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THE IMPACTS OF LAND USE ON GROUNDWATER QUALITY IN THE NORTHEAST YUCATAN PENINSULA REGION

Tesis que presenta

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RECONOCIMIENTO

Por medio de la presente, hago constar que el trabajo de tesis de Daniel Nathan Isaiah Smith titulado "The impacts of land use on groundwater quality in the Northeast Yucatán Peninsula region." fue realizado en la Unidad de Ciencias del Agua, en la línea de Calidad y Uso Sostenible del Agua, en el Laboratorio de Fisicoquímico y Cromatografía, del Centro de Investigación Científica de Yucatán, A.C., bajo la dirección del Dr. Eduardo Cejudo Espinosa y la Dra. Rosa María Leal Bautista, perteneciente al Programa de Posgrado en Ciencias del Agua de este Centro.

Atentamente.

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RESUMEN

La Península de Yucatán tiene un acuífero kárstico somero con fracturas y fisuras que facilitan la infiltración de contaminantes de la superficie hacia el agua subterránea debido a las actividades agrícolas. Las actividades agropecuarias en la región noreste del estado de Yucatán tienen una mayor influencia sobre la concentración de nutrientes en el agua subterránea que las actividades no-agrícolas en el Municipio de Benito Juárez debido al uso excesivo de agroquímicos. Los principales nutrientes en el agua subterránea, como amonio, fosfatos, nitratos, y micronutrientes como sulfatos y potasio, provienen de ambos usos de suelo. Otras sustancias como el herbicida ácido 2,4-diclorofenoxiacético (2,4-D) que se usa en la zona agrícola, pueden indicar la influencia de las prácticas de uso de suelo sobre las concentraciones de nutrientes en el agua subterránea. Un total de 14 pozos en ranchos fueron muestreados en la zona agrícola distribuida en el estado de Yucatán entre los municipios de Tizimín, Sucilá y Panabá, mientras que un total de 16 pozos de AGUAKAN fueron muestreados en la zona no-agrícola del municipio de Benito Juárez en Quintana Roo. El muestreo estacional se realizó para ambas zonas durante las temporadas de lluvias, frente frío y secas. Las muestras fueron procesados a través de membranas de filtro (0.45 µm de tamaño de poro). El análisis de nutrientes fue realizado usando métodos colorimétricos usando espectrofotómetro (Eppendorf Bio Spectrometer) y cromatógrafo de iones (8821C Metrohm). La detección del herbicida se llevó a cabo utilizando el método de extracción en fase sólida en cromatografía líquida de alto rendimiento (HPLC). Los parámetros fisicoquímicos temperatura, conductividad eléctrica, sólidos disueltos totales, pH y potencial redox se mantuvieron estables y mostraron poca variación entre ambas zonas y las tres temporadas. Los promedios de concentración de nutrientes fueron más altos en la zona agrícola que en la zona no agrícola, y los valores más altos se observaron durante la temporada de lluvia. Existen diferencias significativas entre los promedios de concentraciones para nitrato y potasio; durante la temporada de lluvia la concentración de nitratos fue 7.6 mg $N\text{-}NO_3^-$/l para la zona agrícola y de 1.0 mg $N\text{-}NO_3^-$/l para la zona no-agrícola. El potasio tuvo un promedio de 11.4 mg K^+/l para la zona agrícola y 5.4 mg

K^+/l para la zona no-agrícola. Las muestras de herbicida en la zona agrícola durante la temporada de frente frío, mostraron curvas de absorbancia similares a sub-productos del 2,4-D, triclorofenol y diclorofenol. Solo un sitio en la zona no-agrícola tenía trazas de sub-productos del herbicida. El exceso de nutrientes aplicados en los campos agrícolas es susceptible de infiltración, lo que afecta la calidad del agua subterránea. Las buenas prácticas agropecuarias, como las dosis prescritas para la aplicación de agroquímicos, el manejo del ganado y el uso de suelo deben implementarse para reducir el riesgo de contaminación del agua subterránea.

ABSTRACT

The Yucatan Peninsula is a shallow karst aquifer with fractures and fissures that facilitates the infiltration of surface contaminants into groundwater through agricultural activities. Agricultural activities in the northeast region of the state of Yucatán such as the application of agrochemicals have a greater influence on nutrient concentration than non-agricultural activities in the Municipality of Benito Juarez. Main nutrients in groundwater such as ammonia, phosphates, nitrates, and micronutrients such as sulphates and potassium, can originate from both land use types. Other substances such as the herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D), which is used in the agricultural zone, can indicate the influence of land use practices on groundwater quality. A total of 14 wells on ranches were sampled in the agricultural zone distributed in the state of Yucatán among the municipalities of Tizimín, Sucilá and Panabá, while a total of 16 AGUAKAN wells were sampled in the non-agricultural zone in the Municipality of Benito Juárez in Quintana Roo. Seasonal sampling was conducted for both zones during the wet, cold front and dry seasons. Samples were processed through filter membranes (0.45 μm pore size). Nutrient analysis was conducted using colorimetric methods using a spectrophotometer (Eppendorf Bio Spectrometer) and chromatographic methods using an ion chromatograph (8821C Metrohm). The herbicide detection was conducted using the Solid Phase Extraction Method followed by High Performance Liquid Chromatograph-Diode- Array Detection. Physicochemical parameters such as temperature, electrical conductivity, total dissolved solids, pH and redox potential were stable and showed little variation for both zones and among the three seasons; while nutrient mean values were higher in the agricultural zone than the non-agricultural zone, highest in the wet season. Notable differences among mean values for nutrients existed for nitrate and potassium. During the wet season, nitrates had a mean value of 7.6 mg $N\text{-}NO_3^-$/l for the agricultural zone and a mean value of 1.0 mg $N\text{-}NO_3^-$/l for the non-agricultural zone. Potassium had a mean value of 11.4 mg K^+/l for the agricultural zone and a mean value of 5.4 mg K^+/l for the non-agricultural zone. The herbicide samples for two sites in the agricultural zone during the cold front showed absorbance curves similar to 2,4-D by-products trichlorophenol and dichlorophenol

season, one site in the non-agricultural zone had traces of one by-product. However, for the dry season sampling, only one site in the agricultural zone indicated the presence of 2,4-D. Surplus of nutrients applied in agricultural fields is susceptible to infiltration, which later affects groundwater quality. Best practices methods such as prescribed doses for agrochemical application, livestock and land use management should be implemented to reduce the risk of groundwater contamination.

1. INTRODUCTION:

1.1 Groundwater

Groundwater is described as fresh water originating mainly from precipitation that soaks into the soil and then to the aquifer. Groundwater has been extracted for domestic, agricultural and industrial use. Successful methods of extracting groundwater to the surface have increased over time; groundwater is an important resource as it makes up two thirds of the world's fresh water resources (UNESCO, 2004). Groundwater is stored geological reservoirs call aquifers which are made of rocks from different geological ages and types with fluvial deposits such as such as gravel, clay, silt and sandstone (Freeze and Cherry, 1979). Groundwater can exist in aquifers for hundreds and thousands of years or serve as a recharge supply for surface water bodies (USGS, 2017). Secondly, groundwater is found in two zones the unsaturated and saturated zone. The unsaturated zone mainly consisting the soil layers with water retained in its pores, whereas in the saturated zone all pores and rocks are filled with water (USGS, 2017). The unsaturated zone consists of carbonate and evaporate rocks these carbonate rocks are formed from calcium, magnesium, calcite and dolomite (Neven, 1996). Karst aquifers are composed of unconsolidated sediments that originate from the deposition of geological material through the natural process of weathering (Hernandez-Terrones et al.,2011).The vadose zone in shallow karst aquifers have an average thickness ranging from 10-20 m with fractures and fissures that influence infiltration rates (Bauer-Gottwein et al.2011).This characteristic gives karst aquifers high hydraulic conductivity which facilitates the vertical and horizontal flow of water (Hernandez-Terrones et al., 2011). Groundwater is stored in aquifers, which are geological storage systems from which groundwater is extracted for industrial and domestic use. Groundwater water is composed of ions such as magnesium, calcium, potassium, chloride among others that come from the dissolution and precipitation of minerals in karst aquifers (Neven, 1996). Ions originating from precipitated minerals such as calcites, dolomites, aragonite among others (Neven, 1996). The concentration of these ions in groundwater will mainly depend on the dissolution rate which is influenced by seasonal and geological factors, however anthropogenic inputs also contributes to ionic concentration in groundwater (Cabrera et al.,2002).

Groundwater quality is of importance as it is a main source of potable water. Water quality is determined by physical and chemical properties such as dissolved solids, conductivity, redox potential and mineral content (Helmer and Meybeck, 1996). In general, three main factors: natural processes such as weathering of rock material, anthropogenic activities and atmospheric input (Jiang and Yan, 2010) influence groundwater quality. However, groundwater quality can be influenced by two main land use activities such as the use of agrochemicals in agricultural zones and the input from natural processes in non-agricultural zones (Jiang and Yan, 2010). Groundwater water quality is also determined by the percolation rate of the unsaturated zone meaning the time it takes for surface water to reach groundwater through a porous medium, aquifers are vulnerable to contamination with high percolation rate (Harter, 2004). Secondly, the natural attenuation capacity which is the ability of soil to retain or degrade substances before it reaches groundwater is a factor that is considered to determine vulnerability to contamination, however soil capability of degrading organic matter through microbes can influence concentrates of dissolved substances through leaching during the wet season (Harter, 2004). Other factors such as geochemical processes; buffering, redox processes, sorption, dissolution and precipitation which are important in maintaining aquifer functions (Vissers, 2005). Buffering is a process which involves carbonate equilibrium maintaining pH between neutral ranges (6-7 pH). Redox potential involves the process of groundwater sediments and aquatic microbes capacity to reduce oxygen, nitrate, sulphate and other ions (Harter, 2004). A main component of aquifer sediments comes from organic matter which contributes to the dissolution of rock material via carbon inputs coming from the deposition of organic matter increasing carbon dioxide in the vadose zone which acts as a catalyst for the process of karstification. Maintaining water quality is important for sustainable development to ensure resources for the present and future generation. Water quality helps to maintain and improve, human health, reduce poverty, improve food security and preserve ecosystems (UNESCO, 2004). The assessment of water quality includes monitoring to define the condition of a given water body. Water quality monitoring includes quantifying trends in water quality such as dissolved chemical contents in relation to seasonal and anthropogenic factors; also, to define the cause of observed conditions and trends (Helmer and Meybeck, 1996).Water quality is important to determine the adequate use of water sources in the agricultural, industrial and public sectors. Although groundwater is naturally protected from the land surface through soil layers and geological material, potential contamination is caused through the leaching of anthropogenic waste from the land surface. Groundwater has some natural components such as calcium, potassium, sulphate, magnesium among others (UNESCO, 2004).The chemical composition of groundwater determines its usefulness for specific purposes. Groundwater that is of good quality is free of harmful pathogens and chemical substances originating from anthropogenic sources (UNESCO, 2004).

Groundwater is one of the most important natural resources several countries depend mostly on groundwater such as, Tunisia 95%, Belgium 85% and Germany 75% (UNESCO, 2004). In arid countries groundwater is mainly used for irrigation, in the United States of America 45% of the land is irrigated by groundwater, 58% in Iran and 67% in Algeria (UNESCO, 2004). Concerning tropical countries groundwater is of importance for irrigation. In Bangladesh 80% of irrigation water comes from an aquifer, India 60 % and 35 % Pakistan (Shamsudduha, 2013).

1.2 Groundwater in Mexico

In Mexico, water use is regulated by the National Water Commission (Comisión Nacional del Agua, CONAGUA for its name in Spanish). Groundwater is important for the country's socio-economic development, and it represents almost 40% of the total water allocated for consumptive usage (CONAGUA, 2016). In Mexico, there are approximately 653 aquifer systems, 37% of Mexico's potable water sources come from its aquifers (CONAGUA, 2014). Water use in Mexico is divided into five sectors; Agriculture, Public Use, Industry, Energy use and Hydroelectric use. However, groundwater is at risk due to excessive extraction, in the year 2014 a total of 106 aquifers have been reported to be overexploited (CONAGUA, 2015). As population increases, the demand for water increases as well. A recent estimate stated the total national demand for water is more than 97.9 million cubic meters (CONAGUA, 2016). 33.6% of the water used for agriculture comes from aquifers and 40% of the water for public use comes from aquifers on a national basis in Mexico (CONAGUA, 2016).

On an annual basis, Mexico receives about 1,449,471 million cubic meters of water in the form of precipitation. However, about 72.5% goes through the process of evapotranspiration; the other 21.2% is distributed to surface water systems and the remaining 6.4% is infiltrated as groundwater recharge (CONAGUA, 2015). Aquifers in Mexico are distinguishable by 37 administrative regions dividedly mainly by geographic locations (CONAGUA, 2015).The Yucatan Aquifer is divided into three main administrative regions; Yucatan West, Yucatan North and Yucatan East (CONAGUA, 2015). The division of groundwater management gives space for decentralized management through the concessions for groundwater use, where agencies have the responsibility of distributing groundwater and monitoring its quality for public use. In the year 2015 CONAGUA did an estimate for the water balance for the Yucatan Peninsula where they found the water input to be, 1,462.29 million cubic meters per year by natural inputs such as rainfall and surface runoff, natural recharge was 20,350.85 million cubic meters per year. The volumes for outputs were horizontal discharge output, 19,121.2 million cubic meters, groundwater pumping 1,209.2 million cubic meters (CONAGUA, 2015).The coastal outflow of groundwater was estimated to be 0.3-0.4 m^3 km^{-1} s^{-1} (Bauer-Gottwein et al., 2011).

In the state of Yucatan, a total 77,211,000 cubic meters of water is concessional use for agriculture, while 1,256,300 cubic meters is concessional use for public use. The state of Quintana Roo has a concessional for 839,000 cubic meters agricultural use and 723,600 cubic meters for public use (CONAGUA, 2017). However, groundwater resources are at risk by anthropogenic activities in urban and agricultural zones yielding substances potentially pollutants such as sulphates, chlorides and nitrogen among others. Karst aquifers are characterized by groundwater flow through conduits, such as pore spaces in the soil layer which permits the infiltration of water. Karstic aquifers are mainly composed of limestone, a rock largely composed by calcium carbonate ($CaCO_3$) dolomite $CaMg(CO_3)_2$ and gypsum ($CaSO_4$ -$2H_2O$) and other minerals such as aragonite which mainly depends on organic activity such as the production of CO_2 through decaying organic matter by bacterial activity (Cabrera et al.,2002).

The process called karstification is the process of carbonate rocks is transformed into minerals and dissolved ions as per water dissolution (Ford and Williams, 2007). Ions such as Na^+, K^+,Ca^{2+}, Mg^{2+} and SiO_4^{4-} are released through the dissolution of sedimentary rocks creating an alkaline environment (Ford and Williams,2007). The Yucatan Peninsula has a karstic aquifer system that has a porous and fragile geological platform that undergoes geophysical changes frequently such as the weathering and dissolution of rock material (Cabrera et al., 2002) such as quaternary limestone, composed of sediments consolidated of the mineral $CaCO_3$ (Escolero et al., 2005). Conduits such as fractures and intergranular spaces permit groundwater flow; factures in carbonate sediments play also an important role in groundwater flow. There are two types of flows through fractures: laminar and turbulent flow. Turbulent flow involves chaotic changes in pressure and flow velocity, whereas laminar flow is basically the free and parallel flow with no disruptions (Neven, 1996).

The Yucatan Peninsula is one of the largest karstic environments in Central America and the Caribbean having a total groundwater system of 165,000 km^2 (Castro-Graniel and Gil, 2010). The coastal area is more or less 20 km in width, composed of compacted marine carbonate rocks (Castro-Graniel and Gil,2010).The Yucatan Peninsula is unconfined and shallow aquifer with an average depth of 30 meters in which groundwater flow patterns mainly run from inland toward the north and east coast (Perry et al., 2002). The aquifer consists of a fresh water lens and a saltwater lens including a mixing zone in between (Beddows, 2007). Infiltration and groundwater flow is permitted by intergranular voids which creates Pleistocene deposits along the coast (Beddows, 2007). The limestone geological structure of the Peninsula extends to a depth of 1,000 m near Merida (Yucatan) and about 150 meters near the Caribbean

Coast (Beddows, 2007).There is also the presence of sinkholes. The permeable geological structure mainly composed of aragonite, calcite and dolomite serve as a conduit for throughout the geo-hydraulic process such as groundwater flow, aquifer recharge and discharge (Cabrera et al. 2002). Quaternary rock types are found in the coastal zones of the peninsula, with calcite deposits, crystallized calcites can be found up to a depth of 120 meters in the geological structure (Castro-Graniel and Gil, 2010). The Peninsula also has pure carbonate and evaporate rock which when dissolved leaves almost no residues (Perry et al., 2002). Apart from carbonates and evaporates, the Peninsula also consist of anhydrites precipitated from the Miocene (23.03 million years ago) and Cretaceous periods 145.5 million years ago (Rosenfeld, 2002).

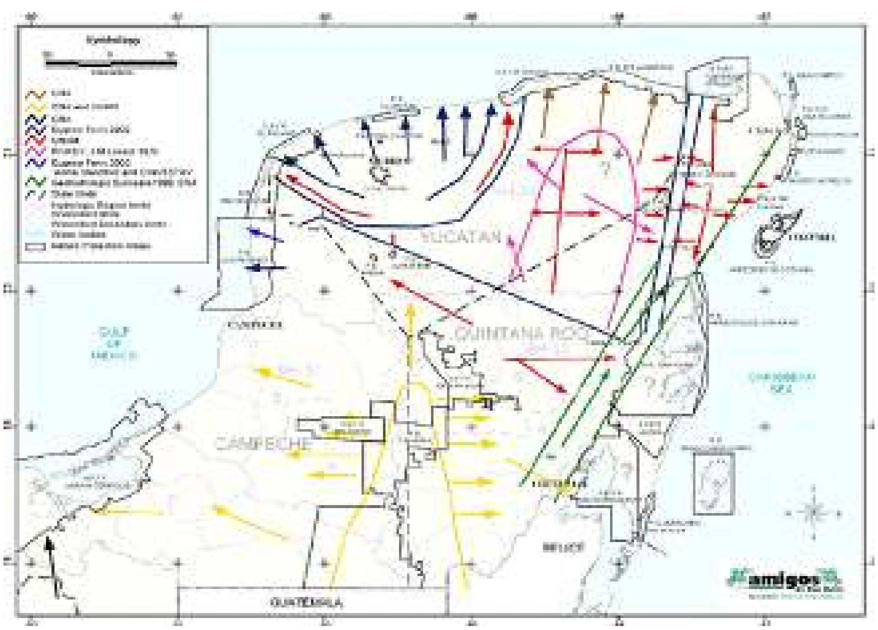

Figure 1: Figure illustrating the suggested flow patterns of groundwater with flow directions from inland to coastal zones. (Taken from Bauer-Gottwein *et al.,* 2011)

1.3 Land Use Change

Land use is the general modification of terrestrial surface through anthropogenic activities (Jiang and Yan, 2010). There are several land use types such as agriculture, urban, grassland, forest and wetlands among others. Land use change from non-agricultural to an agricultural type affects water resources in a specific manner, especially when water is used for crop production which includes deforestation, irrigation and fertilizer use. The amount of water used in the Yucatan Peninsula in 2016 was a total of 3,174.6 million cubic meters, divided into three main land uses; agriculture use (2,060.7 million cubic meters), public use (469.5 million cubic meters) and industrial use (635.4 million cubic meters), other use (9.1 million cubic meters (CONAGUA, 2016). According to these values, the agriculture sector uses more than half of the total amount of the concessional water in the Yucatan Peninsula. This shows that the use of groundwater for agriculture is of high importance; thus, groundwater resources can be considered stressed by agricultural activities. Land use change to agriculture can affect soil structure, which can reduce its retention capacity resulting in rapid infiltration of surface water to the aquifer making groundwater vulnerable to contamination (Jiang and Yan, 2010). The use of agrochemicals to enhance crop production exacerbates the introduction of nutrients into groundwater, in addition to pesticides used for different purposes.

Dissolved substances such as ammonia and phosphates are commonly used as fertilizers (SAGARPA, 1993). The recommended dose for the application of nitrogen to crops is between 92 and 300 kg/ha, the application rates depends on soil condition. Application exceeding recommended doses creates a surplus not used by crop for growth, which in turn can be leached into the aquifer (SAGARPA,1993). Land use management practices such as the application scale of agrochemicals (large or small scale) an the type of farming system (intensive, semi-intensive or non-intensive) have a great effect on water resources (Pacheco and Cabrera,1996).

The method of application can determine the potential infiltration of contaminants into groundwater, meaning manually applied or mechanically applied, also considering seasonality of application (Pacheco and Cabrera, 1996). The practice of mechanical application in an intensive or semi-intensive system determines the quantity of agrochemicals that is entering the unsaturated or vadose zone, which is then prone to leach through meteorological events such as rain, floods and natural disasters like tropical storms (Pacheco and Cabrera, 1996). Soil properties such as pore space, granular size and retention capacity will determine an aquifers vulnerability to contamination (Lerner and Harris, 2009). Last not but not least, once vegetation cover is removed for agricultural use, the soil structure is altered, which also changes porosity and water retention capacity (Lerner and Harris, 2009).

There are several main points as it pertains to the relationship between land use and groundwater. Groundwater underlies most of the landscape, making in prone to contamination by anthropogenic activities; land use affects groundwater resources through changes in recharge patterns (Lerner and Harris,2009). With agricultural development in recharge catchment zones, groundwater is vulnerable to degradation without proper land management practices as it pertains to the use of agrochemicals for crop growth. As a result, zonation for land use practices should be considered to mitigate groundwater contamination (Lerner and Harris, 2009). Secondly, other land use types such as non-agricultural areas, grasslands and forested areas that have minimal anthropogenic influence, tend to have natural inputs of dissolved substances to groundwater (Jiang and Yan, 2010). Natural processes such as the natural dissolution of karst contributes to mainly groundwater chemistry is mainly Ca-HCO_3 (bicarbonate) which is a soluble mineral in karst systems. In non-agricultural areas, dissolved substances such as sulphate can have natural origins from the dissolution of gypsum (Castro et al., 2009).

1.4 Agrochemicals

Agrochemicals are substances that aid crop growth, which are divided into pesticides and fertilizers; the most commonly used ones are fertilizers. An increment in agriculture production has occurred due to the introduction of agrochemicals such as chemical fertilizers since the 1900’s; however, proper application rates of fertilizers are important to prevent leaching in groundwater bodies (Maguire and Alley, 2009). The efficiency of fertilizers is dependent on soil characteristics, such as retention capacity and solubility properties (SAGARPA, 2009). In some cases, calcium carbonate is applied to neutralize soil pH in the occurrence of acidity (SAGARPA, 2009). There are several types of fertilizers such as ammonium nitrate, ammonium sulphate, ammonium phosphate, potassium sulphate, NPK (nitrogen, phosphorus, potassium) among others. Nutrients that are derived from fertilizers are mainly nitrates, phosphates and sulphates, which are important for crop growth and soil health (Pacheco and Cabrera, 1996). Nitrogen-based fertilizers should be applied as close as possible to the time of crop uptake, since nitrates can be lost from soils via leaching (Maguire and Alley, 2009). Agricultural activity requires the use of fertilizers, which is frequently applied in excess. The seasonal application of fertilizers would also determine the probability of leaching, applied just before the rainy season or during the rainy season can facilitate that a given amount of nutrients are leached into groundwater (Pacheco and Cabrera, 1996).

Ammonia is another main nutrient derived from fertilizer use. Ammonia exists in groundwater commonly from the use of nitrogen containing fertilizers (Kamal et al., 2015), but can also be from natural origin such as organic matter degradation. High concentration of ammonia in groundwater is an indicator of recent contamination, as it is not oxidized into forms such as nitrites and nitrates. Other factors such as the anaerobic decomposition of organic matter can influence ammonia concentrations (Kamal et al., 2015). Natural levels of ammonia in groundwater is usually below 0.2 mg $N\text{-}NH_4^+/l$, higher levels of ammonia is usually an indicator of industrial or urban pollution (Kamal *et al.,* 2015). Some of the nitrates in groundwater are derived from nitrification, the oxidation of ammonia into to nitrates. In the Yucatan Peninsula, fertilizers inputs were estimated around 23 kg N ha^{-1} and 48 kg P ha^{-1} into soils; however, surplus concentrations are leached into groundwater (Aranda *et al.,* 2011).

There are health complications associated with high concentrations of nitrates in drinking water, such as methemoglobinemia, a blood disorder in which abnormal amounts of methemoglobin is produced, gastric cancer and lymphoma (Obeidat *et al.,* 2013). Children can suffer adverse health effects because of consuming water contaminated with nitrate concentrations of 10 mg $N\text{-}NO_3^-/l$ or more, causing symptoms such as shortness of breath and even death (Pacheco and Cabrera, 1996). According to the Mexican water quality norms (NOM-127-SSA1-1994), the maximum permissible limit for concentrations of nitrates in water is 10 mg $N\text{-}NO_3^-/l$.

Another substance of interest as it pertains to agriculture is phosphorus. Phosphorus is an important component in agricultural fertilizers and essential element for plant life. However, excess amounts can lead to eutrophication in surface waters (Aranda et al., 2011). As phosphorus is a limiting nutrient and less soluble than other nutrients such as nitrates, it is more susceptible to be in surface runoff which then is transported to aquatic systems (Aranda et al., 2011). Eutrophication is the enrichment of receiving water bodies with mineral nutrients, leading to the production of algae and cyanobacteria which reduces dissolved oxygen (Correll, 1998). It has been estimated that out of a 100% of P contribution to soil from productive activities, agriculture contributes with 22 % portion of P and livestock contributes with 75% (Aranda *et al.,* 2011). Phosphorous concentration is normally lowest in soil solution with a range between 0.8-8 mg P/ kg soil, other clay soil types have ranges with lower values of phosphorus 0.20 – 2.8 mg P/ kg soil (Balik et al., 2009). Lower concentration ranges are attributed to soil retention.

There are other sources of phosphorus such as from the industrial sector contributing a total of 710 tons per year (Aranda et al., 2011) provided that it is mobilized by vertically moving water. Once an overload of phosphorus is present in the soil profile, leaching takes place where phosphorus is transported to the vadose zone and then into aquifers (Aranda et al., 2011). Dissolved oxygen in the unsaturated zone aids the release phosphorus bound to iron oxides but it can precipitate with calcium (Chen et al., 2011).Phosphorus precipitated with calcium, which is not taken up by plants in soluble form, is infiltrated into the aquifer contributing contamination. Inorganic phosphorus is fixed by plants and released back into the soil (Correll, 1998).

Natural fertilizers such cow manure are also used to enhance crop growth. Main nutrient components of manure include potassium, nitrogen and phosphorus (Infascelli et al., 2009). Lopez-Martinez et al., (2001) did a study in northern Mexico and found that potassium is one of the main nutrient in manure having a total of 2.5% composition followed by Nitrogen 1.5% and Phosphorus 0.14%. However, a study conducted by the Manitoba Agricultural Department (Canada) found nitrogen to be the main nutrient in manure. The amount of nutrients in manure was attributed to variable livestock diet composition, which can vary based on local cattle management (Manitoba Agriculture Department, 2015).

Manure use can improve soil porosity, structure and its water holding capacity (Infascelli et al., 2009). However, it can be a sources of pollution to groundwater if not managed properly. In countries where environmental regulations are few, manure is applied to soil continually, which causes nutrient overloads resulting in infiltration. Nitrogen in manure is mainly related to groundwater pollution while phosphorous is related to surface water pollution causing eutrophication (Pinos-Rodriguez et al., 2012). Nutrient needs for crop growth and estimated loss of nutrients after application should be assessed on a case-by-case basis (Infascelli et al., 2009).

Nitrate is termed to be the most mobile nutrient derived from manure. Infascelli et al. (2009) estimated leaked nitrogen from clay-loamy soils to be 25 kg N/ha. With the factor of seasonal influences such as rainy peaks, groundwater becomes more vulnerable to leached nutrients originating from manure application. INIFAP. (2017) also found that N and P loses in soil is a result of excessive fertilizer application. It is assumed that there is a significant correlation between rainfall and Total Nitrogen and Total Phosphorus in runoff after applying fertilizers (INIFAP, 2017). It has been found that nitrates are the main contaminants of surface and groundwater (Jiang and Yan, 2010; Pacheco and Cabrera 1996; Mencio *et al.*, 2011). The agrochemical residues that were not utilized by crops are retained in the soil, which then are transported by vertically moving water from the vadose zone into the aquifer (Pacheco and Cabrera, 1996). This is an important aspect as the vadose zone as it serves as a barrier between the land surface and the aquifer determining infiltration rate of dissolved substances (Gunatilake, 2016).

Finally yet importantly, sulphate is an inorganic compound found naturally in water through the weathering of rocks or water-rock interaction. Sulphates can give water a noticeable taste; and they can be detected in water through chemical testing (Nova Scotia Environment, 2008). Fisher and Mullican (1997) did a study on sulphate relations in groundwater; they showed that sulphate can be associated with other ions such as sodium through the process of continued groundwater flow and mineral-water interaction that causes the saturation of calcite, dolomite and gypsum. This natural input of sulphate can be a result of the dissolution-precipitation reactions in groundwater. However, saltwater intrusion, acid rock drainage, depositions from the burning of fossil fuels and the use of ammonium sulphate fertilizers are also possible sources of sulphates in groundwater (Castro et al., 2009). It is not easy to distinguish the contributions from natural weathering and anthropogenic inputs by assessing the chemical composition of groundwater alone; the relationship between sulphate and electrical conductivity in groundwater between land use types, can aid in identifying origins and the influence of temporal dynamics on groundwater (Jiang and Yan, 2010). Concentration of sulphate at 500 mg SO_4^{2-} /l or above, affects the taste of potable water; high concentrations have a corrosive effect on water pipelines (Gomis et al., 2000). Sulphate cannot be removed from water; however, treatment processes such as anion exchange, distillation and reverse osmosis can improve sulphate-rich water (Castro et al., 2009). High concentrations of sulphates in groundwater can lead to its oxidation by bacteria, which produce sulphuric acid creating an acidic environment (Castro et al., 2009).

The selective use of pesticides to control pests are with the aim of increasing crop production. Most farm systems apply pesticides just before irrigation, which can cause the infiltration of pesticide residues to groundwater (Caldas *et al.,* 2011). In addition, pesticides have the potential to pollute groundwater if it has a high solubility and extended half-life (from 2-3 weeks in soil and longer than 25 weeks in water; Caldas et al., 2011). The herbicide 2 4-Dichlorophenoxyacetic acid (2, 4-D) belongs to phenoxy compounds. These compounds are potentially toxic to humans causing damage to the nervous system, kidney and liver (Bovin et al., 2005). 2,4-D is used to control the growth of broadleaf weeds and grasses in crop lands. It is soluble at pH of 7 to 8 (NPIC, 2008). It is degraded by soil microbes between 20-90 days, in clay soils and loam soils tends to biodegraded within 10 days (Bovin et al., 2005). The herbicide is prone to leaching as sorption in the soil profile takes little over a day to reach equilibrium followed by the degradation process which starts after 10 ten days (Bovin et al., 2005). As 2,4-D is highly mobile in the soil layer, can be used as a tracer of contaminants in groundwater within agricultural zones.

The influx of nutrients in groundwater is not only caused by agricultural activities but also by urban activities (Chen *et al.,*2011). Groundwater is vulnerable to contaminants as it fractures and conduits facilitate the transport of dissolved substances into the aquifer (Vesper et al., 2001). There are non-point and point sources of contaminants. Non-point sources are diffused sources originating from various locations not clearly located. Point source contaminants originate from a localized point, for example, the effluent from a factory or sewage pipeline entering a water body at a specific point (Vesper et al., 2001). Agriculture is often a source of non-point contaminants and wastewater treatment plants are clear examples of point source contamination (Maguire and Alley, 2009).

The Yucatan Peninsula has important economic activities such as agriculture and tourism, which cause a high demand and pressure on the water resources (Bauer-Gottwein et al.,2011).The only available fresh water resource in the Peninsula is groundwater, the permeable limestone geological structure and this soil layer makes the aquifer vulnerable to contamination by the leaching of residues from anthropogenic activities into the aquifer (Bauer-Gottwein et al.2011). Anthropogenic activities such as a fertilizer application and the injection of treated sewage into the aquifer affect groundwater quality increasing concentration of nutrients (Guzman,2016).These values increase with a growing population as more waste is generated from a growing population the Yucatan aquifer is vulnerable to contamination and degradation.

2. PREVIOUS STUDIES

2.1 Dissolved Substances

One of the main sources of external nutrients into aquifers is caused by the excessive use of fertilizers. Natural concentrations of nutrients occur in the top soil to support crop growth; however, fertilizers are applied to enhance production yield (SAGARPA, 1993). A study conducted by Lawniczak *et al.,* (2016) examined the impacts of agriculture on groundwater in the region of central-west Poland by measuring concentrations of nitrates, ammonia and phosphates. They related leaching of nutrients to fertilizer application, timing and method. Thirty-four wells sampled during spring and summer yielded concentration as high as 15.51 mg $N\text{-}NO_3^-$,/l, 0.45 mg $P\text{-}PO_4^{-3}$/l and 11.59 mg $N\text{-}NH_4^+$ /l. Nitrates exceeded the limits set by the World Health Organization (10mg $N\text{-}NO_3^-$/l). This is to show that the surplus of nitrates in groundwater is likely coming from fertilizer application. Lawniczak et al. (2016) did a study on sources of groundwater pollution, leading to the conclusion that runoff from municipal waste and household sewage are main sources of ammonia (0.01 to 1.65 mg $N\text{-}NH_4^+$/l). The practice of fertigation, where farmers fertilize and irrigate soils to enhance crop production, use mainly urea, which is an ammonia based fertilizer. This makes ammonia less susceptible to leaching as it is absorbed in the soil; however, ammonia is nitrified to nitrates, which are negatively charged and not easily absorbed by soil particles, which results in leaching into groundwater (Bohlke et al., 2006).

Phosphorous also affects groundwater quality through the use of agrochemicals. A study conducted by Fronczyk et al., (2016) in an agricultural region in Poland found wells with phosphate concentrations from 0.3 to 1.0 mg $P\text{-}PO_4^{3-}$ /l attributed to the use of ammonium-phosphate based fertilizers. The values did not exceed the maximum permissible limit of groundwater quality set by the Polish authorities; nevertheless, some values were near the threshold value. Another study conducted in the wet and dry regions of Sri Lanka assessed the effects of fertilizers to in a rice paddy production; 12 % of the samples exceeded the maximum permissible limit set by the World Health Organization for potable water (Gunatilake, 2016). These high concentrations were attributed to the timing and quantity of fertilizer application. Although phosphate is useful for crop growth, it is a factor that contributes to algae growth and eutrophication in aquatic environments (Gunatilake, 2016). A similar case of phosphate pollution was assessed in southern India, evaluating groundwater in a region dedicating to rice production. Wells as much as 23 meters in depth were sampled in which water level fluctuations and nutrient concentration correlation was found based on precipitation patterns. Water level varied between 5 meters and 20 meters below ground level. Nutrient concentration increased as water level increased, leading to water exceeding 0.2 mg P-PO_4^{3-}/l (Elango and Rajmohan, 2005).

A study was conducted in China to determine the impact of urban land use on phosphate concentrations in groundwater found that average phosphate concentration in groundwater was 4.3 mg P-PO_4^{-3}/l,(Chen et al., 2011) which exceeded the limit set by the World Health Organization (1.0 mg P-$PO_4^{-3/}$l). According to these findings, high concentrations of phosphates are related to the discharge of untreated sewage and the use of phosphate based domestic products such as detergents from leaky or inefficient sewage. Another study conducted in Florida on 16 shallow wells found that phosphate concentration relates to onsite sewage treatment and disposal. Values of phosphates concentration in three sites ranged from 0.3 to 1.5mg P-PO_4^{-3}/l (Burnett et al., 2002), which surpassed the maximum permissible limit set by the WHO standards for drinking water

A study conducted by Roura-Boy *et al.* (2013) in an intensive agricultural and livestock area in northeastern Spain measure nitrate in karstic springs. Nitrate concentrations in that region yielded values within a range of 8 to 380 mg NO_3^-/l .The effect of fertilizer application does not only provoke high nitrate concentrations, but also high concentrations of phosphates (Roura-Boy et al.,2013). In Mexico, Munoz *et al.* (2004) conducted a study to determine the impacts of the use of ammonium phosphate fertilizers in the Valley of Huamantla (Tlaxcala). As much as 41% of the samples surpassed the limit of 10.0 mg N-NO_3^-/l (N) set by the NOM-127-SSA for human consumption. The varying concentration levels were attributed to dilution by precipitation, nitrate concentration being lower at the end of the rainy season as compared to the beginning. At the end of the rainy season, four samples exceeded the maximum limit, while seven samples passed the maximum limit at the beginning of the rainy season (Munoz et al., 2004).The study concluded that it is important to regulate fertilizer application and timing of irrigation to prevent the leaching of residues into aquifers. Another study related to the use of fertilizers and its effects on nitrate concentrations was completed in an aquifer of high importance in northern Mexico, due to the fact that supplies six municipalities with drinking and irrigation water. A total of 134 wells were sampled in the region, and 34% of the samples had concentration of nitrates that exceeded the maximum permissible limit (Rubio-Arias *et al*., 2007). They provide recommendations such as proper storage and cleaning of fertilizer containers and regulated doses for fertilizer application. Cervantes-Medel and Armienta (2004) did a similar study in the Mezquital Basin in central Mexico. Springs, wells and piezometers were sampled in agricultural zones. Maximum values ranging up to 19.6 mg NO_3^-/l exceeding the Mexican water standard limits for human, with an assumption that the presence of faults and fractures allowed the rapid infiltration of nutrient (Cervantes-Medel and Armienta, 2004)

The Yucatan Peninsula is a region dedicated to the production of short-term crops such as corn, cucumber, tomatoes and livestock production (INEGI, 2009). As a result, balancing the use of fertilizers is needed to mitigate impacts on groundwater quality. Pacheco and Cabrera (1996) conducted a study on the influence of fertilizer use on groundwater quality at the agricultural region south of the state of Yucatan. Concentration of nitrates and sulphates from four water supply wells with depth between 30- 40 meters, exceeded the maximum permissible limits set by the Mexican Norms (10 mg N-NO_3^-/l and 250 mg S-SO_4^-/l respectively). The study attributed high concentrations to the unregulated use of fertilizers. Wastewater disposal is a point source of pollution due to an increase in sanitation facilities and their discharges. This can place a threat on water resources in specific groundwater resources. Leaking of sewer systems and the introduction of wastewater into aquifers are both origins of high concentrations of nutrients in aquifers (Rojas-Fabro et al., 2015).

A study conducted by Obeidat *et al.* (2013) assessed the impact of a wastewater treatment plant on ground water pollution. The findings of this study showed that 50% of the samples yielded nitrate concentrations exceeding the threshold value for the World Health Organization. Nitrate and chloride are often linked with pollution of wastewater origin, since nitrate is a product of organic matter degradation and chlorine is used to disinfect treated wastewater.

There are several examples as it pertains to nitrates contamination from urban sources. For instance, a study conducted by Rojas-Fabro *et al.* (2015) in the city of Merida (Yucatan, Mexico), found that nitrate concentrations from groundwater supply systems ranged from 15.51 to 70.61 mg $N\text{-}NO_3^-$/l, surpassing the maximum permissible limit for drinking water. In addition, a positive correlation existed between nitrates and chlorides, indicating the influence of treated domestic wastewater sewage. Increased nutrient concentration was assumed to originate from septic wastewater plumes. Burnett et al. (2002) used silicate as a conservative tracer providing insight into the superficial origin of phosphates and the extent of wastewater plumes.

A study conducted by Castro et al. (2009) in Ticul western Yucatan, collected water samples from 19 wells with a range of 60-70 meters in depth. During the wet season, the concentrations of sulphates were notably higher in agricultural areas. The study attributed high sulphate concentrations coming from the leaching of ammonium sulphate-based fertilizers instead of natural sources such as the dilution of gypsum, which is a natural source of sulphates. This assumption was made due to the present land use in the area where higher concentration of sulphates were found in intense agricultural zones than less intense agricultural zones. Cervantes-Medel and Armienta (2004) found values as high as 360 mg $S\text{-}SO_4^{2-}$/l exceeding the Mexican water standard limits for human use (200mg $S\text{-}SO_4^{2-}$/l; NOM-127-SSA1-1994). Sanchez *et a*l. (2016) reported high levels of sulphates in a groundwater in the southern region of the

Peninsula. Maximum values as high as 750 mg S-SO_4^{-2}/l were attributed to three possible factors: 1) the presence of evaporite rocks; gypsum; anhydrites, 2) the discharge of wastewater or 3) saltwater intrusion.

2.2 Herbicides

Herbicides such as 2,4-D, are used to eliminate weeds from crop in agricultural lands. Kuwatsuka and Miya (1989) did a study on the effect of soil microbes on the presence of 2, 4-D in soils. This study also found that the degradation of 2, 4-D begins after 10 days in the presence of soil microbes. The leachability of 2, 4-D throughout the soil profile is dependent on soil properties as well as the population of microbes in the profile (Kuwatsuka and Miya, 1989).

Herbicides can be used as supporting evidence that agricultural activities have an effect on groundwater quality since they are applied in the surface and the only source is direct application into crops. A study conducted on the fate of 2, 4-D in an agricultural area in Manitoba (Canada) determined that 2, 4-D remain the soil between 10 and 60 days, which makes possible infiltration of 2, 4-D residues into groundwater .The assumption of the study was that 2, 4-D sorption in soil is facilitated by organic matter in the soil (Gaultier and Farenhorst, 2007).

This substance is important to measure in order to make associations with land use practices and groundwater water quality. Also to determine its concentration within both agricultural and non-agricultural sites, ensuring that concentrations do not exceed the maximum permissible limits of 50 mg/l in water for human consumption set by NOM-127-SSA1-1994. The use of 2,4-D in the Yucatan Peninsula is mostly used to maintain short term crop production such as corn, cucumber, beans among others (Sanchez et al., 2016). A recommended dose of 150mg/ha of 2, 4-D for the control of weeds was suggested by INIFAP.,(2017) for its application on pasture lands in the state of Yucatan. In corn fields, farmers apply 2,4-D when manual control of weeds fails, and application is based on experience on the effectiveness of the product, technical recommendations about the product and aggregated value of crops that requires delicate care (Sanchez et al.,2016). A study was conducted by Carbo *et al*. (2008) in an agricultural area to determine groundwater vulnerability to contamination by 12 pesticides (including 2,4-D) suggested that shallow aquifers are more vulnerable to contamination through leaching and agricultural runoff. The study also suggested the Solid Phase Extraction method using the HPLC-DAD was effective in detecting pesticide residues in water samples. Recommended timely and efficient application of pesticides to crop land will reduce the risk of groundwater contamination by pesticides (Carbo et al.,2008). Trivedi (2015) confirmed the residence time of 2, 4-D in soils to be between 10-50 days, depending on pore size of a given soil, soils that have macro-pores increase soil aeration which increases degradation rate. There are several byproducts derived from 2,4-D two being trichlorophenol and dichlorophenol. Trivedi et al. (2015), studied dichlorophenol as a chlorinated derivative of 2,4-D and found that this compound tends to last longer in the environment than 2, 4-D. Given the residence time of 2, 4-D in the environment, the detection of byproducts can serve as an indicator of the influence of 2,4-D on soil and water.

As it pertains to the use of 2,4-D in non-agricultural zones, as study conducted by Metcalfe et al. (2010) examined contaminants on the coast of the Yucatan Peninsula. The detection of 2,4-D at concentrations as high as 10.5 mg/l was attributed to its use in golf courses and gardens throughout touristic centers along the Rivera Maya strip (Metcalfe et al.2010). Escolero et al. (2005) also detected 2,4-D in groundwater in samples from ten wells near Merida (Yucatan). Some health risks associated with the exposure of 2, 4-D are possible cases of cancer, skin irritation, respiratory disruption and damage to the endocrine system (Vissers,2005). Through oral consumption of contaminated water having concentrations between 2 to 30 ppm exist a possible risk of cancer and potential endocrine disruption in the human body. In the year 2000 the European Union classified 2,4-D as substance that poses adverse health effects, as a result the regulatory use of the substance was implemented (Vissers,2005).

3. JUSTIFICATION

The use of agrochemicals in the agricultural zone of the Northeast region of the Yucatan Peninsula contributes to increased concentration of dissolved substances in groundwater, namely nutrients. As there is natural input of nutrients through the decomposition of organic matter, runoff and the dissolution of geological material, the use of agrochemicals creates a surplus of dissolved substances in groundwater, nutrients and herbicides included.

Groundwater is the primary source of fresh water in the Peninsula of Yucatan, which supports the food and tourism industry. With an increase in population and tourism, the demand for goods and services increases, more space for urban settlements is needed and agriculture produce will be needed in greater demand. Therefore, it is important to know the variability in concentrations of dissolved substances, in order to monitor water quality for its adequate use for human activities and environmental health.

This research aims to increase the knowledge of the current conditions of groundwater, quantifying concentrations of dissolved substances and identifying their dynamics in time and space through seasonal sampling. The importance of conducting seasonal sampling is to compare the effect of the three main seasons on groundwater quality in two different land use situations. Variable precipitation could influence the concentration of some substances in groundwater in areas with different land use activities, namely agricultural and non-agricultural areas. Comparing these two land uses and its effect on concentration of nutrients, micronutrients and pesticides in groundwater is important to identify possible effects of agriculture compared to an area with reduced human activity as an initial step to implement best management practices that mitigate groundwater contamination.

4. HYPOTHESIS

Agricultural land use in the northeast region of the state of Yucatan has a greater influence on the concentration of dissolved substances present in groundwater than the non-agricultural zone within the Municipality of Benito Juarez due to the excessive use of agrochemicals.

5. GENERAL OBJECTIVE

To evaluate the effect of land use on groundwater in one agricultural zone and one non-agricultural zone in the Northeast region of the Yucatan Peninsula by measuring dissolved substances in three different seasons.

6. SPECIFIC OBJECTIVES

- To characterize physicochemically the groundwater in one agricultural zone and the groundwater in one non-agricultural area within the northeast region of the Yucatan Peninsula.
- To distinguish the influence of land use and seasonality on specific dissolved substances, the nutrients ammonia, phosphate and nitrate, and the micronutrients sulphate and potassium in one agricultural zone and one non-agricultural zone.
- To confirm the presence of the herbicide 2, 4-D (2, 4-Dichlorophenoxyacetic acid) as a substance indicative of groundwater contamination from agricultural origin present in groundwater.
- To elaborate groundwater quality maps of the dissolved substances ammonia, phosphate, nitrate, sulphate and potassium, indicating its spatial distribution in groundwater in one agricultural zone and one non-agricultural zone.

7. MATERIALS AND METHODS

7.1 Study Area and Site Selection

The Yucatan Peninsula is a platform that consists of a karst aquifer with an estimated size of 165,000 km^2 including the states of Quintana Roo, Yucatan and Campeche (Mexico, Figure 2). It has a fragile and porous geological structure of Pleistocene and Tertiary rock. The first 120 m depth of the geological structure consists of recrystallized calcites of high permeability (Castro-Graniel and Gil, 2010). Below 220 m in depth, evaporites, dolomites, anhydrites and halite can be found originating from the Paleocene and Eocene. The coastal area of the Yucatan Peninsula is composed of Quaternary rocks which includes sand and clay with calcites formed by the exoskeleton of marine mollusks (Castro-Graniel and Gil, 2010).The Peninsula is approximately near sea level at its lowest point in the coast and 400 meters above sea level at its highest point (CONAGUA,2015). The water in the Peninsula is high in calcium and magnesium, bicarbonate ions and high concentrations of sulphates and chlorides in the coastal regions (Guzman, 2016).

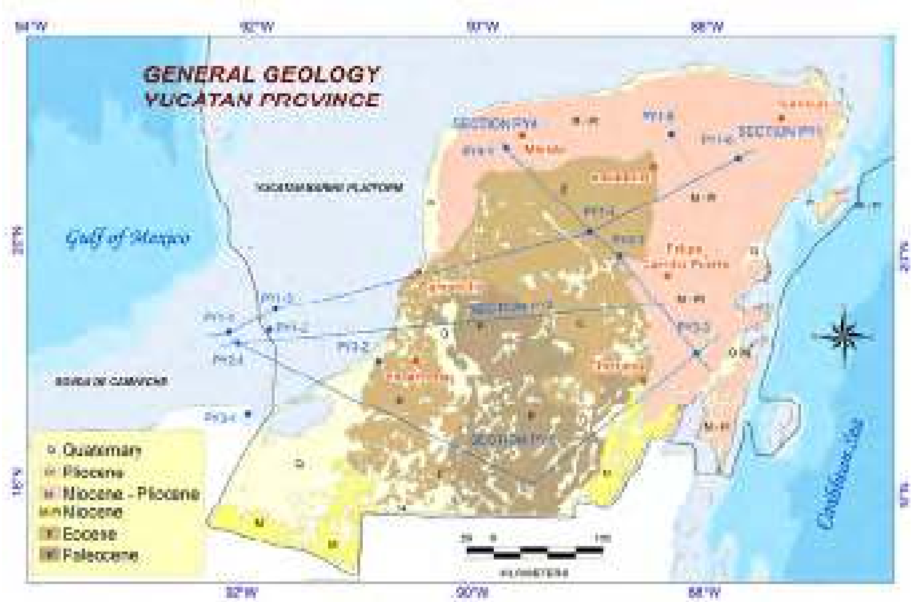

Figure 2. Geological map illustrating the different rock ages represented in the Yucatan Peninsula (Taken from: Jimenez-Davila et al., 2011)

A thin soil layer exists in the Yucatan Peninsula having approximately 20 cm in thickness with organic deposits (Castro-Graniel and Gil, 2010). There are four soil groups in the Yucatan Peninsula; leptosol is mainly shallow soil with weak geological structure (Castro-Graniel and Gil, 2010). As a result, in areas with that type of soil, there are problems with poor soil fertility. Histosol consist mainly of organic matter, having a thickness about 40 centimeters. Vertisol are mainly composed of clay, which changes structure as they change in water content. Lastly, gleysol is a wetland soil type that is saturated mostly with groundwater (Castro-Graniel and Gil, 2010). The vegetation of the Yucatan Peninsula is mainly composed of tropical secondary growth forests, with various vascular plant species. Halophile vegetation and mangrove zones are present in coastal zones (Guzman, 2016). Land use change from forest to agriculture and urbanization permits the succession-expansion of secondary forest growth (Guzman, 2016).The aquifer has a freshwater lens overlying a saline lens; the geological structure makes the underlying aquifer vulnerable to the infiltration of contaminants (Beddows et al., 2007). This eastern portion of the coastal aquifer discharges water into the Caribbean Sea (Escolero et al., 2005). The Yucatan Peninsula has an average rainfall of 1,432.3 mm per year and an average year temperature ranging from 23-28^{o}C (CONAGUA, 2015).

There are three main season in the Peninsula, the dry season from December to May with less than 100 mm monthly precipitation. The wet season from June to October with more than 100 mm monthly precipitation. Finally, the cold front season from January to March with less than 50 mm of monthly precipitation (INEGI 2015, historical data between the years 1949-2016, see figure 3).

The study area includes an agricultural area and a non-agricultural area, located in the state of Yucatan and the state of Quintana Roo respectively (figure 4). The agricultural area considered here comprise three municipalities on the northeast region of Yucatan: Tizimín, Sucilá and Panabá. The estimated total area for the agricultural zone is 2,546 km^2. At all municipalities, geological structure is mainly composed of Neogene and Quaternary platform with sedimentary calcite and a loamy- leptosol soil consisting overlaying calcium carbonate originated from Quaternary rock age (INEGI, 2009).

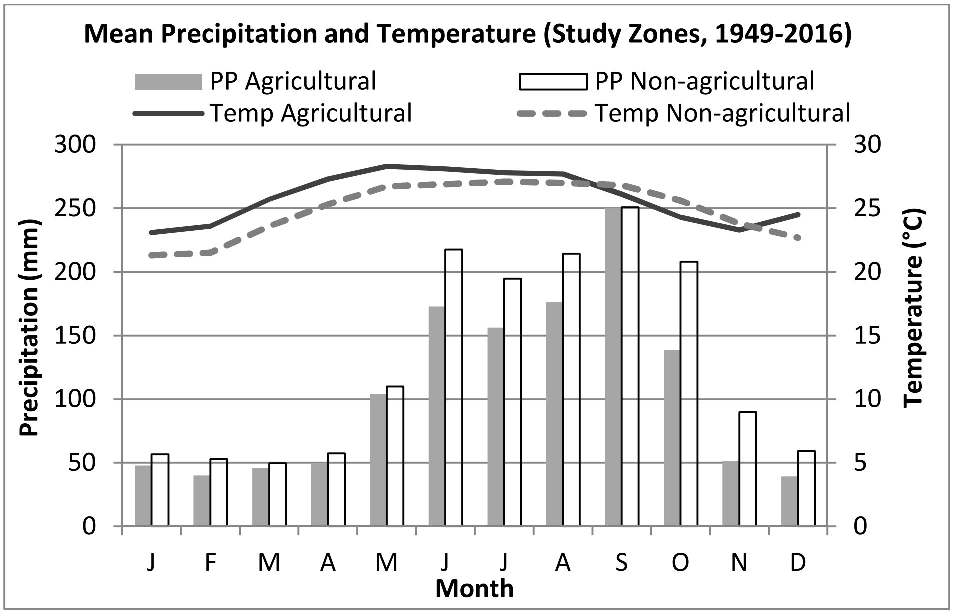

Figure 3.Graph showing historical precipitation and temperature for the study sites. Agricultural zone represented by the station in Valladolid Yucatan and the non-agricultural represented by the station in Kantunilkin,Quintana Roo between the years 1949-2016. Data from CONAGUA.

Tizimin has approximately a population of 77,621 inhabitants, being the leading producer of cattle in the state of Yucatan (INEGI, 2015). It has a mean altitude of 20 meters above sea level; the climatic condition is tropical sub-humid having a mean precipitation of 600 mm per year with an average temperature ranging from 22-28^{o}C (INEGI,2015). The land use is divided as follows: pasture (47%), urban zone (49%) and manglar zone (1.97%; INEGI, 2009). The municipality of Panabá is a region dedicated to the livestock production, with a total population of 7,461 inhabitants. The climatic condition is mainly tropical sub-humid with rains in the summer and mean annual precipitation of 500 mm. Pastures are the main land use in the zone having a percentage of (99.64%) within the remaining divided into; urban zones (0.28%) and original vegetation (0.02%; INEGI, 2009). Sucilá is the third municipality for the agricultural study area, which has a total population of 3,918 inhabitants. The climatic condition is also tropical sub-humid with an average precipitation of 800 mm and a mean temperature ranging from 24-26 °C. The main land use is pastures having a total of percentage of 89.19% and the remaining used in agriculture (0.34%), urban zone (0.69%), and original vegetation (97.7%; INEGI 2009). Figure 5 and Table 1 shows the location of the ranches.

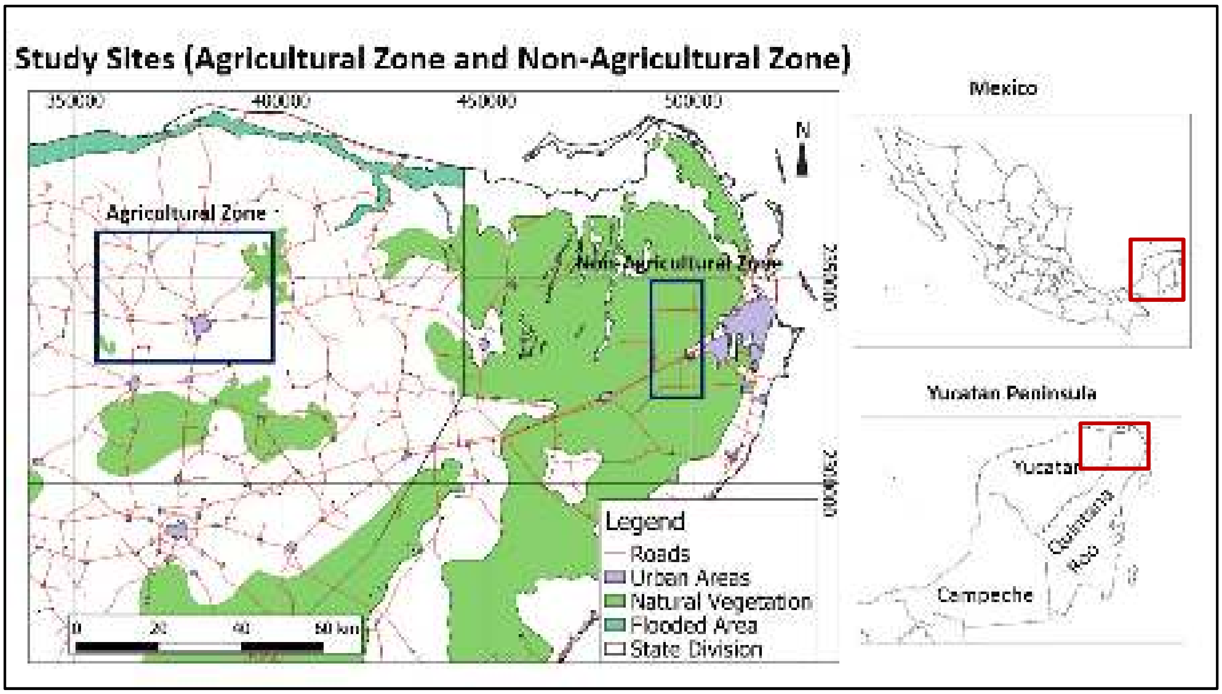

Figure 4. Image depicting the agricultural and the non-agricultural study zones located in the Peninsula of Yucatan Shape files taken from (INEGI, 2015) scale 1:250000

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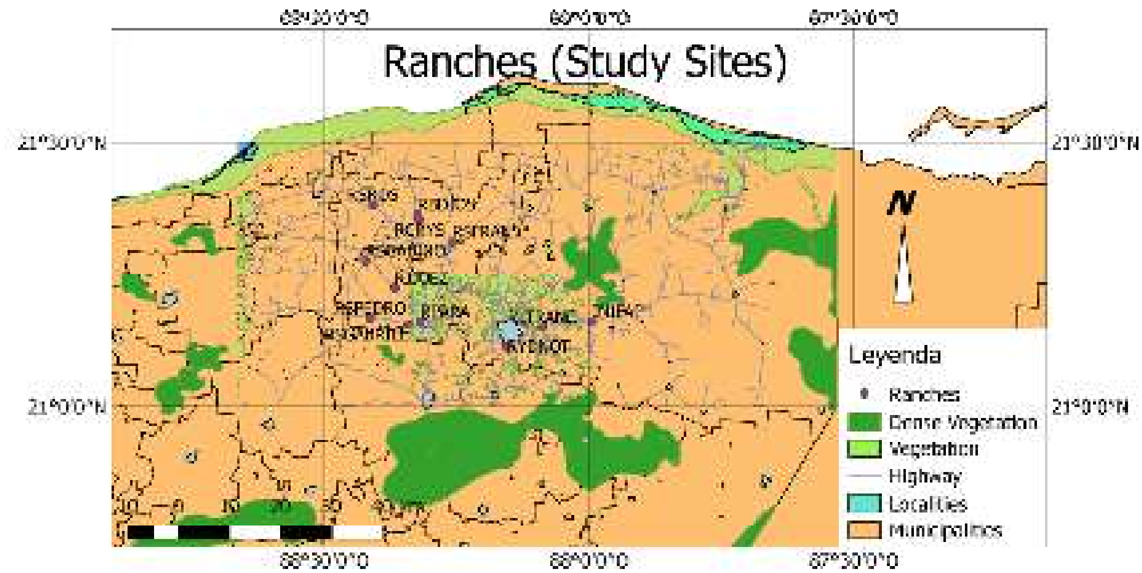

Figure 5.Figure illustrating sampling sites in the agricultural region with a total of 14 sampling sites.

The non-agricultural study area is located in the Municipality of Benito Juarez (Quintana Roo) it had a total population of 743,626 in 2015 (INEGI, 2015). Cancun being one of the main touristic destinations in Mexico has a notable increase amount of visitors. In the year 2017, the state of Quintana Roo received 16,911,163 visitors, approximately 80% arrived to the Riviera Maya (SECTUR, 2017).The climatic conditions is tropical sub-humid with mean annual temperatures between 24-28^{o}C with an annual precipitation of 1,300 mm (INEGI, 2009). The geological structure is Neogene and Quaternary rock with lacustrine deposits of sedimentary calcites with a loamy- leptosol soil (INEGI, 2009). The land use is as follows: urban zones (3.79%), pasture or grazing (1.57%), vegetation (85.72%), mangrove (5.12%), and undefined use (0.22%: INEGI, 2009). Within the 3.70% of the territory for urban zone, the entire population is situated in that small portion of land use which makes it an area of interest to assess the impacts of non-agricultural use on groundwater quality (Figure 6).

Table 1. Study sites for the Agricultural Zone

Location	Municipality	X (East)	Y (North)
Rancho San Francisco 2 (RSFRAN2)	Panabá	362171.80	2365874.35
Rancho San Manuel de Los Conde (RMCOND)	Panabá	371616.70	2358493.26
Rancho Santa Rosa (RSROS)	Panabá	353859.48	2365010.38
Rancho Bendición de Dios (RBDIOS)	Panabá	362545.76	2362865.15
Rancho Crystal (RCRYS)	Panabá	362971.25	2361736.05
Rancho San Francisco (RSFRAN)	Panabá	369330.11	2357169.62
Rancho San Gabino (RSGABI)	Sucilá	352400.42	2353355.79
Rancho Justo Juez (RJJUEZ)	Sucilá	357978.01	2347374.38
Rancho San Pedro (RSPEDRO)	Sucilá	353113.00	2341278.00
Rancho San Gabriel (RSGABR)	Sucilá	360593.91	2339962.36
Rancho Paraíso (RPARA)	Sucilá	362983.35	2340418.96
Rancho Las Trancas (RLTRANC)	Tizimín	386834.94	2339167.83
INIFAP (INIFAP)	Tizimín	396685.40	2340221.34
Rancho Yokdzonot (RYDNOT)	Tizimín	379924.16	2335262.82

The agricultural zone consisted of a total 14 sites located in the northeast region of the state of Yucatan, coordinates x and y were recorded in the Universal Transverse Mercator System.

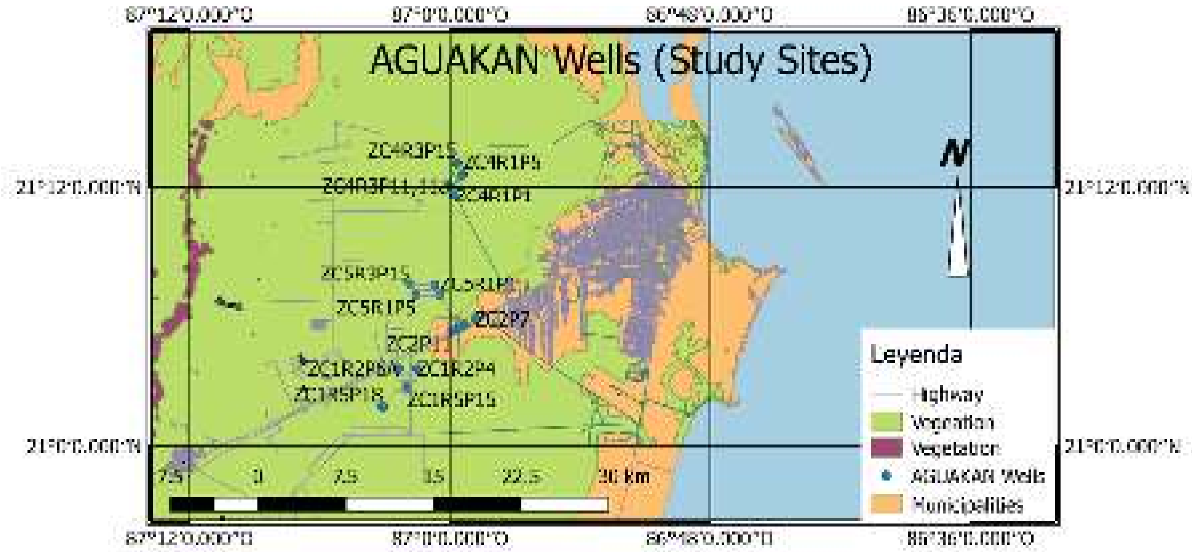

Figure 6. Figure three illustrating sampling sites located in the non-agricultural zone a total of 16 sampling sites.

The production wells (administered by Aguakan) are located in an estimated area of 245 km^2, predominantly covered by secondary growth forests. The area is navigated through feeder roads having small scale farms and subsistence plantations within proximity of the wells. Near the north of the sampling zone “Capture Zone 4” (See Figure 6) increasing urban development is noted as a residential area is being expanded.

In the agricultural area, local cattle owners and organizations were contacted in order to get consent to sample ranches and private wells. The project proposal was presented to presidents from the three cattle ranch associations (Tizimín, Panabá and Sucilá), explaining project objectives and outcomes. Preliminary visits of sites were conducted by visiting cattle ranches to speak with owners and administrators and to identify wells of interest of certain characteristics (see Section 7.1).During the preliminary field visits, sampling sites coordinates were recorded using e Trex Garmin GPS and photographs of the location. These coordinates were recorded in decimal degrees and UTM. The selection of sampling sites was based on spatial distribution was important to have an adequate representation of the agricultural zone.

Table 2. Study sites for the Non-Agricultural Zone

Location	X (East)	Y (North)
Zona de Captación 4 Pozo 11 (ZC4P11)	499919.28	2344371.60
Zona de Captación 4 Pozo 1 (ZC4P1)	500395.00	2343430.9
Zona de Captación 4 Pozo 15 (ZC4P15)	500544.83	2346250
Zona de Captación 4 Pozo 5 (ZC4P5)	501017.65	2345306.2
Zona de Captación 2 Pozo 7 (ZC2P7)	501979.13	2332966.1
Zona de Captación 2 Pozo 9 (ZC2P9)	501116.54	2332486.4
Zona de Captación 2 Pozo 10 (ZC2P10)	500617.42	2332228.2
Zona de Captación 2 Pozo 11 (ZC2P11)	500150.03	2331982.2
Zona de Captación 5 Pozo 5 (ZC5P5)	497227.82	2334939.9
Zona de Captación 5 Pozo 1 (ZC5P1)	499177.86	2334908.9
Zona de Captación 5 Pozo 11 (ZC5P11)	498730.80	2335782.1
Zona de Captación 5 Pozo 15 (ZC5P15)	496763.56	2335853.03
Zona de Captación 1 Pozo 6 (ZC1P6)	495864.69	2328693.2
Zona de Captación 1 Pozo 4 (ZC1P4)	497362.40	2328692.9
Zona de Captación 1 Pozo 15 (ZC1P15)	496574.27	2327162.10
Zona de Captación 1 Pozo 18 (ZC1P18)	494596.81	2325545.6

The non-agricultural zone consisted of a total 16 sites located in the municipality of Benito Juarez, coordinates x and y were recorded in the Universal Transverse Mercator System.

In order to gain access to wells in the non-agricultural zone, the managers of the agency Aguakan were contacted introducing the project objectives and purposes. When access was granted, a preliminary visit of sites was conducted with an official from the company. Coordinates were recorded for each site together with photographs.

The following criteria were implemented for the standardization of sampling methods and data consistency within the three sampling periods. Sampling was seasonal, considering the wet (October 2017), cold front (February 2018) and dry (May 2018) seasons, as which was also conducted in the agricultural zone. A total of 14 wells were selected for sampling in the agricultural zone and 16 wells in the non-agricultural zone ensuring adequate coverage of sampling zone (See Figures 5 and 6). Wells were selected based on certain criteria; in the agricultural zone wells they had to be currently used for irrigation, not exposed to surface runoff input (covered), within an estimated depth of 12-20 meters. Selected wells were drilled by CONAGUA as part of a development project installing deep wells for irrigation. Within the urban zone, the wells are operated by the company DHC-Aguakan, all of them drilled to an approximate depth of 16 meters. Four wells from four water extraction zones on a north to south direction were selected (16 wells, see figure 6).

7.2 Water Sampling

Water samples were collected in high density polyethylene bottles (HDPE) previously washed with phosphate-free detergent and the rinsed with ethanol before conducting field sampling. Water samples were collected directly from outlets and faucets installed at the pumping system using 250 ml high density polyethylene bottles, according to recommendations from the APHA (2017). Labeling of bottles was done according to their respective sites, recording of data (time, date and location), and the initials of the recorder. *In situ*, the physicochemical parameters recorded were; temperature (^{o}C), pH, conductivity (mS/cm), redox potential (mV) and total dissolved solids (mg/l) with sondes (HANNA Instruments Models: HI98129 and HI98130). Parameters were recorded on printed spreadsheet that specified date, time and location.

Samples for chemical analysis were stored in an icebox. Upon arrival to the laboratory, the samples were filtered using filter membranes of 0.45 µm nominal pore size (Pall membrane and a vacuum pump). After filtration, samples were sub-sampled in HDPE bottles of 60 ml for chromatographic analysis (ions) and 30 ml for colorimetric analysis (nutrients) and stored in refrigeration or frozen previous to analysis. Finally, samples for the herbicide 2,4-D were collected in two seasons (cold and dry) in 500 ml glass amber bottles previously rinsed with detergent free of phosphates, ethanol and acetone. Samples of the herbicide were preserved with phosphoric acid to pH 3 and stored in cold.

Figure 6.Pictures depicting extraction faucets in both agricultural (*left*) and non-agricultural (*right*) zones respectively

7.3 Water Analysis of Dissolved Substances

Samples for nutrients analysis were processed within frozen prior to analyses to avoid spoiling of samples. The analysis for ammonia, phosphates, and nitrites were conducted using colorimetric methods with a UV-VIS spectrophotometer (Eppendorf BioSpectrometer). The analysis of nitrates, sulphates and potassium were conducted with an ion chromatography (882 IC Metrohm), stored frozen before analysis.

The quantification for ammonia, nitrite and phosphates was done with UV-Vis spectrophotometry. To determine the presence of ammonia, a reaction occurs with phenol, salicylate and hypochlorite in alkaline conditions to form blue indophenol, colour change is proportional to the concentration of ammonia ion in solution at a wavelength of 650 nm (Solorzano, 1969). The analyses for nitrites were conducted using a reaction of sulfamide in the solution to form a diazonium salt to create a colour change which is proportional to the concentration of nitrite in wavelength of 545 nm. The analyses for orthophosphates is based on reactions specific in detecting orthophosphate ions. The reaction process includes ammonium molybdate and antimony potassium tartrate reaction in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex, the complex is then reduced to an intense blue colour by ascorbic acid. Colour change is proportional to the concentration of phosphates at a wavelength of 650 nm. This method was derived from the Environmental Protection Agency, Method 365.3 for the determination of phosphorus. In all cases, calibration curves were constructed with five standard and one blank; absorbance values were entered into a spreadsheet to generate calibration curves and to convert absorbance into concentrations expressed as mg N as ammonium, N as nitrite and P as phosphates.

The samples for quantification of nitrates, sulphates and potassium were done with an Ion Chromatograph 822 IC (Metrohm). Ion chromatography is a process in which an ion exchanger is used as the stationary phase, and the eluent for determination of anions is typically a dilute solution of sodium hydrogen carbonate and sodium carbonate. Samples were analyzed for anions (NO_3^- and SO_4^{-2}) and the cation K^+ separately. Calibrations curves were generated using stock solutions, with a limit of detection of 0.1 mg/l. 20 ml of sample were injected into at a flow rate of 0.7 ml/min, the mobile phase consisted of 2.7 mM Na_2CO_3/2.5 mM $NaHCO_3$ prepared with Sigma Aldrich reagents with a purity of >99.5% with lot numbers: SLBD9886V and 7BSO423 respectively. Results were presented in milligrams per liter for both nitrates (mg NO_3^-/l) and sulphates (mgSO_4^{-2}/l). The analysis of Potassium was conducted using the chromatography method as well with a Metrosep C 4 250/4 column and mobile phase consisting of HNO_3 with a concentration of 2.7 mM prepared from concentrated nitric acid (99.999%). Results for both the agricultural and non-agricultural zones were entered and organized into and excel spreadsheet to be analyzed statistically.

7.4. Herbicide 2, 4-Dichlorophenoxyacetic acid

A Solid Phase Extraction Method (SPE) derived from Caldas *et al.* (2010) was used for the analysis of the herbicide 2,4-D in agricultural and non-agricultural zones. A total of 14 sites were sampled in the agricultural zone and four in the non-agricultural zone for the cold and dry seasons. The herbicide 2,4-D was used to verify to its presence in groundwater, which can serve as an indicative substance of agricultural activity or use of pesticides affecting groundwater. A 2, 4-D stock solution (2,4-D Pestanal 31518,SIGMA ALDRICH, Lt# SZBD352XV) was prepared in acetonitrile at a concentration of 1,000 mg/l. A total of 100 mg of 2, 4-D standard power was dissolved in 100 ml of acetonitrile. Seven standards were used for the calibration curve with following concentrations: 0.01 mg/l, 0.1 mg/l, 1.0 mg/l, 2.5 mg/l, 5.0 mg/l, 7.5 mg/l and 10.0 mg/l. Absorbance was measured at 210 nm wavelength< the calibration curve had r^2: 0.9843.

A blank sample and a spiked sample of the commercial formulationTordon101® was prepared to be processed and compared with standard and sample absorbance curves in order to confirm the presence of 2,4-D in samples. The spike sample was prepared from a commercial herbicide Tordon 101 having a content of 2,4-D and diethanolamine salt , at a concentration of 240 g active ingredient /l.

The Solid Phase Extraction method was conducted following Caldas et al. (2010) which includes four steps: conditioning, washing, loading and elution. Cartridges Strata C 18-E (55 micro meters, 70A) were conditioned with 3ml of methanol, followed by washing with 1ml of distilled water and finally the loading of 250 ml of sample which was passed through the cartridges to be eluted to a final volume of 1ml using acetonitrile. Samples were then injected into the HPLC-DAD (Agilent ,1290 Infinity, Column kromasil 100-5-C18, 150 mm length) for analysis which consisted of a mobile phase: 50% acetonitrile, 30% methanol, 20% distilled water at a flow rate of 0.5 ml/minute with a total retention time of 2.0 min for 2,4-D detection . Absorbance spectra were used to determine the presence of 2,4-D or possible by-products in samples.

7.5. Data Analysis

Data was organized in Microsoft Excel placing data sets in categories based on study zone, geographical position and season among other attributes. Data collected was organized, analyzed and interpreted via statistical software such as Excel, SPSS 13.0 and Minitab 18. The SPSS 13.0 statistic program was used to create descriptive statistics tables for both physicochemical and nutrient data; also for the creation of box and whiskers plots for concentration values from the agricultural and non-agricultural by season. Box and whiskers plots allowed seeing variability in nutrient concentrations between land use areas and seasonal patterns. After data representation via box plots, the Anderson Darling test of normality was conducting on data sets for nutrients in the agricultural and non-agricultural zone in order to assess normality (Minitab 18). The test for all dissolved substances in both areas showed that all were non-parametric using a level of significance of 95%. Finally, a Post Hoc Dunnett's T3 test was done for identifying differences among median values for the three seasons.

7.6. Geographic Information System

Coordinates for all sampling locations were entered into a Geographic Information System. Available spatial data was used to create maps using the software Quantum-GIS. Coordinates for sampling sites were recorded and converted into a shape file layer, for creating maps of concentrations within the study areas that showed contours with current distribution of dissolved substances. Existing shape file layers were downloaded from INEGI (Instituto Nacional de Estadistica y Geografia) and Geo-information Portal from the National System of Biodiversity Information (CONABIO) at a scale of 1:250000 to depict geopolitical regions, vegetation, municipalities and other land use attributes.

Nutrient contour maps were created for both land use areas and the three seasons. Using Q-GIS, interpolations were conducted to create Triangular Irregular Networks (TIN) files, which is the triangulated connection of sampling points in order to display concentration. TIN have been used by the GIS community for many years and are a common digital mean to represent surface morphology. TINs are a form of vector-based digital geographic data and are constructed by triangulating a set of vertical points (Gandhi, 2016). TINs were used in the research to create contour maps, as it is a compatible geographic file format used to create an interpolation of the concentration of dissolved substances. In addition, it is a geo-process used to demarcate the zone of sampling points in both the agricultural and non-agricultural zone required to create contour lines. Interpolation is the geo-process of connecting sampling points in a vector layer. After interpolation, contours were created using red, green and blue shading to indicate concentration intensity for sampling points in the agricultural and non-agricultural zones. Contour lines were created at every fifth interval on the vector map having a precision of 0.0001 mm between contour lines. Contours were then overlaid on geopolitical layers to give context of geographic location. Contour maps were created from mean values of nutrients such as ammonia, phosphates, nitrates, and the micronutrients sulphates and potassium for the season that yielded the highest concentrations. The contour maps were created to visually display zones of high concentrations, to determine nutrient behavior between sampling zones and seasonal patterns.

8. RESULTS

8.1 Physiochemical characteristics of groundwater: Agricultural and Non-Agricultural Zones

The physicochemical parameters for the wet season are showed in Table 3. Mean values for all parameters in both the agricultural and non-agricultural region had similar data ranges, among sampling sites n= 14 in agricultural, n=16 in non-agricultural conductivity, total dissolved solids, temperature and pH had similar values concerning seasonal patterns in the two land use types (See Tables 3 and 4).

Table 3. Physicochemical parameters measured (mean ± s.d.) for wet, cold front and dry seasons for both land use zones

Parameter	Land Use	Wet ± s.d	Cold Front ± s.d	Dry ± s.d
Temperature (°C)	Agricultural	28.3±2.7	26.6±1.8	28.6±2.2
	Non-Agricultural	25.3±0.3	26.0±0.4	26.1±0.9
Conductivity (mS/cm)	Agricultural	1.6±0.3	1.7±0.3	1.4±0.3
	Non-Agricultural	1.2±0.2	1.2±0.2	1.0±0.1
Total Dissolved Solids (g/l)	Agricultural	0.9±0.2	0.8±0.2	0.7±0.1
	Non-Agricultural	0.6±0.1	0.6±0.1	0.5±0.1
pH	Agricultural	7.1±0.8	7.3±0.5	7.1±0.2
	Non-Agricultural	7.2±0.1	7.7±0.1	7.3±0.1
Redox Potential (mV)	Agricultural	243.9±123.6	287.4±69.7	65.7±13.1
	Non-Agricultural	201.4±52.4	325.3±23.5	53.3±12.4

Difference is noted for the redox potential the mean value being higher in the non-agricultural zone than the agricultural zone during the wet season (See Table 3). There is a high value in pH that could be an abnormal value or a mistake while logging the field data. Several factors could have contributed to this outlier such as the sonde not being stable before the pH was recorded, another factor such as communication error between the reader and the recorder.

8.2 Dissolved Substances: Agricultural and Non-Agricultural Zone

Table 4 shows the mean values for nutrient concentration examined in this research. Ammonia, Phosphates, Nitrates, Sulphates and Potassium had highest mean values for the wet season sampling. The overall mean value for ammonia was highest in the non-agricultural zone during the wet season (0.2 mg, $N\text{-}NH_4^{+}$/L) while the highest overall mean value for phosphates was in the agricultural zone as well during the wet season (0.5 mg $P\text{-}PO_4^{3-}$/L). The overall mean value for nitrate was highest in the agricultural zone during the wet season (7.6 mg $N\text{-}NO_3^{-/}$L).The overall highest mean value for sulphate being the non-agricultural zone during the wet season (19.6 mg S-SO_4^{-2}/L) and potassium had the highest overall mean value for the agricultural zone during the wet season (11.4 mg K^{+}/L). However minimum mean values were noted for phosphates in both the agricultural and non-agricultural zone (See table 6).

Table 4.Concentrations of dissolved substances (mean ± s.d) for the wet, cold front and dry seasons for both land use zones.

Parameter	Land Use	Wet ± s.d	Cold Front ± s.d	Dry ± s.d
(mg N-NO_3^{-}/L)	Agricultural	7.6±5.1	5.5±3.9	6.0±3.4
	Non-Agricultural	1.0±0.8	0.6±0.4	0.7±0.4
(mg N-NH_4^{+}/L)	Agricultural	0.2±0.2	0.1±0.04	0.1±0.07
	Non-Agricultural	0.1±0.1	0.1±0.04	0.1±0.03
(mg P-PO_4^{3-}/L)	Agricultural	0.5±0.2	0.05±0.04	0.0±0.02
	Non-Agricultural	0.3±0.2	0.1±0.1	0.02±0.01
(mg S-SO_4^{-2}/L)	Agricultural	19.1±6.8	15.6±6.3	16.0±4.8
	Non-Agricultural	19.6±3.5	13.3±3.2	19.7±3.2
(mg K^{+}/L)	Agricultural	11.4±16.3	7.3±1.2	7.5±8.6
	Non-Agricultural	5.4±1.0	2.8±0.8	3.0±0.7

Figures 8 to 12 shows the comparison of the dissolved substances among two land use types and three seasons. Ammonia concentrations were more variable in the agricultural zone, with values has high as 0.7 mg N-NH_4^{+}/L. Differences were observed among medians of concentrations by season for the agricultural zone (Kruskal Wallis H=6.06, p=0.048) and also for the non-agricultural zone (H=21.79, p=0.001). In both cases, the wet season had the highest value (Dunnett's post-hoc z=2.41, p>0.05).

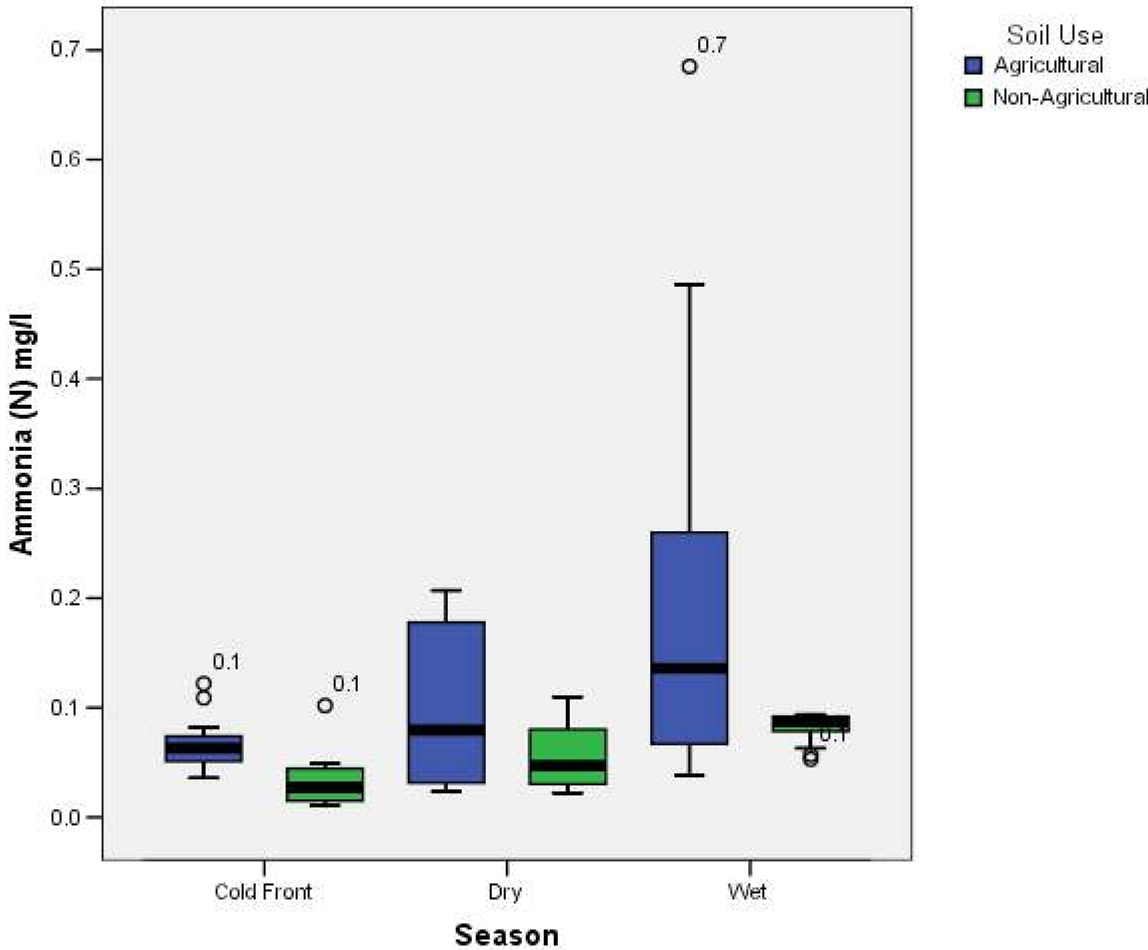

Figure 7. Shows Box plot depicting ammonia values in both agricultural and urban zones for the cold front, dry and wet seasons

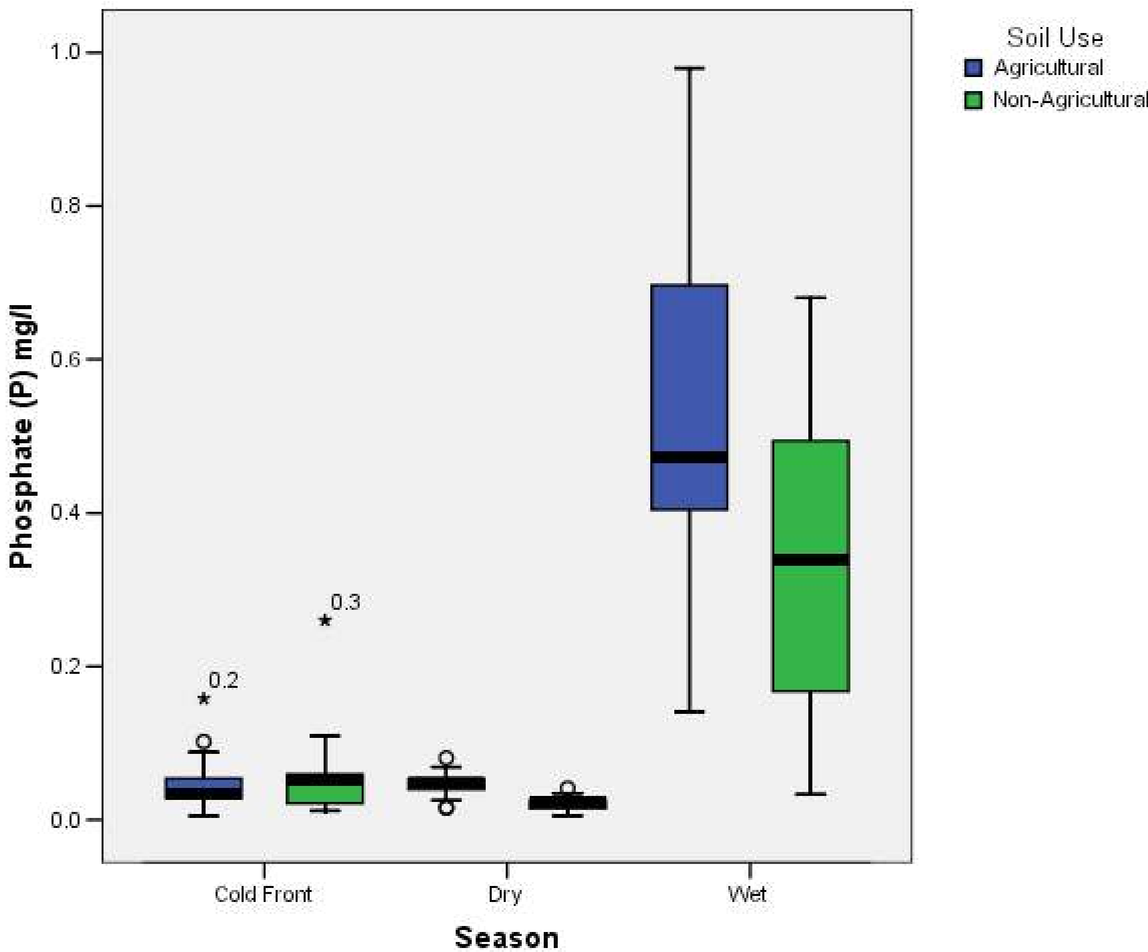

Figure 8.Box plot depicting phosphates values for the Cold Front, Dry and Wet seasons for both the agricultural and non-agricultural zones

Phosphates concentrations were more variable in the agricultural zone during the wet season with values as high as 1.0 P-PO_4^{3-}/l. Differences were observed among medians of concentrations among the three seasons for the agricultural zone (Kruskal Wallis H=26.8, p=0.001) also for the non-agricultural zone (H=29.74, p=0.001). In both cases the wet season had the highest value (Dunnett's post-hoc z=5.2, p<0.05).

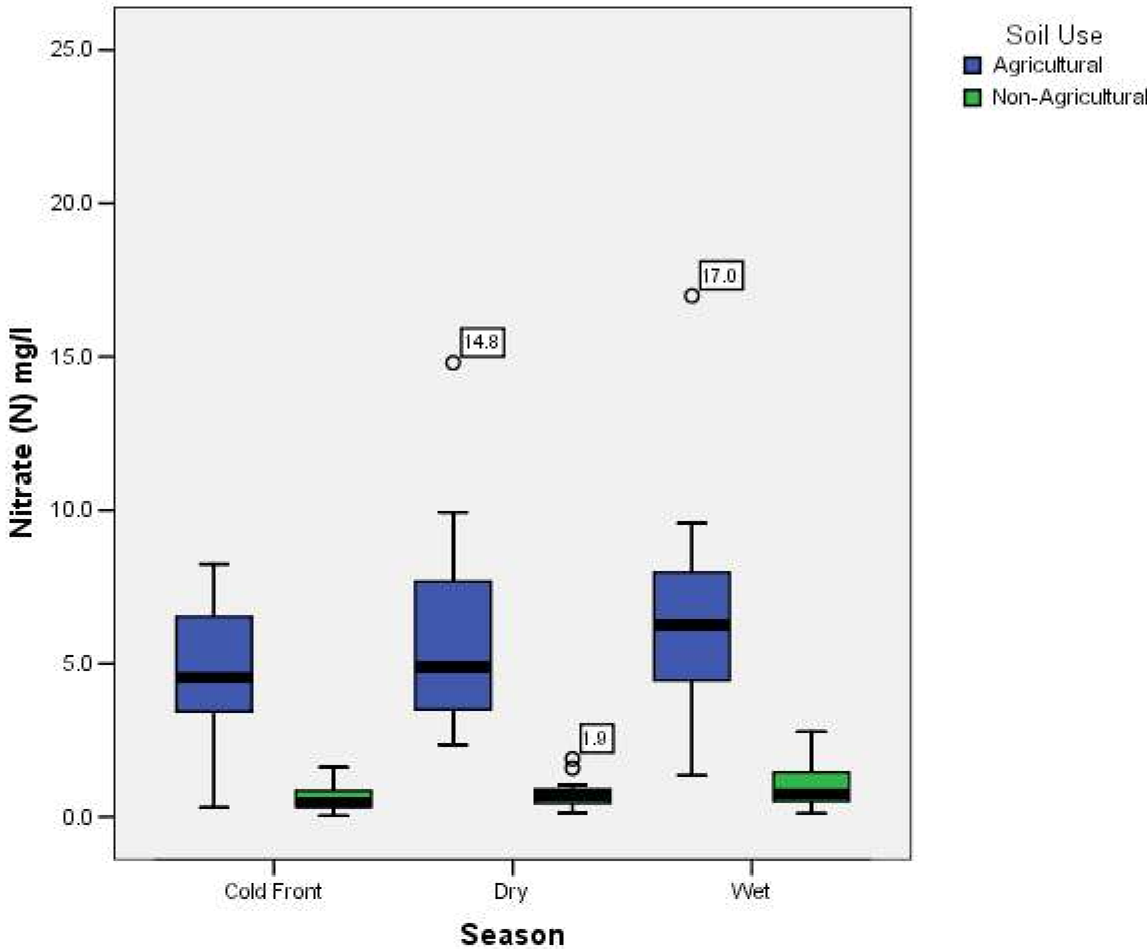

Figure 9.Box plot depicting nitrate values for the Cold Front, Dry and Wet seasons for both the agricultural and non-agricultural zones.

Nitrates concentrations were more variable in the agricultural zone during the wet season with values as high as 17.0 mg $N\text{-}NO_3^{2}$ /l. Differences were not observed among medians of concentrations among the three seasons in the agricultural zone (Kruskal Wallis (H=2.7, p=0.26). In both cases differences did not exist between seasons (Dunnett's post-hoc p>0.05).

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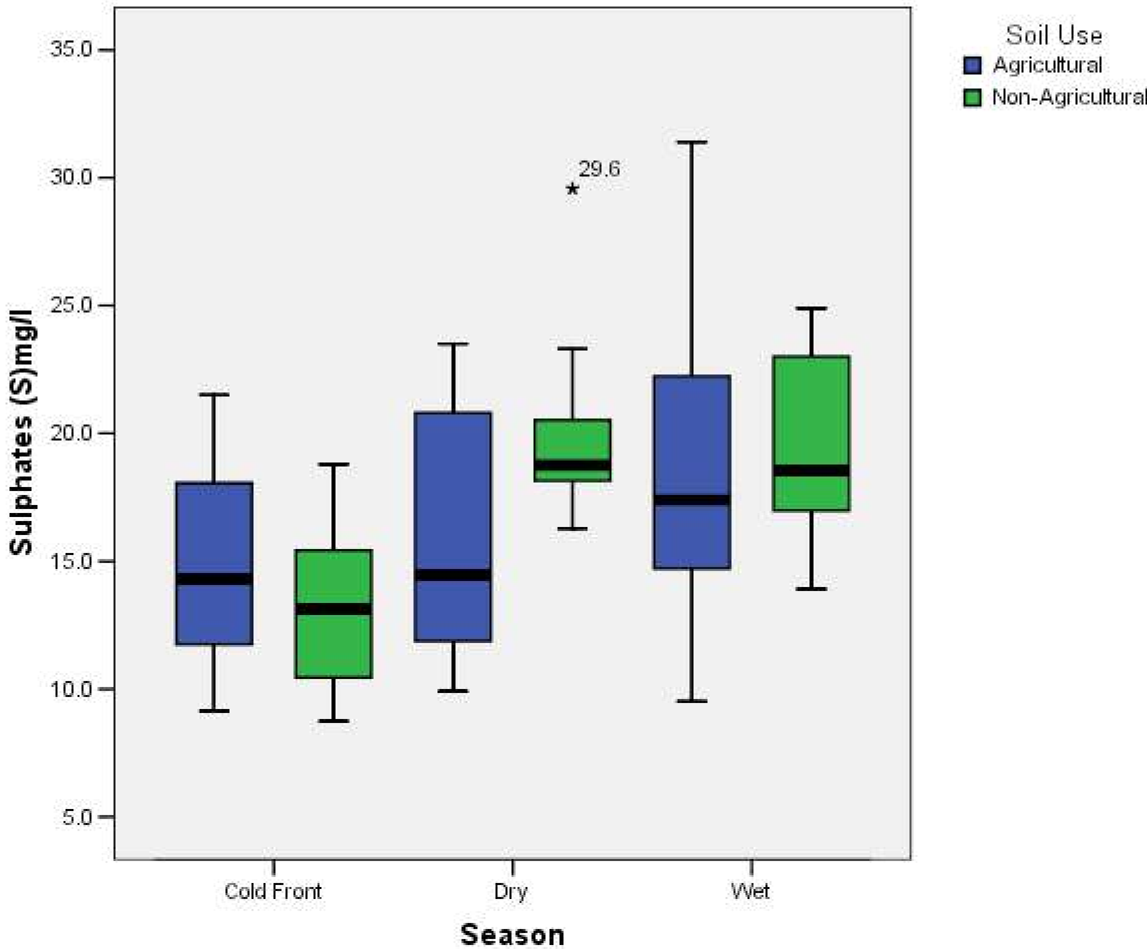

Figure 10.Box plot depicting sulphate values for the Cold Front, Dry and Wet seasons for both the agricultural and non-agricultural zones.

Sulphate concentrations were more variable in the non-agricultural zone during the dry season with maximum values as high as 29.6 mg S-SO_4-^{2}/l. Differences were observed among medians of concentrations among the three seasons for the non-agricultural zone (Kruskal Wallis H=22.4,p=0.001). In the non-agricultural zone the dry season had the highest value (Dunnett's post-hoc z=1.7, p<0.05).

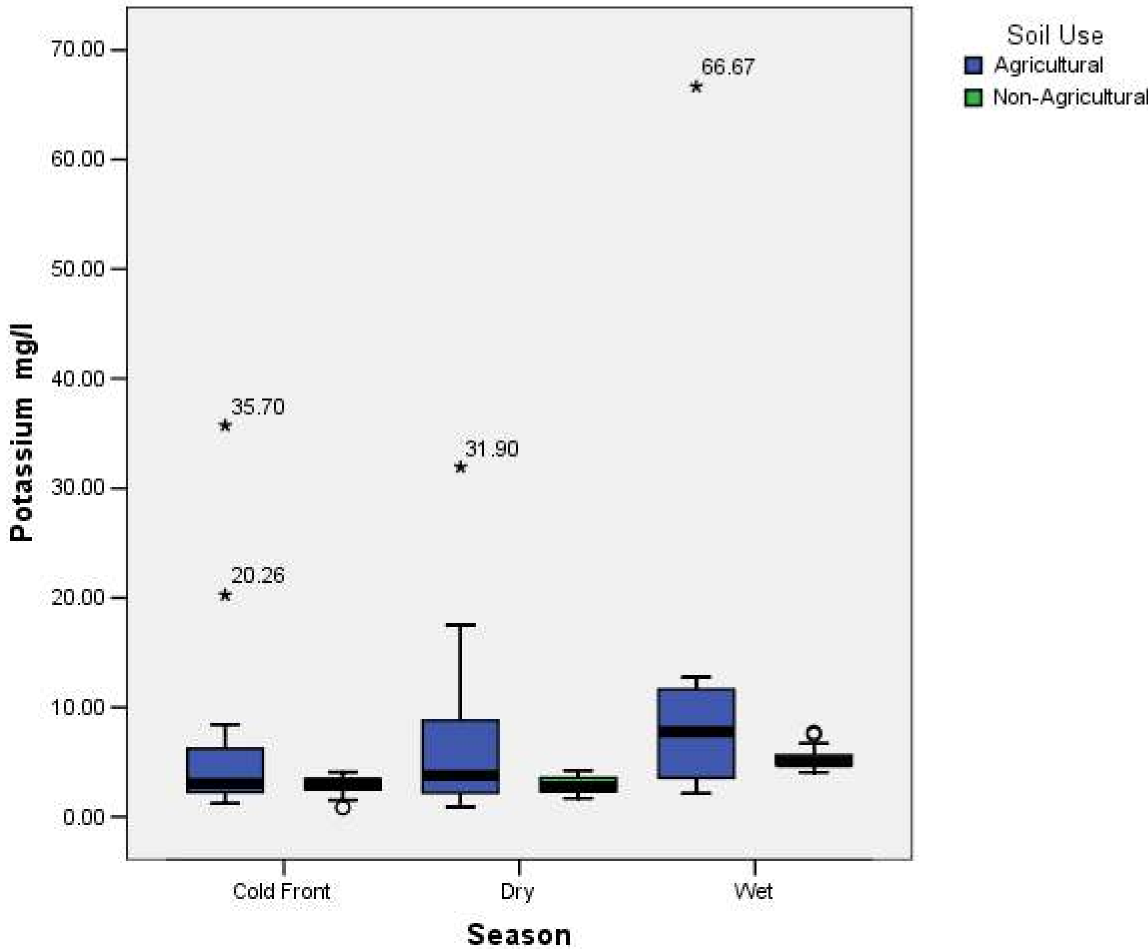

Figure 11.Box plot depicting potassium values for the Cold Front, Dry and Wet seasons in both the agricultural and non-agricultural zones.

Potassium concentrations were more variable in the agricultural zone during the dry season, however values were higher in the agricultural zone during the wet season with vales as high as 66.7 mg K^+/l. Differences were observed among medians of concentrations among the three seasons for the non-agricultural zone (Kruskal Wallis H=30.62,p=0.001). With higher values for the wet season in the non-agricultural zone (Dunnett's post-hoc z=5.53, p<0.05).

8.3 Herbicide 2, 4-D

The presence of the herbicide 2, 4-D was included as supporting evidence which suggests agricultural activities such as the application of agrochemicals have an effect on groundwater. An HPLC-DAD with detection limit of 1.0 ppm of 2, 4-D standard, was used to develop a standard curve for the herbicide 2, 4-D with an analytical standard (See Annexes). 2,4-D was detected during the dry season in one agricultural site and its by-products detected during the cold front season in two agricultural sites and one non-agricultural site.

Table 5.Detection of 2,4-D and its by-products in the agricultural and non-agricultural zones during the cold front and dry seasons.

Season	Location	Similar UV Spectrum
Cold Front	R.B.Dios (Agricultural)	Trichlorophenol
	R.J.Juez (Agricultural)	Dichlorophenol
	ZC5P1 (Non-Agricultural)	Tricholophenol
Dry	R.Para (Agricultural)	2,4-D standard and (Tordon-101®)

8.4 Dissolved Substances Contour Maps

Contour maps were created to display nutrient concentrations values encountered during the thesis research their spatial and temporal dynamics in groundwater for the agricultural zone. Although the main purpose of contour maps in this research is to visually display nutrient concentration values encountered further analysis of interpolation methods can be used for predictive studies. Figures 13 to 17 shows vectorial maps for the distribution of ammonia, phosphate, nitrate, sulphate and potassium for the agricultural zone during the wet season.

Overall higher values for nitrates were noted mainly in the southern region of the agricultural zone. While higher values for sulphates were noted in the northern region, and concentrations being minimal for ammonia and phosphates. Nevertheless nutrient concentrations were higher in the wet season as compared to the cold front and dry seasons.

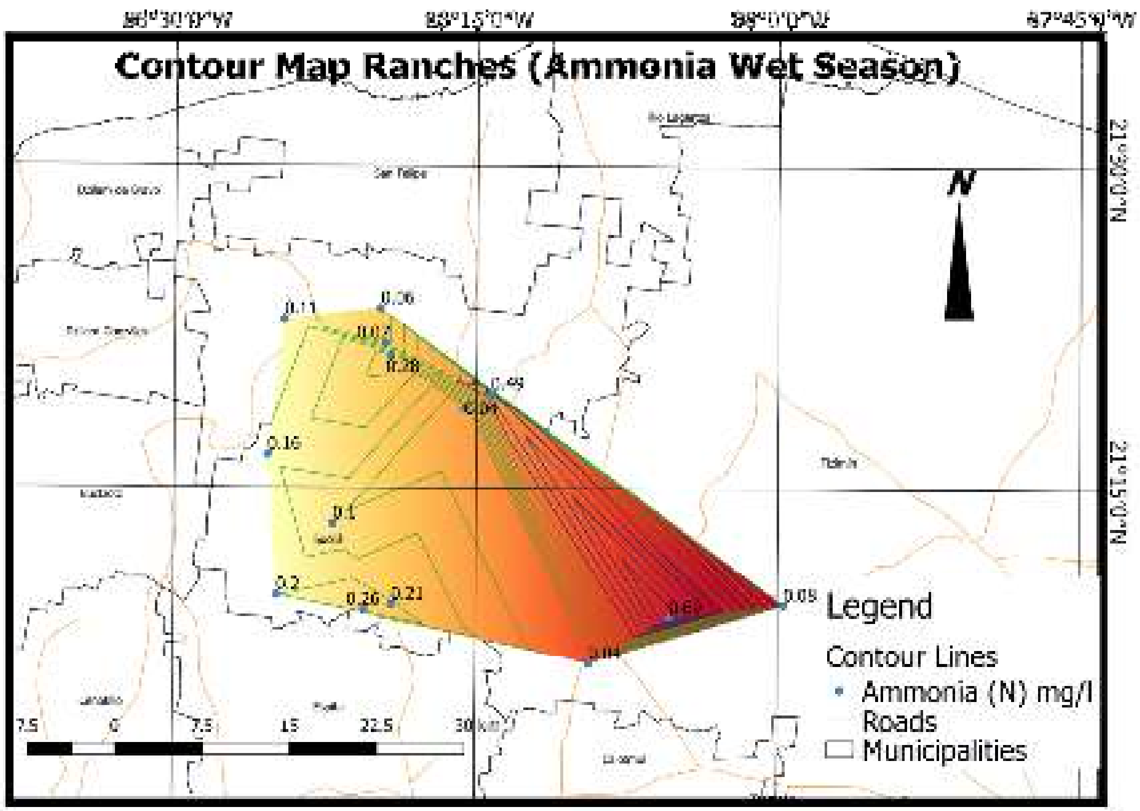

Figure 12. Contour Map for the ranches in the agricultural area which includes a total of 14 sampling points, showing the highest values for ammonia in milligrams per litre during the wet season. The maximum value for ammonia is a total concentration of 0.69 mg $N\text{-}NH_4^+$/l while the lowest was located in the northern area of the study zone 0.04 mg $N\text{-}NH_4^+$/l.

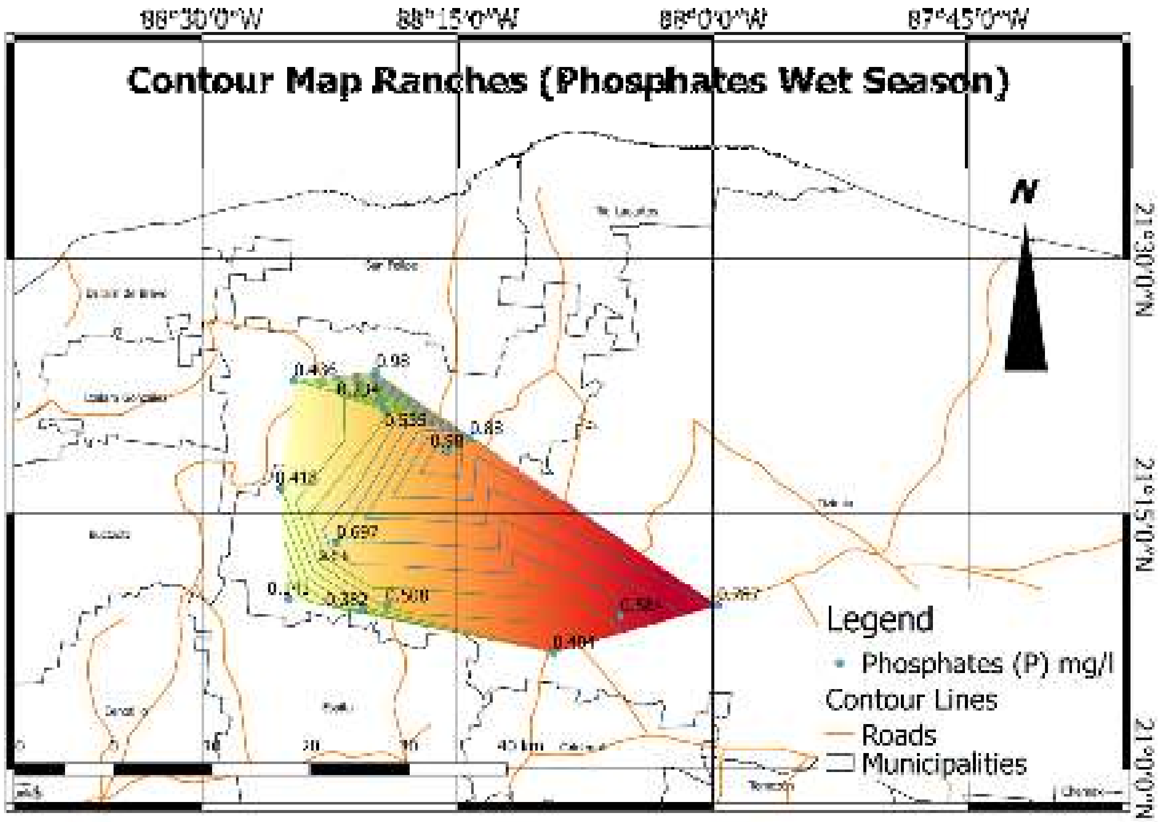

Figure 13.Contour Map for the ranches in the agricultural area with a total of 14 sampling points, showing the highest values for phosphates in milligrams per litre during the wet season. Maximum values for phosphates mainly noted during the wet season, maximum values yielded 0.88mgP-PO_4^{3-}/l and 0.98 mg P-PO_4^{3-}/l (P) in the northern in the study area.

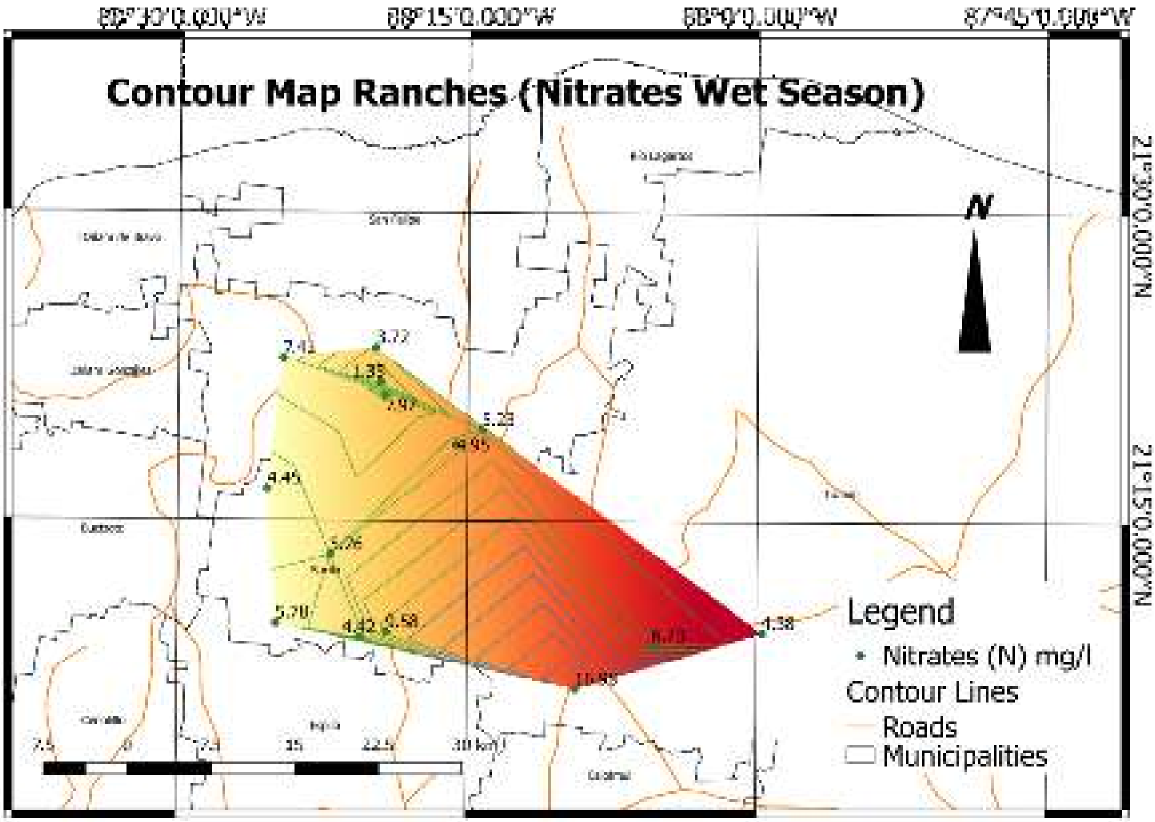

Figure 14.Contour Map for the ranches in the agricultural area with a total of 14 sampling points, showing the highest values for nitrates in milligrams per litre during the wet season. Maximum values for nitrates were noted in the wet season mainly in the southern area of the agricultural study zone, the highest value being at 16.98.N-NO_3^- mg/l.

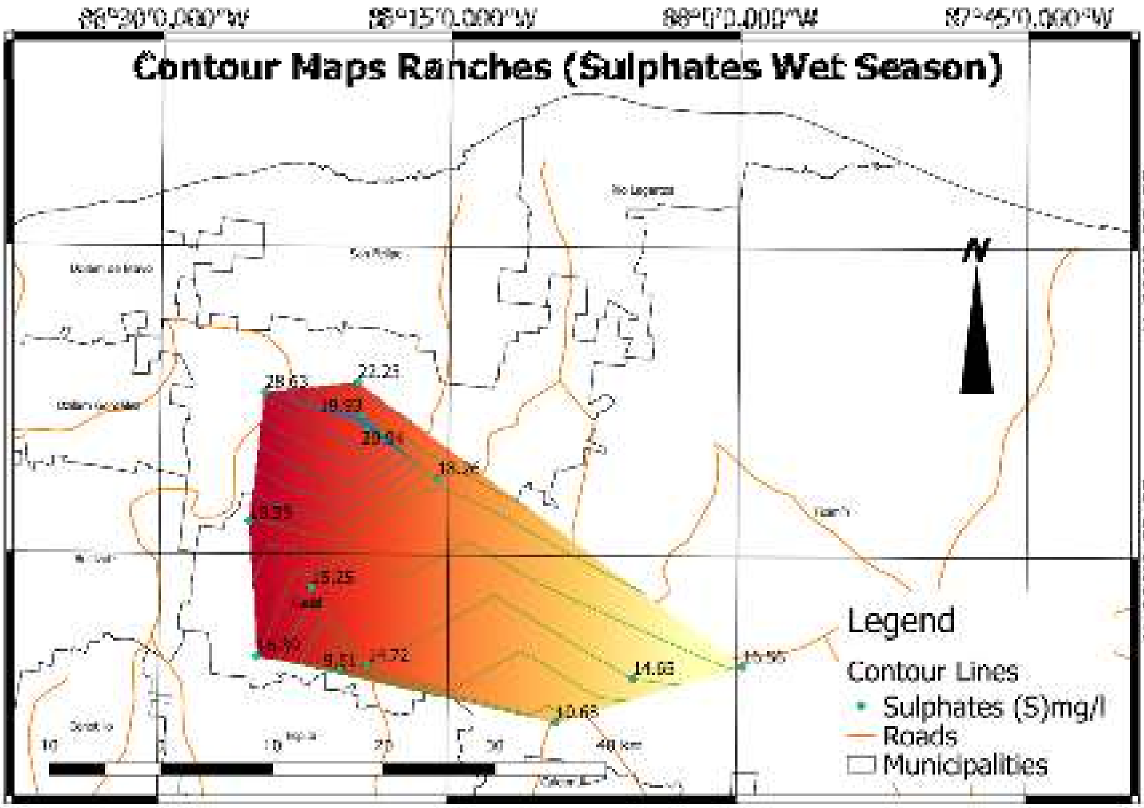

Figure 15. Contour Map for the ranches in the agricultural area with a total of 14 sampling points, showing the highest values for sulphates in milligrams per litre during the wet season. Sulphate values in the agricultural region are higher in the northern area of the study zone maximum values ranging from 15.25 S-SO_4^{2-}mg/l -29.94 S-SO_4^{2-} mg/l.

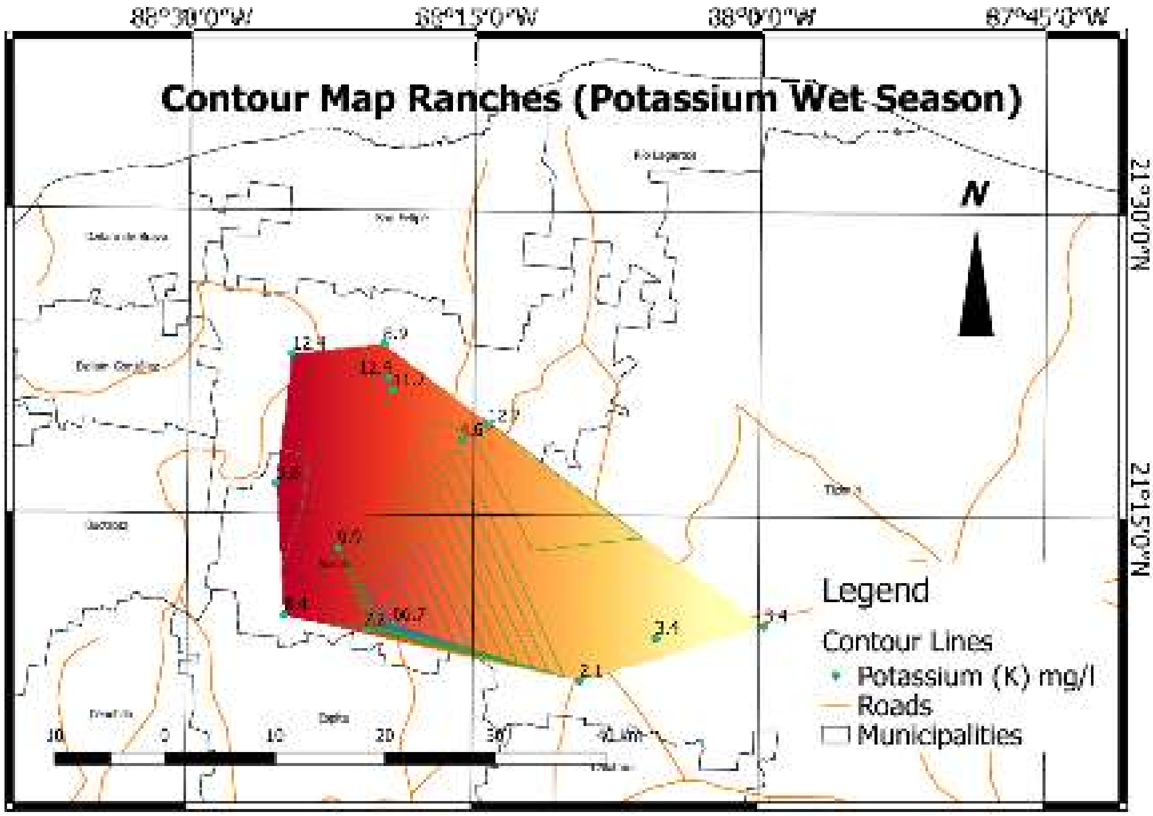

Figure 16. Contour Map for the ranches in the agricultural area with a total of 14 sampling points, showing the highest values for potassium, in milligrams per litre during the wet season. Maximum values for potassium were mainly in the southern region of the study area during the wet season having the highest maximum value of 66.7 K^{+}mg/l.

Contour maps for the non-agricultural zone were created to illustrate nutrient concentrations in groundwater, displaying their spatial and temporal behaviour. Figures 18-22 shows vectorial maps for the distribution of ammonia, phosphate, nitrate, sulphate and potassium for the non-agricultural zone, also for the wet season.

Higher values for sulphates were noted mainly in the northern region of the non-agricultural zone and minimal values in the southern region. Secondly higher values for potassium were noted in the central and southern region, while concentrations being minimal for ammonia and phosphates and nitrates. Overall nutrient concentrations were higher in the wet season unlike sulphate concentrations which were higher in the dry season.

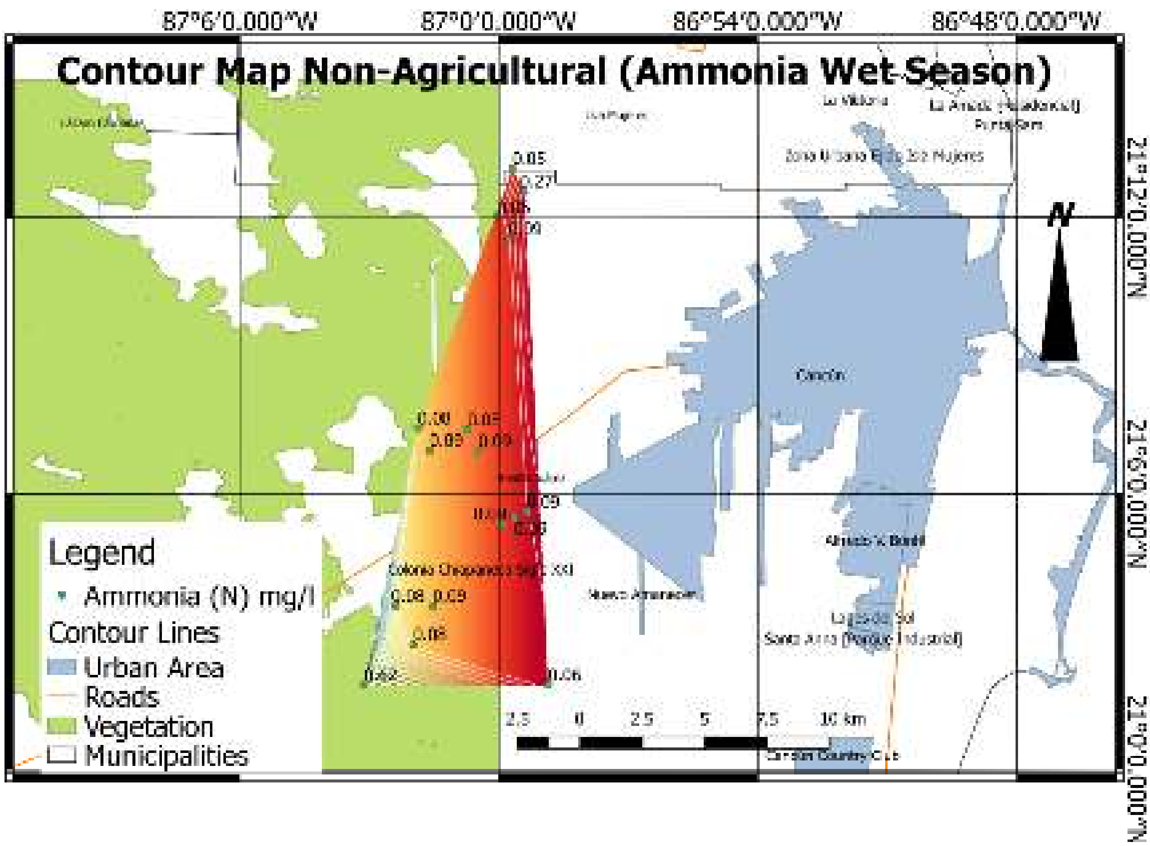

Figure 17. Contour Map for the non-agricultural study site includes a total of 16 sampling points, showing the highest values for ammonia in milligrams per litre during the wet season. Values for ammonia in the AGUKAN area were central region of the study area with a mean value of 0.09 mg N-NH_4^+/l mg/l.

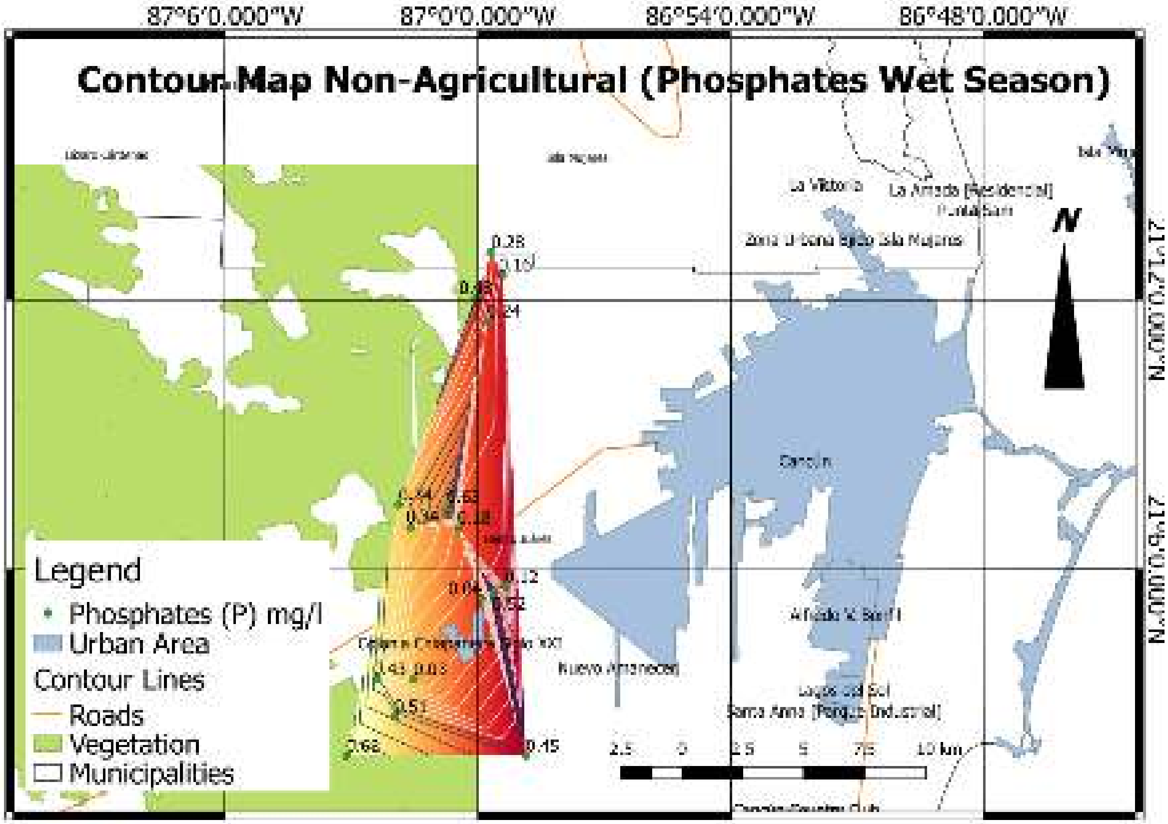

Figure 18. Contour Map for the non-agricultural study site a total of 16 study sites showing the highest values for phosphates in milligrams per litre during the wet season. The values for phosphates that were higher are noted in the mid region as well having values ranging from 0.34 - 0.63 mgP-PO_4^{3-}mg/l.

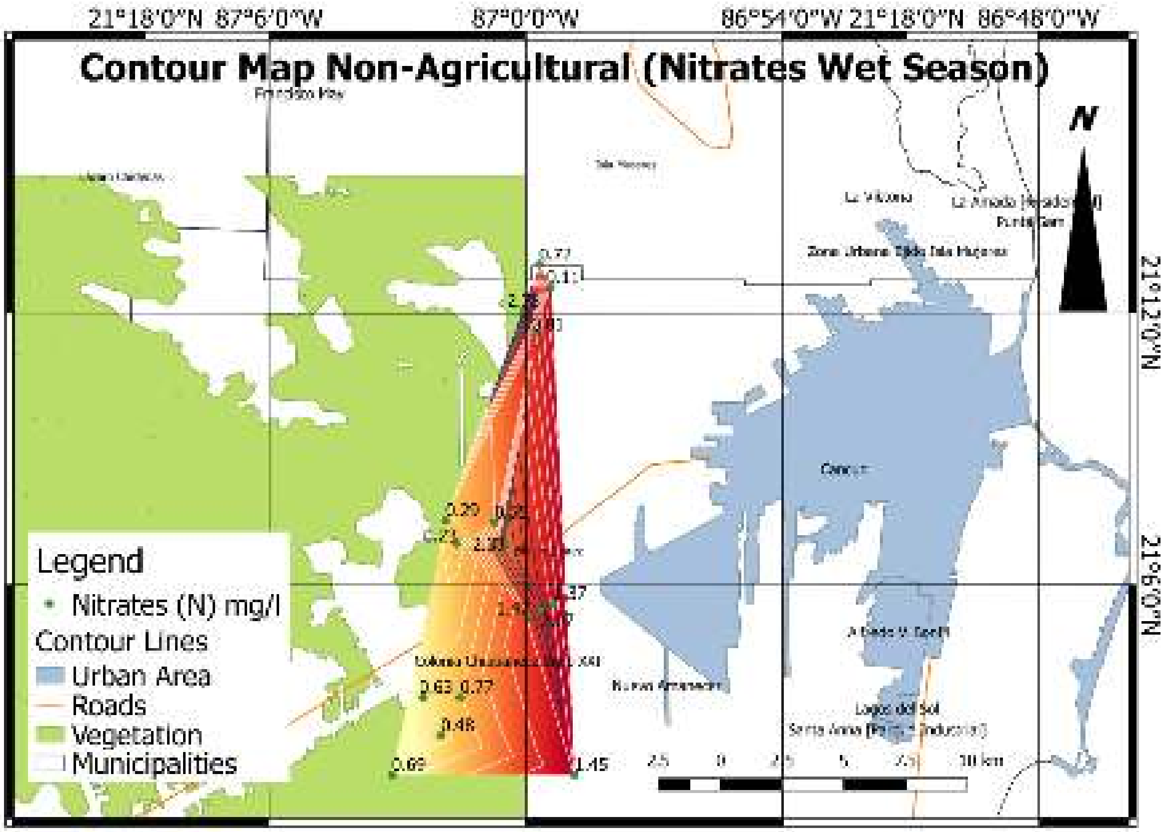

Figure 19. Contour Map for the non-agricultural study site a total of 16 study sites showing the highest values for nitrates in milligrams per litre during the wet season. Nitrates values had the highest value in the northern area of the non-agricultural zone 2.78 N-NO_3^-mg/l.

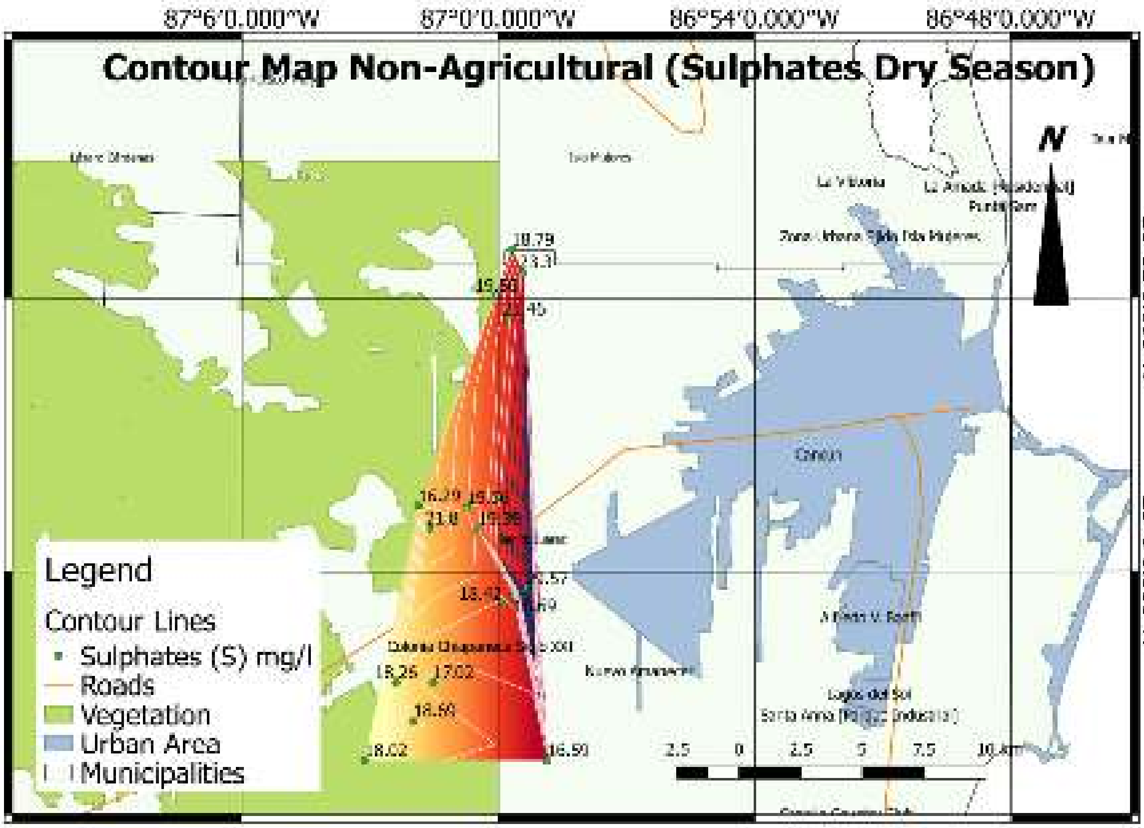

Figure 20. Contour Map for the non-agricultural study site a total of 16 study sites showing the highest values for sulphates during in milligrams per litre the dry season. Sulphate values were higher in the lower region of the non-agricultural zone ranging from 16.29 to 29.57 S-SO_4^{2-}mg/l during the dry season.

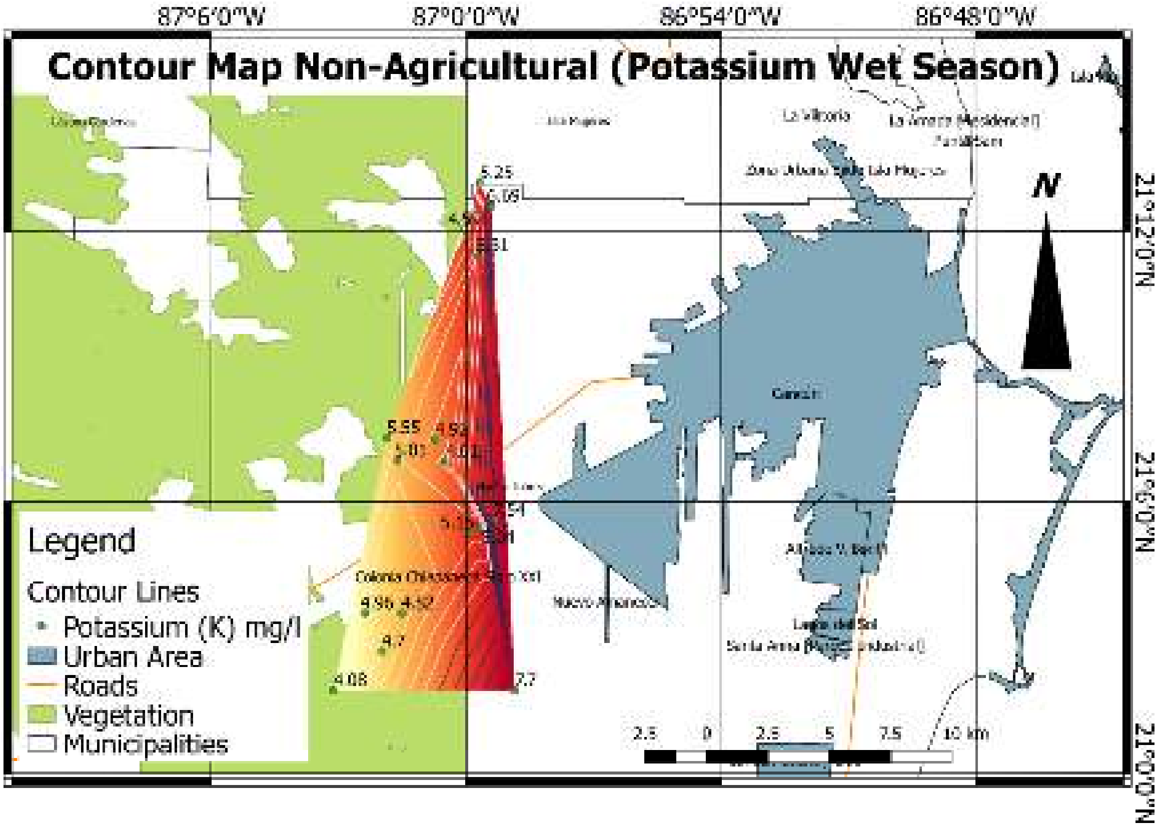

Figure 21.Contour Map for the non-agricultural study site a total of 16 study sites showing the highest values for potassium in milligrams per litre, during the wet season. Values for potassium are higher in the northern area of the non-agricultural zone having maximum values up to 6.69 K^{+}mg/l during the wet season.

9. DISCUSSION

9.1 Land use effect on Dissolved Substances

Physicochemical parameters for both the agricultural zone and the non-agricultural zone did not show significant seasonal variation between land uses, however comparing land use, concentration values were higher in the agricultural zone. According to Hernandez-Terrones et al. (2011) found mean temperatures to be an average of 26.8 °C for groundwater springs in the northern Yucatán coast suggesting groundwater temperature to be lower as compared to surface water temperature due to lack of solar radiation exposure. A study done by Gonzalez and Flores (2015) in the Sucila agricultural area found temperatures ranging from 22.8 to 26.8 °C during the wet and dry seasons which were considered to represent stable groundwater conditions, temperature values for this thesis research had a range of similar values for both the wet and dry seasons.

The pH values for both the agricultural and non-agricultural region had an overall mean of 7.28.Values did not surpass the maximum permissible limit of a pH of 8.5 set by the World Health Organization. The pH of groundwater depends on the process of karstification, which contributes to ionic concentration in groundwater given that the amount of hydrogen ions due to the dissolution of calcium carbonate influences alkalinity of groundwater (Neven, 1996).

Total dissolved solids were higher mainly within the rainy season in the agricultural zone, in which the maximum value was 1.16 g/l, whereas also in the non-agricultural zone it was 0.8 g/l.Total dissolved solids are derived from water rock interactions, surface runoff, leaching, weathering and dissolution of minerals, leading to an increase in dissolved solids (Gonzalez and Flores 2015).

Electrical conductivity was higher during the wet season having a mean value of 1.7 mS/cm for the agricultural zone and 1.2 mS/cm for the non-agricultural zone. However, values were similar for the wet, cold front and dry seasons which suggest stable environmental conditions and water coming from similar sources. According to

Gonzalez and Flores (2015) electrical conductivity is an indicator of ion concentration, high electrical conductivity values can be attributed to anthropogenic activities creating high mineralization of organic load. Dissolved substances such as sulphates, chlorides and sodium contribute to electrical conductivity. Gonzalez and Flores (2015) found electrical conductivity to be higher in cultivated areas especially during the rainy season, which could be a possible contribution of agricultural activities such as fertilizer application, thus increasing groundwater water ionic composition. The parameter that varied the most was Redox. According to Gonzalez and Flores (2015) redox potential is influenced by the varying concentration of dissolved substances in groundwater such as; ammonia, nitrates, sulphates, phosphates among others which increase the reduction capacity of groundwater.

Ammonia is found in groundwater naturally as a result of anaerobic decomposition of organic material due to microbial activity that aids in the decomposition of organic matter; however external factors such as leaching from fertilizers, organic waste disposal and leaking of sewage systems, can also contribute to ammonia concentrations in groundwater (Bohlke et al., 2006). Natural concentrations of ammonia in groundwater can range up to 3mg N-NH_4^+/l (Bohlke et al., 2006) which, which in aerobic conditions can then be oxidized into nitrites and nitrates. Ammonia concentration yielding higher values during the wet season can be possibly caused by surface leaching induced by precipitation after the application of manure or fertilizers just before the wet season to enhance the growth of fodder grass, due to the fact that manure´s content is approximately 1.7% of nitrogen (Maguire and Alley, 2009). Higher values measured in the agricultural zone (compared to the non-agricultural zone) might be due to agricultural land use practices such as deforestation, pasture cultivation and other activities that create a surplus of organic matter prone to decomposition. Although ammonia occurs naturally in groundwater, abrupt changes in concentration can be attributed to recent contamination from anthropogenic activities (human waste and fertilizer application; Bohlke et al., 2006).Concentration trends observed in the agricultural zone showed higher concentrations during the wet season and lower during the cold front and dry seasons (See section 7.3). This can be attributed to land management practices such as the application of manure just before the wet season, which makes dissolved substances more susceptible to infiltrate into groundwater in addition to natural inputs. Given the concentrations were lower in the non-agricultural zone as indicated in section 7.3; this condition can be attributed to natural inputs such as the decomposition of vegetal tissue, soil organic matter and surface run off. Concentration trends were similar among the three seasons, suggesting stable conditions originating from close to natural conditions. The maximum value for ammonia during the wet season surpassed the maximum permissible limit of 0.50 mg N-NH_4^+/l set by the NOM-127-SSA-1 Mexican water standards. This value could be attributed to characteristics of the particular site such as application of fertilizers and additional organic matter input as manure. Rojas-Fabro et al.(2015) mentioned that abrupt increases in ammonia concentration could be linked to recent point source contamination, however manure application is not a point-source and simultaneous application of manure in several ranches can lead to this increase. In optimal conditions ammonia oxidation to nitrites and nitrates occurs rapidly, which leaves little to no trace of ammonia in groundwater but leading to an increase in nitrate.

Phosphorus leaching occurs in soils with low sorption capacity which depends on soil composition. As phosphorus reaches groundwater, it is distributed by advection and diffusion being more stable in groundwater than surface water due to less turbulent flow (Withers et al., 2005). Phosphate mean value concentrations were higher in the agricultural zone than the non-agricultural zone, suggesting that agricultural activities involving the application of agrochemicals and manure, could be the origin of this dissolved substance in the aquifer (Chen et al., 2011). Seasonal trends such as higher concentration in the wet season in the agriculture region can be attributed to the leaching of phosphate into groundwater mobilizing with rainwater as it infiltrates (Chen et al., 2011). Several factors such as, low soil retention, water infiltration and external inputs from anthropogenic activities, could have contributed to high phosphate concentration in the agricultural region particularly high during the wet season.

Maximum values for both zones exceeded the World Health Organization maximum permissible limit (1.00 mg P-PO_4^{3-}/l) for phosphates in groundwater. Higher values of phosphates in the agricultural area can be attributed to the use of manure and agrochemicals, the time when it is applied (just before the wet season) and the quantity applied to crops. Sahoo et al. (2016) did a study on the concentration of dissolved substances in groundwater in a livestock intensive area. The assumption of the study was that localized intensive livestock farming permits the rapid infiltration of nutrients into groundwater. Management strategies such as keeping livestock in parcel within a certain distance from wells (30 to 60 m) would likely prevent the influence of manure on groundwater. This strategy could also be applied in the northeast Yucatan area where livestock management uses parcels and compartments for grazing, proper livestock care would help mitigate the influence of manure on groundwater in the region. Other management strategies suggested water budgeting, and the creation of diversion canals and vegetation buffers to filter infiltrating runoff (Sahoo et al., 2016). As it pertains to the agricultural zone in the Yucatán Peninsula, vegetation buffers such as water tolerant plant species can be cultivate in low lying areas that serves as recharge points which would help in filtering surface runoff that may contain excess nutrients.

High nitrates in the agricultural zone are assumed the result of the amount of agrochemicals and manure applied and then leached from the land surface into groundwater. The application of agrochemicals is a factor affecting dissolved such as nitrates ammonium (Pacheco and Cabrera, 1996). The application of fertilizers leads to the rapid infiltration of the non-assimilated nutrient to the aquifer, leading to high concentrations in groundwater (Pacheco and Cabrera, 1996). Pacheco and Cabrera (1996) did a study on the effect of fertilizer application on the concentration of dissolved substances in groundwater within the state of Yucatan. High nitrate concentrations were attributed to the use of manure in agricultural zones, high concentrations were observed from November to February. Concentrations found in this study site in state of Yucatan were similar to concentrations reported in this research in the southern area of the agricultural zone (Municipality of Tizimín). Similarities in concentrations could be a result of similar agricultural practices such as the application of fertilizers before and during the wet season. A study done by Cervantes-Medel and Armienta (2004), measured nitrate concentration in the Huamantla Valley (Tlaxcala, Mexico). They found nitrates values to be lower at the end of the wet season than at the beginning of the wet season, assumed to be dilution of the dissolved substance by precipitation (Cervantes-Medel and Armienta, 2004). As compared to the agricultural area of this thesis, it was observed that seasonal differences affects the concentration of dissolved substances in groundwater, likely due to increased leaching caused by an increases in precipitation and surface runoff. A study done by Gonzalez and Flores (2015) in the cattle production zone near the municipality of Sucila found nitrate concentration to be higher during the peak of the wet season October-November and also near areas of intense cattle rearing. The highest nitrate concentration was measured at a site in the southern region of Tizimin, where intensive agricultural practices were observed. Manure is a natural fertilizer that is commonly applied in the study area. One of its main components is nitrogen in the form of ammonia, which can be oxidized to nitrites and nitrates via microbial activity and water interaction (Asyraf et al., 2017). Higher values of nitrates in the agricultural zone than in the non-agricultural zone was possibly caused by the application of manure which caused additional leaching. High values were consistently observed in locations within the agricultural zone where livestock was in close proximity to wells thus influencing groundwater quality.

The source of nitrates in the non-agricultural zone can be of natural origin, it was not possible to identify contributions from seeping sewer pipelines, domestic, or municipal wastewater. The nitrate-chloride concentrations ratio (NO_3^-/Cl^-) has been used as supporting evidence for urban sources, correlation coefficients close to 0.650 are associated to urban influence (Pacheco and Cabrera, 1996; Rojas-Fabro et al., 2015). The correlation coefficient for the wet and dry season for the non-agricultural zone in the Municipality of Benito Juarez was 0.25, lower than the suggested significant correlation coefficients. This suggests that the nitrate measured in the non-agricultural area is likely from natural sources.

Sulphate (S) concentration did not vary much between the two zones. Sulphate can be related to natural inputs such as the dissolution of sulphate containing minerals such as gypsum and anhydrites (Castro et al., 2009). The precipitation of sulphate is a factor that reduces its presence in groundwater in areas that are prone to salt water intrusion; however, the dissolution of gypsum and anhydrite contributes to sulphate concentration in groundwater, precipitation-dissolution process is influenced by factors such as temporal patterns which can affect the dilution of sulphate concentration in groundwater (Castro et al., 2009). In addition a study did in the Sucila area by Gonzalez and Flores (2015) found sulphate values to be higher during the peak wet season (October-November) however values were lower in drying months such as May. However data values did not show much variation between the wet and dry season. Fisher and Mullican (1997) suggested that the dissolution of carbonate creates sulphate associations such as $Ca\text{-}SO_4^-$ and $Mg\text{-}SO_4^-$ which gives more mobility to sulphate in groundwater. However, sulphate concentrations did not show much variation between the agricultural and non-agricultural zones, which suggest that sulphate concentrations in both zones are possibly from natural origin, as both zones contain sulphate-containing rocks.

The analysis of the ion potassium showed maximum values in the agricultural zone, having an extreme value of 66.67 mg K^+/l during the wet season for a sampling site located in the municipality of Sucila, where livestock farming is intensive, compared to the highest value (See section 8.2) . This indicates a possible influence of land use practices such as the application of manure and seasonality, within the agricultural zone with high concentration of potassium during the wet season. Lopez-Martinez et al., (2001) did an analysis of cattle manure and found that manure is composed of 2.5% potassium, 1.8% nitrogen and 0.14% for phosphorus, with potassium being the dissolved substance with the highest percentage. This suggest that manure use is a possible explanation for high concentration of potassium in groundwater samples for the agricultural zone, especially during the wet season. Followed by sulphate, potassium has the second highest concentration yielded for the three seasons for the agricultural zone suggesting that manure has an effect on groundwater quality.

9.2 Seasonal Patterns Dissolved Substances

The seasonal trend for dissolved substances observed in this research was higher concentration during the wet season, followed by the dry season, then the cold front season. This trend suggests the influence rain on the concentration of dissolved substances in groundwater. Elango and Rajimonhan (2005) conducted a study on the seasonal trends of phosphates and found that phosphate ions are adhered to soil particles during the dry season and then flushed into groundwater during the wet season. As phosphates values were very low during the dry season, it was possible that the above mentioned phenomenon of phosphates from during the wet season could have occurred. While in the non-agricultural region phosphates showed similar seasonal trends their variability was lower; and the lowest mean value for the dry season due to possible immobilization in soil. In groundwater, during low pH conditions (less than pH 6) promotes the dissolution of calcium carbonate introducing calcium into groundwater and then forming calcium-phosphates bonds making phosphates more stable in groundwater (Neven,1996).However conditions in both zones were not acidic in both zones. It is not known if calcium concentrations does have an effect on phosphate concentrations in both zones.

Nitrate had the highest mean values for the agricultural region, providing supporting evidence on the influence of the use of agrochemicals and manure on groundwater. In addition, intensity of agricultural practices and fertilizer management are factors than can influence concentrations of dissolved substances in groundwater (Sahoo et al., 2016). Manure is one of the main sources of dissolved substances in the agricultural region; due to the fact that is inexpensive. It is rich in potassium followed by nitrate and phosphates. Prolonged application of manure and agrochemicals in the agricultural zone could have led to an increase in the surplus of nutrients in soil, which is then infiltrated into groundwater through rainfall and surface runoff, finally recharging water with high concentration of dissolved substances.

Higher values of nitrates during the dry season than the cold front season could be a result of reduced bacterial activity during cold front season, as microbial populations are more active during dry than during the cold front seasons due to changes in soil moisture and temperature (Roura-Boy et al., 2013). Another factor that could have contributed to higher concentrations in the dry season was that a tropical depression affected the study area a couple days during the last week of the month of May, before dry season sampling, thus increased rainfall could have promoted infiltration of dissolved substances into groundwater. However values were lower in the non-agricultural zone than the agricultural zone. These concentrations were below the maximum permissible limit set by the NOM-127-SSA1-1994 for limits for potable water (10.0 mg N-NO_3^-/l). This is important because the non-agricultural zone represents the well field for water extraction for the municipality of Benito Juarez (Quintana Roo).

Concerning seasonal patterns, sulphates had similar mean values for both the agricultural zone and non-agricultural zone. However, the variability observed in the non-agricultural zone during the dry season could be the occurrence of a tropical depression in the month of May a couple days before the dry season sampling. Given that the non-agricultural zone is on the Caribbean coast the geological strata is thinner than that of the agricultural zone, dissolution and the infiltration of sulphate containing minerals could have occurred faster than in the agricultural zone (Perry et al., 2002).

Ranches near the municipality of Sucilá showed higher values for potassium as compared to ranches located in Tizimín and Panabá. During field sampling farmers from the Sucilá area mentioned the frequent use of manure before and during the wet season to increase grass growth for cattle. This could explain with the highest mean value for potassium was in the wet season in the agricultural zone. Also, in areas of high values wells were in close proximity to areas of grazing which could increase manure and potassium influence on groundwater. Results from both the agricultural and non-agricultural zones indicated that increased precipitation during the wet season likely had an influence on dissolved substances concentrations in groundwater, while values were lower in the dry and cold front seasons where precipitation is reduced compared to the wet season. This seasonal variation of dissolved substances can be attributed to flushing and runoff of these substances that were absorbed or store in soil during the rest of the year from the soil surface into the aquifer especially during the wet season. Secondly, soil use had an effect on concentrations of dissolved substances in groundwater. According to farmers, the use of manure is mainly used to enhance pasture growth as is mainly applied just before the season, which represents an input of dissolved substances into groundwater. Nutrient management is a key factor that determines its infiltration into ground water, management practices such as method of application, time of application, volume, dosage and livestock management such as rotation within parcels and keeping livestock 100-200 feet away from wells, can mitigate groundwater contamination (Sahoo et al.2016).

The 2, 4-D analysis in field samples did not yield absorbance peaks equivalent to the 2, 4-D analytical standard, however, the absorbance spectra had similar peaks compared to two by-products of 2, 4-D such as dichlorophenol and trichlorophenol. As stated by Trivedi et al. (2015), 2, 4-D starts to degrade in the soil layer between 10-60 days. Contributes to the possibility of the 2, 4-D by-products that were mainly encountered in the agricultural and non-agricultural zone during the cold front season. The absorbance peaks for the sample R.B.Dios located in the municipality of Panabá was similar to a by-product of 2, 4-D trichlorophenol (Trivedi et al., 2015).The absorbance peak for the sample R.J.JUEZ in the cold front season was similar to that of the by-product dichlorophenol (Haughland et al., 2001).Degradation of the herbicide by soil microbes could have helped to increase degradation rate and the reason of observing signals similar to by-products (Kuwatsuka and Miya, 1989). Degradation can also occur in groundwater by microbes that are attached to organic matter that enters groundwater through leaching (USGS, 2017).This is a possible explanation for the detection of by-products in the thesis research which indicates the previous application of the 2,4-D. This is evident as farmers suggested the use of the herbicide before and during the wet season as sampling took place during the cold front and dry seasons which is a possible explanation of the detection of by-products as a result of degradation by microbes. As stated by Trivedi et al., (2015) 2,4-D residues are usually associated with organic matter which makes it prone to degradation by microbes. The presence of 2, 4-D by-products suggests that associated dissolved substance such as herbicides and agrochemicals in general may come from agricultural origin. Since both sampling sites indicated the possible presence of 2, 4-D by-products and confirmed by surveys, where farmers stated the use of the 2, 4-D containing Tordon 101 herbicide (see Annex). Through informal conversations, approximately 60% of farmers stated the use of 2, 4-D just before the wet season, hence a possibility for the observed results. During the dry season sampling one site showed evidence of 2,4-D (R.Paraiso) at this site physical evidence such as empty bottles of 2,4-D were found while conducting sampling suggesting the recent use of 2,4-D herbicide. (pers.obs.).

Kuwatsuka and Miwa (1989) suggested that traditional practice of farmers applying 2, 4-D to crops before the rain could have implications on water quality as it will cause the infiltration of herbicide residues to groundwater.To avoid groundwater contamination by herbicides, best practices should be considered such as proper storage of pesticide waste bottles, and proper method and dosage of application, among others. Method of application must be considered with the total residence time in soil as this will determine the amount of substance absorbed and the potential remaining active ingredient that could infiltrate to groundwater (Boivin et al., 2005). In the non-agricultural zone only one sampling site showed a trace of possible 2, 4-D by product (See Results section 7.4). Detection of possible by-products of the herbicide 2, 4-D in the non-agricultural zone suggests that herbicide use occurred nearby. Although 2, 4-D was not expected to be found in the non-agricultural zone its by-product was detected in one site which suggested which suggest its possible use in area for maintenance purposes of extraction well or the possible influence of its use from a nearby anthropogenic activities.

9.3 Spatial Patterns (Contour maps)

The contour maps generated with the results of this thesis, indicated that in the agricultural zone, nitrates, potassium and ammonia were higher in the southern area of the study zone; while in the non-agricultural zone sulphates and ammonia maximum values were noted in the mid-section of the study zone, in closer proximity to the highway (as compared to other section of the study zone).

Highest nitrate concentration was measured in one ranch of intense agricultural activity in the southern area of the agricultural zone, which has large parcels of short term crops, large number of cattle and heavy equipment used for sowing and reaping. While in the non-agricultural area, which is mainly composed of secondary growth forest with minimal influence from agricultural activity, the nitrate concentration was higher in the south part of the study zone; while sulphates have values as high as 29.94 mg $S\text{-}SO_4^{2-}/l$ in the northern area of the study zone. The rest of the values for sulphates in the non-agricultural zone were similar to concentrations measured in the agricultural zone.

Finally, a table comparing previous studies in other regions (karstic and non-karstic) is showed relative to the results obtained in this research (Table 6). The values for ammonia compared to previous research (Cervantes-Medel and Armienta., 2004, Kamal et al., 2015, Lawniczak et al., 2016) showed much higher for ammonia concentration values than data collected in this thesis. This could be a result of more intense agricultural activities within the other zones studied the variability in time span in which data was collected and analyzed. On the other hand values for phosphates and sulphates were higher compared to previous studies. Differences in the study area and intensity of anthropogenic activities can be possible causes for the contrast between data. However, nitrate values of the thesis data were higher than values from previous studies. This could be due to the fact that study zones from previous studies are located in different parts of Mexico where anthropogenic practices and geological conditions are different, in addition to the intensity of cattle farming in the northeastern Yucatan.

Table 6.Comparing maximum values of dissolved substances for the study area to maximum values encountered in the Yucatan region and other regions.

Author (year)	**Land use**	**Dissolved Substances**	**Concentration reported**	**Thesis Data (2017-2018)**
Cervantes-Medel and Armienta (2004)	Agricultural	$mgN\text{-}NH_4^+/l$	4.3-29.4	0.02-0.7
Lawniczak et al. (2016)	Non-Agricultural	$mgN\text{-}NH_4^+/l$	0.01-1.7	0.01-0.2
Kamal et al. (2015)	Non-Agricultural	$mgN\text{-}NH_4^+/l$	0.5-11.2	0.01-0.2
Gonzalez and Flores (2015)	Agricultural	$mgP\text{-}PO_4^{3-}/l$	0.1-2.7	0.1-1.0
Hernandez-Terrones et al. (2011)	Non-Agricultural	$mgP\text{-}PO_4^{3-}/l$	0.02-1.0	0.01-1.0
Chen et al. (2011)	Non-Agricultural	$mgP\text{-}PO_4^{3-/}l$	0.3-4.4	0.01-1.0
Muñoz et al. (2004)	Agricultural	$mgN\text{-}NO_3^{-2}/l$	2.1-10	0.3-20.3
Cervantes-Medel and Armienta et al., (2004)	Agricultural	$mgN\text{-}NO_3^{-2}/l$	4.3-12.5	0.3-20.3
Pacheco and Cabrera (1996)	Agricultural	$mgS\text{-}SO_4^{-2}/l$	250-355	9.2-23.5
Castro et al. (2009)	Agricultural	$mgS\text{-}SO_4^{-2}/l$	11.9-250	9.2-23.5
Gonzalez and Flores (2015)	Agricultural	$mgS\text{-}SO_4^{-2}/l$	13.4-46.2	9.2-23.5
Sanchez et al. (2016)	Non-Agricultural	$mgS\text{-}SO_4^{-2}/l$	4.32-326	8.7-29.6

Although agricultural activities have an impact on groundwater, only sulphates have a maximum permissible limit in the Ley Federal de Derechos de Agua para Riego, (2009) 250 mg $S\text{-}SO_4^{2-}/l$. High concentrations of sulphates can contribute to soil acidification and reduce crop yield. Data values from a previous study conducted by Pacheco and Cabrera (1996) in Ticul Yucatan reached the maximum limit of (250 mg $S\text{-}SO_4^{2-}/l$);

however, sulphate values reported in this thesis did not reach nor surpass the maximum limit for sulphate concentration set by the Ley Federal de Derechos de Agua para Riego. High values found in the previous study in Ticul Yucatan was attribute to possible agricultural activities such as the application of agrochemicals. Sulphate values in the agricultural zone for this research did not reach or exceed the maximum permissible limit which suggests possible natural origin such as the dissolution of sulphate containing minerals.

Fertilizer application methods and land use management strategies should be improved to reduce the risk of groundwater contamination. Farmers in the agricultural zone should only apply the recommended doses of fertilizer and herbicide indicated on each commercial agrochemical to reduce the surplus of dissolved substances that is prone to leach into groundwater. In addition farmers should consider a change of method as applying agrochemicals not near and during the wet season; however the timely use among the three seasons and not the accumulated use during the wet season. Also after the use of commercial agrochemicals waste bottles should be secured and stored in a designated area to prevent exposure of residues to the environment which can result in leaching. Concerning the non-agricultural zone the management agency of extraction wells should monitor wells near highways and urban development where higher concentrations of dissolved substances were encountered. In addition, updated studies should be conducted to evaluate factors that affect groundwater quality within both zones.

10. CONCLUSIONS

High concentrations of dissolved substances encountered in the agricultural zone can be a result of the use of agrochemicals such as fertilizers and herbicides which residues are possibly leaked into groundwater in higher amount during the wet season.

Values for the agricultural zone showed more physicochemical variation than values for the non-agricultural zone; however, land use and seasonal patterns did not have a significant influence on physicochemical properties as it had on dissolved substance.

Dissolved substances values were higher in the agricultural zone as compared to the non-agricultural zone suggesting the influence of anthropogenic activities on groundwater such as the application of agrochemicals, manure and cattle farming.

Concentrations of dissolved substances in groundwater were affected by seasonal patterns. Data values varied more in the agricultural zone especially during the wet season. This suggests the influence of infiltration of dissolved substances through higher precipitation and surface runoff during the wet season. Through informal conversations with farmers in the agricultural zone approximately 60% of farmers stated they use agrochemicals prior and during the wet season.

Ammonia had higher mean values in the agricultural zone than the non-agricultural zone. Significant differences were observed in nitrates in the agricultural zone, higher than mean values in the non-agricultural zone. Nitrates were one of the dissolved substances with the highest values in the agricultural zone during the wet season high concentrations found mainly in the southern area of the study zone.

Phosphates values were slightly higher for the agricultural zone and during the wet season, but not statistically different.

There were no significant differences for sulphates among land use and the seasons. Concentration slightly higher in the non-agricultural zone during the dry season are interpreted as influence of natural inputs through water rock-interactions the dissolution of sulphate containing minerals.

Higher values of potassium were found in study sites located in the western area of the agricultural zone, where famers admitted to use manure as a fertilizer to grow cattle grass, especially during the wet season. Potassium concentrations in the non-agricultural zone are considered from natural inputs.

The 2,4-D analysis resulted in three samples tested positive for possible by-products of 2,4-D, namely trichlorophenol and dichlorophenol. Through informal conversations in the agricultural zone approximately 60% of farmers stated the use of 2,4-D before the wet season, which serves as supporting evidence that land use practices such as the application of agrochemicals in the agricultural zone has an influence on dissolved substances in groundwater.

Nutrient management strategies are needed in agricultural zones, as nutrient loss through excessive application of fertilizers can increase nitrogen, phosphorus and potassium concentrations in groundwater, impacting its quality.

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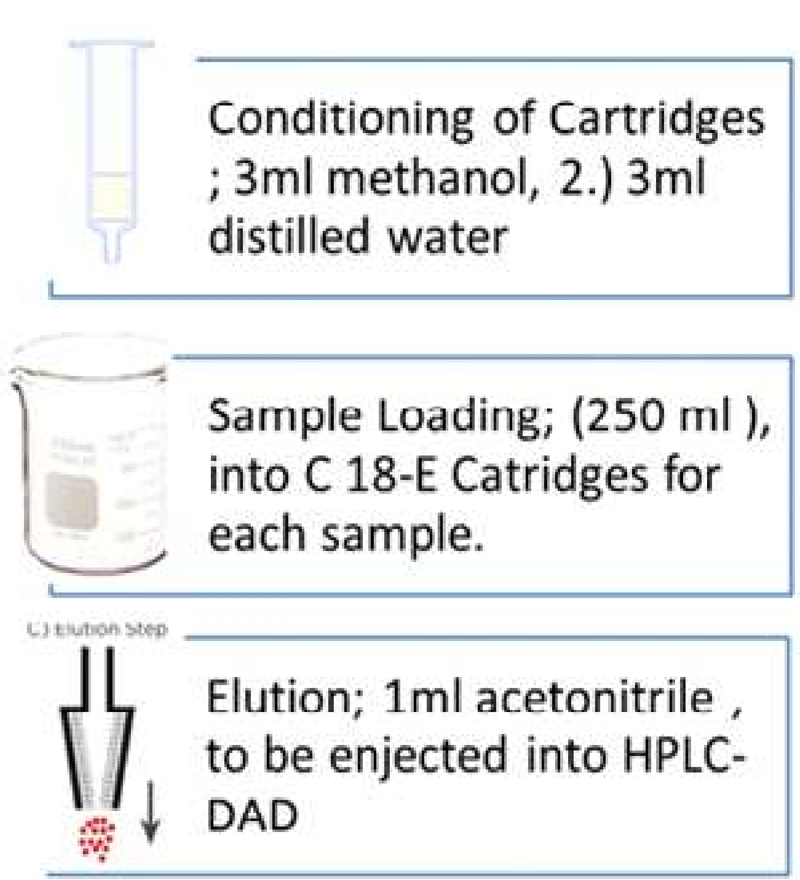
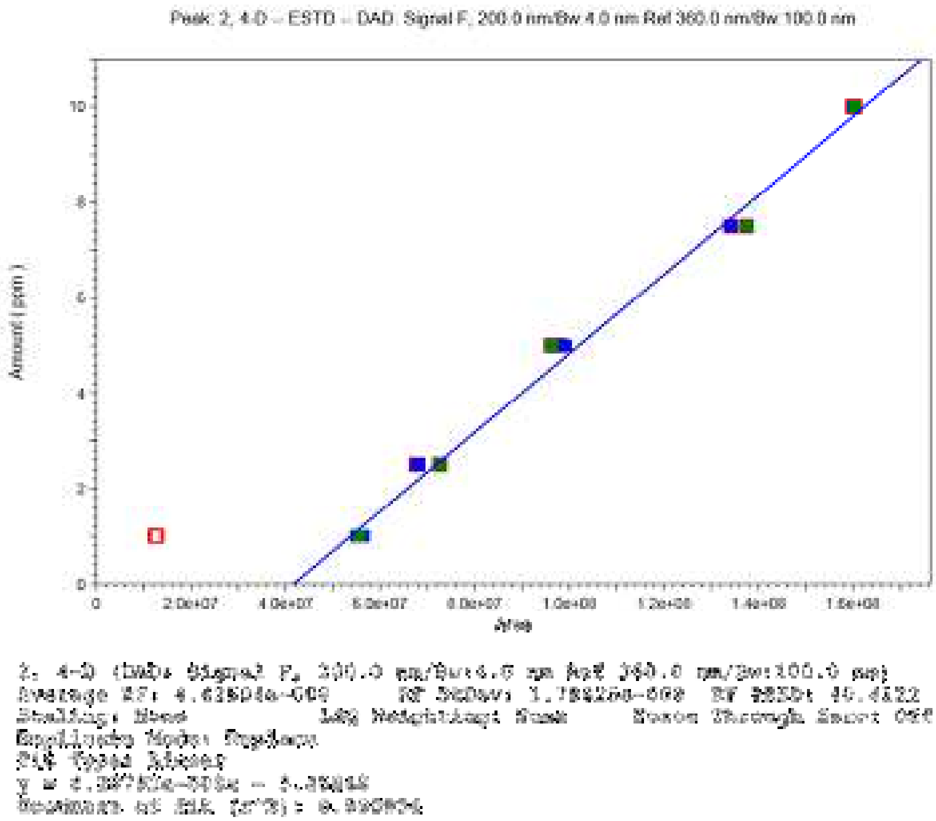
12. ANNEXES

Example of vials used for phosphate analysis (UV analyses) for the wet season in the urban zone having a total volume of 7ml.

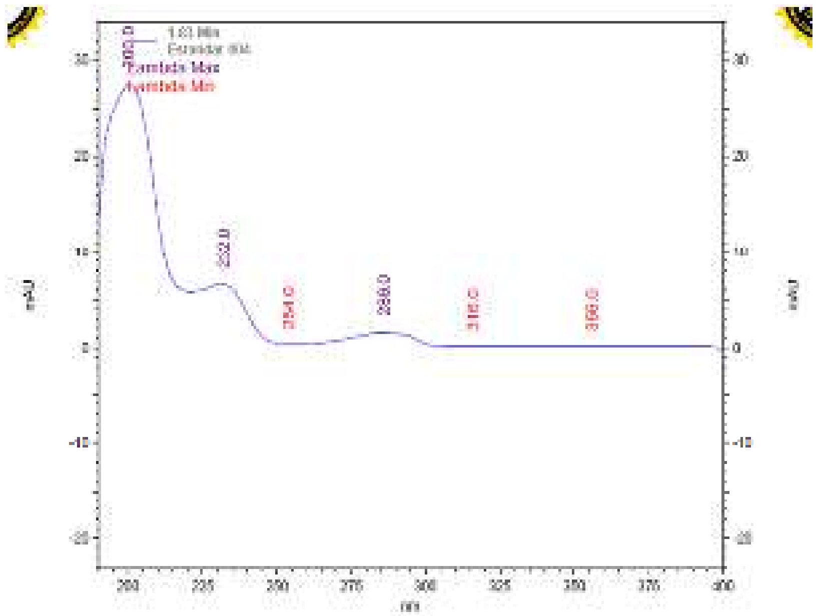
Flow Diagram for the solid phase extraction method (Caldas et al, 2010). Condition C18-E strata cartridges with 3ml methanol. Loading of 250 ml of sample and passed through funnel at a flow rate at approximately 10 ml/min. Elution of cartridges was conducted with 1 ml acetonitrile and placed in 2ml amber sample bottles to be analyzed.



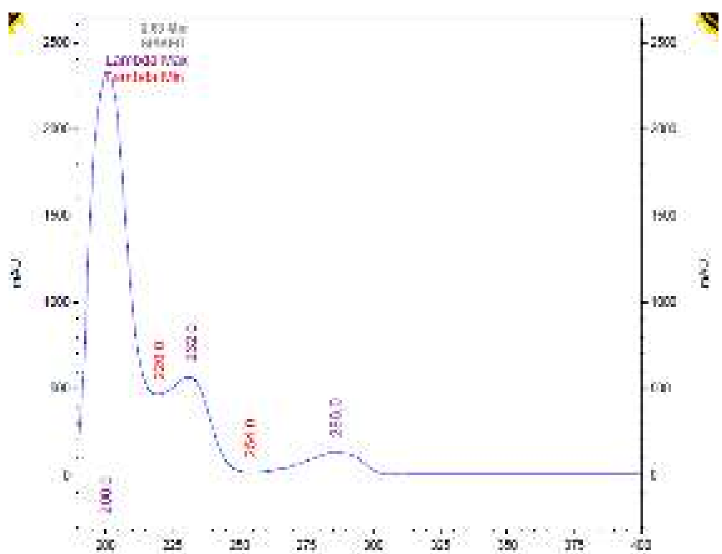
Example of Standard Calibration Curve for the detection of 2, 4-D with a HPLC-DAD. A total of five standards were prepared from a stock of 2, 4-D having a total concentration of 1000 mg/l. The five standards were prepared using acetonitrile with a total of 10ml for each one. Method derived from Caldas et al. (2010) *Herbicide Persistence in Rice Paddy Water in Southern Brazil*.



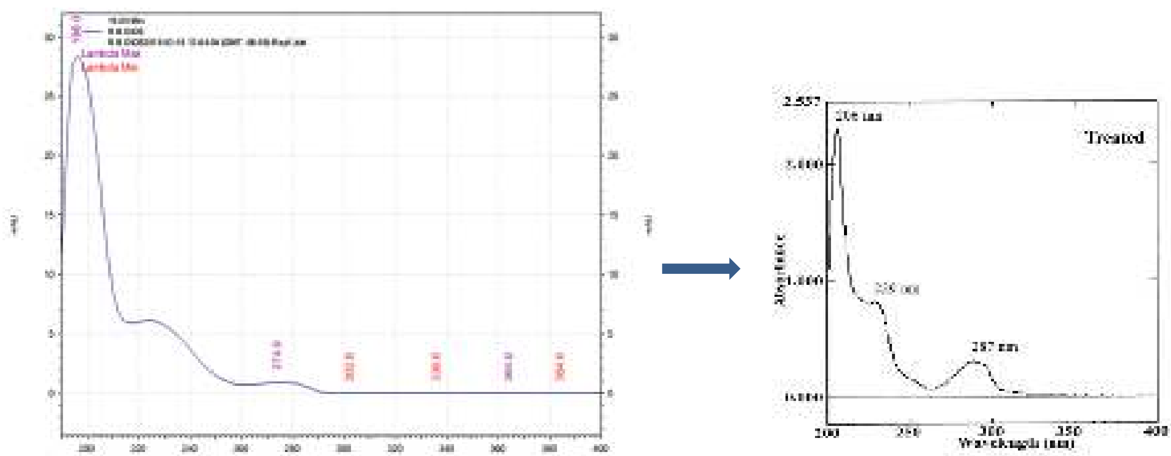
Absorption spectrum for the dry season sampling in the agricultural zone. Peak values yielded for this specific standard were; 200.0 nm, 232.0 nm and 286.0 nm which were similar to peak values for the spike and values of the sample tested positive for 2,4-D.



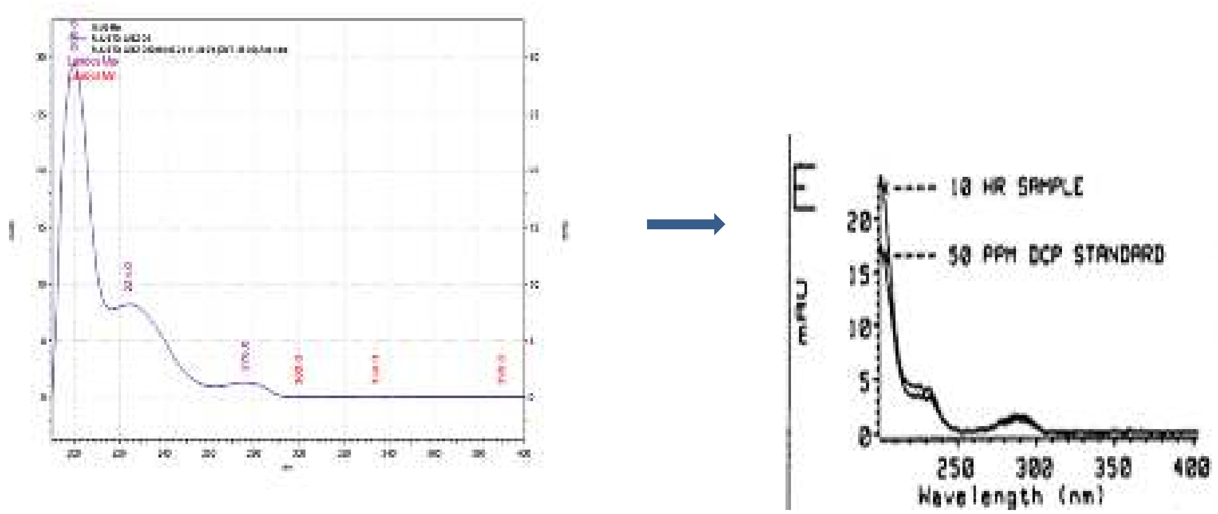
Absorption spectrum of the commercial formulation with Tordon101®. Absorbance peaks were; 200.0 nm. 232.0 nm and 286.0 nm which are also similar to that of the spectra of the 2,4-D standard.



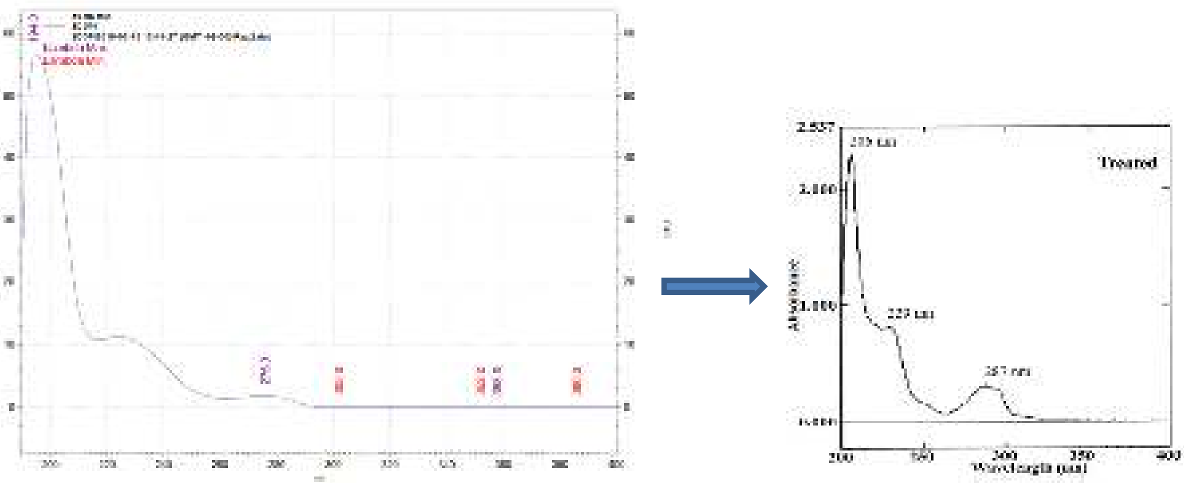
Absorption spectrum from HPLC analysis of 2,4-D showing absorbance peaks of substance in the agricultural zone (R.BDIOS) showing similarity to Trichlorophenol spectrum, a 2,4-D by-product. From Trivedi et al. (2015).



Absorption spectrum from HPLC analysis of 2,4-D showing absorbance peaks of substance in the agricultural zone (R.J.JUEZ) showing similarity to Dichlorophenol spectrum, a 2,4-D by-product. From Haugland et al. (1990).



Absorption spectrum from HPLC analysis of 2,4-D showing absorbance peaks of substance in the non-agricultural zone (ZC5P1) showing similarity to Trichlorophenol spectrum, a 2,4-D by-product. From Trivedi et al. (2015).



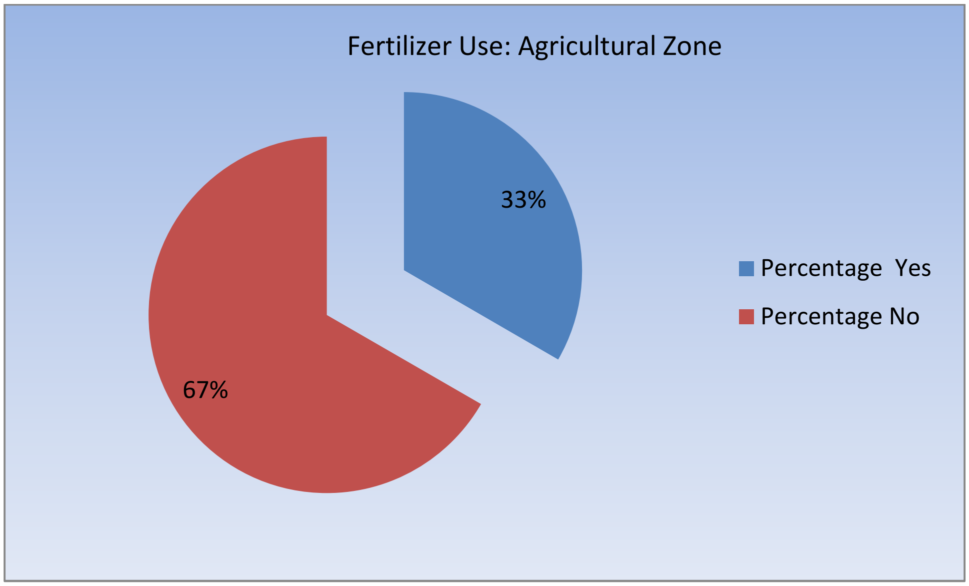
Example of field sheet used to record physicochemical parameters for the cold front season sampling for both the agricultural and non-agricultural zones. Physicochemical parameters such as pH, conductivity, total dissolved solids, redox potential and temperature were recorded for each sampling site as well as the date and time.

Hoja de Campo Salida #2 (Época: Nortes)

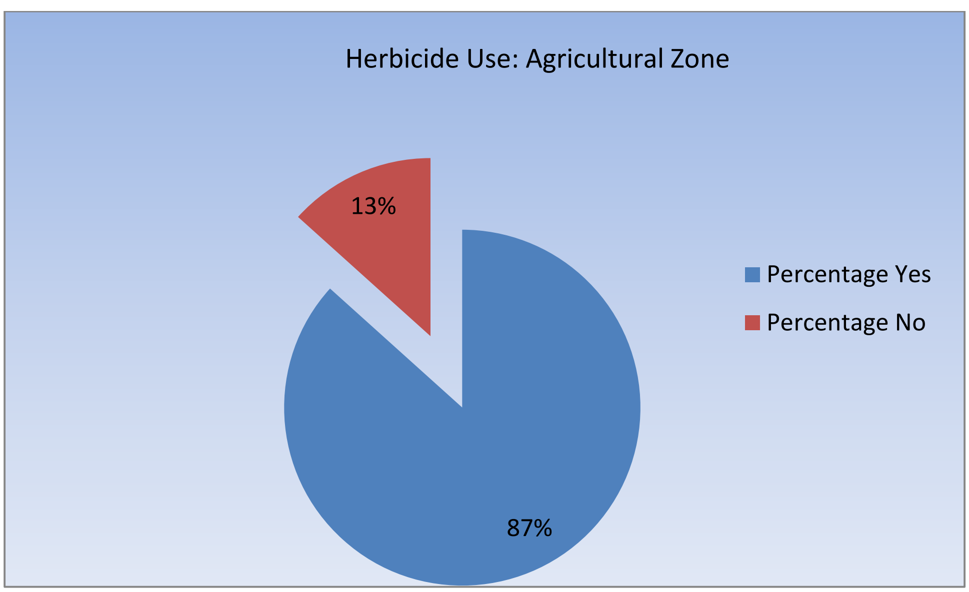
Fecha	Hora	Lugar	pH	Conductividad	TDS	Potencial Redox	Temperatura	Comentarios

Example of extraction wells. *Left*: AGUAKAN in the non-agricultural zone in the Municipality of Benito Juarez. *Right*: agricultural zone (Panabá) used for irrigating cattle feeding grass (Taiwan Grass)

Pie chart showing the percentage of fertilizer use in the agricultural zone: 67% confirmed non-use of fertilizers and 33% confirming the use of fertilizers



Pie chart showing the percentage of herbicide use within the agricultural zone: 87% of farmers confirmed the use of herbicides, 13% answered non-use of fertilizers



Pie chart showing seasonal percentage use of agrochemicals between the wet, cold front and dry seasons. More than half users (60%) admitted to the use of agrochemicals before and during the wet season.