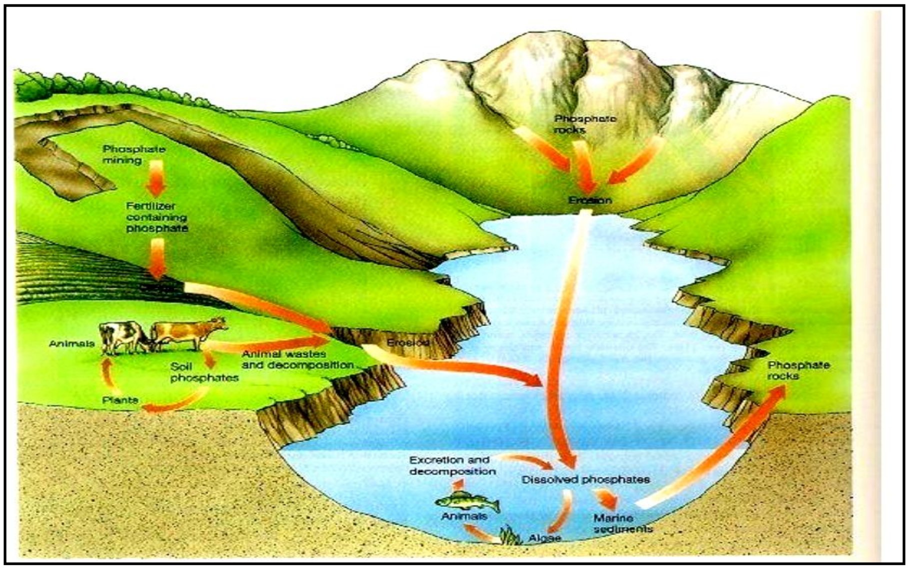


Figure 3.3 Phosphate cycle (http://mastermanapes.pbworks.com/f/phosphorus-cycle.jpg)

Phosphorus occurs only in a small quantity in the soil for uptake by plants; hence it is a limiting factor for plant growth. Runoff of phosphate fertilizers from farmlands might lead to eutrophication of the receiving water bodies' especial lakes. The situation might eventually cause algae bloom thereby lowering the water quality.

3.9. Soil Environment

The definition of soil as a dynamic natural body that composed of mineral and organic solids, gases, liquids and living organisms (Brady and Weil,1999) provides a good understanding of soil environment. It clearly distinguished between soil water as liquids, soil atmosphere as gases and soils organisms as living organisms. The main environmental variables affecting life in the soil includes soil moisture, temperature, aeration (i.e. the absence or presence of sufficient oxygen), organic matter and inorganic nutrients to be phosphorus and nitrogen. The balance of these factors controls the availability and abundance of micro-organisms as well as some animals in the soils. These organisms influence essential processes on the soil for example aggregation and degradation of plant, animal residues and the nutrient cycling that latter accompany these processes.

To comprehend life in the soil; the soil can be viewed as an extremely heterogeneous collection of microhabitats. The soil is a matrix of solid including sand, silt, clay and organic particles. Hence, depending on the mix of environmental variables that thrive, prevailing conditions can vary remarkably.

3.9.1. Soil water

Soil water is usually derived from rain or some other forms of overland flow. The amount of water that enters the soil is a function of the soil structure and the texture. Because of the burrowing activities of soil organisms, which facilitate soil water movement, these organisms are very beneficial to the soil.

Water movement through the soil is principally by mass flow and capillary action. The mass flow of soil water is water movement through larger particles while capillary action is the slower movement of soil water through highly tortuous network of very small channels and pores. Mostly soil water is held in these systems of capillary pores and channels and can be held quite firmly through physical interactions with the solid components of the soil matrix. Matrix water is held in small (usually microscopic) pores and is often absorbed in particle’s surface, which can be held rather tightly. These interactions of soil matrix essentially bind soil water. On the part of the plant and soil microbes, they require energy to extract these soil waters. The force required by the plant to obtain the soil water is known as matrix potential or pressure and it is an indicator of how tightly water is held in the soil (Texas A &M University, 2012).

The matrix potential is a function of soil texture. Silts and clay can hold moisture at very low matrix potential because of the greater amount of small particles with finer pores, which absorb and retain water. These smaller soil particles offer greater surface area that is vital for soil water holding capacity. On the contrary, larger soil particles with coarse texture like sand do not retain much water because of larger pore spaces. In a similar way, clay soil tends to return more nutrient and other chemicals than sandy soils. Most of these nutrients leach easily through the sandy soil.

The water that occupies the soil pore is known as soil solution. This water is never pure and contains dissolved salts and gases. This is the most available one to the plants and soils microbes. Soil waters are important in the transportation of and cycling of nutrients between the plants and the soils (Davidson et al., 1998).

3.9.2. Soil atmosphere

Soil atmosphere refers to the mixture of gases occupying the soil pores, which are not filled with soil water. These gases are derived from overlying air. The soil atmosphere contains less oxygen than the air with more carbon dioxide. The soil atmosphere is responsible for transpiration of the plants root systems. These might be due to aerobic activities taking place in the soil by organisms inhabiting the soil. The soil atmosphere facilitates the chemical processes taking place in the soil pore spaces.

3.9.3. Processes involve in the fate of Nitrate, phosphate and potash

3.9.3.4. Leaching

Soils have varied retentive properties depending on their texture, organic matter content, and cation exchange capacity (CEC) that influence the mobility of nitrate in the soil (Powell and Gaines 1994). Sandy soils have less retention capacity than finer clay soil. This is due to the fact that sand has less clay and silt which gives rise to lower cation exchange capacity (CEC) (Brandy, 1974). CEC is defined as the sum total cation (An ion carrying a positive charge which moves towards the cathode during electrolysis [OED]).that the soil can absorb. However, nitrate is an anion that can readily leach through the soil profile, soils with significant quantity of silt and clay and organic matter will also retain more NO_3-N than soils without much clay and silt (Powell and Gaines 1994). The soil texture also affects the water permeability or percolation rate of a soil. Percolation is the downward movement of free water and is often referred to as the saturation hydraulic conductivity rate. Coarser particle size soil has faster hydraulic conductivity rate and the finer particle size soil has slower hydraulic conductivity rate.

3.9.3.2. Plant uptake

In the soil, nitrate in solution with soil water primarily flow to the root of plant and the plants inspires the soil water. The soil water contains nitrates since they are not absorbed by soil particles. The movement of nitrate to the root of plants via soil water rarely limits its up take. Ammonium on the other hand is attached to soil particles so; only a portion of it is available in the soil water at any time. Ammonium concentration at the root surface can limit plants uptake at certain times. In soils of high CEC, or high fixation capacity (clay soils), ammonium in solution is insufficient to support high oxygen intake by plants (Walkers and Bernal, 2008). Under dry conditions, soil moisture may limit the movement of ammonium to the root and plant uptake may be hindered. In irrigated land, the movement of ammonium especially in sandy soil does not limit plants uptake.

The soil nitrogen has the ability to affect the soil in two ways, which are by influencing the pH of bulk soil (soil that is not directly adjacent to plants root) as well as the pH of the rhizosphere (soil that is directly in contact with the plants root) (Walker and Bernal, 2008). The application of nitrate containing fertilizers generally increases soil pH. The plants cause the increase in the soil pH, as nitrate is taken into the roots and hydroxyl ion (OH^-) is released to the soil. However, when the ammonium is the primary form of nitrogen, the plant releases acid (H^+) and the pH close to the root is decreased. The soil pH can significantly alter the population of soil microbial organisms that aids in nutrient transportation processes.

3.9.3.3. Phosphate adsorption/absorption

Soil phosphate can either result from an organic source (decomposition of dead remains of plants and animals) or from inorganic source (from phosphate fertilizers). The fate of both sources of phosphate to the soil barely follows same pattern. The dominant species of phosphate ions in the soil occurs are H_2PO^{2-} and H_2PO^-(Hinsinger, 2001). Basically, two types of inorganic reactions control the concentration of these phosphate ions in solution. The two reactions are precipitation-dissolution and sorption-desorption. Precipitation-dissolution reactions involve the formation and dissolving of precipitates. Sorption-desorption reactions involve the sorption and desorption of ions and molecules from the surface of mineral particles. The movement of phosphate into plants also influences soil solution concentration and helps to facilitate dissolution and desorption reactions. Soil generally contains crystalline and near-amorphous minerals in clay size particles. These minerals are combined with an equal wide range of poorly characterized organic compounds which modifies the chemical and physical properties of clay. Hydrous and aluminum oxides, and alumino silicates occur widely in the soil. They will react with phosphate solutions to produce an isomorphous series of iron and aluminum phosphate. Studies have confirmed that phosphate ions are strongly adsorbed by hydrous metals surface. The metallic phosphate oxides can be coated with hydrous ferric oxide and effectively slows the rate at which they dissolved.

Adsorption occurs when phosphate ions are removed from solution and become attached to the surface of soil particles. Then if the adsorbed phosphate ions diffused into the solid, they are said to be absorbed. Phosphate binds to clay minerals through exchangeable ions like iron and aluminum as well as hydroxyl group on the broken edge of clay (Hemwall, 1957). At higher concentration of between 6.8 to 7.2 ppm, precipitation occur rapidly forming iron and aluminum phosphate which becomes insoluble with increasing time and pH (Muljadi et al. 1966). The absorption of organic phosphate to the soil increases with increased pH. This is because clay saturated with calcium and magnesium shows greater adsorption for nuclide acid than clay saturated with potassium and sodium (Sparankle P. et al. 1975).

3.9.3.5. Precipitation

Precipitation is amongst the factors that influences the fate of plants nutrients in the soils. In regions with high precipitation, the rate of loss of plants nutrients from the soils increases via surface runoff for phosphate and potash into the surface water resources. While, nitrate loss to the environment will also increase via the process of leaching to the ground water resources. In winter and early spring, precipitation is high and influence the rate of surface runoff and leaching of phosphate, potash, and nitrate respectively (Liang et al., 1991). During summer, there is usually very little or no precipitation and consequently, the irrigation water are responsible for the nutrients nutrient loss via leaching process.

CHAPTER 4
MATERIALS AND METHODS

Having set out in chapter two the general principles of soil chemistry and identified the main problems of analyzing soils for fertilizer residues, the goal of this chapter is to present the materials and methods of the soil analysis which were conducted on samples from the Guzelyurt citrus orchards.

The first part of this chapter explains the approach adopted to soil sample collection in the chosen district of study, and is closely followed explanation of the actual conduct of my analysis of soil samples. Sampling design involves the selection of the most efficient method for choosing the samples that are used to estimate the properties. The definition of population to be sampled is centered by the initial formulation of research study (Pennock, 2004). The different methods of sampling a population for soil analysis are haphazard sampling, judgment sampling, and probabilistic sampling. Haphazard sampling involves a series of non-reproducible, idiosyncratic decisions of the sampler and no systematic attempt is made to ensure that samples taken are representatives of the population being sampled (Kim, 2005). This type of sampling is not good for scientific design since they are non-reproducible. On the other hand, judgment sampling involves sampling points based on prior knowledge held by the researcher. Judgment sampling can results in accurate estimate of population parameters such as mean and total but cannot provide measure of accuracy of these measurements (Kim, 2005). Moreover, the reliability of these estimates is only as good as the judgment of the researcher. While probabilistic sampling involves the selection of sampling points at random locations using a range of sample layouts and the probability of sample points selection can be calculated for each designed sampling. Probabilistic sampling design defines how specific elements will be selected from the population and this sampled element forms the sampled population.

Given the purpose of this study, however, a combination of judgment and probabilistic sampling methods were used. Thus when identifying the classes or types of orchards to be sampled within the district, judgment-based sampling was used, whereby judgments based on information regarding the quantity of fertilizer application, type of fertilization practice and ages of citrus trees were used. The reason for judgment sampling for the choice of orchards was based on available background knowledge. By contrast, when it came to identifying the points at which soil samples were to be obtained within the *orchards* was based on probabilistic sampling (random sampling). In other words to avoid bias of results, the sampling points in every chosen orchard were sampled randomly for soil collection. Nevertheless although sampling points within each orchard was identified probabilistically, samples were always taken from soils within 0.5 meters (m) of the drip irrigation or 1meters (m) from the an individual citrus tree.

4.1. Sample collection

Soil sample collection involves the selection from a total population of a subset of individuals upon which measurements are made. The measurements made on these subsets were then used to estimate the soil residual nitrate, nitrite, phosphate, and potash from the total population. Sampling is inherent to field research of soil science because measuring the total population is impossible for any realistic study. Soil samples for any form of soil test take into consideration some of the soil formation factors. Pedon constitute the sampling unit (Kim, 2005). The parent rock material and their mineralogical content from which the soil particles are derived are of great importance for soil testing. The exclusive purpose of this research is to investigate the potential residue impact of an important but small set of agrochemical fertilizers to the soil environment through nitrates, phosphate, and potash residue measurement in soil samples. It is not an attempt to measure groundwater contamination by these fertilizers.

In this study, three classes of orchards were taken into consideration: organic orchards (in which no synthetic fertilizers had been applied), synthetically fertilized orchards (sometimes referred to as ‘inorganic orchards’) and an abandoned orchard. In total ten orchards were sampled; two were organic orchards, seven orchards received synthetic chemical fertilizers, and one was an abandoned orchard.

While much attention is paid to laboratory procedures, the process for obtaining soil for analysis, it is worth noting that soil sampling soil sampling standard (Kim, 2005). A good sampling plan and procedures provides the measure of the average soil fertility as well as the measure of other environmental variables. If the soil samples are not representative of the field under consideration, the resulting analysis will be meaningless or difficult to interpret. Usually ‘field errors’- which refers to the possible errors that may occur in the field during sample collection such as wrong labeling of samples, mixing up samples from different depths, during sample collections - are much greater in distorting effect than analytical errors because field errors accumulate through the whole process (Jenkins et al, 1997). To minimize such errors in this study, four sampling points were selected at each orchard. That is to say, at each depth, the soils samples obtained at each of the four points for every depth was mixed up properly.

‘Analytical errors’ refer to possible errors that may occur during the analysis in the laboratory. To minimize the errors that may occur during laboratory analysis, the laboratory experiments were repeated for each sample at all depth. Therefore, collecting good representative samples from the field is the most important and first aspect for obtaining good and meaningful soil analysis.

The soil sampling processes are aimed at collecting seemly uniform sub-samples representing a field with similar cropping and soil management history. There is no universally accepted sub-sample number for different field situations.

A pedon may range in area from 1-2m^2 and it is broadened on all four sides by vertical sections or soil profile (Kim, 2005). This sampling unit is also considered as the single soil population. The validity of the sampling unit as representative of the soil as a whole depends upon the following criteria (Kim, 2005):

- **The degree of homogeneity of the sampling volume**: Sufficient homogeneity of the sampling volume in soil science is an unquestioned requirement for any analytical reference to justify the accuracy of the investigated properties. Homogeneous sampling volumes yield better results that can be reproducible than sampling volumes that are heterogeneous.
- **The method of sampling**: The sampling method is of major concern because it is one of the greatest aspects whereby field errors can occur. Samples are better selected from a pit by exposing the soil profile.
- **The number of sampling units**: The use of several small sampling units instead of one large sampling unit may yield a result that might provide a closer approximation of the estimated property of the soil under investigation.

There are different ways in which soil samples are collected from the field for soil testing:

- Cross strip in uniform field
- Test plot in uniform field
- Zigzag method
- Diagonal method in uniform field
- Two way diagonal in uniform field
- Ideal way of field sampling (random method).

Random sampling is the simplest and the most widely used method that is used to obtain representative samples from the Guzelyurt citrus orchards. In this method, every sampling unit has an equal and independent probability of being drawn (Kim, 2005). Randomly selected samples simply mean every possible sampling unit in the target population (soils of citrus orchards in Guzelyurt) has an equal chance of being selected ((US EPA, 1998). Simple random samples can be either sample in time and/or space and are often appropriate at an early stage of an EPA [QA/G-9 1.3 - 2 QA 96] investigation in which little is known about systematic variation within the site or process. With a simple random sample, the term "random" should not be interpreted to mean haphazard; rather, it has the explicit meaning of equiprobable selection (US EPA, 1998).

There are different standard methods for soil sample collection that depend on the purpose for which the samples are collected. However soil sample collection is an integral part of any research work that has to do with soil and water analysis.

Inappropriate collection (for example, not take into account all the criteria of homogeneity in sampling volume, correct method of sampling and the number of sample units) of soil samples from the field to the laboratory and mishandling in the laboratory during analysis are possible sources where errors might occur and alter the result.

For this study the soil samples were collected based on a horizontal and vertical base (Mussa et al., 2009).The sampling depth ranges from 0-90 centimeters (cm) at each sampling point and were denoted as taken from depths of 0-30, 30-60 and 60-90 cm together with the name of their locations before they were brought to the laboratory.

However the sampling was done at intervals of 30 cm depth in a vertical profiling with a spade and a helical auger. Samples collected from each depth were approximately 1 kilogram (kg) (all of the sampling units had equal volume or mass). These samples were then mixed in a plastic bag to get a composite soil sample. The bag was turned around a few times, in order to make the soil homogeneous. Plant residues and stone pieces were removed by hand picking and then soil sample was transferred to a sample bag. Sampling date, location and sampling number were marked on the bags and samples were brought to laboratory. Sampling was completed before the next fertilizing period that usually starts around spring.

4.2. Soil sample collection tools

Spade: for cleaning the surface of the soil before sample collection. These were also used to collect the top 0-30 cm depth of soil samples in the field.

Helical auger: for the collection of soil samples at depths deeper than 30 cm.

Plastic bags: to hold the soil samples until the samples are brought to the laboratory.

Global positioning system (GPS): to note the location and elevation above sea level at points of sampling in the field.

4.3. Sampling time

Soil sample collection can be done at any time of the year. However, sampling after soil fertilization or amendment should be avoided. A total of ten orchards were sampled on the 21st to 23rd of March, 2012. The ten orchards were selected randomly based on pre-knowledge of the soil types, citrus type, and the age of the citrus plants. It is important to sample at a similar period of the year for reliable comparison of the results. In this research, sampling took place in the beginning of spring shortly before the application of fertilizers in the citrus orchards in preparation for a new farming season.

4.4. Sampling locations

Sampling locations were chosen on the bases of soil types, orchards age, and fertilization practice (judgment sampling was used in orchard selection). In TRNC, most farmers apply mixed fertilizers to their crops and orchards while very few of those are practicing organic farming. These fertilizers are applied both in granular form and as solvent in solution (which means the fertilizer is dissolved in water before application.) through the irrigation pipes. Orchards with matured citrus trees receive approximately 50 kg of fertilizer per donum (1333m^2) while those with younger trees receive approximately 25 kg per donum. Orchards of citrus trees that were ten years or younger were considered to be 'young' orchards; those older than ten years are considered to be 'old' orchards. The ten orchards selected were considered to represent an overall picture of soil degradation in citrus orchards in Guzelyurt district.

The Figure 4.2 represent a plot map showing the GPS points that samples were collected in the study area. The location where all samples were collected was recorded with a GPS and the ages and types of citrus plants grown in the orchards were recorded as well.

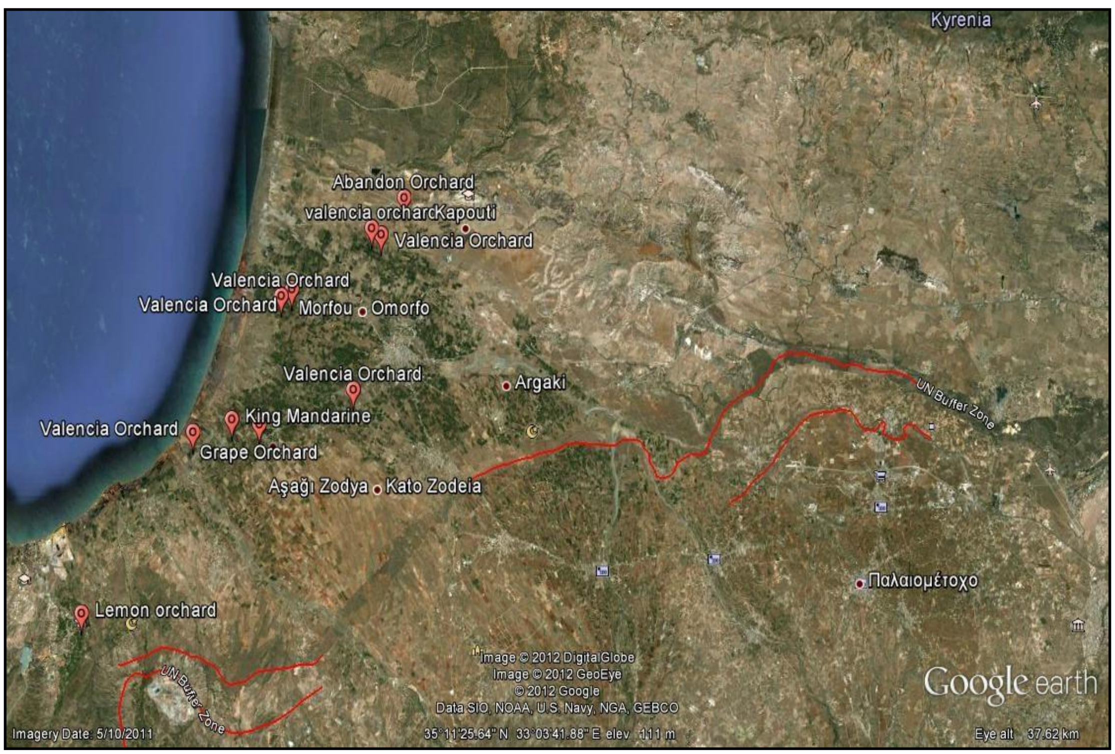


Figure 4.1 GPS location point of sample orchards and types of citrus orchards (Google Earth)

4.5. Laboratory analysis

4.5.1. Nitrate and nitrite analysis

There are various methods for determining nitrate and nitrite in soil. The most popular of these methods is the reduction of nitrate ions to ammonia followed by steam distillation (Norman and Stucki, 1981). The reduction of nitrates ions to ammonia is a method of analyzing soil nitrate. However, most studies have identified that the use of Ultraviolet spectrophotometer (UV spectrophotometer) is the best because of the relative ease and accuracy of measurement (Norman and Stucki, 1981). The soil samples were therefore extracted with potassium chloride as described by ISO method (ISO/TS 14256-1:2003(E))for the determination of soil nitrate.

In order to extract nitrate and nitrite in soil 40.0 g of soil samples were weighed into bottles, 200ml of 1M potassium chloride (KCl) solution was added and mixture was shaken for an hour at 20 ±2˚C as described in ISO/TS 14256-1 2003(E) testing kit (ISO/TS 14256-1:2003(E)). Then approximately 60ml of the extract suspensions were poured into tubes and centrifuged for 30 minutes at around 3000 G. The supernatant solutions were decanted into glass vessels that were then ready for the measurement of nitrate and nitrite by UV spectrophotometer.

The standard method requires that after the extracts have been prepared; they should be used immediately or stored at a temperature lower than 4˚C for one week at most. In this study, the extracts were stored in the refrigerator only for two days before analyses. The soil extracts and the solutions for the kit were for nitrate testing. The soil extract solution and the kits solutions were mixed up and allowed for to complete reactions that forms the colure that the UV spectrophotometer measures. Ten ml of soil extract solution was placed into a small stoppered bottle, two ml of nitrate kit solution reagent (in sulphuric acid and phosphoric acid solution, nitrate ions reacts with 2,6-dimethylphenol to form 4-nitro-2,6-dimethylphenol that was determined photometrically) The 4-nitro-2,6-dimethylphenol is a complex organic compound that gave coloration of each sample. In acidic solution nitrite ions react with sulphanic acid to form diazonium salt, which in turn reacts with nitrogen N-(1-naphthy) ethylenediamine dihydrochloride to form a red violet azo dye. This dye was determined photometrically. The pH was noted with the aid of litmus paper. The pH was noted with the aid of litmus paper. This mixture is allowed to stand for thirty minute before testing so that the coloration process should be completed. During the process of the formation of the complex azo dyke, a clear solution gradually changes colour into a purple colour solution depending on the nitrate concentration in the solution. The coloured solutions are then placed in a UV spectrophotometer (spectroquant NOVO 60 by Merck) that measures the intensity of the coloration and this gives the concentration of nitrate which is recorded. Nitrite is measured in similar manner.

4.5.2. Potash analysis

The soil potash was measured by flame photometer simply by measuring potassium ion concentration through an automated flame test from the soil samples.

The potassium in the soil sample was uncovered with ammonium acetate solution. 1 M ammonium acetate solution prepared and then the pH was adjusted to 7.0 by the addition of ammonia. This solution was then used as the extraction solution.

Ten gram of the soil sample was mixed with 25 ml of extraction solution in a glass bottle, shaken thoroughly and kept overnight at room temperature. Then the mixture was filtered with a vacuum filtration set-up using Whatman 589 filter paper. The filtration process might be repeated if the solution is not clear (Tuzuner, 1990).

4.5.3. Phosphate analysis

Soil phosphate was measured by Jenway Ultra Violet (use of a UV) spectrophotometer at 882 nm. In the determination of soil residues of phosphate, the Murphy and Riley method was applied on the soil extract. This method actually measures the relative available orthophosphate with the aid of $NaHCO_3$ as or in the extraction solution. The development of a blue colour in the samples indicates the formation of molybdophosphate complex. This is reduced by ascorbic acid in the presence of antimony for the determination of soil phosphate concentration (Carter, 2002).

When extracted with this method, phosphorus corresponds to the most biologically available forms of phosphorus that can be organic or inorganic as well as fractions of microbial forms. This method is suitable for basic, neutral or acid soils. The extracting agent decreases the concentration of the calcium in solution by precipitating insoluble calcium carbonate. The solubility of calcium phosphates increases with a decrease in calcium activity (effect of lining on phosphorus availability). Half molar $NaHCO_3$ extraction solution was prepared in a 5000ml volumetric flask. The pH of the extraction solution was adjusted to 8.5 with 1M NaOH. In the process of extraction, CO_2 is driven off from the bicarbonate, the pH of the solution increases and the bicarbonate is converted to carbonate. Consequently, when there is lower calcium activity, calcium carbonate is formed thereby increasing the quantity of phosphate in the solution (Rodríguez et al., 1994).

Phosphorus in the soil extract solution reacts with molybdenum in acidic medium to form the blue complex. This molybdenum blue reaction is always carried out under well-defined conditions of pH, temperature and reaction time to move the equilibrium towards the most condense form**.** The reaction consists of a series of combining molybdic acid with the ortho form of phosphorus. The condensation in the complex formation process is only possible. A reducing agent (ascorbic acid and sulphuric acid) and catalyst (antimony tartrate) facilitate the formation of the blue colour phosphomolybdic acid anion (Pansu and Gautheyrou, 2006).

Five grams of dried soil sample were mixed with100ml of 0.5 M $NaHCO_3$ solution using a shaker with a speed of 120 rpm (revolution per minute) for 30min. Then supernatant was filtered via Whatman 42 paper within 1 to 10 minutes. After filtration, 5.0 ml of 2.5 M H_2SO_4 was added to the soil extracts with a pipette to lower pH from 8.5 to 5.0 in a 25.0 ml flask. Each extract in the volumetric flask was swirled gently for about 3-5 min until all of the CO_2 was removed. To the extract, 4 ml of the reducing reagent was added to get 25.0 ml of solution with de-ionized water.

Hundred ml of intermediate P (phosphorus) standard solutions (1.0 mg/l and 10 mg/l) was prepared using 100 mg/l P stock solution. Then 1.0, 2.0, 3.0, 4.0 and 5.0ml were pipetted from 1.0 mg/l and 10.0 mg/l P stock solutions in to 25 ml volumetric flasks. Then, 5.0 ml of 0.5 M $NaHCO_3$ solution was added to each flask. The pH of the standard solution was lowered from 8.5 to 5.0 with 2.5 M H_2SO_4.The volume of 2.5 M H_2SO_4 solution that would be added to standards was determined daily, by taking 5.0 ml of 0.50 M $NaHCO_3$ solution and adding 2.5 M H_2SO_4 solution. Then the determined volume of 2.5 M H_2SO_4 solution was added and the solution was swirled until all of the CO_2 was removed. Then 4.0 ml of reducing reagent (sulphuric acid-molybdate, antimony potassium tartrate-ascorbic acid) was added to each flask. The volume was made to 25.0 ml with distilled water (Kim, 2005). After this, the calibration curve was prepared with stock solutions of known concentrations in the UV spectrophotometer.

4.5.4. Lime content

The Scheibler Method measures calcium carbonate ($CaCO_3$) amount in the soil (Altfelder et al., 2007). Scheibler calcimeter consists of a glass tube and a burette connected with plastic tubing (Fig. 4.1). Tubes were filled with water and the volume of carbon dioxide (CO_2) gas that evolved from the reaction of hydrochloric acid (HCL) with carbonate was measured. A weight and a bottle were used for the adjustment of the water level. The carbonates present in the soil sample were converted into CO_2 by adding hydrochloric acid (HCl) to the sample while temperature and pressure were recorded. The reaction in simplified form is represented below:

$$CaCO_3 + 2H^+Ca^{2+} + H_2CO_3 \rightarrow H_2CO_3\ H_2O + CO_2\ (g)$$

CO_2 releases as a result of the reaction that causes the water level to rise. The height of the level was measured to calculate the carbonate content, which was expressed as % (w/w) calcium carbonate. All measurements were carried out under the same conditions.

One gram of soil sample was weighed and placed into the calcimeter bottle (A) as shown on the diagram below. At the same time a plastic cup was filled with 5.0 ml of concentrated hydrochloric acid (HCl). The cup containing the acid was placed in the reaction vessel containing the soil sample. There was no contact between the hydrochloric acid and the soil before the reaction vessel was connected to the calcimeter (Scheibler unit). The apparatus was closed with the rubber stoppers and connected to the reaction vessels. Stopcock (B) was closed and the water level was checked once again to be equal in the arms of glass U-tube (Nuh 2010).

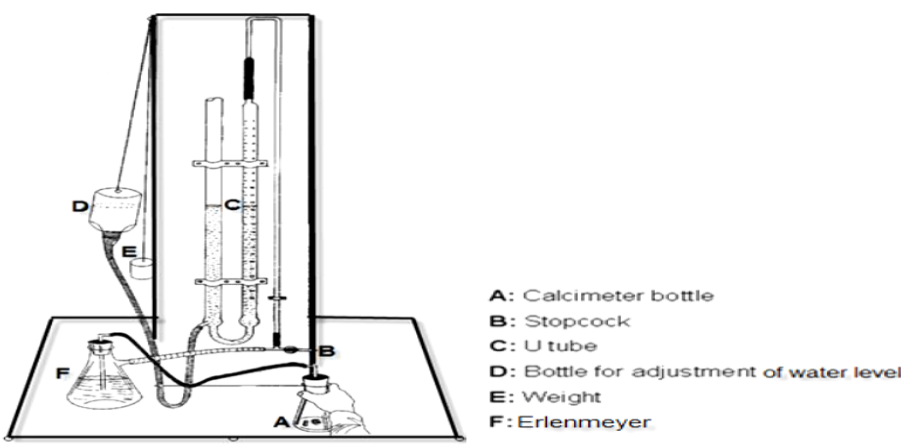


Figure 4.2 Schematic diagram of a calcimeter (Nuh, 2010)

4.5.5. Organic matter content

The Walkley-Black wet-chemical oxidation technique was developed in 1930 (Walkley and Black, 1934) and is currently one of the most widely used techniques in the direct determination of soil organic matter (Cartherine and Rock, 2008). Potassium dichromate ($K_2Cr_2O_7$) determines the end point during titration. To apply the Walkley-Black technique for calcareous soils, it should be preceded by the elimination of carbonates using strong-acid digestion. The samples were heated to 150˚C on a hot plate to increase the efficiency and precision of the dichromate digestion. The determined value was then converted to organic matter using the Van Bemmelen correction factor of (100/58=1.724) that assumes soil organic matter is 58% (w/w) carbon (Cartherine and Rock, 2008).

For analysis 10.0 ml of 1.0 N(normal) $K_2Cr_2O_7$ solution was prepared and mixed with 20.0 ml of concentrated H_2SO_4 solution (98 % grade by Merck-Chemicals) then added to 1.0 g of soil. This solution was swirled and allowed to cool to room temperature, because of exothermic reaction. The solution was then kept at 150˚C for 1 min on a hot plate and then cooled to 26˚C. Green colour shows high organic matter amount in the sample; another 10.0 ml of 1.0 N $K_2Cr_2O_7$ should be added and the same procedure repeated (Tuzuner, 1990). A 200.0 ml of water and 12–13 drops of 0.16 % diphenylamine-4-sulfonic acid barium salt were added as an indicator solution for coloring the soil samples during titration.

4.5.6. Soil type analysis

The percentage of sand, silt and clay in the soil was measured using hydrometer method. This method is based on Stoke's law governing the rate of sedimentation of particles suspended in water. The soil samples were treated with sodium hexametaphosphate to form a complex with cations that binds clay and silt particles into aggregates. Density of soil was determined and read in grams of solid per liter after the sand settles out and after silts settles. Corrections of temperature interference were made during the calculation of the percentage of the soil particle size analysis. Table 4.1 shows the soil types based on particle size analysis at all depths in the sampling locations.

Table 4.1 Soil location, orchard size and age and soil types at various depths from particle size analysis by hygrometer method

Orchards	Locations	Size (donum)	Age (years)	0-30 cm	30-60 cm	60-90 cm
Inorganic	Lefke	30	35 - 40	sandy loam	sandy loam	N/A
	Gaziveren-1	12	7 - 10	loam sand	sandy loam	sandy loam
	Gaziveren-2	8	35 - 40	clayey loam	clayey loam	clayey loam
	Aydinkoy	15	30-35	loam	clayey loam	clayey loam
	Guzelyurt - 1	5	35-40	loam	loam	loam
	Yayla-1	12	35-40	clayey loam	clayey loam	clayey loam
	Yayla-2	10	45-50	clayey loam	clayey loam	clayey loam
Organic	Guzelyurt-2	10	35 - 40	clayey loam	sandy loam	sandy loam
	Guzelyurt-3	8	45-50	Clayey loam	sandy loam	sandy loam
Abandoned	Kalkanli	8	45 - 50	loam sand	Loam sand	sand

4.5.7. pH Analysis

pH was measured with an automated EcoMeT P 25 pH meter with a graphite electrode that had been calibrated automatically. pH values of saturated soil samples were measured by tipping the electrode rod into the stirred homogeneous suspension at 20°C ± 2°C. The electrode was dipped; left in the suspension for about 2 minutes and pH values of were recorded. Soil sample with pH values between 6 and 8 are considered as neutral. Those below 6 are acidic soils while above 8 are considered to be alkaline soil.

4.5.8. Soil electrical conductivity Analysis

The electrical conductivity (EC) of the soil indicates the quantity of soluble salt ions (electrolytes) that present in the soil. The determination of soil electrical conductivity was done with a conductivity cell by measuring the electrical resistance of the saturated soil suspensions using Jenway4520 Laboratory Conductivity/TDS Meter. Measurement range is between 0 and 1999± 1 μS/cm. This instrument compensated automatically for the temperature variation during measurements. The instrument was calibrated manually with 0.010 M potassium chloride, which had an electrical conductivity of 1413 μS/cm at 25 °C. The conductivity cell was filled with the soil suspension. Then it was shaken to settle the suspension and further additions of suspension were done until the cell was completely full (Tuzuner, 1990). Table 4.2 is an electrical conductivity (EC) chart used for comparing the salinity of the soil according to the total salt content.

Table 4.2 Electrical conductivity values and total salt content (Nuh, 2010)

Total Salt (%)	**Conductivity (μS/m)**	**Salinity**
0.00-0.15	0.0-4.04	Not salty
0.16-0.35	4.1-8.0	Slightly salty
0.36-0.65	8.1-15.0	Moderately salty
65	15.0	Strongly salty

CHAPTER 5
RESULTS AND DISCUSSION

5.1. Evaluation standards

There are no published standards for the evaluation of residual soil nitrates, nitrite, potash, and phosphate; therefore, in this thesis drinking water standards have been used as a criterion. The United States Environmental Protection Agency clearly states that the units for drinking water standards are in milligrams per liter (mg/l) unless otherwise noted. This simply means the amount of contaminant or pollutant that can be found in a million parts of a given sample, for instance soils.

The US Environmental Protection Agency (EPA) maximum contaminant level (MCL) for nitrate in drinking water of 10 mg/l nitrate-nitrogen (nitrate-N) (equivalent to 45 mg/l as nitrate-NO_3) and 1 mg/l for nitrite-N. The World Health Organization (WHO) guideline (WHO 2004b) of 11 mg/l as nitrate-N(equivalent to 50 mg/l as nitrate-NO_3) were promulgated to protect against methemoglobinemia, or “blue baby syndrome,” to which infants are especially susceptible.

However, based on the European Union (EU) drinking water standards, nitrite and nitrate amounts cannot exceed 0.5 mg/l nitrite nitrogen and 50 mg/l nitrate-NO_3, respectively. In some cases, potassium in the form of alum is added in the drinking water for purification to replace chlorine. However, phosphate has a limiting value of plants growth at about 0.02 mg/l (Sharpley and Tunner, 2000; US EPA, 1998), and when this limited value is exceeded, it turns to kill the plants and when in surface water surface, it promotes algae bloom. These standards are as summarized on the table 5.1 below

Table 5.1 Maximum contaminant level of nitrate and nitrite in drinking water

Chemical contaminants	Drinking water standards for maximum contaminant level
nitrate	11 mg/l nitrate-N and 45 mg/l nitrate-NO_3
nitrite	0.5 mg/l nitrite-N
phosphate	Not applicable
potash	Not applicable

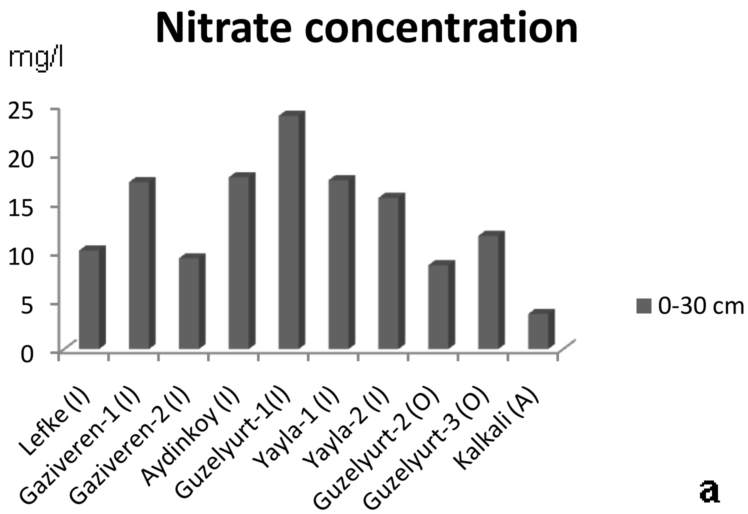
5.2. Results

The results for below were measured in mg/l nitrate-NO_3 and mg/l nitrite-N for nitrate and nitrite respectively. Table 5.2 shows nitrate, nitrite, phosphate and potash residues at 0-30 cm

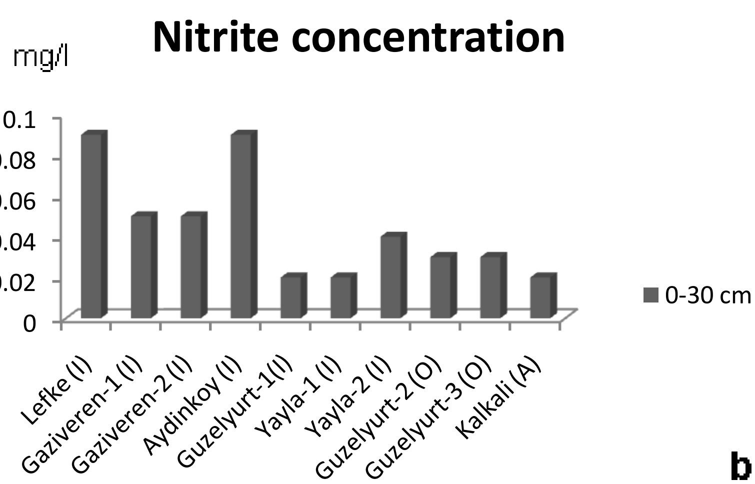
Table 5.2 Nitrate, nitrite, phosphate and potash residues at depth of 0-30 cm

Measured residues in different orchards		Nitrate-NO_3^- (mg/l)	Nitrite (mg/l)	Phosphate (mg/l)	Potash (mg/l)
Inorganic (I)	Lefke	10.1	0.09	0.09	0.45
	Gaziveren-1	17.1	0.05	0.36	0.89
	Gaziveren-2	9.3	0.05	0.52	1.40
	Aydinkoy	17.6	0.09	0.44	2.50
	Guzelyurt-1	23.9	0.02	0.34	0.89
	Yayla-1	17.3	0.02	0.35	2.89
	Yayla-2	15.5	0.04	0.30	1.39
Organic (O)	Guzelyurt-2	8.6	0.03	0.04	0.89
	Guzelyurt-3	11.6	0.03	0.19	1.39
Abandoned (A)	Kalkanli	3.6	0.02	0.12	1.20

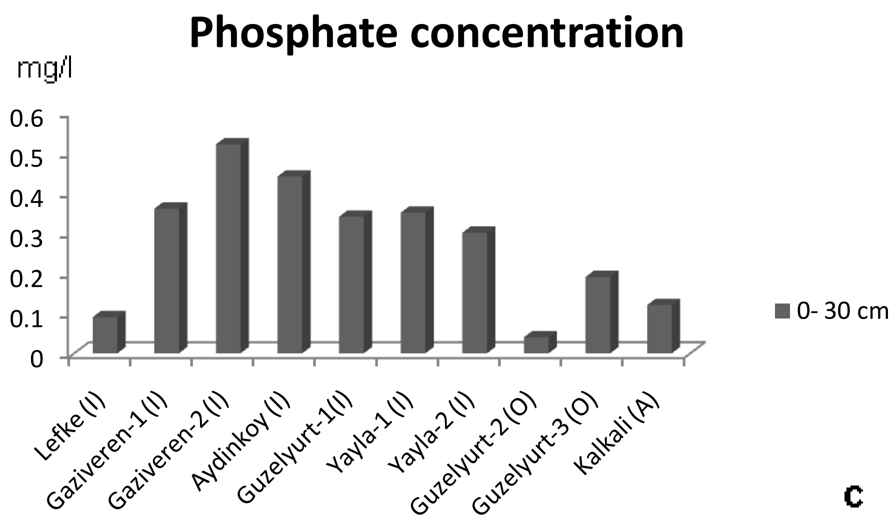
The Figure 5.1 below shows a distribution of nitrate, nitrite, phosphate and potash measured residues of soils samples obtained from ten citrus orchards within the Guzelyurt district at 0-30 cm depth. Within this depth, nitrate has the highest concentration in mg/l., this is followed by potash residues at same depth and then phosphate and nitrite are the least measured residues. However, the values of nitrate concentration in the soil for all locations at this depth were below the 45 mg/l maximum contaminant level. The concentrations of nitrite also were below the maximum contaminant level of 0.05mg/l at the depth for all location exception at Aydinkoy that was 0.09 mg/l.


Nitrate concentration
mg/l
25
20
15
10
5
0
Lefke (I)
Gaziveren-1 (I)
Gaziveren-2 (I)
Aydinkoy (I)
Guzelyurt-1(I)
Yayla-1 (I)
Yayla-2 (I)
Guzelyurt-2 (O)
Guzelyurt-3 (O)
Kalkali (A)
0-30 cm

a


Nitrite concentration
mg/l
0.1
0.08
0.06
0.04
0.02
0
Lefke (I)
Gaziveren-1 (I)
Gaziveren-2 (I)
Aydinkoy (I)
Guzelyurt-1(I)
Yayla-1 (I)
Yayla-2 (I)
Guzelyurt-2 (O)
Guzelyurt-3 (O)
Kalkali (A)
0-30 cm

b



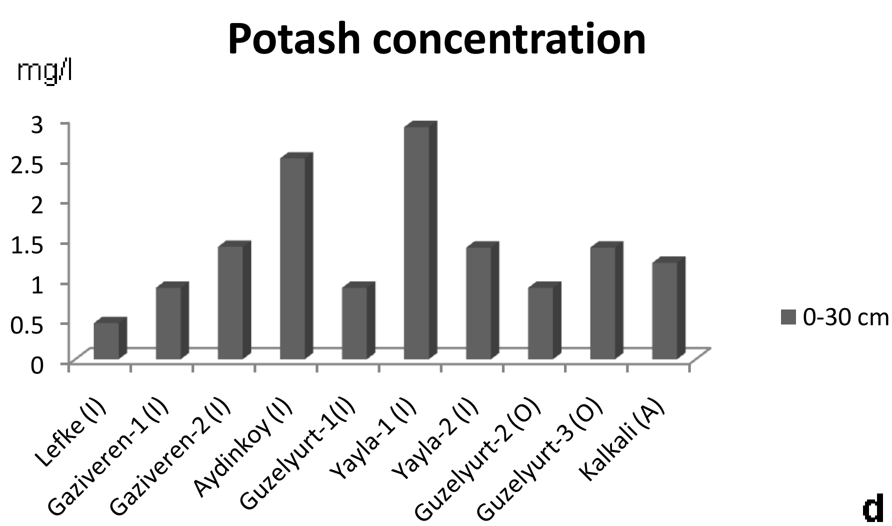


Figure 5.1 Distribution of (a) nitrate, (b) nitrite, (c) phosphate and (d) potash concentrationsat 0-30 cm depth

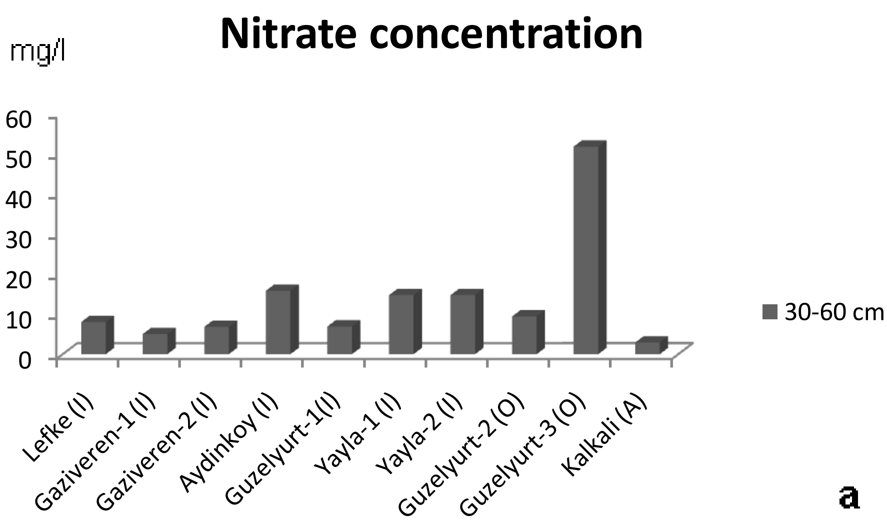
The highest nitrate concentration at this depth was recorded at Guzelyurt-1.This is not an expected result. The soil texture at this location is sandy loam and thus it may allow leaching by surface wash off, as indicated earlier. Nitrite residues are very low because nitrite is highly unstable. For potash, at this depth, Yayla-1 has the highest residue concentration. Both clayey loam texture and low conductivity may help rising the potash accumulation at Yayla-1. Lefke has the least potash residue. In relation to the sandy loam soil type at this location, it may be easy for most of the residues to have percolated to the underground water resource. For phosphate, Gaziveren-2 has the highest residue concentration. The soil texture at this location is clayey loam and might be having an influence on potash accumulation. Lefke has the least potash residue. In relation to the sandy loam soil type at this location, it is easy for most of the residues to have percolated to the underground water resource. For phosphate, Gaziveren-2 has the highest residue concentration and this might be due to the soil texture as well. Kalkanli has the least phosphate because no fertilization practice is done on the orchard. Nitrite residues are very low because nitrate is highly unstable.

Table 5.3 Nitrate, nitrite, phosphate and potash residues at depth of 30-60 cm

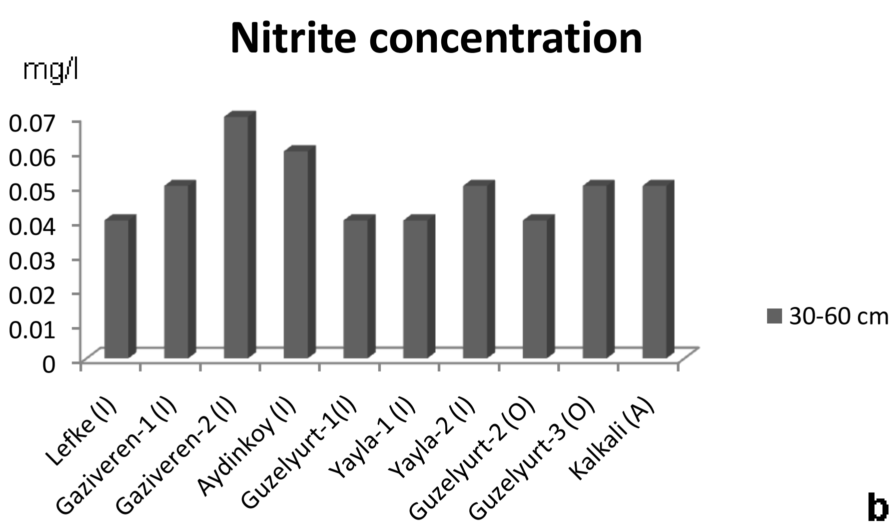
Measured residues in different orchards		Nitrate (mg/l)	Nitrite (mg/l)	Phosphate (mg/l)	Potash (mg/l)
Inorganic (I)	Lefke	8	0.04	0.09	0.29
	Gaziveren-1	5	0.05	0.17	1.69
	Gaziveren-2	6.8	0.07	0.28	1.09
	Aydinkoy	15.8	0.06	0.31	1.29
	Guzelyurt-1	6.9	0.04	0.08	1.79
	Yayla-1	14.7	0.04	0.65	1.79
	Yayla-2	14.7	0.05	0.01	1.00
Organic (O)	Guzelyurt-2	9.4	0.04	0.00	1.79
	Guzelyurt-3	51.7	0.05	0.02	0.59
Abandoned (A)	Kalkanli	2.9	0.05	0.59	0.07

The Figure 5.2 below shows that at depth of 30-60 cm for all locations, nitrate residues were the highest, followed by potash, then phosphate and nitrite. Generally, at this depth, the highest amount of nitrate was recorded at Guzelyurt-2 orchard (organic orchard) as 51 mg/l as shown on Figure 5.2a below. The concentration of nitrate at Guzelyurt-2 is slightly higher than the maximum contaminant level of 45 mg/l. The concentration of nitrate for the other location remains relatively lower than the maximum contaminant level. Nitrite concentration at is depth were higher than the maximum contaminant level of 0.05 mg/l for sample from Gaziveren-1 and Aydinkoy.

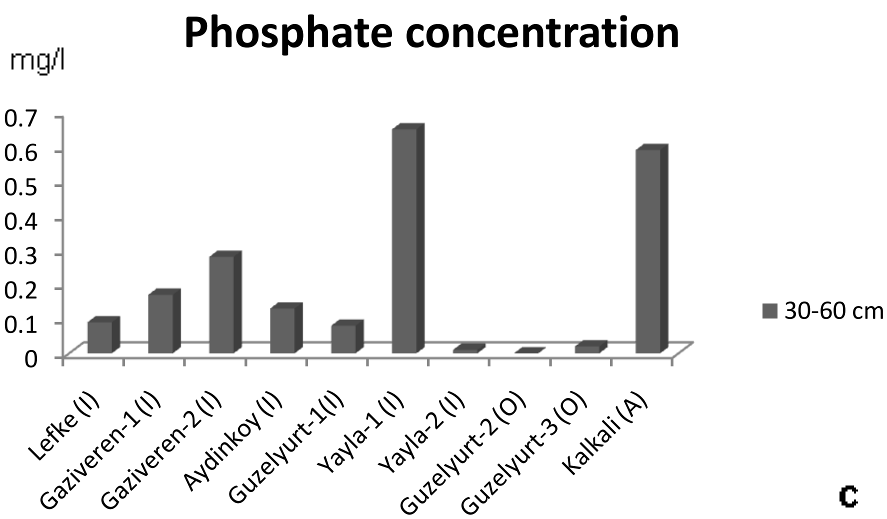
These two locations recorded values of 0.07 mg/l and 0.06mg/l respectively whereas sample from the rest were either 0.05mg/l or slightly below as shown on Figure 5.2b.



a



b



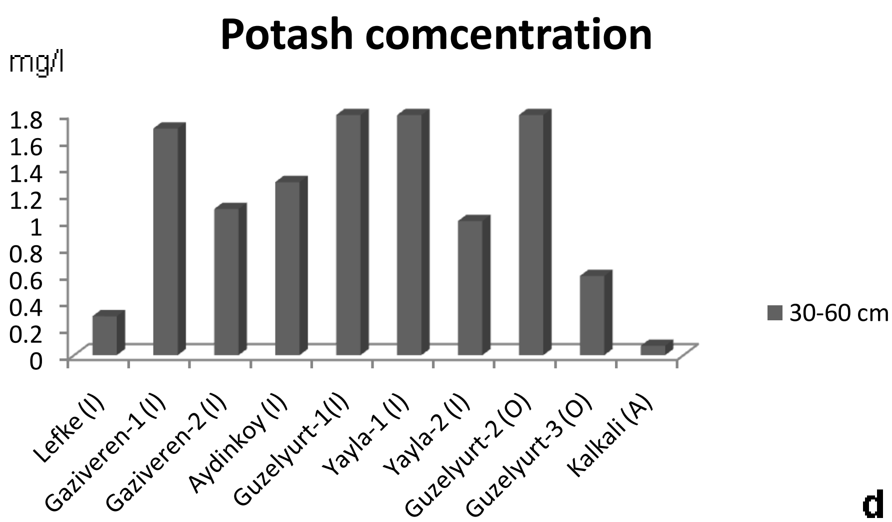


Figure 5.2 Distribution of (a) nitrate, (b) nitrite, (c) phosphate and (d) potash concentrationsat 30-60 cm depth

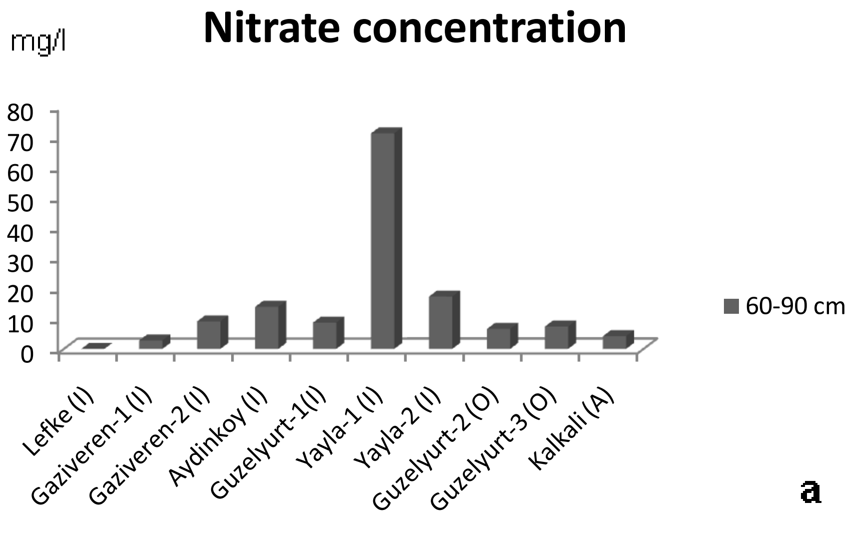
For potash, Gaziveren-1, Guzelyurt-1, Yayla-1 and Guzelyurt-2 were highest while Lefke and Kalkanli were the least. Phosphate and nitrate are present in small quantities relative to nitrate and potash.

Table 5.4 below shows nitrate, nitrite, phosphate and potash residues that measured from all locations at 60-90 cm, in mg/l.

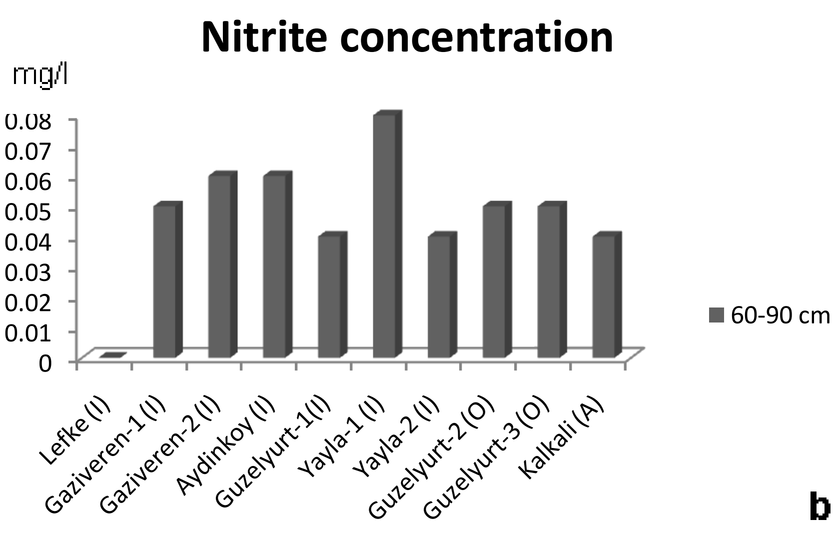
Table 5.4 Nitrate, nitrite, phosphate and potash residues at depth of 60-90 cm

Measured residues in different orchards		Nitrate (mg/l)	Nitrite (mg/l)	Phosphate (mg/l)	Potash (mg/l)
Inorganic (I)	Lefke	N/A	N/A	N/A	N/A
	Gaziveren-1	2.8	0.05	0.17	0.69
	Gaziveren-2	9.1	0.06	0.13	0.69
	Aydinkoy	13.9	0.06	0.20	1.20
	Guzelyurt-1	8.7	0.04	0.10	0.39
	Yayla-1	71.2	0.08	0.31	0.89
	Yayla-2	17.3	0.04	0.00	0.89
Organic (O)	Guzelyurt-2	6.6	0.05	0.30	0.89
	Guzelyurt-3	7.4	0.06	0.00	0.40
Abandoned (A)	Kalkanli	4.2	0.04	0.00	0.29

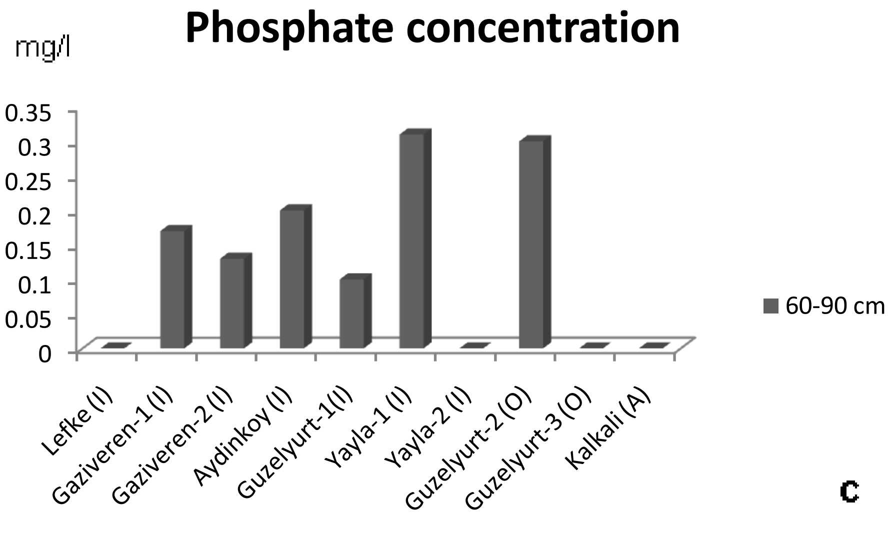
The Figure 5.3 show a general pattern like the others at this depth of 60-90 cm with nitrate dominating, follwed by potash, then phosphate and nitrite. Figure 5.3a shows that Yayla-2 has the highest amount of nitrate with value of 71.2 mg/l. This value is higher than the maximum contaminant level of 45 mg/l. The rest locations were far below this amounts. Figure 5.3b shows that Gaziveren-2, Aydinkoy, Guzelyurt, Yayla and Guzelyurt-3 recorded nitrite concentration above the maximum contaminant level of 0.05 mg/l


Nitrate concentration
mg/l
80
70
60
50
40
30
20
10
0
60-90 cm
Lefke (I)
Gaziveren-1 (I)
Gaziveren-2 (I)
Aydinkoy (I)
Guzelyurt-1(I)
Yayla-1 (I)
Yayla-2 (I)
Guzelyurt-2 (O)
Guzelyurt-3 (O)
Kalkali (A)

a


Nitrite concentration
mg/l
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
60-90 cm
Lefke (I)
Gaziveren-1 (I)
Gaziveren-2 (I)
Aydinkoy (I)
Guzelyurt-1(I)
Yayla-1 (I)
Yayla-2 (I)
Guzelyurt-2 (O)
Guzelyurt-3 (O)
Kalkali (A)

b



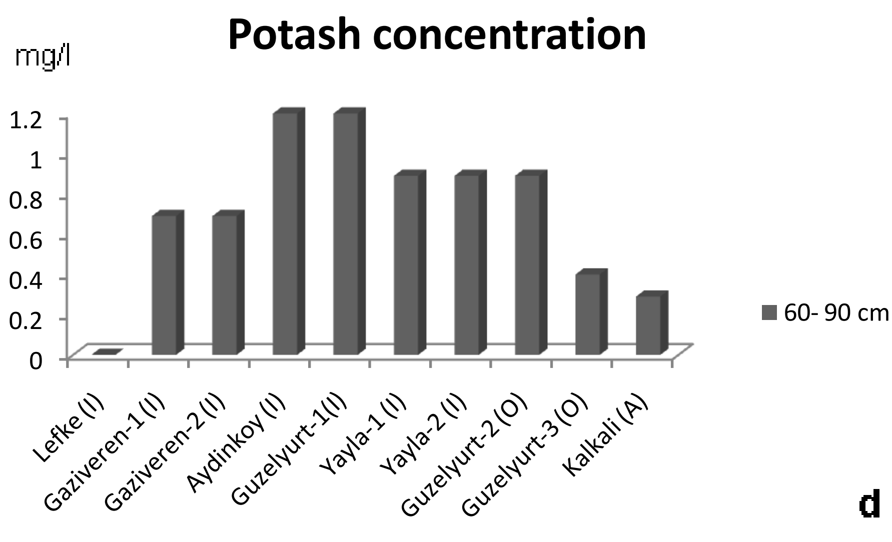


Figure 5.3 Distribution of (a) nitrate, (b) nitrite, (c) phosphate and (d) potash concentrations at 60-90 cm depth

For nitrate, Yayla-1 records the highest ampount of nitrate at this depth followed by Yayla-2, Aydinkoy, then Gaziveren-2 and Gaziveren-1 and Kalkanli are the least.

Potash, phoshate and nitrite are at this depth are relatively small as compared to nitrates.

5.2.1. Nitrates

The determination of inorganic nitrogen (N) residue in the soil is in nitrate-(NO^{3-})form and is often useful, because despite their usually low levels, these inorganic forms are readily available for plant uptake. However, they constitute major environmental and human health hazards. In warm, well-aerated, slightly acid to slightly alkaline soils, the nitrogen from the soil absorbed by plant is predominantly in the nitrate form (Mussa et. al., 2009).

Figure 5.4 shows the relationship between the nitrate concentration and the depths of the soil for all sampled location.

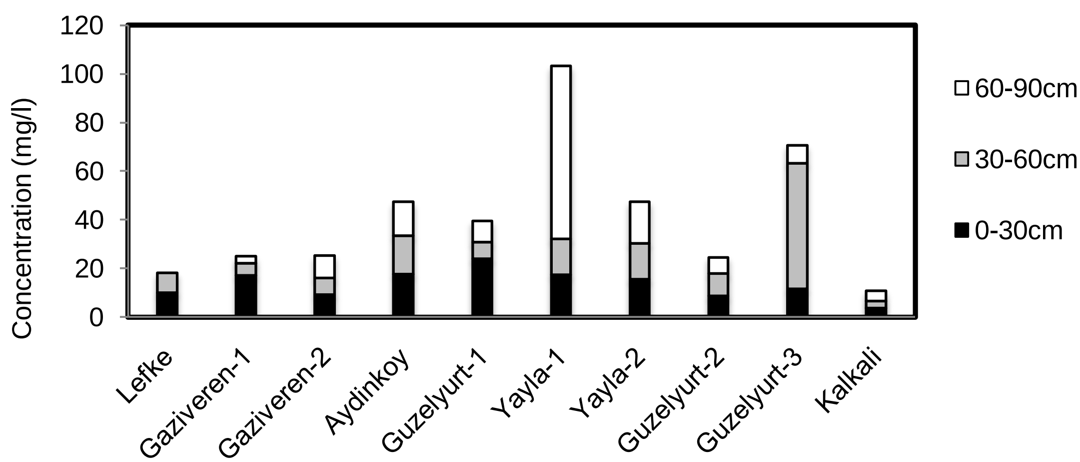
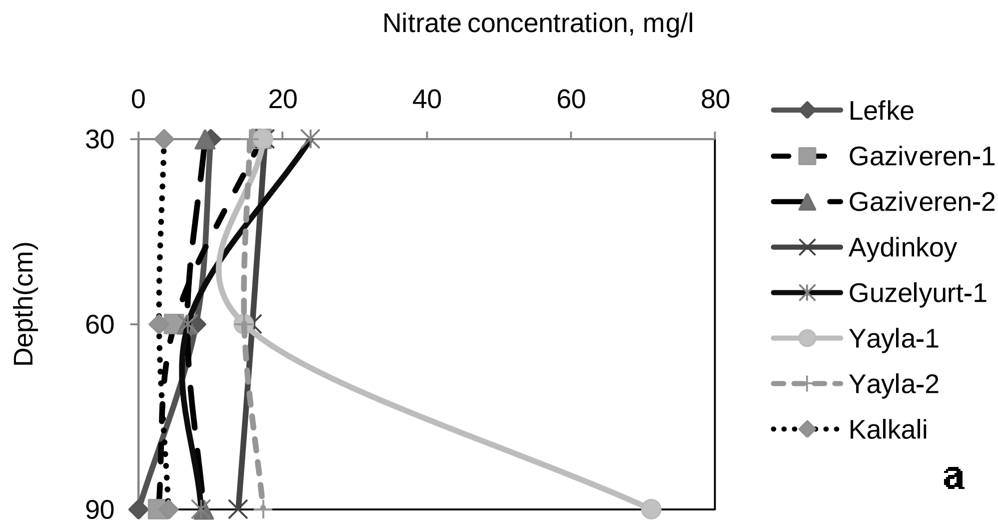


Figure 5.4 Nitrate residue concentration distribution in the soil at depth 0-90 cm



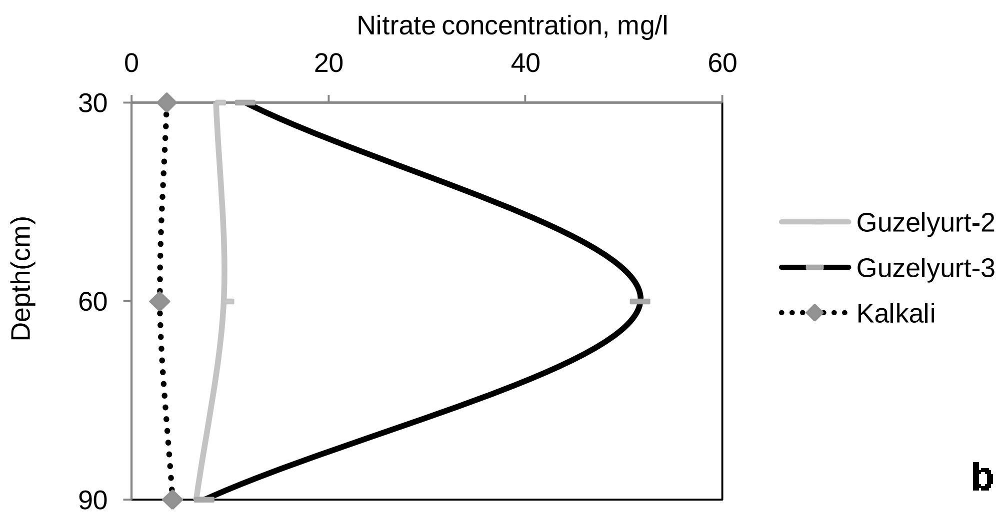


Figure 5.5, Nitrate residue concentration in the soil at depth 0-90 cm for (a) inorganic (b) organic orchards.

Nitrates accumulation shows great variation with depth across the three depths in the citrus orchards in Guzelyurt in TRNC. Within the top 0-30 cm and 30-60 cm depth, the nitrate concentrations in the inorganic orchards ranges from 9.3 to 23.9 mg/l, and 5 to15.8 mg/l, respectively. This might be accounted by the fact that, 0-60 cm is the zone, where the plant roots are highly concentrated, and tend to absorbed most of the available nitrogen from this zone into the plant system.

Analysis of Figure 5.4 and Figure 5.5show that,

i) The highest concentration of nitrate in the study area was found from soil samples for the inorganic orchards collected from Yalya-1 at depth of 60-90 cm depth. For the organic orchard, highest was recorded at Guzelyurt-3 at 30-60 cm depth.

ii) Only soil samples collected at Guzelyurt-3 at depth of 30-60 cm and Yalya-2 at depth of 60-90 cm has values of residues that are above both the U.S EPA, WHO and EU drinking water limit for maximum contaminant level.

The general pattern shows a decrease in nitrate residues from 0-30 cm, 30-60 cm and 60-90 cm. For instance, nitrate residues for Aydinkoy is highest at 0-30 cm, decreases at 30-60 cm and is least at 60-90 cm. However, there are some anomalies. For instance, at Yayla-1 nitrate concentration was highest at 60-90 cm and Guzelyurt-3, the residue is highest at 30-60 cm depth. These anomalies can probably be accounted for by the local variation in soil particle size distribution (texture) within the Guzelyurt district.

For the three different orchard categories at 0-30 cm, the highest nitrate residues recorded for inorganic orchard at Guzelyurt-1 was 23.9 mg/l and was followed by Aydinkoy with 17.6 mg/l and then Yayla-1 with 17.3 mg/l whereas the least for this category of orchards was 9.3 mg/l at Gaziveren-2. For the two organic orchards, Guzelyurt-3 recorded the highest of 11.6 mg/l. The abandon orchard recoded nitrate concentration residue of 3.6 mg/l.

For the three different orchard categories at 30-60 cm, for the inorganic orchards, Aydinkoy orchard was the highest with residue value of up to 15.8mg/l. This was closely followed by Yayla-1 and Yayla-2 with residues concentration measuring 14.7mg/l and Gaziver-1 was the least with 5 mg/l. For the organic orchards, Guzelyurt-3 shows and anomalous nitrate concentration of 51.7 mg/l and Guzelyurt-2 was 9.4mg/l. The abandon orchard, show a concentration of 2.9 mg/l.

For the three different orchard categories at 60-90 cm, for the inorganic orchards, Yayla-1 recorded the highest residues concentration of 71.2mg/l, followed by Yayla-2 with 17.3 mg/l and Aydinkoy with 13.9 mg/l and the least was Gaziveren-1 with

2.8nmg/l . For the organic orchard, Guzelyurt-3 was 7.4 mg/l and Guzelyurt-2 with 6.6 mg/l. For the abandon orchard, the nitrate residue concentration was 4.2mg/l.

5.2.2. Nitrites

Figure 5.6, shows nitrite residues that were recorded at the different location for all three depths.

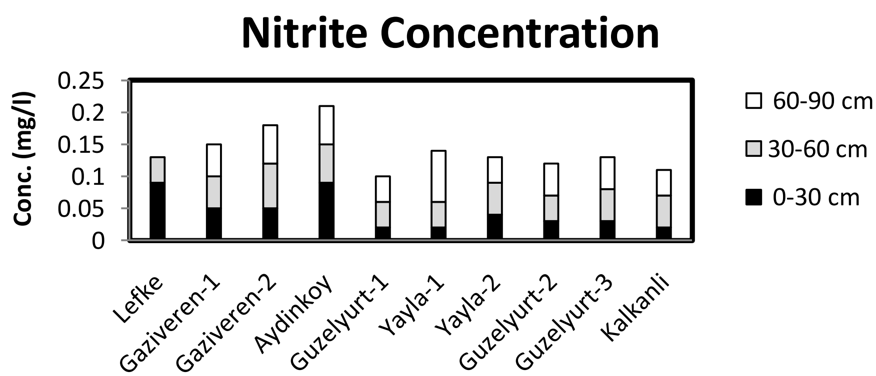
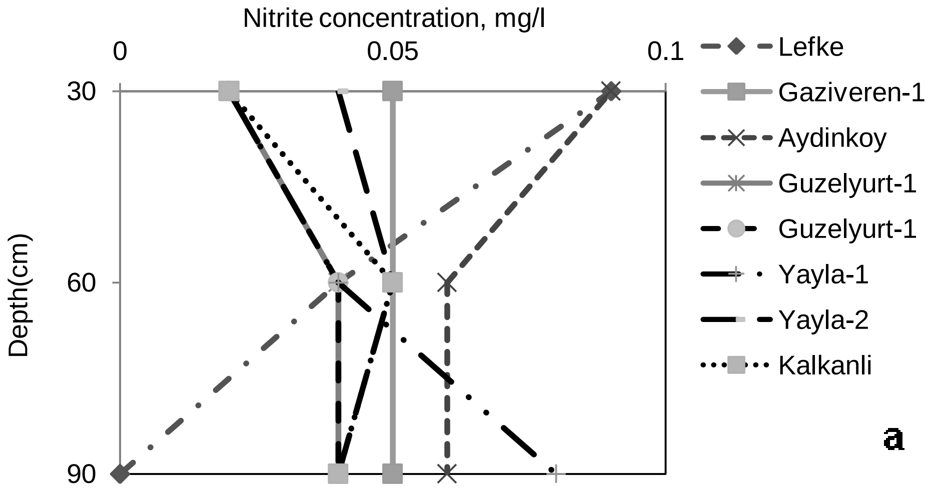


Figure 5.6Nitrite residue concentration distribution in the soil at depth 0-90 cm

Generally, nitrite residues in the soil are very low with because nitrite is an intermediary compound formed during nitrification as well as denitrification (Oswald and Adullahi, 1995/1996). For the inorganic orchard at 0-30 cm depth, Lefke and Aydinkoy had the highest nitrite concentration. This is then followed by Gaziveren-1 and Gaziveren-2. For the organic orchards, both had the same concentration. The abandoned orchard had the least residue. The other depths shows irregular pattern of nitrite residues for all categories of orchards.



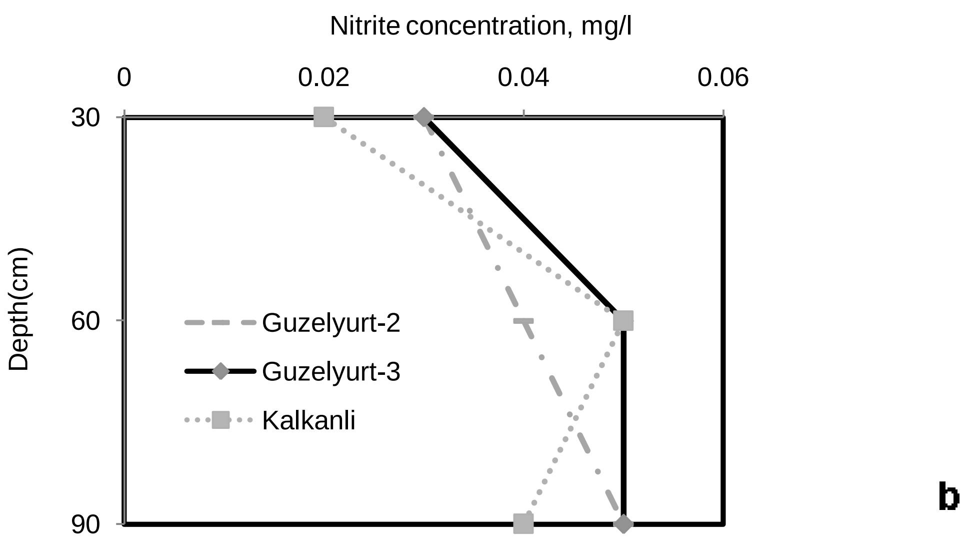


Figure 5.7Nitrite residue concentration in the soil at depth 0-90 cm for (a) inorganic (b) organic orchards

5.2.4. Phosphate

Soil phosphorus occurs as phosphate and both in the organic and in organic form are of major importance in plant-soil-water interaction, and in the general phosphorus biogeochemical cycling in natural systems. The majority of agricultural soils usually cannot meet crop demands for P, and fertilization is required (Mussa et. al., 2009)

Plants generally absorb most of their P as $H_2PO_4^-$and smaller amount as HPO_4^{2-} depending on the pH i.e. lower pH values will increase the absorption of H_2PO_4 ion, whereas, higher pH values will increase the absorption of HPO_4^{2-}ion (Mussa et. al., 2009).

The Figure 5.8 shows the relationship between residue concentration and depth of the soil. There is a general decrease in phosphate residues concentration with increasing depth at each location.

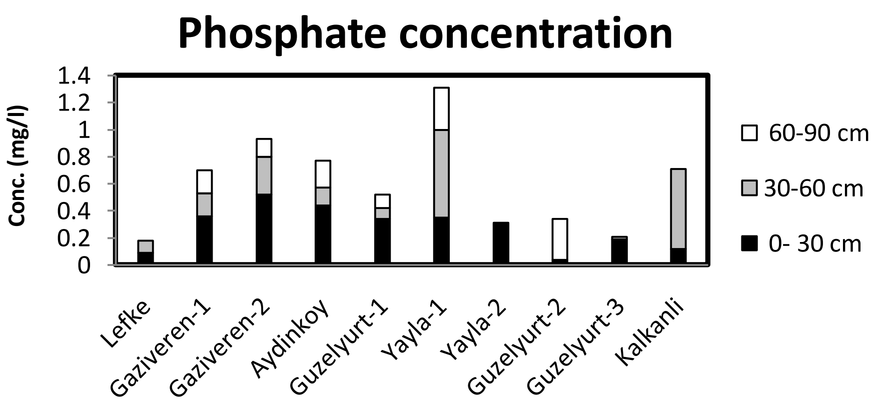
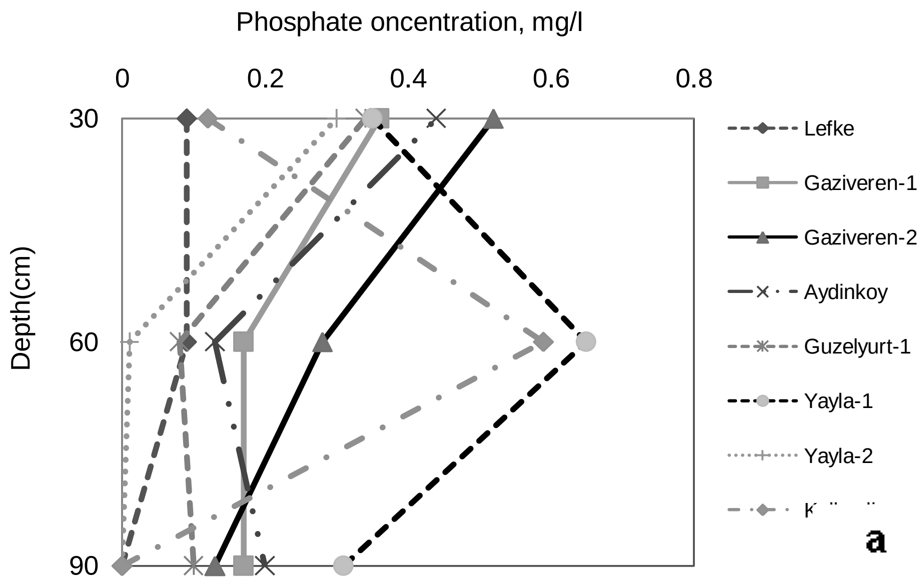


Figure 5.8 Phosphate residue concentration in the soil at depth 0-90 cm for inorganic orchards



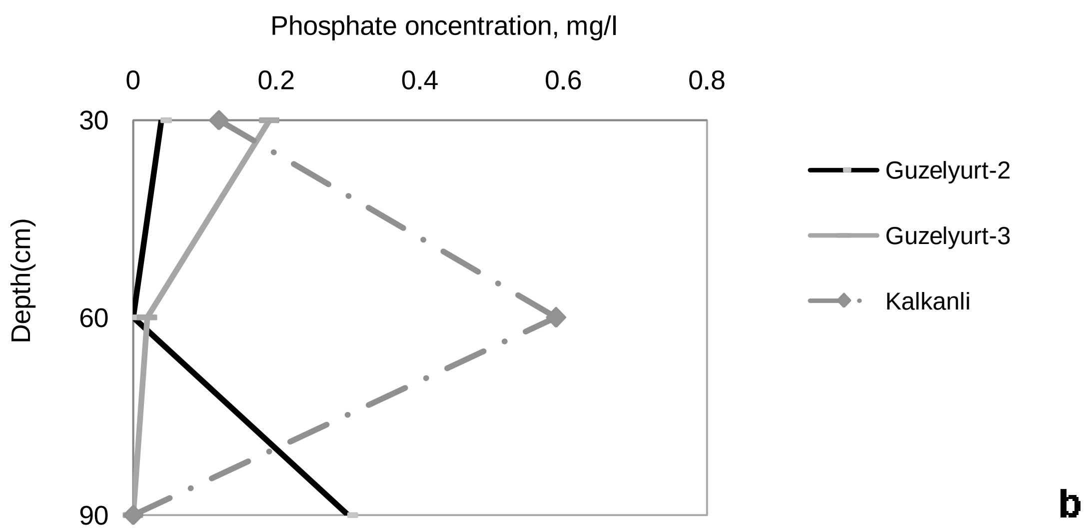


Figure 5.9 Phosphate residue concentration in the soil at depth 0-90 cm for (a) inorganic (b) organic orchards

In general, inorganic orchards show the highest phosphate residues and this is followed by the organic orchards and then the abandoned orchard. Figure 5.9 shows:

i) Most of the phosphate is found in the top soil. This may be because the samples were collected on the month of April in which there was no rainfall for leaching the anions. However, the other studies have confirmed that most phosphate mostly accumulate at this depth. This can be due to the fact that there is high potential for adsorption and absorption of phosphate.

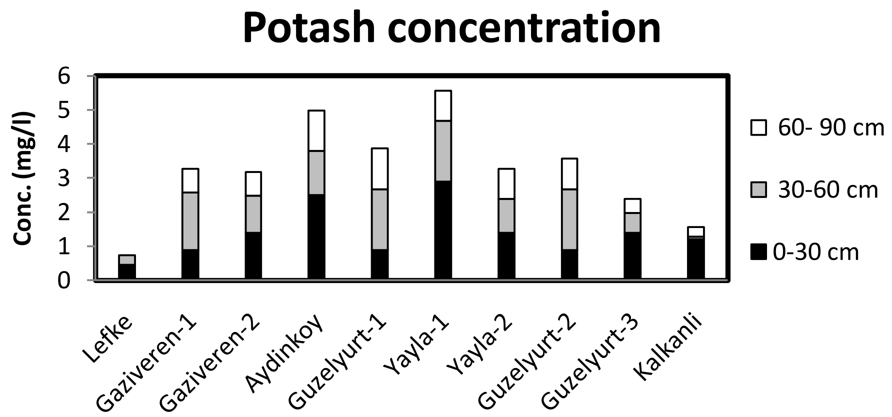
ii) The highest amounts are found in samples collected from inorganic orchard (Gaziveren-2 and Aydinkoy at depth between 0-30 cm). At depth between 30 and 60 cm, it was Yayla-1 that has high pH value for the inorganic orchard and Guzelyurt-2, which is also an organic orchard, generally these amounts decrease with increasing depths due to the absorption by plant. However, there are some anomalous cases.

iii) The depth as well as the soil types and pH influence the amount of phosphate residues on the soil.

As shown on Table 5.4, phosphate residues for all samples were the highest at the 0-30 cm depth. The lowest amounts of these residues were recorded at depths of 60-90 cm. For instance, in Yayla-1, at depth of 0-30 cm, the soil phosphate residue was 0.30 mg/l, 30-60 cm depth it was 0.01 mg/l, and at 60-90 cm it was 0.00 mg/l. These values imply that phosphate residues mostly accumulate in the top soil as opposed to the subsoil.

5.2.3. Potash

The Figure 5.10 shows potash concentration in mg/l verses depths in cm for all categories of orchards in the study region.



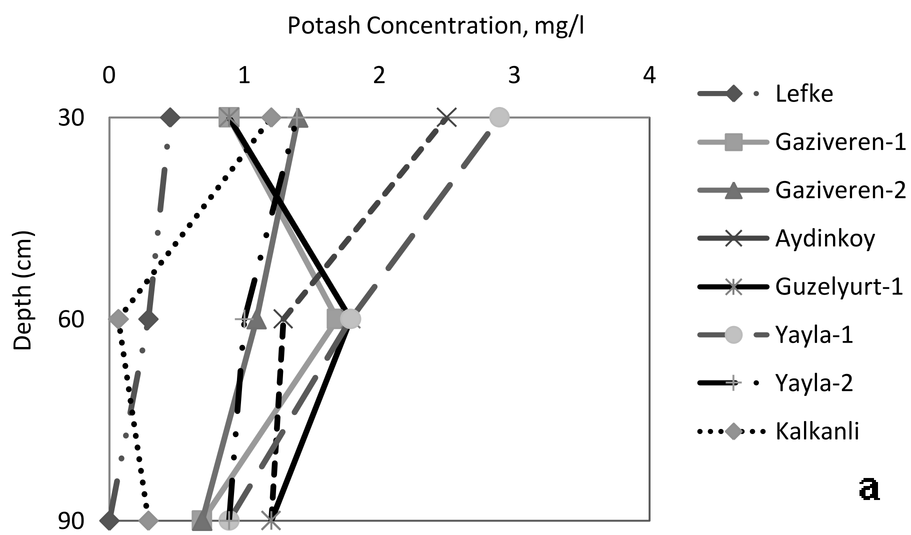


Figure 5.10 Potash residue concentration distribution in the soil at depth 0-90 cm

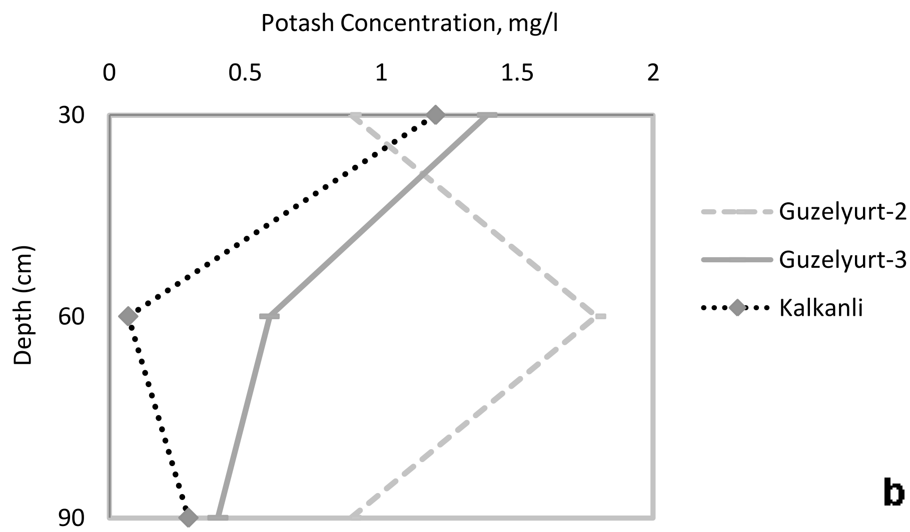


Figure 5.11, Potash residue concentration in the soil at depth 0-90 cm for (a) inorganic (b) organic orchards

Generally, the potash residues decrease with increase depth. For the inorganic orchards, at 0-30 depth, Yayla-1 had the highest potash residues, and is closely followed by Aydinkoy. Lefke is the least. On the other hand, for the organic orchards, Guzelyurt-3 is highest and is approximately half the residues in Yayla-1; this is followed by Guzelyurt-2.

5.2.5. pH and conductivity

Soil pH values and electrical conductivities at all locations in the study areas are shown in Table 5.5 and Table 5.6, respectively. The pH values of all the location ranges between 6 and 8 that mean soil samples. The electrical conductivity (EC) values show that samples are not salty because the measured EC values were within the range of 0.0-4.04 μS/m according to Table 4.2.This implies that the study area and the results obtained in this study have not been affected by the salinity as confirmed by the pH and conductivity values.

Table 5.5 pH and Electrical conductivity (EC) of the soil samples collected from 0 to 90 cm depths from orchards

Measured parameter		pH			Electrical conductivity (μS/m)		
Sampled depths (cm)		0-30	30-60	60-90	0-30	30-60	60-90
Inorganic orchards	Lefke	7.1	7.3	N/A	0.06	0.06	N/A
	Gaziveren-1	6.9	7.2	7.3	0.10	0.07	0.10
	Gaziveren-2	7.1	7.1	7.0	0.11	0.12	0.16
	Aydinkoy	6.7	6.9	6.9	0.14	0.12	0.80
	Guzelyurt -1	7.4	7.7	7.7	0.10	0.16	0.16
	Yayla-1	7.5	7.7	7.7	0.01	0.17	0.60
	Yayla-2	7.5	7.6	7.6	0.08	0.07	0.06
Organic orchards	Guzelyurt-2	7.6	7.6	7.6	0.14	0.20	0.04
	Guzelyurt-3	7.7	7.6	7.6	0.05	0.03	0.04
Abandoned orchard	Kalkanli	7.3	7.6	7.6	0.02	0.04	0.05

The electrical conductivity of the abandoned orchard was the lowest. The pH values of all three classes of orchards falls within a narrow range in the neutral pH that, shows the application of fertilizer on the soils of citrus orchards does not affect the soil pH significantly.

Table 5.6overleaf shows a statistical representation of the data generated from the 29 samples obtained at the 10 different locations within the study areas.

Table 5.6 Computed means, medians, standard deviations, standard errors andfor all residues of inorganic and organic orchards for all depths.

Inorganic orchard												
D	0-30 cm				30-60 cm				60-90 cm			
R	NO_3^-	NO_2^-	$P_2O_5^{-}$	K_2O	NO_3^-	NO_2^-	$P_2O_5^{-}$	K_2O	NO_3^-	NO_2^-	$P_2O_5^{-}$	K_2O
M	15.80	0.05	0.34	1.49	10.27	0.05	0.21	1.28	20.50	0.05	0.15	0.79
Md	17.10	0.5	0.35	1.39	8	0.04	0.17	1.29	11.50	0.05	0.15	0.79
SD	4.60	0.03	0.12	0.83	4.25	0.01	0.16	0.50	23.12	0.01	0.09	0.25
SE	1.81	0.01	0.07	0.33	1.73	0.01	0.06	0.20	10.3	0.01	0.04	0.11
N	7	7	7	7	7	7	7	7	6	6	6	6
Organic orchard												
D	0-30 cm				30-60 cm				60-90 cm			
M	10.10	0.03	0.12	1.39	30.55	0.05	0.01	1.19	7.00	0.05	0.15	0.64
Md	-	-	-	-	-	-	-	-	-	-	-	-
S D	4.81	0.00	0.10	0.35	29.91	0.01	0.01	0.84	0.56	0.01	0.21	0.11
SE	1.5	0.00	0.06	0.25	21.15	0.05	0.01	0.60	0.40	0.01	0.15	0.25
N	2	2	2	2	2	2	2	2	2	2	2	2

Where :

R = residues D = depth M= mean Md=median

SD=standard deviation SE=standard error N=number of samples

Table 5.5 shows the mean, median, standard deviation, and standard error all residues in both the inorganic and the organic fertilization application. The mean values and the standard error margin of **nitrate residues** in the inorganic orchards decreases from 15.80 ± 1.81 mg/l at depth of 0 to30 cm to 10.27 ± 1.73 mg/l at depth 30 to 60 cm and the increases again to 20.50 ± 10.3 mg/l. For the organic orchards, the mean nitrate residues increases from 10.10 ± 1.5 mg/l at depth of 0 to 30 cm to 30.55 ± 21.15 mg/l at depth of 30 to 60 cm and decreases to 7.00 ± 0.40 mg/l at depth of 60 to 90 cm.

The mean values and the standard error margin of **phosphate residues** in the inorganic orchards decreases from 0.34 ± 0.07 mg/l at depth of 0 to 30 cm to 0.21 ± 0.06 mg/l at depth 30 to 60 cm and further decreases to 0.15 ± 0.04 mg/l. For the organic orchards, the mean phosphate residues increases from 0.12 ± 0.06 mg/l at depth of 0 to 30 cm to 0.01 ± 0.01 mg/l at depth of 30 to 60 cm and decreases to 0.15 ± 0.15 mg/l at depth of 60 to 90 cm.

The mean values and the standard error margin of **potash residues** in the inorganic orchards decreases from 1.49 ± 0.33 mg/l at depth of 0 to 30 cm to 1.28 ± 0.20 mg/l at depth 30 to 60 cm and a further decreases again to 0.79 ± 0.11 mg/l. For the organic orchards, the mean potash residues increases from 1.39 ± 0.25 mg/l at depth of 0 to 30 cm to 1.19 ± 0.25 mg/l at depth of 30 to 60 cm and decreases to 0.64 ± 0.25 mg/l at depth of 60 to 90 cm.

5.4. Discussion

The accumulation of nitrate residues in soil in citrus orchards may show that nitrates might contribute to environmental degradation. In the study area, 2 soil samples obtained from Guzelyurt-3 at depth of 30-60 and Yayla-1 at depth of 60-90, (constitute about seven percent) of the total sample were found have nitrate-NO_3 above nitrate drinking water standard of 50 mg/l. This implies that the soils at these locations and depths have high affinity to store nitrate. As a result, the ground water underneath such locations might be safer relative to nitrate contaminant level for drinking water. Ninety three percent of the soil this implies most of the nitrate might have been taken up by the plants or leached into the ground water resources. Some sample orchard has nitrate concentration below the drinking water limit at different depths. Nitrate movement process in soils of citrus orchards across all three sampling depth in this study area, is evident and this may put the ground water resource at risk of nitrate pollution. In the study, it has been noticed that, 25 kg of soluble mixed NPK fertilizer per donum are generally recommended for orchards with younger citrus trees while the orchards with older citrus trees receive 50 kg per donum of the same fertilizer. The nutrient uptakes of both young old citrus plants are not similar. In terms of nutrients residues in both cases of orchard types, there was no significant difference. This can be accounted for by the fact that the younger plants will generally need less nutrients as compared to the older plants that puts the ground water resource at risk of nitrate pollution.

In summary, the nitrate residues in soils of citrus orchards might be an indication that the amount of NPK fertilizer and organic manure application on the soils exceeded the plant uptake.

In the soil, nitrogen exists in different form (nitrate, nitrite and ammonium ions) which interacts with one another and the plants, animals and microorganisms. These interaction processes together with other factors like the soil texture, cation exchange, climate, irrigation practice, and the timing, type and quantity of fertilizer application controls the fate of nitrogen in the soil.

Guzelyurt has climatic conditions which are typical of the Eastern Mediterranean geographic location with temperature rising to above 40˚C in summer and an annual rainfall of approximately 280mm. Precipitation and irrigation water is responsible for the facilitation of leaching processes across the soil profile. Hence the climatic condition of very hot summer and mild rainfall tends to increase nitrate accumulation in the soil. The climatic conditions give a better range of temperature conditions for soil bacteria (nitrosomonas and nitrobactas) to thrive (Morrill and Dawson, 1967). These bacteria together with other soil organisms facilitate the conversion of soil nitrogen from synthesized N, P, K fertilizer, composed fertilizer and manure in the soil to nitrate, nitrate and ammonium compounds interchangeably via a reversible process like nitrification, mineralization and denitrification.

Nitrosomonas *Nitrobacter*

Ammonium $\uparrow \leftrightharpoons$ Nitrite $\uparrow \leftrightharpoons$ Nitrate

Higher temperature and pH range of 5.5 to 10 with optimum pH of 7are favorable conditions for the chemical transformation of nitrate to nitrite and vice versa. The occurrence of microorganisms in the soils might be correlated with soil reaction and other acidity related properties. *Nitrosomonas* and *Nitrobacter* organism numbers and proliferation characteristics influenced by soil environment accounted for the four nitrification patterns observed in the above chemical reaction. At high temperature, the forward reaction is favoured whereas, at low temperature, the backward reaction is favored. This explains why the values for nitrite are very low as compared to that of nitrate as shown in Figure 5.1 and Figure 5.2, respectively. The pH values in Guzelyurt falls within optimum range for nitrosomonas and nitrobactas activities. Hence, these microorganisms can be used to control soil nitrogen.

In summer with very high temperature and irrigation by drip method in the citrus orchards, the leaching potential is low. However, the evaporation of soil water increases. In winter and spring, there is a higher potential of leaching of nutrients to groundwater resources by precipitation.

The organic orchards (Guzelyurt-2 and Guzelyurt-3) also show high values of nitrate soil residues. These organic orchards are mostly fertilized with animal waste and compost manure. This implies that the animal waste and compost manure also has high nitrogen content. Guzelyurt-2 and 3 nitrate residues were 8.6 and 11.8 mg/l, respectively as compared to Guzelyurt 1 that is 23.9 mg/l at depth of 0-30 cm. At depths of 30-60 cm, the nitrate value for Guzelyurt was very high 51.7 gm/l.

Guzelyurt shows great variation in soil texture in different locations and at different depths ranging from sandy loam, loamy sand, loam, loamy clay, clayey loam soil. These different soil types have different cation exchange abilities. The sandy soils in Kalkanli though in an abandoned orchard generally show less nitrate retention because it has the least cation exchange capacity with relatively larger particle grain sizes that influence percolation of soil water and soluble nitrate. Although nitrate can leach readily within the soil profile, soils with more silt and clay (clayey loam) texture like Gaziveren, Aydinkoy, Yayla turns to measure more nitrate than the other locations with similar soil texture. This can be account for by other facture like amount of irrigation water and citrus tree density within the orchards. In orchards with denser the trees, the evaporation of soil water becomes less as compared with sparely populated orchards. Dense orchards mean large over-soil canopy surface area. As a result, less evaporation which implies decreased in the soil nitrate concentration that can eventually leached to ground water resources. Hence, leaching of nitrate beneath the plants root zones is controlled by a good number of factors.

Plants uptake of nitrogen supplied to the soil is also a controlling factor of how much residues can be measure in the soil sample obtained from any particular location at any point in time. The soil water containing the soluble nitrate generally flows via the soil since they are not absorbed into the root systems of the plants.

These results closely tally with nitrate-N residue in soils of citrus orchards in Guzelyurt in Northern Cyprus across three sampling depths of soil. The nitrate in soil of inorganic orchard at depth of 0-30 cm ranges from 9.3 to 23.9 mg/l, at depth of 30-60 cm, it ranges from 5 to 15.8 mg/land at depth of 60-90 cm; it ranges from 2.8 to 71.2 mg/l.

The soil textures show slight variation with depth from 0-90 cm in some of the orchards. The variations also affect the fate of plants nutrients (nitrate, nitrite, phosphate and potash) in the soils different ways. In the study area, the variation in soil texture with depth in some orchards might be due to transported soils from other locations to enhance the orchards soil quality. Such soils turn to have different chemical and mineralogical composition. As a result, the cation exchange ability of orchards with transported soils is altered across the different depths. The nitrate from both inorganic and organic manure will be absorbed by the clay minerals in clay rich soils. In such situations, the leaching potential for nitrate in orchards with transported clay soils will reduce, consequently increasing the nitrate concentration in soils at such deeps. The implication is that ground water might be least affected by nitrate pollutants in soils that are rich in clay minerals. On the other hand, in orchards with high proportion of sand across depths, the nitrate concentration is low. This might have leached through the soil profile to pollute the ground water resource.

The variation in nutrient residues (nitrate and nitrite) accumulation across the sampling depths might be accounted for by the microorganisms' population which plays a leading in the conversion of nitrate to nitrite and verse versa. Across the different depth, the soil pH and temperature influence the microorganisms' population. This also explains why at certain depths there are more nitrite residues than others in the different orchards.

A comparison of phosphate residues on in inorganic, organic and abandon orchard shows that at the end of a complete citrus farming season, there is phosphate accumulation on the soil that might possibly have resulted from the inorganic and organic fertilization practice. However, the amount of soil phosphate residues in the soil at different sampling location and at different depths varies greatly because of the heterogeneous nature of the soil. These variations can be attributed to a good number of factors such as climatic conditions, amount of irrigation water, and the biogeochemical processes that are involved in the fate of inorganic and organic phosphate in the soils.

The mean phosphate amount of 0.35 mg/l for inorganic orchard, at depth of 0-30 surport the fact that phosphate accomulates most at the topmost profile of the soil as opposed to 0.21 mg/l and 0.15 mg/l for depth of 30-60 cm and 60-90 cm respectively.

The accumulations of soil phosphate residues were significantly higher in the inorganic, and organic orchards were significantly higher than that of the abandon orchard. The biogeochemical processes like phosphate adsorption and absorption that controls the fate of phosphate in the soil are influenced by soil physical properties like texture, mineralogy and porosity. In this study, Yayla-1 with loamy soil texture shows the highest concentration of phosphate. This is due to the fact that loamy soils are generally rich in plants nutrients. Although loamy soil has approximately balanced amount of sand, silt and clay, the mineralogical content of the clay portion of the soil in Yayla-1 might be very rich in hydrous and aluminum oxides, and alumino silicates. They will react with phosphate solutions to produce an isomorphous series of iron and aluminum phosphate thereby increasing phosphate concentration in this location.

In this study, the relationship between plant age and soil nutrient residues has not been investigated. However, the young citrus trees might be having a lesser amount of nutrient uptake as compared to the older citrus trees because the residue measured at the different orchards does not tally much.

CHAPTER 6
CONCLUSION

The amount of nitrate, nitrite, and phosphate and potash residues accumulating in the soil is determined primarily by a survey twenty nine soil samples obtained from ten citrus orchards in Guzelyurt district and this was followed by laboratory analysis of the samples. Based on the analysis of the soil samples of the inorganic, organic and the abandoned orchards, the main factors contributing to the residues in the soil can be attributed to over application of manure and excessive fertilizer application that exceeds plants uptake.

The results of this work may imply that agrochemical fertilizer application on citrus orchards in TRNC may have a long term effect on ground water quality of the Guzelyurt aquifer. After evaluation of twenty nine soil samples, some amount of nitrate, nitrite, potash, and phosphate were deposited. This study has confirm that nitrate residues in the study area in TRNC citrus orchards at the season of investigation, ranges from 9.3 to 23.9 mg/l, at depth 0-30 cm, 5 to 15.8 mg/l at depth of 30-60 cm and 2.8 to 71.2 mg/l at depth of 60-90 cm for the inorganic orchard. The emphasis is places on nitrate because of it direct implication of human health.

The average nitrite was 0.05 mg/l across all sampling depths. For phosphates, average values of 0.34, 0.21 and 0.15 mg/l were recorded at depths of 0-30, 30-60 and 60-90 respectively. For potash, average values of 1.49, 1.28 and 0.79 mg/l were recorded for the inorganic orchards.

The two types of fertilization practice that are common in TRNC are inorganic (agrochemical fertilizers) and organic (animal manure).The most common inorganic fertilizers were found to be the mixed soluble NPK fertilizer. This soluble mixed NPK fertilizer that is applied to the citrus orchards in TRNC contains 20% by volume of nitrogen (nitric nitrogen 6%, ammonium nitrogen 4% and urea nitrogen 10%), 20% by volume of water soluble phosphorus as phosphate (P_2O_5) and 20% by volume of water soluble potassium as potash (K_2O). This is the requirement to maintain sustainable soil nutrient management for citrus cultivation. After all these required nutrients are applied by the farmers in their orchards through different forms and types of fertilizers, the residues on the soils in any quantity contributes significantly to soil quality degradation.

This study confirms that in TRNC citrus orchards, the soils weather fertilized or unfertilized, contains some amount of nutrient residues, abandoned orchard values can be considered to be the background residual level and throughout this study for nitrate, nitrite, phosphate and potash. However, these nutrient residues vary greatly based on the soil texture, climatic conditions, biogeochemical processes and fertilization practice. In an attempt to quantify nitrate, nitrite, phosphate and potash residues that are being deposited on the soils of citrus orchards at the end of 2012 farming season, it can be concluded that both fertilizer and organic manure contributes to nitrate residues on the soils. However, some quantities of potash and phosphate residues were also recorded from some of the samples of both the organic and in organic orchards. Some of the soil samples from the organic orchards and from the abandoned orchard recorded zero phosphate residues. Based on the results, at the end of the each citrus growing season, significant amount of nitrate, nitrite, potash and phosphate residues were recorded from soil samples obtained at different depths following both fertilization application practice within the study area. Assuming the abandon citrus orchard (Kalkanli orchard) as control orchard for the investigation, that orchard has the lowest values for nitrate and nitrite residues at all depths.

Since the soil is a component of the environment, there is no doubt that agrochemical fertilizer application on soils of citrus orchards is gradually degrading the soil quality and leading to soil contamination. This implies that over time, the soil contamination problem will increase if no action is taken as a result of the cumulative effects of these residues. Since, this research has confirm residues of nitrate, nitrite, potash and phosphate in the soil that might be resulting from agrochemical fertilizer application, there is need to sensitize the farmers on good soil management practice that can sustain the soils of their orchard.

It is worth noting that this work is the first research on potential environmental impact of agrochemicals residues of this kind on soils of citrus orchards in TRNC and therefore forms the ultimate fundamentals of further research in similar domain. Additionally, this work has created research collaboration between Middle East Technical University, European University of Lefke and the Local Municipal laboratory of Guzelyurt. These ties were very useful in the transfer of technical know-how throughout the research. It is suggested that these ties should be further strengthen to bridge the gap research collaboration between institutions and government authorities in TRNC.

6.1. Limitations and Recommendations for further research

The duration for this research study was relatively short for carrying out periodical sampling and laboratory analysis to generate a good number of data that could be used for further statistical analysis. As a suggestion it is therefore recommended that in the future, further studies should be done, with sampling undertaken at least three times across all the chosen orchards per year: That is to say, before the first fertilization period; before the second fertilization period and after the harvest. This periodic sampling can be done for approximately 5 years in order to be able to calculate the annual rate of residue accumulation.

The biogeochemical processes of the fate of agricultural fertilizers and other pesticides in an agro-ecosystem (soils and groundwater) of Guzelyurt were not done because it is outside the scope of this research investigation. Hence, it is recommended that a further research should be conducted that will monitor the role of microorganisms on the fate of agricultural fertilizers in Guzelyurt district.

It is also recommended that a survey of nitrate contamination of groundwater resources in the underlying aquifers from wells that are supplying irrigation water should be tested along soil the soil samples to know the level of ground water contamination.

With sampling depth of 0 to 90 cm, at interval of 30 cm depth, it is not possible to have a graphical representation of residue concentration variation with depth. It is also recommended that a similar research should be conducted with increased number of sampling depths in other to be able better visualized the residual concentration variation with depths.

In addition, it is recommended that the farmers in TRNC should use agrochemical fertilizer carefully and be aware of their possible effect on the environment. The farmers can ensure that plants used up most all of the nutrients applied in the fertilizers or other soil amendments by following three basic principles which are:

- Apply fertilizer / soil amendment at rates recommended *after* soil and plant tissue testing.
- *Match* fertilizer /soil amendment application with time of plant need.
- *Minimize* run-off, soil erosion and leaching.

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