SPATIOTEMPORAL PATTERNS OF SALT AND NUTRIENT CONTAMINATION IN LOS ANGELES COUNTY'S GROUNDWATER BASINS

by

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Abstract

Salts and nutrients are common contaminants in urban groundwater systems, and at certain levels these pollutants have been associated with adverse effects on agriculture, corrosion and mineral deposits on industrial piping, a decrease in the drinkability of water, and serious health problems. Groundwater pollution can stem from both natural and anthropogenic sources and given the high costs of remediation, groundwater managers are tasked with monitoring groundwater contamination and controlling its sources. With its large population, close proximity to the coastline and arid climate, Los Angeles County provides an important study area for the spatial and temporal analysis of salt and nutrient constituents across each of its 10 groundwater basins.

This thesis study utilizes the California Regional Water Quality Control Board data set consisting of groundwater quality samples drawn from underground storage tanks, site clean-up programs and land disposal sites to determine the spatiotemporal patterns across each basin. Results show that no spatiotemporal pattern was recognized, except that the salt constituents routinely exceeded the respective Basin Plan limits (unlike the nutrient constituents). In the end, more conclusive results could be determined with additional analysis and modeling that was better designed for sample collection and better controlled over the locations and depths at which the samples were taken.

Chapter 1 – Introduction

1.1 Groundwater and Sources of Contamination

Groundwater provides an important source of drinking water throughout the world. One half of the drinking water and 40% of the irrigation water used in the U.S. come from groundwater supplies (Corwin et al., 1997). However, multiple substances can contaminate groundwater leaving it unfit for human consumption. In 1993, the U.S. Environmental Protection Agency identified more than 200 chemical compounds present in groundwater, many of which negatively impact the quality (Ducci, 1999). Salts and nutrients are common contaminants in groundwater pollution. Excessive levels of salt in groundwater can create adverse effects for agriculture, corrosion and mineral deposits on industrial piping, and decrease the drinkability of water (Matsumoto, 2010). Excessive nutrients have been linked to serious health problems including low oxygen levels in the blood stream of infants, known as methemoglobinemia (Gardner and Vogel, 2005; Hudak, 1999, 2000; Hudak and Sanmanee, 2003; Lee et al., 2006; Masetti et al., 2008; Nolan et al., 1997, 2002; Pacheco and Cabrera, 1997), an increased risk of non-Hodgkin's lymphoma (Gardner and Vogel, 2005; Hudak, 1999, 2000; Hudak and Sanmanee, 2003; Masetti et al., 2008; Nolan et al., 1997, 2002; Strebel et al., 1989), and increased cancer risk through production of N-nitroso compounds in the body (Nolan et al., 2002; Pacheco and Cabrera, 1997; Strebel et al., 1989).

Salt and nutrient pollution in groundwater has been attributed to both natural and anthropogenic sources. Salts, such as sulfate and chloride, are naturally present in evaporite minerals: sulfate, anhydrite, and halite, as well as in sedimentary rocks that contained seawater during deposition (Hudak and Sanmanee, 2003). Salts also occur naturally through seawater intrusion and salinization in arid regions (Uliana, 2005). Nutrients are found naturally from weathering of nitrogen-bearing rocks, degradation of organic matter in soils and atmospheric deposition (Böhlke, 2002). Natural characteristics of soils and sedimentary layers also increase the ability for anthropogenic sources to contaminate groundwater. Unconfined aquifers combined with shallow water tables and coarse-grained, highly permeable unsaturated zones (Hudak, 1999; Nolan et al., 1997) provide conditions that favor salts and nutrients at the surface percolating through the soil to the groundwater table.

Anthropogenic sources of salt and nutrient pollution are numerous. Land use has a direct influence on the quality of groundwater because of the types of chemicals that can be introduced at the surface (Eckhardt and Stackelberg, 1995). Residential, municipal, commercial, industrial and agricultural activities all have the ability to harm groundwater quality (Nas and Berktay, 2010). Salts are contributed to groundwater from sources such as agricultural fertilizers and other chemicals, oil field brine, sewage, landfill leaching, industrial effluent and deicing salts from roadways (Hadak and Sanmanee, 2003). Nutrients are contributed to the environment through crop and lawn fertilizer, animal manure, septic systems (Hudak and Sanmanee, 2003), and the combustion of fossil fuels, which increases the levels of atmospheric nitrogen deposition (Puckett, 1994). Groundwater contamination can also be driven by human interaction with the groundwater table. Over pumping groundwater from deep aquifers can accelerate the movement of contaminants through the aquifer system (Kehew et al., 1996). Pumping can also increase the levels of salt water intrusion that occurs in groundwater basins near the coastline.

Point sources of pollution, such as sewage pipes and leaking septic tanks, provide a straightforward target for monitoring and regulation. These sites have attracted the attention of groundwater resource managers as they have worked to identify and contain highly toxic concentrations of salts and nutrients that pose an immediate threat to human health (Corwin et al., 1997). Nonpoint source pollutants, such as fertilizers, deicing salt and road runoff, are dangerous because their contaminant contributions are more difficult to limit and monitor. While these sources provide smaller concentrations of pollutants, their accumulation through time may persist over several years or decades (Corwin et al., 1997). Nonpoint source pollutants provide a different challenge to groundwater managers because they do not respect political boundaries (Corwin et al., 1997), leading to an increased need for a unified approach to monitoring and regulation.

Groundwater remediation is a costly, difficult, and slow process. The possible remediation strategies include excavation, surface capping, subsurface barriers, and chemical and biological treatment, among others (Ahn and Chon, 1999). With a strong dependence on groundwater aquifers for potable water, identifying areas where groundwater is at risk for contamination is an important and valuable step in managing and protecting this natural resource (Masetti et al., 2008; Tesoriero and Voss, 1997; Wilson et al., 1993). Oenema et al. (1998) examined the efficiency of policies the Netherlands imposed for nitrate and phosphorus management for farmers, requiring reports of all incoming and outgoing nutrients in imported and exported products on an annual basis. The management strategies recommended in this study were expected to lower the nitrate concentration from 40% in 1985 to 12% by 2037, although the authors believed that additional policies would be necessary in areas of high concern.

1.2 Groundwater Investigations and Geographic Information Systems

Groundwater quality studies are of interest to governments and management agencies, to help direct and fortify their policy decisions, as well as for university researchers, looking to document changes in groundwater quality while seeking to understand the sources of these pollutants. The latter is a substantial challenge because the various stocks and flows that characterize the natural hydrology cycle vary tremendously over space and time, and human modification of these systems more often than not adds to this complexity.

These complexities have led to numerous approaches for examining groundwater pollution and their sources. Studies have been conducted at different scales to uncover varying extents of groundwater pollution. While state (e.g. Navulur and Engel, 1997) and national scale (e.g. Nolan et al., 1997; Puckett, 1994) investigations are important for highlighting the global patterns of pollution and their sources, there are multiple variables that are site dependent and localized studies are recommended for developing support of individual groundwater management decisions (Nolan et al., 2002). Groundwater investigations set out to accomplish various goals, including the determination of sources of pollution, predicting the areas that are vulnerable to pollution, and measuring the spatial and temporal trends of the pollution.

Geographic Information Systems (GIS) have provided a new and useful means of supporting groundwater quality investigations. GIS provides suites of software tools that combine database management with digital mapping and analysis capabilities for spatially-oriented data (Fritch et al., 2000). There are many advantages of GIS for environmental monitoring, including groundwater analysis, advanced cartographic abilities, the capacity to organize and synthesize large amounts of data for spatial examination, and the capability to discover and display spatial relationships using specialized empirical and statistical models (Corwin et al., 1997). The utilization of GIS with a groundwater monitoring investigation allows the analyst to investigate the different outcomes using several models with numerous datasets across various scales (e.g. Araghinejad and Burn, 2005; Corwin et al., 1997; Goovaerts et al., 2005). The coupling of groundwater analysis with GIS increases the speed and ease in which results can be attained and conclusions can be drawn, enabling the ability to analyze larger datasets with more complicated models across larger spatial extents.

1.3 Purpose of this Thesis

This thesis study was designed to complement the development of salt and nutrient management plans by the Los Angeles Regional Water Quality Control Board, the agency responsible for designating specific standards for groundwater quality in Los Angeles and Ventura Counties. The purpose of this groundwater quality investigation is to characterize the spatial and temporal patterns of salt and nutrient groundwater quality in the 10 groundwater basins in Los Angeles County, California. In addition, the variables of depth to groundwater and the distance to the coastline are examined to determine the correlation of either variable with an increase in groundwater pollution in any of the 10 basins.

1.4 Thesis Organization

The remainder of the thesis contains four chapters. Chapter 2 summarizes prior work characterizing groundwater quality across a variety of natural and built environmental settings. Chapter 3 discusses the data and methodology used for this groundwater quality study. The study area, the methods of data collection, management and analysis are described in detail. Chapter 4 presents and discusses the results of the groundwater study, including maps of the spatial extent of pollution and the temporal patterns uncovered. Chapter 5 presents the conclusions that can be drawn from the analysis and proposes areas of further research.

Chapter 2 – Past Work

2.1 National and State Groundwater Contamination Studies

Small scale groundwater contamination studies provide an important understanding of the broader context of groundwater quality. These studies are conducted on national (e.g. Lake et al., 2003; Oenema et al., 1998, Puckett, 1994) and state (Ceplecha et al., 2004) scales. Small scale groundwater quality studies look at very broad datasets that require wide coverage with uniform data standards, often only available in the form of state or national published datasets. With these data sources, small scale groundwater quality studies typically utilize overlay and regression methods for their analysis to determine the extent of high groundwater pollution, or areas highly vulnerable to groundwater pollution.

Nolan et al. (1997), for example, produced a national nitrogen vulnerability map of the U.S. The map was created by overlaying national datasets including nitrogen loading and population density, as the nitrogen input variables, and soil drainage characteristics and woodland to cropland ratio, as the aquifer vulnerability input variables. The resulting map displayed areas with the combination of high and low nitrogen loading with high and low aquifer vulnerability. The largest areas identified as high vulnerability and high nitrogen loading were found in the Midwest, including Nebraska, Kansas, Iowa, northern Illinois, southern Wisconsin and western Michigan, in addition to central California, eastern Washington and southeast Pennsylvania. Additionally, areas with high vulnerability, regardless of nitrogen loading levels, can be utilized to identify where monitoring of groundwater pollution should occur.   Nolan et al. (2002) utilized regression modeling to predict nitrate contamination in shallow groundwater across the U.S. The regression model used national datasets for nitrogen loading, percent cropland, human population density, percent of well drained soils, depth to groundwater and presence of a fracture zone in the underlying aquifer. The resulting regression model was found to be well-correlated with observed groundwater data and depicted high probability areas in the High Plains of the Midwest, the central California basin, southeastern Washington and western Texas, all areas with extensive agricultural operations.

State scale groundwater contamination studies typically offer more detailed assessments of contamination. Hudak (2000), for example, conducted a state wide groundwater quality study of Texas, utilizing 7,793 wells from the Texas Water Department Board database to compile, map and evaluate regional patterns of nitrate using GIS spatial analysis. The study determined the percentage of polluted wells in each county, as well as the statistical correlation between nitrate concentration and well depth, total area fertilized, and market value of livestock. While the latter two variables were not found to be significant, there was a statistically significant inverse-correlation between concentration and well depth.

National and state scale studies provide an important view of the groundwater quality as a whole, identifying regional issues and characterizing groundwater pollution patterns. Policy makers and monitoring agencies can utilize small scale maps in order to better identify areas where localized groundwater studies would be appropriate as well as the areas to distribute funding for such studies. However, small scale studies ignore the contributions of local variables since they are not significant on the national scale, causing the study results to be inappropriate for local management to utilize for supporting decisions (Nolan et al., 2002).

2.2 County and Local Groundwater Contamination Studies

Urban groundwater is a large scale problem because it involves processes that occur in urban areas, most commonly counties or smaller areas. Large scale groundwater studies (conducted at the county scale or finer) provide a closer insight to groundwater quality by utilizing site-specific data. These local scale groundwater studies provide more meaningful results for groundwater managers because they include local conditions, exceptions and field data analysis. The finer scale approach requires fewer assumptions about the conditions applied in groundwater analysis methods, producing clearer results. This approach also supports the use of tailored data collection and the inclusion of site-specific factors that can contribute to groundwater contamination, providing a clearer picture of the processes affecting groundwater pollution in specific areas.

Multiple methods have been used for groundwater investigations on the local scale. One approach is the development of groundwater and constituent fate and transport models (Kehew et al., 1996; Mitchell et al., 2001; Wilson et al., 1993). Almasri and Kaluarachchi (2007), for example, developed a nitrate fate and transport model that utilized land use data and examined the relationship between point and non-point sources and nitrate levels in the soil. Their model, which was successfully verified with groundwater monitoring data, utilized the spatial distribution of on-ground nitrogen loadings, a simulation of soil nitrogen processes including mineralization, nitrification and denitrification, and a model of the groundwater flow processes. Lee et al. (2006) achieved similar success using a nutrient fate and transport model to describe the nitrogen content in the groundwater. Both of these models provide groundwater managers with important information about those processes that affect pollutants transport beyond the water table.

Another approach to large scale groundwater studies has been through the coupling of GIS software and statistical studies to examine the sources and spatial distributions of groundwater pollution (Ahn and Chon, 1999; Kaçaroğlu and Günay, 1997; Pacheco and Caberera, 1997). Hudak and Sanmanee (2003) best demonstrate this method of groundwater analysis in a selection of counties in central Texas. Their study uses GIS and statistical analysis to examine the correlations between solutes (nitrate, chloride, sulfate and fluoride), well depth and land use. The study concluded that there was no statistically significant correlation between solute samples exceeding the maximum contaminant level (MCL) for drinking water and land use. However, there was a positive correlation determined between chloride and sulfate samples exceeding the MCL limit, as well as an inverse correlation found between nitrate samples exceeding the MCL limit and well depth, a conclusion also noted by several other studies (Ahn and Chon, 1999; Eckhardt and Stackelburg, 1995; Gardner and Vogel, 2005; Hudak, 1999, 2000; Pacheco and Cabrera, 1997; Tesoriero and Voss, 1997). Groundwater managers can utilize these studies to understand the spatial patterns of pollution in their region.

Another approach to local groundwater pollution studies is the use of weighted overlay or regression methods to demonstrate the correlation between groundwater pollution and its sources. In general there are two such approaches, regression models withpredetermined variables and exact weights, such as DRASTIC and SINTACS (Fritch et al., 2000; Ducci, 1999; Masetti et al., 2008; Napolitiano and Fabbri, 1996; Van Stempvoort et al., 1993), or regression models that determine the degree of correlation between possible variables and instances of groundwater pollution (Eckhardt and Stackelberg, 1995; Gardner and Vogel, 2005; Kaown et al., 2007). These methods produce maps which show the probability or susceptibility of each area to groundwater pollution based on the weighted combination of the examined explanatory variables. The DRASTIC and SINTACS models use the variables depth to water, net recharge, aquifer media, soil media, topography, impact of vadose zone media and hydraulic conductivity, while other regression models have examined variables such as land use and population density. Groundwater susceptibility maps help groundwater managers identify vulnerable areas in regions that should be monitored for pollution levels.

A final approach to local groundwater quality studies utilizes geostatistics (Goovaerts et al., 2005, Lin et al., 2001, Liu et al., 2004; Pozdnyakova and Zhang, 1999). Geostatistics produces a continuous surface using collected groundwater samples and utilizing spatial relationships and statistics to determine the most likely values for the resulting surface at unmeasured locations. One of the major benefits of geostatistics is the lowered cost of field data collection while producing equally, if not more, accurate results. For groundwater quality studies, interpolated surfaces can show the constituent pollution across an area, and can be combined with other interpolated surfaces to create a groundwater quality map (Nas and Berktay, 2010). However, since the most important part of utilizing geostatics is the selection of the interpolation model, many studies have focused on comparing and determining which model produces the most accurate results for their data set (D'Agostino et al., 1998; Dash et al., 2010).

2.3 Groundwater Contamination in California

Numerous studies have examined groundwater quality in the state of California, including some groundwater quality studies that have focused on the groundwater basins in Los Angeles County. The five most notable studies and their findings have been outlined in Table 1 and discussed below. In 2003, the California Department of Water Resources completed the fifth update to the Bulletin 118 series, a set of groundwater studies that began in 1952. This groundwater study investigated thousands of public supply wells in the South Coast regional study area, which included basins from parts of Los Angeles, Ventura, Orange, Riverside, San Bernardino and San Diego Counties. The study determined 16% of wells exceeded maximum contaminant levels for nitrates and 5% exceeded maximum contamination levels for inorganics, such as total dissolved solids (TDS) (California Department of Water Resources, 2003).

The U.S. Geological Survey (USGS) has also completed two notable studies on groundwater quality in Los Angeles County. From 1995 to 2002, the USGS conducted a spatial analysis of the groundwater quality in the four sub-basins of Los Angeles Coastal Plain basin: Central, West Coast, Santa Monica and Hollywood (Figure 1). The study collected hydraulic, geologic and chemical data from 20 new and 58 existing wells across the basin. The instances of TDS and chloride contamination were found to be strongly correlated ($r^2 = 0.98$) and were spatially concentrated along the coast of the study area

Table 1: Summary of notable Los Angeles County groundwater contamination studies.

Study	**Period**	**Location**	**Noted Contamination**
California Department of Water Resources, Bulletin 118	2003	Basins from Los Angeles, Ventura, Orange, Riverside, San Bernardino and San Diego Counties	Nitrates and TDS contamination
U.S. Geological Survey	1995-2002	Los Angeles Coastal Plain basin	Chloride, sulfate and TDS contamination
U.S. Geological Survey GAMA Study	2005	San Fernando, San Gabriel and Raymond basins	Nitrate and TDS contamination
U.S. Geological Survey GAMA Study	2006	Los Angeles Coastal Plain basin	Boron, chloride, sulfate, and TDS contamination
U.S. Geological Survey GAMA Study	2007	Santa Clara River Valley basin	Chloride, sulfate and TDS contamination

and deeper in the groundwater basin. Sulfate contamination was found along the south coast of the study area but showed no trend of contamination with depth. There were no instances of contamination by nitrates (Reichard et al., 2003).

The Groundwater Ambient Monitoring Assessment (GAMA) Program is the second notable study completed by the U.S. Geological Survey. This study was completed in cooperation with the State Water Resource Control Board and included three separate studies of groundwater basins in Los Angeles County. Twenty-four wells were monitored in the San Fernando, San Gabriel and Raymond groundwater basins from May to July 2005. Multiple groundwater solutes and variables were examined, including salt and nutrient constituents. The nutrient constituent measurements were compared against the U.S. maximum contaminant levels (MCL-US) as well as the California maximum contaminant levels (MCL-CA); often these limits are the same. The chloride, sulfate and TDS salt constituents were also compared to the California Department of Public Health secondary maximum contaminant levels (SMCL-CA), which have both an upper and lower threshold for each constituent. The boron samples were compared against the California Department of Public Health notification level limits (NL-CA). Nitrate exceeded the MCL-US threshold in one well and TDS exceeded the SMCL-CA lower threshold in six wells (Land and Belitz, 2008).

Twenty-six wells were monitored in the Santa Clara River Valley Basin from April to June 2007 as a part of the GAMA study. These wells exceeded the SMCL-CA lower thresholds for chloride, sulfate and TDS in one, nine and eight wells, respectively, and the SMCL-CA upper thresholds in four, ten and 18 wells, respectively (Montrella and Belitz, 2009). Nineteen wells in the four sub-basins of the Los Angeles Groundwater Basin (Central, Hollywood, Santa Monica and West Coast) were monitored from June to November 2006 in this study as well. Sulfate and TDS concentrations exceeded the SMCL-CA lower threshold in one well each; the chloride, sulfate and TDS concentrations exceeded the SMCL-CA upper threshold in one, one and 13 wells, respectively, and the boron concentration exceeded the NL-CA level in one well (Mathany et al., 2009). The monitoring periods were not long enough to examine temporal trends and no attempts were made to analyze spatial patterns in these studies either.

Chapter 3 - Data and Methods

3.1 Study Area

Los Angeles County provides an important study area for salt and nutrient groundwater contamination due to the large urban population, the proximity to the ocean and the semi-arid climate. The geologic conditions of the basin provide the most direct contribution to the quality and availability of groundwater. The regional geology is dominated by the large bend in the San Andreas Fault which formed an east-west mountain range, the Transverse Ranges, splitting Los Angeles County in half. The basins that have formed in and around the Transverse Ranges are filled with alluvium eroded from the mountains. The periodic change in sea-level also provided a source of intermittent marine sediment deposition across the southern portion of the county.

The resulting geology consist of deposits, varying in thickness, of marine and alluvial sediments, comprised of sand, gravel, and conglomerate with intermittent silt and clay beds, of Holocene, Pleistocene, and Pliocene age (Mathany et al., 2009). The unconsolidated and semi-consolidated sedimentary composition of these basins provides the perfect setting for groundwater aquifers, while the intermittent layers of clay form impenetrable barriers, known as aquitards, creating confined aquifers. The Los Angeles County basins each contain multiple layered aquifers that vary in thickness. While the top unconfined aquifers are subject to the direct leaching of pollution from the surface, over time the pollution is able to travel between layers through cracks and faults into the confined aquifers below. The pollution of these lower aquifers poses a larger problem because the water flows slower at these depths creating an accumulation of pollution that can take a long time to revert.

There are other natural conditions of the study area which contribute to the quality and availability of groundwater in Los Angeles County including climate and the proximity to the coastline. The county's semi-arid climate, with an average of 15.5 inches of precipitation each year (National Weather Service Forecast Office, 2012), is broken into a dry season from May through October, and a wet season from November to April during which almost all of the annual precipitation falls. This small amount of precipitation provides moderate recharge to the groundwater basins during the winter and nearly no recharge during the summer. Los Angeles County also has 75 miles of coastline, creating the threat of salt-water intrusion to the basins closest to the coast. While this issue has been addressed through the use of injection wells that pump water into the groundwater table, pushing the intruding seawater plume back toward the coastline (Johnson, 2007; Mathany et al., 2009), it remains an active concern for Los Angeles County's groundwater managers.

With a population of 9.8 million people in Los Angeles County there are multiple sources of urban groundwater pollution that can negatively affect the underlying groundwater basins. Urbanization impacts the quantity of available groundwater through the large proportion of impenetrable surfaces, such as paved roads, parking lots and buildings, which limit the ability for precipitation to seep through the soil and recharge the groundwater (Barrett, 2008). The land use of the county includes urban residential, commercial, and industrial, each of which produces its own salt and nutrient contaminants that can infiltrate and pollute a groundwater basin. Urban storm water runoff is a form of non-point source pollution including, street litter, animal wastes, combined sewer overflows, and construction and industrial activity wastes, among others (Nussbaum, 1990). This run-off may carry the pollution into the groundwater where infiltration and percolation occur. Other sources of urban water pollution include underground storage tanks, landfills, leaking sewers and industrial and retail locations that spill chemical solvents (Lerner, 2008).

This thesis study investigates four salt contaminants that commonly appear as urban groundwater pollutants: boron (B), chloride (CL), sulfate (SO_4) and total dissolved solids (TDS). Boron is often used as an additive in detergent, fertilizer, glass, ceramics and cosmetics (Zhao and Liu, 2010), all of which are common contributors to pollution in urban sewage, landfills and storm water runoff. Household sewage, landfill leachate, industrial effluent, urban runoff and saline intrusion have all been noted as sources of chloride (Nas and Berktay, 2010; Hudak and Sanmanee, 2003). Sulfates are used commercially in the chemical industry and are discharged into groundwater through industrial wastes (Nas and Berktay, 2010) as well as through sewage and landfill leachates (Hudak and Sanmanee, 2003). The constituent total dissolved solids (TDS) measures the minerals, metals and other compounds in solution (Nussbaum, 1990). Elevated total dissolved solids concentrations have been attributed to fertilizers, oil field brines, industrial discharges and sewage effluents (Matsumoto, 2010).

Four nitrogen contaminants common in urban groundwater pollution were also investigated in this thesis study: nitrite-nitrogen (NO_2-N), nitrate (NO_3), nitrate-nitrogen

(NO_3-N) and nitrite-nitrogen plus nitrate-nitrogen (NO_2-N+NO_3-N). Leachate from septic systems, urban runoff, and combined sewage overflow are important urban sources of nitrogen (Puckett, 1994). Urbanization also provides a large source of nitrogen pollution that can infiltrate groundwater through the combustion of fossil fuels (Puckett, 1994; Hudak and Sanmanee, 2003). The dense population of motor vehicles in Los Angeles County has contributed to the degradation of the air quality, providing conditions that are commonly referred to as 'smog.' The chemicals released into the air through the burning of fossil fuels are redistributed to the ground through atmospheric deposition, another large source of nitrogen pollution to the area.

There are 10 groundwater basins within Los Angeles County (Figure 1). These basins vary greatly in their size as well as the current state of groundwater quality and availability. The smallest basins include Malibu Valley (613 acres), Russell Valley (3,100 acres), Raymond (26,200 acres), and Santa Clara River Valley East (66,200 acres). The Malibu Valley groundwater basin, located along the west coast of Los Angeles County, drains toward the coastline to the south. Both the Russell and Santa Clara River East groundwater basins, located in the northwest corner of Los Angeles County, flow into larger groundwater basins located in Ventura County to the north. The Raymond groundwater basin, located between the San Fernando and San Gabriel basins, flows directly into the San Gabriel basin, located to the southeast. The San Fernando (145,000 acres), San Gabriel (154,000 acres) and the Los Angeles Coastal Plain (310,900 acres) are the largest groundwater basins in Los Angeles County. The San Fernando and San Gabriel basins are located within the Transverse Ranges; these groundwater basins flow south, through the small drainage pathways that wander through the mountains and into the Central sub-basin of the Los Angeles Coastal Plain basin. The Los Angeles Coastal Plain basin is broken into four sub-basins: the Santa Monica basin (32,100 acres) to the northwest, the Hollywood basin (10,500 acres) to the north, the West Coast basin (91,300 acres) to the west and the Central basin (177,000 acres) to the east. The groundwater flow patterns in this area are affected by sea-water intrusion injection along the coastline in the west and southwest portions of the basin, which directs the groundwater flow away from the coast. The groundwater flows in a southeast direction in the remainder of the basin.

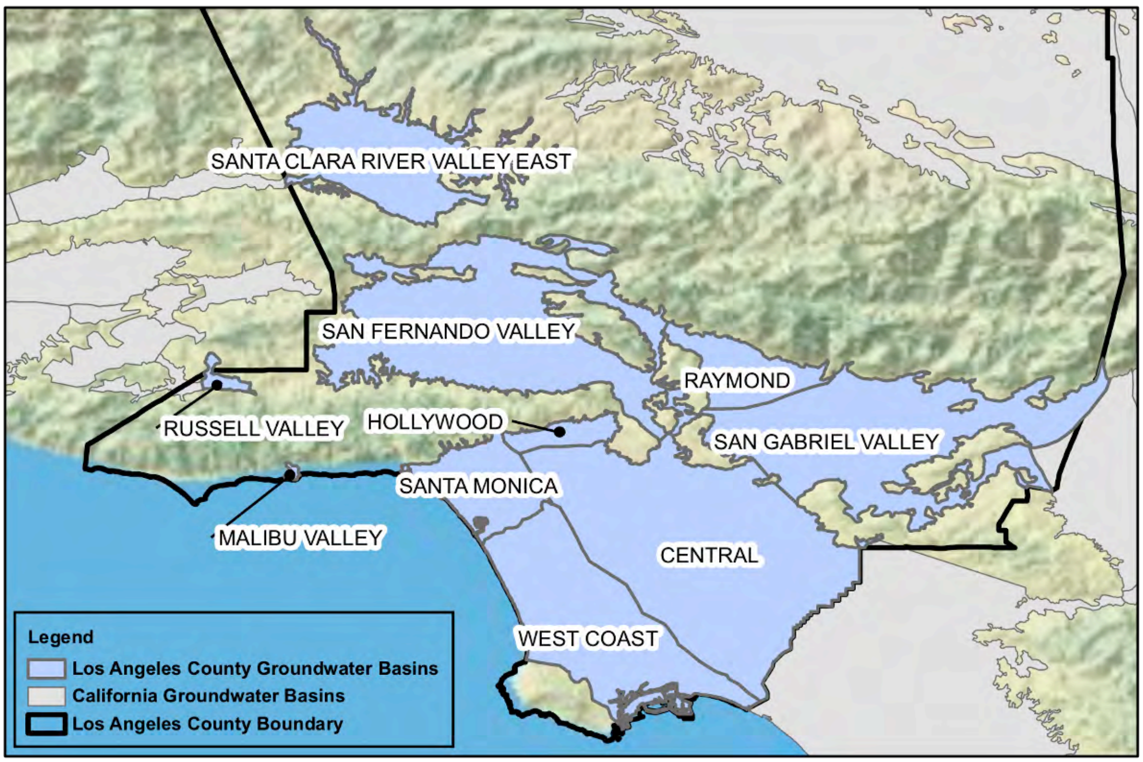

Figure 1: Los Angeles County's groundwater basins.

There are documented salt and nutrient groundwater quality issues in several of the Los Angeles County groundwater basins. Both the San Fernando and San Gabriel

Basins have historically contained high concentrations of nitrate from subsurface sewage disposal and past agricultural activities (California Regional Water Quality Control Board, 1994). With discontinuous confining layers in these alluvial basins, the pollutants have been able to seep through to the groundwater. In the San Gabriel Basin, approximately 20% of the groundwater production for municipal use has been closed due to pollution (California Regional Water Quality Control Board, 1994). The four sub-basins of the Los Angeles Coastal Plain groundwater basin have documented salt and nutrient groundwater quality issues including seawater intrusion near the coastline and organic as well as inorganic pollutants originating from leaking tanks, leaking sewer lines and illegal discharges (California Regional Water Quality Control Board, 1994). The issue of seawater intrusion has been addressed through injection wells which have formed a freshwater barrier along the coastline; however, their effectiveness must be continuously monitored. In addition, the discontinuous confining layers in these alluvial basins have also provided a path for pollutants to slowly filtrate to deeper aquifers (California Regional Water Quality Control Board, 1994).

The State Water Resource Control Board (State Board) is the California agency in charge of designating the beneficial uses of the surface and groundwater as well as the narrative and numerical objective that must be attained and maintained for acceptable groundwater quality. In Los Angeles County, the Los Angeles Regional Water Quality Control Board (Regional Board) is the local agency in charge of these designations. The Basin Plan began setting numerical limits for Los Angeles and Ventura County groundwater quality in 1952. Since then there have been multiple revisions to address the changes in groundwater quality and management, the most recent being completed in 1994. The 1994 Basin Plan revision designates the numerical limits that each of the eight constituents in this thesis study must meet to maintain an acceptable level of groundwater quality. The limits attributed to the four salt constituents vary by basin and are summarized in Table 2. In addition, salt constituent limits vary across each basin, but since this thesis is conducting analysis at the basin scale, the lowest limits designated for each constituent were applied to the whole basin. The nutrient limits are uniform across all county basins: ground waters shall not exceed 1 mg/L as nitrite-nitrogen (NO_2-N), 45 mg/L as nitrate (NO_3), 10 mg/L as nitrate-nitrogen (NO_3-N) and 10 mg/L nitrogen as nitrate-nitrogen plus nitrite-nitrogen (NO_2-N + NO_3-N) (California Regional Water Control Board, 1994). Nitrate and nitrate-nitrogen are both varieties of the nitrate nutrient which occur in nature in two different forms. The nitrate nutrient is 4.4 times heavier in molecular weight than the nitrate-nitrogen nutrient; therefore, the nitrate limit is approximately 4.4 times larger than the nitrate-nitrogen limit (45 and 10 mg/L, respectively).

These eight salt and nutrient constituents, also generally referred to as analytes, commonly exceed their designated standards, which has led the Regional Board to begin the development of individual salt and nutrient management plans for each of the groundwater basins in the county. The goal of salt and nutrient management planning is to understand the present level of pollution, calculate the assimilative capacity of each salt and nutrient and develop a remediation strategy to obtain lower levels of salt and nutrient pollution in each basin. This thesis study will support the salt and nutrient plan

Table 2: Groundwater constituent limits (in mg/L) by groundwater basin (California Regional Water Control Board, 1994).

Basin	Sub Basin	Boron	Chloride	Sulfate	TDS
Los Angeles Coastal Plain	Central	1.0	150	250	700
Los Angeles Coastal Plain	Hollywood	1.0	100	100	750
Los Angeles Coastal Plain	Santa Monica	0.5	200	250	1,000
Los Angeles Coastal Plain	West Coast	1.5	250	250	800
San Fernando		1.5	100	300	700
San Gabriel		0.5	100	100	450
Raymond		0.5	100	100	450
Russell Valley		1.0	250	500	1,500
Malibu Valley		2.0	500	500	2,000
Santa Clara River Valley	Santa Clara River Valley East	0.5	100	150	700

process by characterizing the spatiotemporal patterns of four salt constituents and four nutrient constituents and their instances of exceeding the limit in each of Los Angeles County's 10 groundwater basins.

3.2 Groundwater Data Collection and Management

Groundwater data was downloaded from the State Water Resources Control Board Geotracker website (http://geotracker.waterboards.ca.gov/). Geotracker is the State Water Resource Board's data management system that contains information on all sites which are both managed by the State Water Resource Board and impact groundwater, including active and closed underground storage tanks, site clean-up programs, and land disposal sites. This system allows for sites to upload electronic groundwater data as required by their regulatory permits. The system compiles these data and provides an interactive GIS interface to view the sites and makes the data available for download by county.

The data used in this study was downloaded in September 2011 from the 'Download ESI Data" page of the Geotracker data management site. Three files were obtained: (1) the EDF dataset - Electronic Deliverable Format data which contains every constituent measurement at every site that has been submitted electronically to the Regional Board, and similarly, (2) the Geo_XY dataset - a table of all of the sites in Los Angeles County and their geographic coordinates, and (3) the Geo_Well dataset - a table of all of the depth to groundwater measurements taken at each site. The data dictionaries for these three tables were also obtained from the Geotracker data management site and used for reference.

GIS data describing the boundaries of the 10 groundwater basins in Los Angeles County were also obtained. Specifically, a polygon shapefile was downloaded from the Department of Water Resources Bulletin 118 groundwater basin maps and descriptions website (http://www.water.ca.gov/groundwater/bulletin118/gwbasin_maps_descriptions.cfm). The file contained the polygon areas of all the groundwater basins in California, of which the 10 groundwater basins in Los Angeles County were selected and clipped for use in this thesis study. In addition, the GIS data for the boundary of Los Angeles County was acquired from the Los Angeles County GIS Data Portal website (http://egis3.lacounty.gov/dataportal/).

The EDF data file was imported into SAS Business Analytics Software in order to extract the data for the eight targeted constituents of this study: boron (B), chloride (CL), sulfate (SO_4), total dissolved solids (TDS), nitrite nitrogen (NO_2-N), nitrate (NO_3), nitrate-nitrogen (NO_3-N) and nitrate-nitrogen plus nitrite-nitrogen (NO_3-N+NO_2-N). The exported data was cleaned up by removing measurements made in units that were unable to translate to mg/L because they required a density calculation in order to be converted (i.e. mg/kg, PPM and percent), resulting in the removal of 0.09% of the data. All measurements in μg/L units were converted into mg/L. The remaining data were then joined to the Geo_XY data table to provide geographic locations for the constituent measurements to be analyzed spatially. The Geo_XY locations were only matched to 75% of the EDF data, and further, only 66% of the data points fell within the boundaries of the 10 groundwater basins in Los Angeles County.

Each of the returned data points was next assigned to a season based on the day that the constituent measurement was taken: summer, coded as S.YY, (May through October) and winter, coded as W.YY-YY, (November through April) according to the annual precipitation patterns in Los Angeles County. The EDF data ranged from July 2001 through June 2011; because summer 2001 and summer 2011 did not contain data for every month in the season, these data points were removed from the set. Taken as a whole, 64% of the original data set was retained and used for the evaluation conducted in this thesis study.

The removal of some of the original data might have altered the spatiotemporal patterns that characterize Los Angeles County in this thesis study. Table 3 was used to investigate how this data cleaning process might have affected the characteristics of the data. The comparison shows that the average concentrations decreased for all of the salt constituents (boron, chloride, sulfate, and TDS), whereas the concentrations increased for three of the four nutrient constituent averages (nitrate, nitrate-nitrogen, and nitrite-nitrogen plus nitrate-nitrogen) following data removal. The nitrite-nitrogen constituent showed the least change. Overall, these changes suggest that the salt constituent data used in this study will most likely contain a smaller fraction of samples exceeding the standard than the larger, all-inclusive dataset, while the nutrient constituent data used in the study will more than likely contain a larger fraction of samples exceeding the standard than the larger, all-inclusive dataset. This effect on the data set was taken into account when analyzing the results of the analysis.

Table 3: Changes in constituent statistics following data removal as directed in the text.

	Dataset	# Samples	Average	Std. Dev.	Minimum	Maximum
B	Original	5,185	0.84	1.71	0	34
	Final	2,707	0.59	1.24	0	23
CL	Original	16,474	289.81	1,118.74	0	24,100
	Final	8,629	226.68	849.68	0	20,000
SO4	Original	54,892	528.11	1,746.89	0	93,000
	Final	37,285	512.04	2,024.48	0	93,000
TDS	Original	12,885	2,342.52	6,510.53	0	315,000
	Final	6,817	2,117.17	5,694.50	0	97,500
NO2N	Original	5,713	0.12	1.62	0	88
	Final	3,336	0.10	1.63	0	88
NO3	Original	8,608	10.07	24.04	0	560
	Final	4,839	10.93	25.05	0	460
NO3N	Original	40,167	4.32	11.30	0	800
	Final	28,407	4.48	10.90	0	800
NO3-NO2N	Original	1,341	12.35	75.40	0	978
	Final	734	20.99	101.00	0	978

The final EDF data set was then joined to the Geo_Well table using SAS to match the well depth measurements taken on the closest day to the date each sample was taken in the final EDF data set. Well depths were matched to 96% of the final EDF data. In addition, the distance to the coastline was calculated with the Near analysis tool in the ArcGIS Analysis Toolbox and added as a field to the final EDF table. These last data management steps completed the final dataset utilized for the spatiotemporal analysis of groundwater quality characteristics in Los Angeles County. The GIS analysis was conducted using Esri's ArcGIS 10.0 mapping software. The data set was documented in the metadata as having been collected in the North American Datum of 1983 (NAD 83) and was mapped in ArcMap 10.0 in the Geographic Coordinate System (GCS) North American 1983.

3.3 Methods of Analysis

Data exploration, the first step of the analysis, began with an evaluation of the spatial characteristics of the Geotracker dataset. Since these samples were all collected from monitoring wells at permitted sites, the samples are found in clusters across the groundwater basins. Figure 2 displays the clusters as they can be observed at the basin and sub-basin scales. The limited spatial distribution of this data reveals the limited options for methods of spatial analysis because the location, depth and time interval variables of the sampling events are not controlled, an assumption that many spatial analysis techniques make.

With the limiting spatial analysis options, a tabular analysis was conducted first on each of the salt and nutrient constituents in each of the groundwater basins to determine the presence of increasing or decreasing trends in the percentage of samples exceeding the respective Basin Plan limits (see Tables 4 through 10). Once the tables were analyzed, certain constituents required graphs to further aid in the visualization and recognition of trends in the percent of samples exceeding the respective Basin Plan limits (see Figures 3, 5, 7 and 9). Additional analysis was conducted to examine spatiotemporal

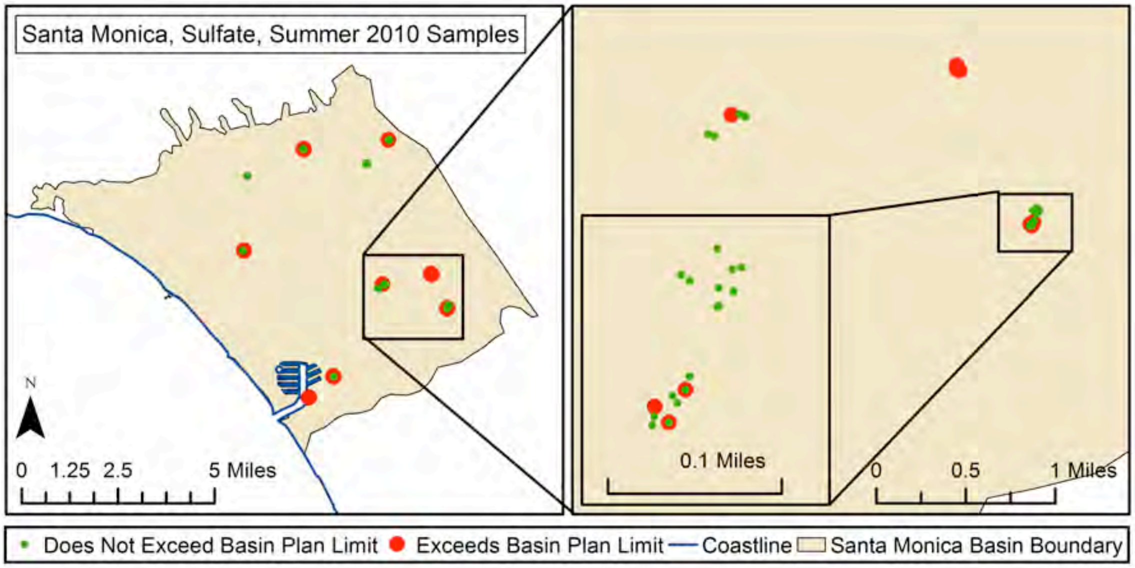

Figure 2: Maps showing clusters of samples that dominate the Geotracker dataset.

trends of select constituents in select basins to aid in the determination of the impact of the changes in samples sizes and locations of sampling sites on the identified trends in the percentages of samples exceeding the respective Basin Plan limits (see Figures 4, 6, and 8).

Groundwater basins comprised of alluvial material, like the 10 basins in Los Angeles County, have multiple deposits of alluvium forming both permeable (aquifers) and impermeable layers (aquitards). The groundwater quality can be substantially different in each layer of these alluvial basins based on the amount of pollution that permeates to each depth and the vertical rate of flow of the groundwater. In order to better understand from what depth the groundwater quality data is originating from, the depth to water was analyzed in comparison to the percentage of samples exceeding the respective Basin Plan limits for each constituent in the 10 Los Angeles County basins. The depth to groundwater was divided into equal sample quintiles with the following class limits: -0.91 to 14 feet, 14.01 to 24.47 feet, 24.48 to 35.57 feet, 35.58 to 60.56 feet, 60.57 to 780.47 feet, and samples with no corresponding depth to groundwater measurements, 'no data.' The salt or nutrient constituent's total and percentage of samples exceeding the standard was analyzed for each of the groundwater depth classes (see Table 11; Figures 10 and 11).

Due to the documented groundwater quality issues of salt water intrusion in the four basins of the Los Angeles Coastal Plain groundwater basin (Central, Hollywood, Santa Monica and West Coast), the distance to the coastline was analyzed together with the percentage of samples exceeding the Basin Plan limit to better characterize the links, if any, between salt water intrusion and groundwater quality degradation. The distance to coastline was broken down into five equal distance intervals: nearest (0 to 3.74 miles), near (3.75 to 7.48 miles), mid (7.49 to 11.23 miles), far (11.24 to 14.97 miles) and furthest (14.98 to 18.71 miles). The relationship between the fraction of samples exceeding the respective Basin Plan limits and the distance to the coastline intervals was analyzed for each salt constituent (see Table 12).

Chapter 4 - Results and Discussion

4.1 Groundwater Spatiotemporal Analysis

4.1.1 Salt Constituents

Boron was sampled 2,707 times in Los Angeles County from November of 2001 to April 2011 and 11% of these samples exceeded the respective Basin Plan limits. The Central, West Coast, San Fernando, San Gabriel and Santa Clara basins contained the majority of boron sampling events (Table 4). Consistent sampling in each of these basins was established during different seasons (San Fernando, summer 2004; West Coast, San Gabriel and Santa Clara, winter 2004-2005; and Central, winter 2005-2006) and has continued since without interruption. The Central and Santa Clara basins contained higher levels of boron, with 21% and 24% of the samples exceeding the corresponding Basin Plan limits, respectively. A winter and summer seasonal trend was not found in any of the basins. The San Fernando and San Gabriel basins displayed consistently low percentages of boron samples exceeding the respective Basin Plan limits. The Central, West Coast, and Santa Clara basins all displayed increasing percentages of samples exceeding the respective Basin Plan limits. However, each of these basins increased at different rates: the Santa Clara basin rapidly increased in summer 2006, the Central basin increased gradually between summer 2006 and summer 2008, and the West Coast basin steadily increased from summer 2008 to present day. In addition, each of these three basins contained widely varying sampling sizes in each season; this may have contributed to the trend of increasing percentages of samples exceeding the respective Basin Plan limits in these instances.

Table 4: The number and fractions of boron samples exceeding the respective Basin Plan limits, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	0%	0%	-	-	-	-	-	-	-	-	0%
	# Samples	1	4	-	-	-	-	-	-	-	-	5
S.02	% Exceed	-	-	-	-	-	-	-	-	-	-	-
	# Samples	-	-	-	-	-	-	-	-	-	-	-
W.02-03	% Exceed	-	-	-	-	-	-	-	-	-	-	-
	# Samples	-	-	-	-	-	-	-	-	-	-	-
S.03	% Exceed	-	0%	-	-	-	-	-	-	0%	-	0%
	# Samples	-	16	-	-	-	-	-	-	5	-	21
W.03-04	% Exceed	0%	0%	-	-	-	-	-	-	0%	-	0%
	# Samples	3	19	-	-	-	-	-	-	6	-	28
S.04	% Exceed	-	0%	0%	-	7%	-	-	-	0%	-	3%
	# Samples	-	7	9	-	15	-	-	-	3	-	34
W.04-05	% Exceed	-	0%	0%	0%	4%	0%	-	-	0%	13%	4%
	# Samples	-	17	21	20	27	3	-	-	3	30	121
S.05	% Exceed	-	-	0%	0%	25%	0%	-	-	-	17%	11%
	# Samples	-	-	7	20	16	10	-	-	-	36	89
W.05-06	% Exceed	0%	-	-	0%	0%	0%	-	-	-	17%	6%
	# Samples	1	-	-	25	25	9	-	-	-	36	96
S.06	% Exceed	5%	-	0%	9%	0%	0%	-	-	-	25%	9%
	# Samples	56	-	7	23	46	13	-	-	-	57	202
W.06-07	% Exceed	3%	100%	0%	0%	0%	0%	-	-	-	31%	10%
	# Samples	33	6	5	72	30	14	-	-	-	42	202
S.07	% Exceed	14%	-	0%	0%	0%	0%	-	-	-	31%	10%
	# Samples	22	-	6	33	44	15	-	-	-	42	162
W.07-08	% Exceed	9%	-	0%	0%	0%	0%	-	-	-	31%	9%
	# Samples	35	-	6	32	44	15	-	-	-	42	174
S.08	% Exceed	30%	0%	0%	0%	16%	0%	-	-	-	29%	13%
	# Samples	61	50	15	49	44	25	-	-	-	38	282
W.08-09	% Exceed	27%	0%	-	6%	6%	0%	-	-	-	25%	13%
	# Samples	74	33	-	33	64	36	-	-	-	36	276
S.09	% Exceed	27%	0%	0%	10%	0%	0%	-	-	-	21%	15%
	# Samples	75	2	2	52	29	26	-	-	-	38	224
W.09-10	% Exceed	21%	-	17%	5%	0%	0%	-	-	-	25%	12%
	# Samples	67	-	35	105	30	17	-	-	-	36	290
S.10	% Exceed	21%	-	27%	10%	2%	0%	-	-	-	17%	12%
	# Samples	72	-	15	72	56	27	-	-	-	30	272
W.10-11	% Exceed	38%	-	0%	31%	1%	0%	-	-	-	30%	21%
	# Samples	58	-	2	36	76	13	-	-	-	44	229
Totals	% Exceed	21%	4%	8%	6%	3%	0%	-	-	0%	24%	11%
	# Samples	558	154	130	572	546	223	-	-	17	507	2707

Chloride was sampled 8,629 times in Los Angeles County from November 2001 through April 2011; 35% of these measurements exceeded the respective Basin Plan limits. During this time, the Raymond, Russell, and Malibu basins had few or no chloride samples collected, therefore these basins were not analyzed with the other seven basins (Table 5). A trend between the winter and summer seasons was not observed in any of the basins. The Central, Santa Monica and Santa Clara basins maintained consistent percentages of samples exceeding the respective Basin Plan limits throughout the analysis period. The fraction of samples exceeding the Basin Plan limit in the San Fernando basin decreased over the time period (Figure 3), but this trend was coupled with an increase in the number of samples collected per season. This change in sample support might have contributed to the decrease in the percentage of samples exceeding

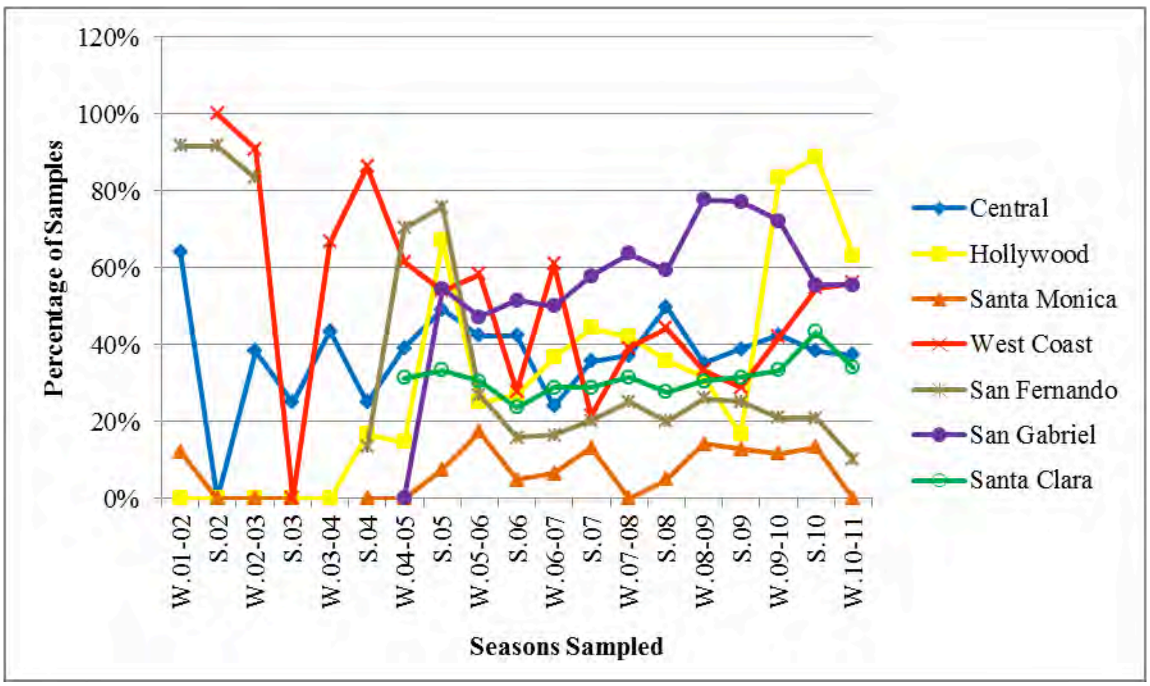

Figure 3: The percentage of chloride samples exceeding the respective Basin Plan limits, during each season, in the seven analyzed basins.

Table 5: The number and fractions of chloride samples exceeding the respective Basin Plan limits, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	64%	0%	12%	-	92%	-	-	-	-	-	24%
	# Samples	14	19	82	-	12	-	-	-	-	-	127
S.02	% Exceed	0%	0%	0%	100%	92%	-	-	-	-	-	13%
	# Samples	1	15	72	2	12	-	-	-	-	-	102
W.02-03	% Exceed	38%	0%	0%	91%	83%	-	-	-	-	-	41%
	# Samples	26	17	1	11	6	-	-	-	-	-	61
S.03	% Exceed	25%	0%	0%	0%	-	-	-	-	0%	-	4%
	# Samples	12	30	19	1	-	-	-	-	5	-	67
W.03-04	% Exceed	43%	0%	-	67%	-	-	-	-	0%	-	28%
	# Samples	23	36	-	21	-	-	-	-	6	-	86
S.04	% Exceed	25%	17%	0%	86%	13%	-	-	-	0%	-	33%
	# Samples	12	24	9	22	15	-	-	-	3	-	85
W.04-05	% Exceed	39%	15%	0%	62%	70%	0%	-	-	0%	31%	38%
	# Samples	148	41	37	78	27	5	-	-	3	35	374
S.05	% Exceed	49%	67%	8%	54%	76%	55%	-	-	-	33%	51%
	# Samples	67	73	40	150	29	33	-	-	-	36	428
W.05-06	% Exceed	42%	25%	17%	58%	27%	47%	-	-	-	31%	42%
	# Samples	158	52	104	276	78	36	-	-	-	36	740
S.06	% Exceed	42%	27%	5%	28%	16%	52%	-	-	-	24%	28%
	# Samples	203	52	61	172	176	33	-	-	-	38	735
W.06-07	% Exceed	24%	37%	6%	61%	17%	50%	-	-	-	29%	31%
	# Samples	137	49	77	123	109	34	-	-	-	38	567
S.07	% Exceed	36%	44%	13%	22%	20%	58%	-	-	-	29%	28%
	# Samples	176	36	68	88	173	38	-	-	-	38	617
W.07-08	% Exceed	37%	42%	0%	39%	25%	64%	-	-	-	32%	34%
	# Samples	287	38	38	74	139	33	-	-	-	38	647
S.08	% Exceed	50%	36%	5%	44%	20%	59%	-	-	-	28%	39%
	# Samples	313	120	39	106	155	37	-	-	-	36	806
W.08-09	% Exceed	35%	32%	14%	33%	26%	78%	-	-	-	31%	34%
	# Samples	278	98	28	93	184	54	-	-	-	36	771
S.09	% Exceed	39%	17%	13%	29%	25%	77%	-	-	-	32%	34%
	# Samples	285	54	31	83	147	44	-	-	-	38	682
W.09-10	% Exceed	43%	83%	12%	42%	21%	72%	-	-	-	33%	38%
	# Samples	312	18	68	107	119	36	-	-	-	36	696
S.10	% Exceed	38%	89%	13%	55%	21%	56%	-	-	-	43%	39%
	# Samples	211	27	15	97	148	27	-	-	-	30	555
W.10-11	% Exceed	37%	63%	0%	56%	10%	56%	-	-	-	34%	32%
	# Samples	107	19	2	98	186	27	-	-	-	44	483
Totals	% Exceed	40%	33%	9%	48%	23%	61%	-	-	0%	31%	35%
	# Samples	2770	818	791	1602	1715	437	-	-	17	479	8629

the Basin Plan limit, but this result does suggest that a decrease in chloride concentrations has occurred in the San Fernando basin since 2001. There is also a sudden decrease in the percentage of samples exceeding the respective Basin Plan limits during the winter 2010-2011 season in six of the seven basins (excluding the West Coast basin), which could have been caused by a regional scale factor, such as a lower than average precipitation during this winter season.

The San Gabriel and West Coast basins contain the highest levels of chloride readings across the 10-year period, 61% and 48% of samples exceeded the corresponding Basin Plan limits, respectively. The percentages of samples exceeding the respective Basin Plan limits in the San Gabriel and Hollywood basins increased with time (Figure 3) given relatively consistent numbers of samples in each season. While there were several spatiotemporal analyses that would illustrate the chloride trends in Los Angeles County groundwater basins, a spatiotemporal analysis was completed on the Hollywood basin in order to further investigate if the reason for the increase in samples exceeding the Basin Plan limit could be ascribed to changes in sampling locations or rather a real increase in chloride concentration (Figure 4). The spatiotemporal analysis showed that the samples collected in the Hollywood basin since 2001 were clustered around 10 sites, where multiple samples were collected at a finer scale. Due to the lack of scattered samples, spatial trends are difficult to determine. However, a relationship is seen in seasons where a high percentage of the samples exceeding the Basin Plan limit were collected almost exclusively from the southwest corner of the basin (summer 2005, winter 2009-2010,

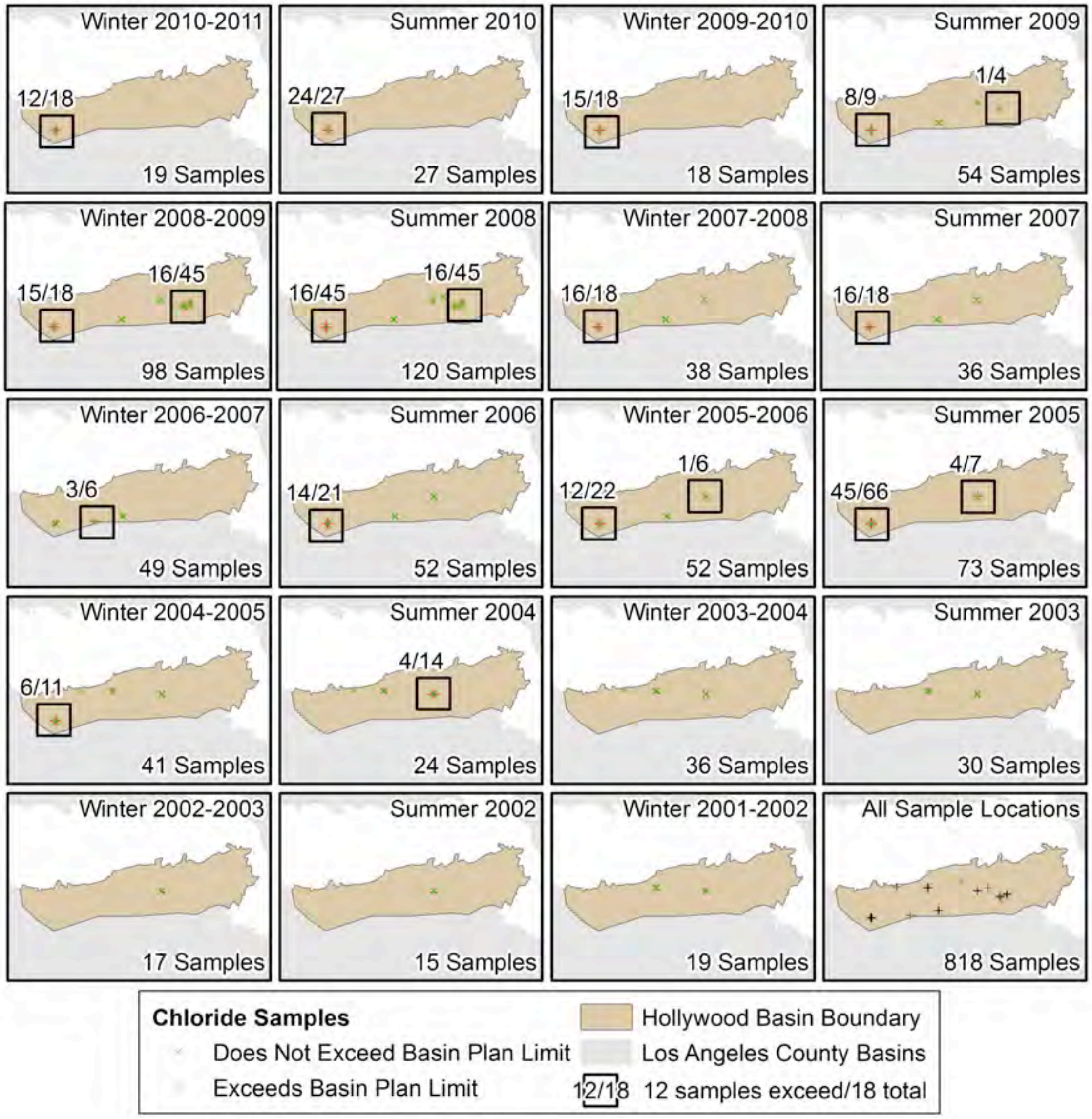

Figure 4: Spatial distribution of chloride samples in the Hollywood basin, during each season.

summer 2012 and winter 2010-2011), whereas seasons in which samples were collected from multiple locations displayed a lower percentage of samples exceeding the Basin Plan limit (winter 2005-2006 through summer 2009). This relationship indicates that the groundwater in the southwest corner of the basin contains higher levels of chloride than the other sites across the basin.

A total of 37,285 sulfate samples have been collected in Los Angeles County since November 2001; 37% of these samples exceeded the respective Basin Plan limits. Both the Raymond and Malibu Valley basins did not have continuous sulfate sampling over the 10-year period, and were excluded from further analysis (Table 6). None of the eight analyzed basins displayed a trend between the summer and winter seasons. The eight analyzed basins can be divided into two groups based on the ranges of the percentage of samples exceeding the respective Basin Plan limits. The Central, Santa Monica, West Coast and San Fernando basins have the lower range of percentages, all below 50%, while the Hollywood, San Gabriel, Russell and Santa Clara basins have a higher range of percentages, all above 55% (Figure 5). All of the basins have displayed consistent percentages over the 10-year time period, except for the Russell basin, which

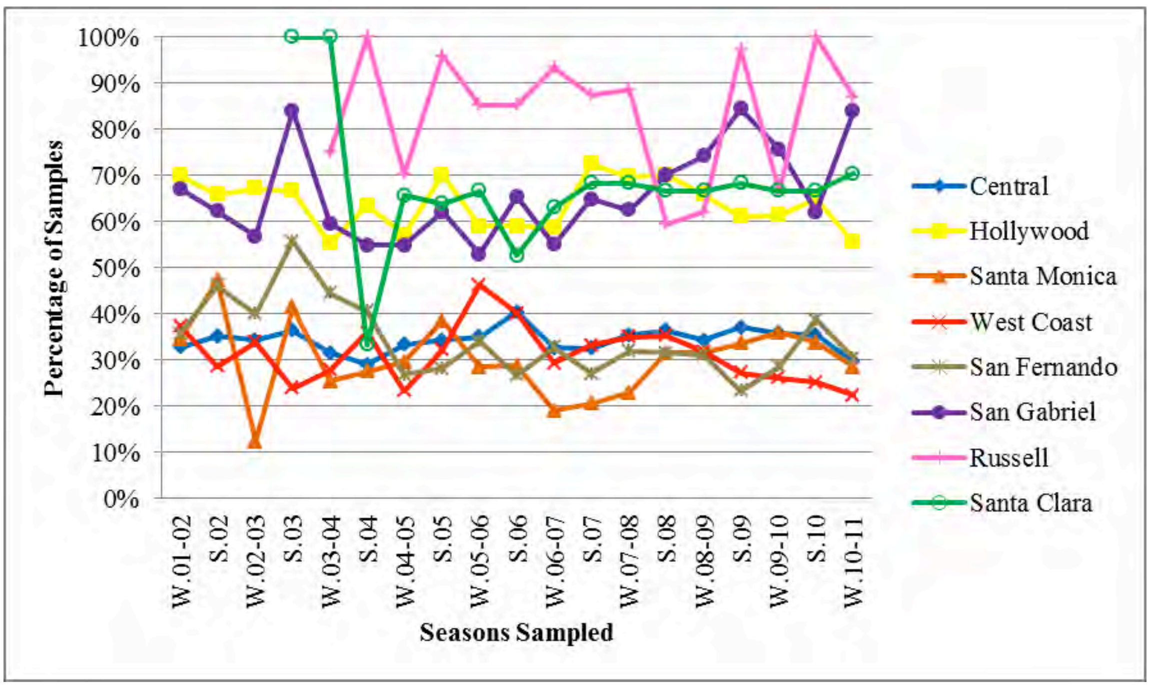

Figure 5: The percentage of sulfate samples exceeding the respective Basin Plan limits, during each season, in the eight analyzed basins.

Table 6: The number and fractions of sulfate samples exceeding the respective Basin Plan limits, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	33%	70%	35%	37%	36%	67%	-	-	-	-	37%
	# Samples	648	30	147	364	257	70	-	-	-	-	1516
S.02	% Exceed	35%	66%	47%	29%	46%	62%	-	-	-	-	39%
	# Samples	786	44	163	335	286	69	-	-	-	-	1683
W.02-03	% Exceed	34%	67%	12%	34%	40%	57%	-	-	-	-	36%
	# Samples	801	58	81	374	180	58	-	-	-	-	1552
S.03	% Exceed	36%	67%	41%	24%	56%	84%	-	-	20%	100%	41%
	# Samples	594	69	99	325	260	44	-	-	5	3	1399
W.03-04	% Exceed	32%	55%	25%	28%	45%	60%	-	75%	0%	100%	35%
	# Samples	681	76	55	331	238	62	-	16	6	3	1468
S.04	% Exceed	29%	63%	27%	36%	41%	55%	-	100%	0%	33%	35%
	# Samples	682	63	131	308	222	51	-	18	3	6	1484
W.04-05	% Exceed	33%	57%	30%	23%	27%	55%	-	70%	0%	66%	33%
	# Samples	833	91	172	424	265	91	-	37	3	35	1951
S.05	% Exceed	34%	70%	39%	32%	28%	62%	-	96%	80%	64%	38%
	# Samples	818	121	223	517	354	119	-	25	5	36	2218
W.05-06	% Exceed	35%	59%	28%	46%	34%	53%	-	85%	86%	67%	40%
	# Samples	947	93	246	649	376	136	-	34	7	36	2524
S.06	% Exceed	40%	59%	29%	40%	27%	65%	-	85%	100%	53%	39%
	# Samples	869	122	302	682	528	136	-	34	7	38	2718
W.06-07	% Exceed	33%	59%	19%	29%	33%	55%	-	93%	100%	63%	35%
	# Samples	936	87	230	536	487	138	-	61	5	38	2518
S.07	% Exceed	33%	73%	21%	33%	27%	65%	-	88%	83%	68%	36%
	# Samples	780	80	209	542	508	148	-	40	12	38	2357
W.07-08	% Exceed	35%	70%	23%	35%	32%	63%	-	89%	100%	68%	38%
	# Samples	923	76	183	531	485	152	-	44	8	38	2440
S.08	% Exceed	36%	70%	32%	35%	32%	70%	89%	59%	57%	67%	40%
	# Samples	939	141	149	451	546	124	9	74	7	36	2476
W.08-09	% Exceed	34%	66%	32%	32%	31%	74%	-	62%	88%	67%	39%
	# Samples	1005	173	155	503	603	167	-	74	8	36	2724
S.09	% Exceed	37%	61%	34%	27%	23%	85%	100%	97%	-	68%	40%
	# Samples	570	72	86	315	265	110	8	36	-	38	1500
W.09-10	% Exceed	36%	61%	36%	26%	29%	76%	100%	67%	-	67%	37%
	# Samples	719	96	139	421	325	66	8	39	-	36	1849
S.10	% Exceed	35%	65%	34%	25%	39%	62%	-	100%	-	67%	38%
	# Samples	565	60	80	310	302	74	-	22	-	30	1443
W.10-11	% Exceed	30%	56%	29%	22%	30%	84%	86%	87%	-	70%	34%
	# Samples	531	45	42	308	407	50	7	31	-	44	1465
Totals	% Exceed	34%	64%	30%	32%	33%	65%	94%	80%	68%	66%	37%
	# Samples	14627	1597	2892	8226	6894	1865	32	585	76	491	37285

had highly variable readings, and the San Gabriel basin, which exhibited a modest increase in the percentage of samples exceeding the Basin Plan limit over time. The sampling size per season also varied in the San Gabriel basin, providing a possible explanation for the increase in percentage of samples exceeding the respective Basin Plan limit in addition to the conclusion that sulfate concentrations were in fact increasing in the basin. To investigate further a spatiotemporal analysis was conducted (Figure 6) for the sulfate trends in the San Gabriel basin, which showed that the samples collected are concentrated along the southern portion of the basin, with the exception of a small cluster of sample sites in the center of the basin. Unfortunately, the limited spatial distribution of sites indicates that the results that are shown for San Gabriel basin may not be indicative of the basin as a whole. However, since the samples were concentrated in the southwest, the increase in the percentage of sites exceeding the respective Basin Plan limit shows that the sulfate concentration in the southern portion of San Gabriel basin has increased over time. Additionally, the sole sampling site in the center of the basin does not contain samples exceeding the respective Basin Plan limit until the final two seasons (summer 2010 and winter 2010-2011), suggesting that the sulfate levels may be increasing in other portions of the basin as well.

A total of 6,817 total dissolved solids (TDS) samples have been collected in Los Angeles County since November 2001. The TDS samples exhibited the highest percentage of samples exceeding the respective Basin Plan limits (78%) of the eight constituents analyzed in this thesis study. Due to a lack of TDS sampling in the Raymond, Russell and Malibu basins, these basins were excluded from further analysis

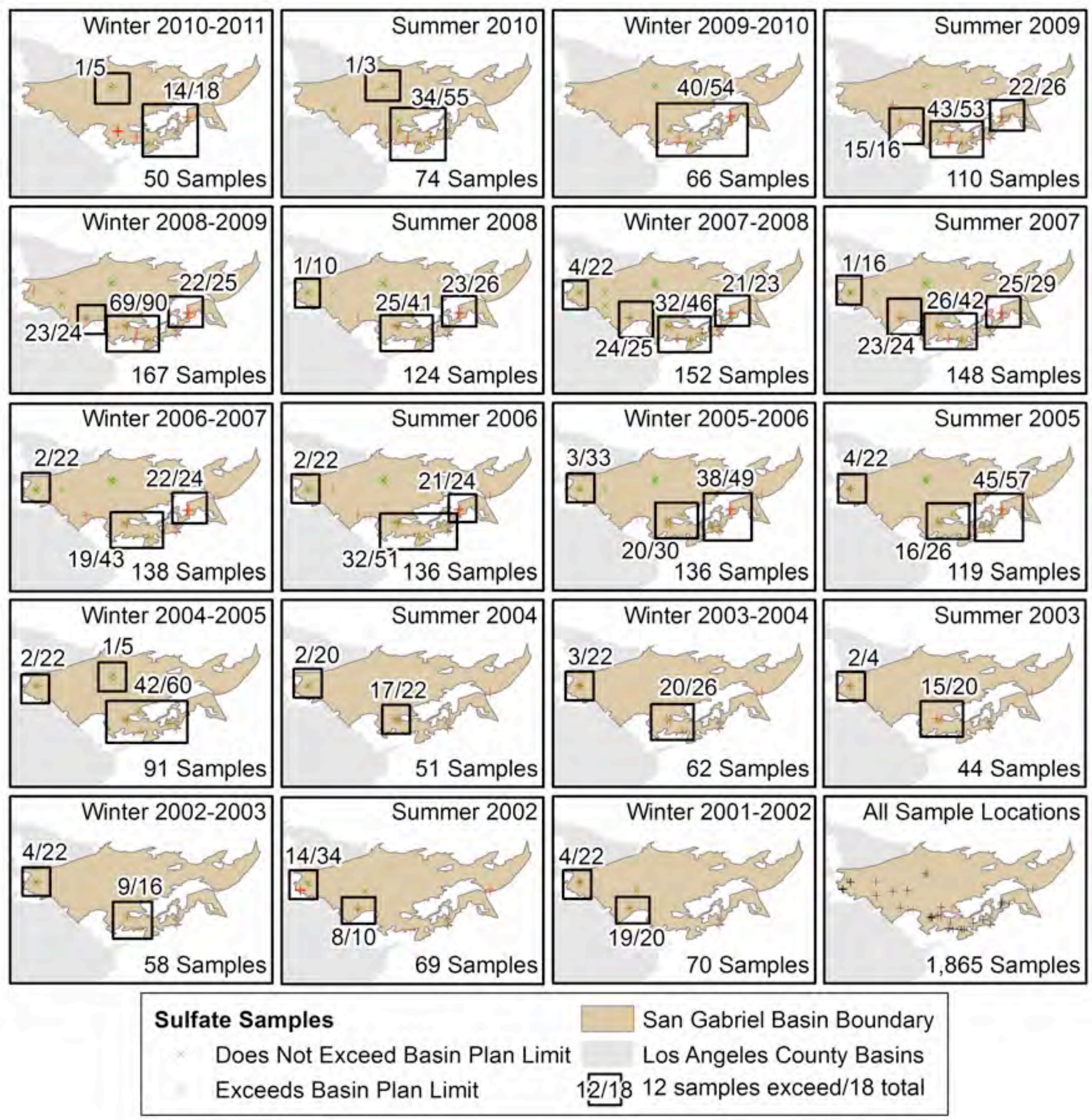

Figure 6: Spatial distribution of sulfate samples in the San Gabriel basin, during each season.

(Table 7). In four of the remaining seven basins, continuous TDS sampling began at varying times (Santa Monica and San Fernando basins, summer 2004; San Gabriel and Santa Clara basins, winter 2004-2005). A winter and summer trend was not recognized in any of the analyzed basins. The Central, West Coast, San Fernando and San Gabriel basins displayed the highest percentages of samples exceeding the respective Basin Plan

Table 7: The number and fractions of TDS samples exceeding the respective Basin Plan limits, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	100%	58%	58%	90%	100%	-	-	-	-	-	69%
	# Samples	3	19	40	10	13	-	-	-	-	-	85
S.02	% Exceed	100%	53%	-	100%	100%	-	-	-	-	-	77%
	# Samples	1	15	-	2	12	-	-	-	-	-	30
W.02-03	% Exceed	91%	53%	0%	100%	100%	-	-	-	-	-	81%
	# Samples	22	17	1	11	6	-	-	-	-	-	57
S.03	% Exceed	100%	83%	-	100%	-	-	-	-	0%	-	80%
	# Samples	12	30	-	2	-	-	-	-	5	-	49
W.03-04	% Exceed	100%	64%	-	76%	-	-	-	-	0%	-	70%
	# Samples	16	36	-	21	-	-	-	-	6	-	79
S.04	% Exceed	100%	71%	0%	100%	95%	-	-	-	0%	-	83%
	# Samples	39	24	9	22	21	-	-	-	3	-	118
W.04-05	% Exceed	81%	68%	0%	74%	88%	60%	-	-	0%	57%	68%
	# Samples	119	41	21	23	24	10	-	-	3	35	276
S.05	% Exceed	88%	85%	29%	79%	82%	85%	-	-	-	58%	77%
	# Samples	34	73	24	108	51	33	-	-	-	36	359
W.05-06	% Exceed	87%	64%	59%	88%	95%	80%	-	-	-	58%	80%
	# Samples	166	44	103	222	38	35	-	-	-	36	644
S.06	% Exceed	94%	57%	43%	94%	97%	85%	-	-	-	58%	84%
	# Samples	194	44	60	216	63	33	-	-	-	38	648
W.06-07	% Exceed	86%	59%	35%	80%	83%	85%	-	-	-	53%	72%
	# Samples	191	49	86	110	53	34	-	-	-	38	561
S.07	% Exceed	95%	75%	46%	86%	98%	87%	-	-	-	63%	81%
	# Samples	129	36	90	132	86	38	-	-	-	38	549
W.07-08	% Exceed	90%	79%	40%	87%	89%	85%	-	-	-	61%	79%
	# Samples	143	38	57	89	64	33	-	-	-	38	462
S.08	% Exceed	88%	60%	21%	89%	91%	86%	-	-	-	64%	75%
	# Samples	185	102	63	87	77	37	-	-	-	36	587
W.08-09	% Exceed	82%	58%	38%	87%	71%	94%	-	-	-	61%	74%
	# Samples	168	86	40	84	145	54	-	-	-	36	613
S.09	% Exceed	88%	44%	21%	89%	79%	95%	-	-	-	68%	77%
	# Samples	142	52	24	64	39	44	-	-	-	38	403
W.09-10	% Exceed	88%	89%	24%	77%	81%	94%	-	-	-	58%	77%
	# Samples	171	18	42	83	101	36	-	-	-	36	487
S.10	% Exceed	86%	89%	29%	90%	76%	93%	-	100%	-	63%	82%
	# Samples	145	27	21	100	63	27	-	4	-	30	417
W.10-11	% Exceed	85%	83%	0%	89%	80%	81%	-	-	-	61%	81%
	# Samples	109	18	2	75	118	27	-	-	-	44	393
Totals	% Exceed	88%	66%	38%	87%	85%	88%	-	100%	0%	60%	78%
	# Samples	1989	769	683	1461	974	441	-	4	17	479	6817

limits. The Hollywood and San Gabriel basins displayed matching patterns between their respective percentages of samples exceeding the Basin Plan limits and the number of samples collected each season, where an increase or decrease in percentage was coupled with a respective comparable increase or decrease in the number of samples. This pattern indicates that the number of samples and their spatial distribution could have an impact on the percentage of samples exceeding the respective Basin Plan limits.

The percentages TDS samples exceeding the basin limits have gradually diminished in three of the four basins (Central, West Coast and San Fernando basins) with the highest percentages over the 10-year monitoring period (Figure 7). These three basins also exhibited varying numbers of samples collected per season, which could be a contributing factor to the decrease in percentage of samples exceeding the TDS Basin

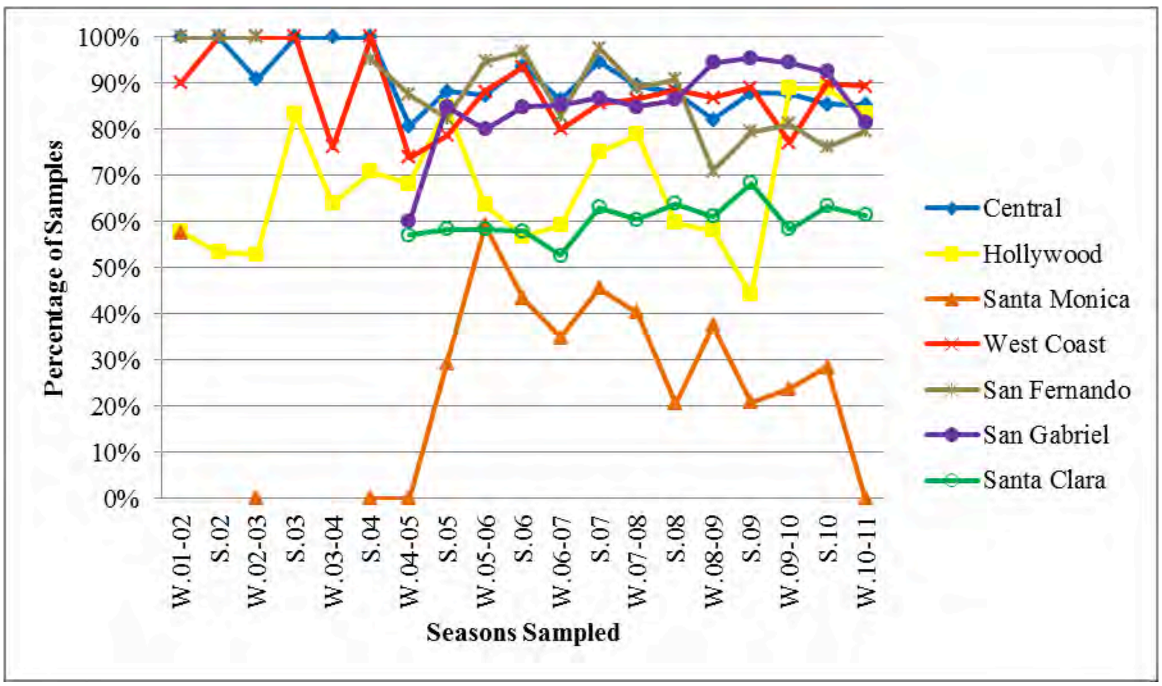

Figure 7: The percentage of TDS samples exceeding the respective Basin Plan limits, during each season, in the seven analyzed basins.

Plan limits. To gain a better understanding if the varying numbers of samples per season may help to explain the decreasing trend in these three basins, a spatiotemporal analysis was completed. Due to its high percentage of samples exceeding the Basin Plan limit and its highest number of samples collected during the 10-year monitoring period, the Central basin was selected for this analysis (Figure 8). The spatiotemporal analysis shows that samples have been collected in a more dispersed pattern across the basin in recent years and this fact, coupled with the consistency of samples exceeding the limit displayed in Figure 8, suggest that the denser sampling gives a more accurate picture of groundwater quality and that the TDS groundwater quality may be improving. Additional spatiotemporal analyses completed for the San Fernando and West Coast basins (not shown) displayed a similar dispersed pattern in recent years coupled with an increase in consistency in the sampling size, additionally supporting that the larger sampling size in recent years is providing an increasingly accurate picture of the TDS groundwater pollution in these three basins.

Overall, the San Gabriel basin had the worst salt constituent readings during the 10-year period, containing the highest percentages of samples exceeding the respective Basin Plan limits for chloride and TDS, and the second highest percentage of samples exceeding the respective Basin Plan limits for sulfate. The San Gabriel basin also displayed increasing percentages of samples exceeding the respective Basin Plan limits for the same three salt constituents over the 10-year period. The Hollywood, Central, West Coast and Santa Clara basins also displayed a large and sometimes increasing fraction of readings for these salt constituents exceeding the respective Basin Plan limits.

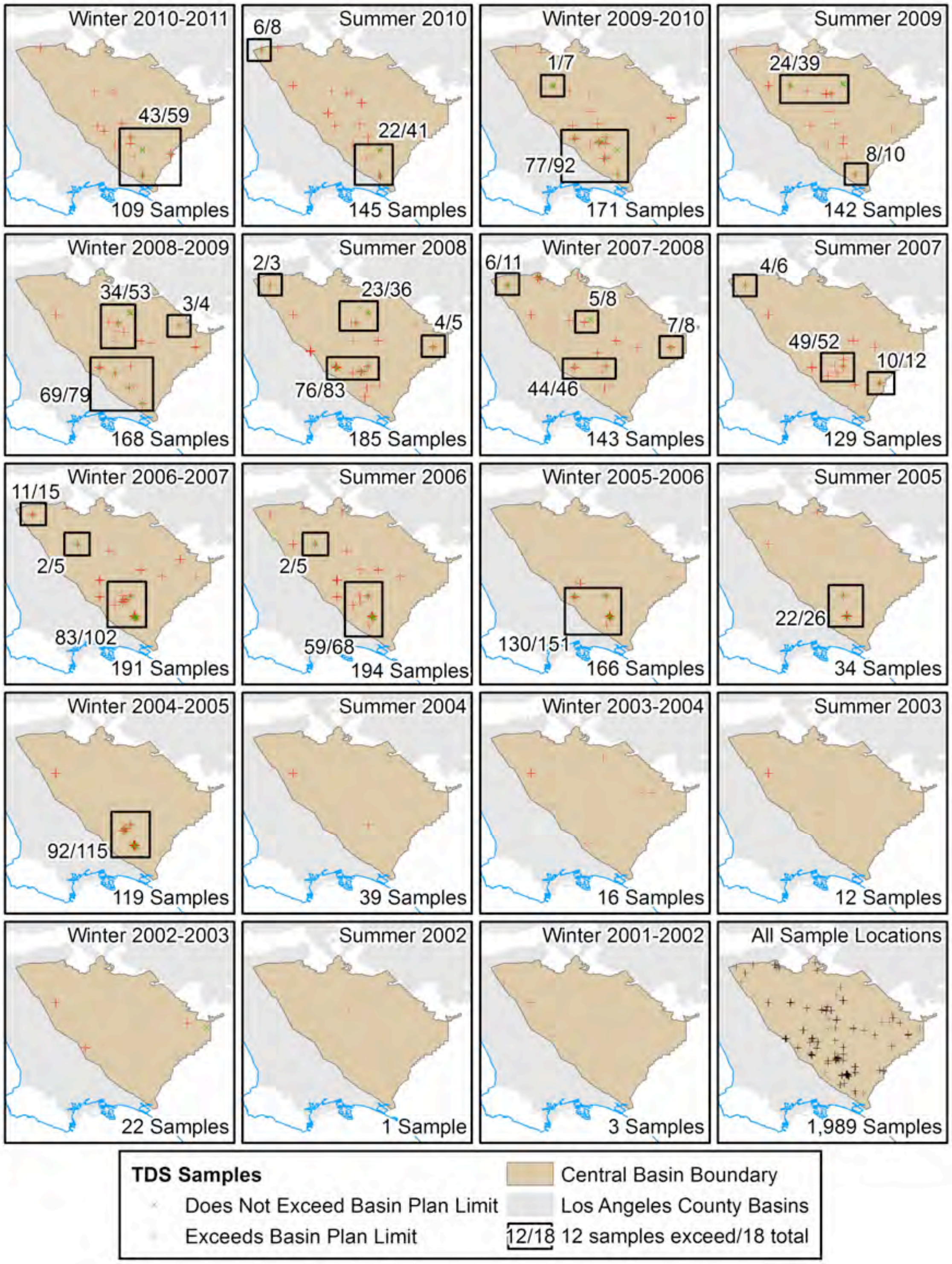

Figure 8: Spatial distribution of TDS samples in the Central basin, during each season.

The Hollywood basin exhibited an increasing trend in the percentage of samples exceeding the respective Basin Plan limits for both chloride and TDS; and the Central, West Coast and Santa Clara basins were all in the highest groups of samples exceeding the respective Basin Plan limits for two of the analytes (Central, boron and TDS; West Coast, chloride and TDS; Santa Clara, boron and sulfate). While number and spatial pattern of sampling locations could have affected the high percentages observed, it is likely that high salt constituent concentrations are also contributing to the trend. The only basin to exhibit a decreasing trend for multiple salt constituents was the San Fernando basin, which was observed to have decreasing percentages of samples exceeding the respective Basin Plan limits for two of the four analytes (chloride and TDS). While variations in sampling numbers and locations during each season in the San Fernando basin could have contributed to the decrease in percentage, it is likely that the concentrations of both salt constituents are falling and that the groundwater quality in the San Fernando basin is improving.

4.1.2 Nutrient Constituents

A total of 3,336 nitrite-nitrogen (NO_2-N) samples have been collected in Los Angeles County since November 2001. The nitrite-nitrogen readings were the lowest of any of the analytes analyzed in this thesis study, with just 1% of the samples exceeding the Basin Plan limit. No nitrite-nitrogen sampling in the Hollywood, Raymond, Russell and Malibu basins included continuous samples across the 10-year period; therefore, these four basins were excluded from further analysis (Table 8). In the remaining six basins, the Central basin was the only basin with continuous sampling for the entire study

Table 8: The number and fractions of nitrite-nitrogen samples exceeding the Basin Plan limit, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	0%	0%	8%	-	0%	-	-	-	-	-	6%
	# Samples	2	4	40	-	8	-	-	-	-	-	54
S.02	% Exceed	0%	-	0%	0%	0%	-	-	-	-	-	0%
	# Samples	1	-	20	2	7	-	-	-	-	-	30
W.02-03	% Exceed	0%	0%	0%	0%	-	-	-	-	-	-	0%
	# Samples	12	2	1	11	-	-	-	-	-	-	26
S.03	% Exceed	0%	0%	0%	-	-	-	-	-	0%	-	0%
	# Samples	3	14	19	-	-	-	-	-	5	-	41
W.03-04	% Exceed	0%	0%	-	10%	-	-	-	-	0%	-	4%
	# Samples	3	17	-	21	-	-	-	-	6	-	47
S.04	% Exceed	0%	0%	-	5%	-	-	-	-	0%	-	2%
	# Samples	1	15	-	22	-	-	-	-	3	-	41
W.04-05	% Exceed	3%	0%	0%	0%	-	0%	-	-	0%	0%	2%
	# Samples	105	13	20	17	-	8	-	-	3	30	196
S.05	% Exceed	0%	0%	0%	17%	0%	0%	-	-	-	0%	2%
	# Samples	35	7	56	24	13	3	-	-	-	30	168
W.05-06	% Exceed	0%	-	0%	0%	3%	0%	-	-	-	0%	1%
	# Samples	36	-	53	72	68	3	-	-	-	30	262
S.06	% Exceed	2%	-	0%	26%	0%	0%	-	-	-	0%	2%
	# Samples	90	-	149	19	131	7	-	-	-	34	430
W.06-07	% Exceed	2%	-	0%	5%	0%	0%	-	-	-	0%	1%
	# Samples	44	-	48	19	74	8	-	-	-	34	227
S.07	% Exceed	0%	-	0%	2%	0%	0%	-	-	-	0%	0%
	# Samples	36	-	42	42	109	7	-	-	-	34	270
W.07-08	% Exceed	2%	0%	3%	0%	0%	0%	-	-	-	0%	1%
	# Samples	53	10	34	6	96	8	-	-	-	34	241
S.08	% Exceed	0%	0%	0%	32%	0%	0%	-	-	-	0%	5%
	# Samples	71	11	6	37	93	9	-	-	-	32	259
W.08-09	% Exceed	0%	0%	0%	2%	1%	0%	-	-	-	0%	1%
	# Samples	57	14	6	53	102	9	-	-	-	14	255
S.09	% Exceed	2%	0%	0%	0%	0%	0%	-	-	-	0%	0%
	# Samples	45	8	22	21	74	8	-	-	-	32	210
W.09-10	% Exceed	0%	-	0%	0%	0%	0%	-	-	-	0%	0%
	# Samples	67	-	38	24	44	6	-	-	-	32	211
S.10	% Exceed	0%	0%	0%	0%	1%	0%	-	-	-	0%	1%
	# Samples	27	2	2	55	83	5	-	-	-	26	200
W.10-11	% Exceed	0%	0%	-	0%	0%	0%	-	-	-	0%	0%
	# Samples	20	1	-	23	78	6	-	-	-	40	168
Totals	% Exceed	1%	0%	1%	6%	0%	0%	-	-	0%	0%	1%
	# Samples	708	118	556	468	980	87	-	-	17	402	3336

period, the other five basins all began continuous sampling at different times (West Coast, winter 2003-2004; Santa Monica, San Gabriel and Santa Clara, winter 2004-2005; San Fernando, summer 2005). None of the basins analyzed demonstrated a winter and summer seasonal trend across the 10-year period. Overall, the percentage of samples exceeding the Basin Plan limit was very low in each basin. Three basins (San Fernando, San Gabriel and Santa Clara) displayed an overall average of zero percent of samples exceeding the Basin Plan limit, while the Central, Santa Monica and West Coast basin had percentages of one, one, and six percent, respectively. The ranges varied from 0-3% in the Central and San Fernando basins over the 10-year period, unlike the Santa Monica and West Coast basins which exhibited higher fluctuations of percentages of samples exceeding the Basin Plan limit from season to season, ranging from 0 to 8% in the Santa Monica basin and 0 to 33% in the West Coast basin. Additionally, the four basins with the largest percentages of samples exceeding the Basin Plan limit were the four sub-basins of the Los Angeles Coastal Plain basin. The presence of higher readings of nitrite-nitrogen in the Los Angeles Coastal Plain sub-basins can presumably be attributed to local sources of groundwater pollution that are found in these coastal basins, such as higher numbers of leaking sewers or larger volumes of urban runoff.

A total of 4,839 samples have been collected for nitrate (NO_3) in Los Angeles County since November 2001; 8% of these samples were found to exceed the Basin Plan limit. During this time the Central, West Coast and San Fernando basins were the only basins with sufficient continuous data to analyze trends (Table 9). None of these basins displayed a winter and summer trend. The San Fernando basin displayed the highest

Table 9: The number and fractions of nitrate samples exceeding the Basin Plan limit, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	9%	-	8%	1%	19%	0%	-	-	-	-	8%
	# Samples	142	-	66	114	72	22	-	-	-	-	416
S.02	% Exceed	7%	0%	0%	1%	33%	3%	-	-	-	-	8%
	# Samples	133	7	55	98	64	33	-	-	-	-	390
W.02-03	% Exceed	8%	0%	0%	1%	0%	7%	-	-	-	-	5%
	# Samples	185	10	4	101	42	29	-	-	-	-	371
S.03	% Exceed	4%	0%	0%	0%	3%	25%	-	-	-	-	3%
	# Samples	142	9	6	128	71	8	-	-	-	-	364
W.03-04	% Exceed	3%	0%	0%	0%	9%	10%	-	0%	-	-	4%
	# Samples	156	29	6	100	65	31	-	9	-	-	396
S.04	% Exceed	5%	0%	0%	10%	2%	15%	-	0%	-	17%	6%
	# Samples	118	11	19	77	56	13	-	18	-	6	318
W.04-05	% Exceed	1%	0%	0%	6%	3%	25%	-	0%	-	-	4%
	# Samples	69	3	12	31	63	8	-	9	-	-	195
S.05	% Exceed	4%	0%	0%	0%	3%	50%	-	-	-	-	4%
	# Samples	109	3	12	35	29	4	-	-	-	-	192
W.05-06	% Exceed	4%	0%	0%	8%	3%	50%	-	-	-	-	5%
	# Samples	151	3	5	61	35	4	-	-	-	-	259
S.06	% Exceed	7%	0%	-	7%	6%	50%	-	-	-	-	8%
	# Samples	101	3	-	43	35	4	-	-	-	-	186
W.06-07	% Exceed	4%	-	-	8%	13%	20%	-	-	-	-	6%
	# Samples	141	-	-	62	40	5	-	-	-	-	248
S.07	% Exceed	11%	0%	65%	5%	71%	-	-	-	-	-	26%
	# Samples	105	3	20	42	38	-	-	-	-	-	208
W.07-08	% Exceed	13%	-	-	5%	34%	-	-	-	-	-	15%
	# Samples	87	-	-	40	35	-	-	-	-	-	162
S.08	% Exceed	15%	0%	0%	8%	29%	-	-	-	-	-	14%
	# Samples	111	3	21	48	35	-	-	-	-	-	218
W.08-09	% Exceed	15%	0%	0%	16%	35%	-	-	-	-	-	16%
	# Samples	80	18	21	81	37	-	-	-	-	-	237
S.09	% Exceed	7%	0%	0%	8%	44%	-	-	-	-	-	18%
	# Samples	54	3	6	61	55	-	-	-	-	-	179
W.09-10	% Exceed	0%	0%	0%	13%	30%	0%	-	-	-	-	13%
	# Samples	32	7	10	71	43	2	-	-	-	-	165
S.10	% Exceed	0%	0%	0%	3%	6%	0%	-	0%	-	-	3%
	# Samples	48	10	9	34	47	8	-	4	-	-	160
W.10-11	% Exceed	2%	0%	0%	6%	0%	0%	-	-	-	-	2%
	# Samples	60	7	9	48	46	5	-	-	-	-	175
Totals	% Exceed	7%	0%	6%	5%	17%	11%	-	0%	-	17%	8%
	# Samples	2024	129	281	1275	908	176	-	40	-	6	4839

percentage of samples exceeding the Basin Plan limit. Overall, the percentages of samples exceeding the Basin Plan limit were relatively low from November 2001 until the summer of 2007 when the percentage spiked to 71%. Since the summer 2007 season the fraction has declined to zero percent of samples exceeding the Basin Plan limit in the winter 2010-2011 season. The Central and West Coast basins displayed comparable trends where the height of the percentage of samples exceeding the Basin Plan limit in each basin was reached in the winter 2008-2009 season; which has since declined through the winter 2010-2011 season. The large sampling effort recorded throughout the study period within these three basins suggests that the decreasing trend in recent years is due to a decrease in nitrate concentrations. Since these basins are also widely dispersed across Los Angeles County, the decrease displayed in all three basins may be due to a real decrease in rainfall or some other region-wide factor that affects nitrate contamination of groundwater.

A total of 28,407 samples have been analyzed for nitrate-nitrogen (NO_3-N) in Los Angeles County since November of 2001; 14% of these samples exceeded the Basin Plan limit. During this time period the sampling effort in the Raymond and Malibu basins was too sparse to determine trends in groundwater quality (Table 10). A winter and summer seasonal trend was not found in any of the eight analyzed basins. The San Fernando basin contained the highest percentage of samples (25%) exceeding the Basin Plan limit. Meanwhile, the Russell and Santa Clara basins, which did not begin continuous sampling until the winter 2004-2005 season, contained two of the lowest percentages of the samples exceeding the Basin Plan limit with only three and one percent, respectively. A

Table 10: The number and fractions of nitrate-nitrogen samples exceeding the Basin Plan limit, in each basin, during each season.

Season		Los Angeles Coastal Plain				San Fernando	San Gabriel	Raymond	Russell	Malibu	Santa Clara	L.A. County
		Central	Holly-wood	Santa Monica	West Coast							
W.01-02	% Exceed	10%	13%	0%	18%	37%	0%	-	-	-	-	15%
	# Samples	346	15	15	163	83	4	-	-	-	-	626
S.02	% Exceed	10%	13%	8%	11%	26%	17%	-	-	-	-	13%
	# Samples	516	23	80	208	141	12	-	-	-	-	980
W.02-03	% Exceed	8%	4%	8%	15%	18%	0%	-	-	-	-	10%
	# Samples	601	45	77	267	131	29	-	-	-	-	1150
S.03	% Exceed	8%	11%	8%	17%	24%	6%	-	-	0%	0%	13%
	# Samples	442	44	93	197	177	36	-	-	5	3	997
W.03-04	% Exceed	12%	0%	2%	11%	16%	0%	-	14%	0%	67%	12%
	# Samples	505	28	49	228	173	31	-	7	6	3	1030
S.04	% Exceed	10%	0%	10%	13%	19%	0%	-	-	0%	-	11%
	# Samples	542	45	93	231	151	38	-	-	3	-	1103
W.04-05	% Exceed	14%	5%	3%	10%	24%	8%	-	11%	0%	0%	12%
	# Samples	757	66	143	367	185	88	-	28	3	30	1667
S.05	% Exceed	16%	4%	4%	10%	24%	13%	-	4%	0%	0%	14%
	# Samples	701	52	169	457	316	115	-	25	5	30	1870
W.05-06	% Exceed	14%	9%	5%	10%	26%	16%	-	9%	0%	0%	14%
	# Samples	784	44	164	511	329	132	-	34	7	30	2035
S.06	% Exceed	12%	3%	6%	16%	24%	16%	-	3%	0%	0%	14%
	# Samples	741	74	241	464	450	132	-	34	7	38	2181
W.06-07	% Exceed	13%	0%	13%	18%	28%	14%	-	0%	0%	0%	16%
	# Samples	748	38	151	392	389	133	-	61	5	34	1951
S.07	% Exceed	9%	2%	16%	20%	33%	13%	-	0%	0%	0%	17%
	# Samples	646	60	138	441	436	148	-	40	12	34	1955
W.07-08	% Exceed	10%	0%	17%	18%	30%	15%	-	0%	0%	0%	16%
	# Samples	768	48	145	436	424	152	-	44	8	34	2059
S.08	% Exceed	11%	0%	18%	17%	21%	12%	0%	0%	0%	0%	14%
	# Samples	766	32	91	360	474	124	9	74	7	32	1969
W.08-09	% Exceed	10%	1%	13%	16%	26%	20%	-	5%	0%	0%	15%
	# Samples	850	71	106	383	525	147	-	74	8	32	2196
S.09	% Exceed	7%	0%	23%	23%	28%	15%	0%	0%	-	0%	15%
	# Samples	473	23	65	230	188	98	8	37	-	32	1154
W.09-10	% Exceed	10%	0%	6%	15%	29%	28%	0%	3%	-	0%	14%
	# Samples	627	52	84	290	236	60	8	39	-	32	1428
S.10	% Exceed	8%	6%	18%	18%	21%	20%	-	0%	-	0%	14%
	# Samples	378	17	44	214	228	49	-	18	-	26	974
W.10-11	% Exceed	8%	0%	10%	16%	21%	34%	0%	3%	-	2%	13%
	# Samples	400	20	31	220	288	41	7	31	-	44	1082
Totals	% Exceed	11%	3%	9%	15%	25%	15%	0%	3%	0%	1%	14%
	# Samples	11591	797	1979	6059	5324	1569	32	546	76	434	28407

decreasing trend in the percentage of samples exceeding the Basin Plan limit was observed in the Hollywood and Russell basins, while the San Gabriel basin exhibited an increasing trend (Figure 9). However, each of these basins had widely varying sample numbers during each season, which may have contributed to the identified increasing and decreasing trends.

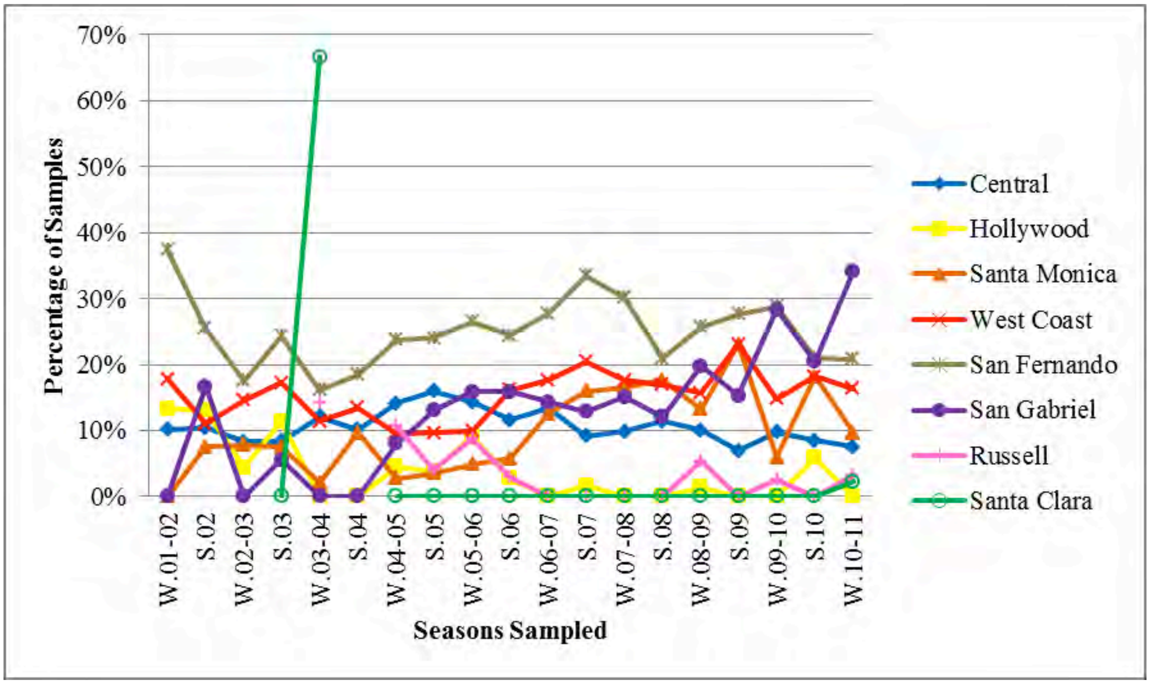

Figure 9: The percentage of nitrate-nitrogen samples exceeding the Basin Plan limit, during each season, in the eight analyzed basins.

A total of 734 samples have been analyzed for nitrite-nitrogen plus nitrate-nitrogen (NO_2-N + NO_3-N) in Los Angeles County since November 2001; 14% of these samples have exceeded the Basin Plan limit. However, none of the 10 basins contained sufficient data to identify spatiotemporal trends. Therefore, nitrite-nitrogen plus nitrate-nitrogen data was not further analyzed in this thesis study.

Overall, the San Fernando basin contained the highest percentages of samples exceeding the Basin Plan limits for two of the three analyzed nutrient constituents with

17% of nitrate samples and 25% of nitrate-nitrogen samples exceeding the respective Basin Plan limits. Additionally, the West Coast basin displayed the highest percentage of samples exceeding the Basin Plan limit for nitrite-nitrogen (6%) and the second highest percentage of samples exceeding the Basin Plan limit for nitrate-nitrogen (15%). Overall, the nutrient constituents changed little over the 10-year time frame. Both nitrate and nitrate-nitrogen exhibited small decreases over the 10-year period in two basins each (nitrate, Central and West Coast basins; nitrate-nitrogen, Hollywood and Russell basins). The number of samples varied across seasons in the Hollywood and Russell basins, but the sample effort in the Central and West Coast basins was relatively consistent. The latter provides a stronger argument for the decreasing trend being tied to a real decrease in the nitrate concentration in these basins. Apart from these trends, all of the other constituents in each of the analyzed basins exhibited no clear trend.

4.2 Additional Groundwater Spatial Analyses

In addition to the spatiotemporal analysis completed for each constituent, two additional spatial analyses were conducted on the Los Angeles County groundwater data: the first examined the relationship between the percent of samples exceeding the respective Basin Plan limits for salt and nutrients and the depth to groundwater and the second examined the percentage of samples exceeding the respective Basin Plan limits for salts and the distance from the coastline. The depth of the groundwater table surface has a recognized inverse correlation to the level of groundwater pollution in a basin (Ahn and Chon, 1999; Eckhardt and Stackelburg, 1995; Gardner and Vogel, 2005; Hudak, 1999, 2000; Pacheco and Cabrera, 1997; Tesoriero and Voss, 1997). Shallow groundwater tables collect water more recently infiltrated from the surface, providing less time for the soil to filter the groundwater pollutants. Deeper groundwater aquitards collect water that has traversed a longer flow path and provided more time for groundwater pollutants to be filtered out. In order to understand at what depth the samples exceeding the plan limits for each constituent are located, the total depth range was divided into five equal sample classes. The percentage of samples with values exceeding the respective Basin Plan limits was analyzed for each depth category for each constituent (Table 11).

Table 11: The number and fractions of samples exceeding the respective Basin Plan limits for each constituent at each equal sampled depth.

		-0.91 to 14 ft.	14.01 to 24.47 ft.	24.48 to 35.57 ft.	35.58 to 60.56 ft.	60.57 to 780.47 ft.	No Data	Total
Boron	% Exceed	21%	13%	8%	12%	12%	6%	11%
	# Samples	211	383	594	266	1025	228	2707
Chloride	% Exceed	30%	20%	40%	41%	35%	24%	35%
	# Samples	517	752	1761	1989	2744	866	8629
Sulfate	% Exceed	43%	45%	40%	31%	25%	32%	37%
	# Samples	6410	8486	7745	7603	5889	1152	37285
TDS	% Exceed	78%	83%	83%	71%	74%	93%	78%
	# Samples	925	878	1141	1369	2135	369	6817
Nitrite-N	% Exceed	3%	0%	0%	1%	1%	4%	1%
	# Samples	111	173	337	682	1531	502	3336
Nitrate	% Exceed	9%	7%	6%	6%	11%	24%	8%
	# Samples	768	1013	1304	899	687	168	4839
Nitrate-N	% Exceed	14%	12%	12%	15%	19%	13%	14%
	# Samples	5520	6603	5428	5689	4495	672	28407
Nitrite-N + Nitrate-N	% Exceed	12%	14%	10%	18%	61%	17%	14%
	# Samples	138	267	240	44	33	12	734

The nitrate-nitrogen and the nitrite-nitrogen plus nitrate-nitrogen constituents increased in percentage of samples exceeding the respective Basin Plan limit with increasing depth class. The chloride and nitrate constituents displayed fluctuating percentages of samples exceeding the respective Basin Plan limits, however, both chloride and nitrate showed an overall increasing percentage of samples exceeding the respective Basin Plan limits with increasing depth class. The sample sizes for each of these constituent varied significantly. Overall, nitrate-nitrogen and nitrite-nitrogen plus nitrate-nitrogen decreased in sample size with increasing depth class, while the chloride sample size increased with increasing depth class, and the nitrate constituent experienced an increase and then decrease in sample size with increasing depth.

Since the nitrate-nitrogen constituents had relatively the highest number of samples and a similar sample supply across the five depth classes, a spatial analysis was conducted in order to investigate if the location of the samples influenced the increasing concentrations that were exhibited with increasing depth (Figure 10). The Central and Hollywood basins contained sampling and evenly spatially distributed samples at all of the depth sections. The San Fernando, San Gabriel, West Coast and Santa Monica basins displayed an increase in spatial distribution across each basin in the deeper sections. This change in the distribution of groundwater sampling in the deeper sections could be influencing the increase in nitrate-nitrogen samples that are exceeding the respective Basin Plan limits but it is likely that nitrate-nitrogen concentration is increasing with increasing depth class.

Meanwhile, the boron, sulfate, TDS and nitrite-nitrogen constituents show decreases in percentages of samples exceeding the respective Basin Plan limits with depth (Table 11). All four constituents showed inconsistent sampling numbers with each

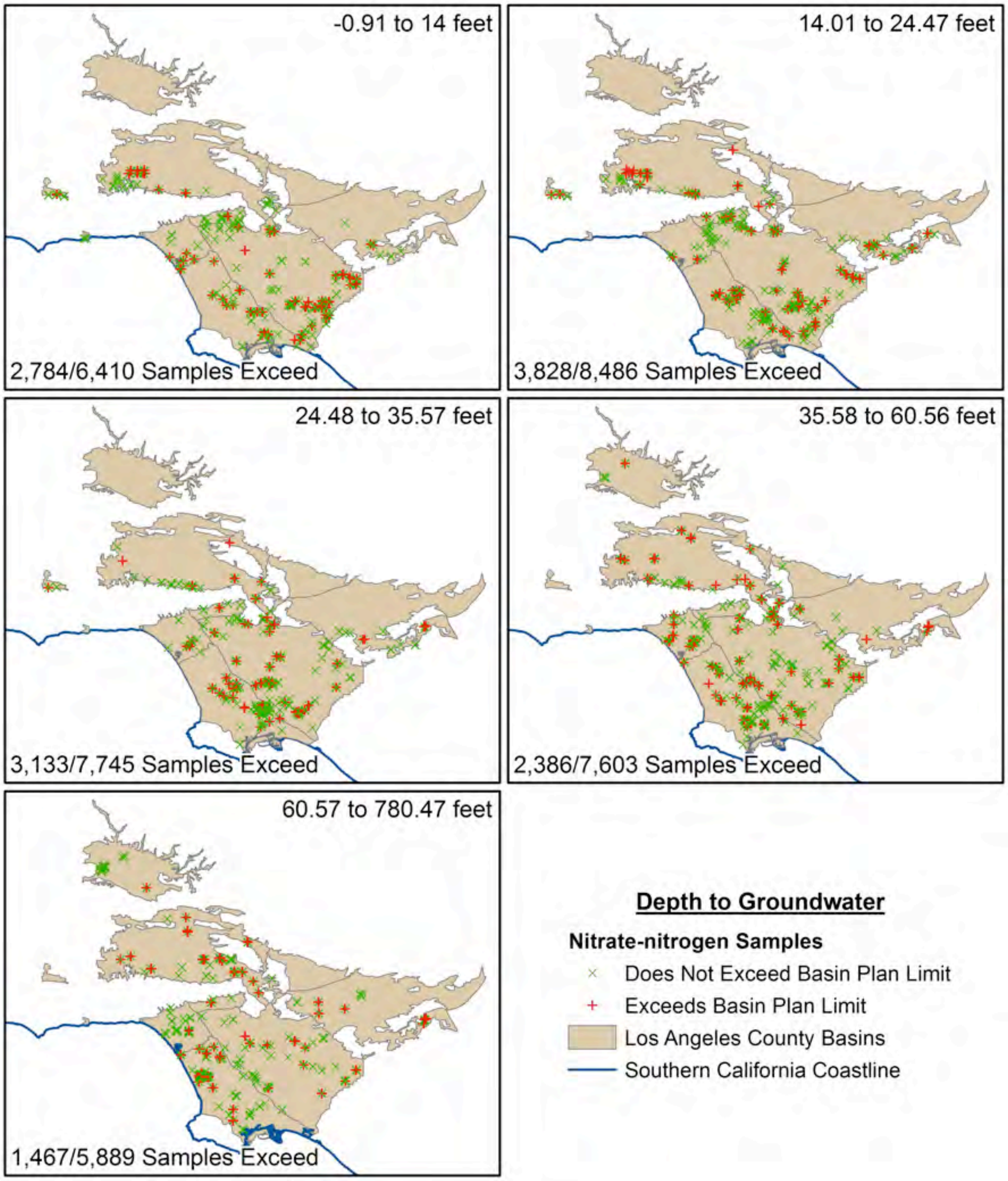

Figure 10: The spatial distribution of nitrate-nitrogen samples in each of the five depth classes.

depth class. Due to the higher sampling numbers, the sulfate data was analyzed further to determine any trends and clues that might explain the decrease in fraction of samples exceeding the respective Basin Plan limits with increasing depth (Figure 11). Across each of the basins it is clear that in the deepest two sections, the sampling is more widely distributed. This trend is especially evident in the Santa Clara, San Gabriel and West Coast basins. Looking more closely at the pattern of samples not exceeding the

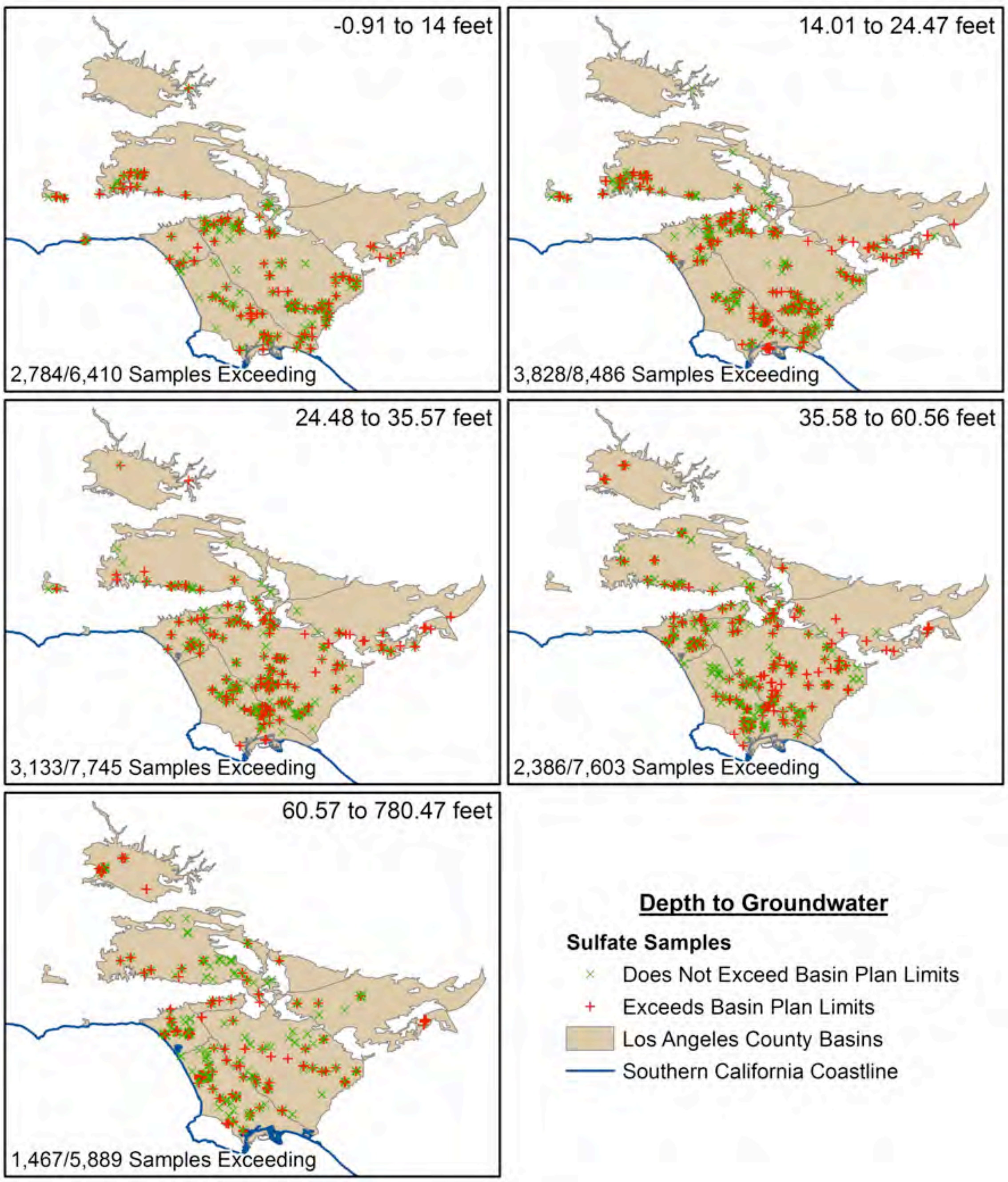

Figure 11: The spatial distribution of sulfate samples in each of the five depth classes.

respective Basin Plan limits, this increase in the spatial distribution of sampling locations is the most likely explanation for the decrease in the percentage of sulfate samples exceeding the respective Basin Plan limits with groundwater depth.

The distance of a site to the coastline can have an influence on the salt constituents that are measured in a sample. Since salt-water intrusion is a problem that only affects basins close to the coastline, the Central, Hollywood, Santa Monica, West Coast and Malibu basins were used for this portion of the analysis. However, as displayed in the spatiotemporal analysis tables (Tables 4-10); the Malibu basin did not contain adequate sample sizes to provide a significant contribution to the analysis. Therefore, only the four sub-basins of the Los Angeles Coastal Plan basin were analyzed comparing the distance to the coastline to the percentage of samples exceeding the respective Basin Plan limits for each of the four salt constituents (Table 12). With increasing distance from the coastline, the percentage of samples exceeding the respective Basin Plan limits increased for three of the four salt constituents (boron,

Table 12: The numbers and fractions of samples exceeding the respective Basin Plan limits for each salt constituent at various distances from the coastline.

		Nearest	Near	Mid	Far	Farthest	Total	All LA Basins Total
Boron	% Exceed	6%	14%	9%	34%	-	12%	11%
	# Samples	491	509	287	127	0	1414	2707
Chloride	% Exceed	35%	45%	32%	31%	7%	37%	35%
	# Samples	1938	1990	1792	218	43	5981	8629
Sulfate	% Exceed	28%	36%	43%	38%	14%	35%	37%
	# Samples	7676	9665	5654	3882	465	27342	37285
TDS	% Exceed	69%	85%	72%	95%	14%	77%	78%
	# Samples	1708	2054	844	253	43	4902	6817

sulfate and TDS), until the farthest distance category where the percentages dropped dramatically in each of the basins. The decline in sampling number may explain some of this decrease. The percentage of samples exceeding the chloride Basin Plan limit decreased with distance, suggesting that saltwater intrusion may still contribute to higher chloride levels at sites closer to the coast.

Chapter 5 – Conclusions

5.1 Groundwater Quality in Los Angeles County

Sulfate and nitrate-nitrogen were the two constituents monitored most intensely with 37,285 and 28,407 samples, respectively, collected during the study period. The salts are routinely higher than the nutrients in terms of the percentage of samples exceeding the respective Basin Plan limits. The nutrient constituents have been sampled less frequently (nitrate, 4,839 samples; nitrite-nitrogen, 3,336 samples; and nitrite-nitrogen plus nitrate-nitrogen, 734 samples) and have much lower percentages of samples exceeding the respective plan limits (nitrate-nitrogen, 14%; nitrite-nitrogen, 14%; nitrate, 8%; nitrite-nitrogen, 1%). Therefore, the noted sources of salt constituents are most likely occurring in higher volumes in Los Angeles County than the noted sources of nitrogen constituents. The TDS, sulfate and chloride measurements exceeded the respective Basin Plan limits 78%, 37% and 35% of the time, respectively. Industrial effluent is the most commonly noted source of these three constituents, and therefore could be the leading contributor to groundwater pollution in Los Angeles County.

The Central Basin experienced the largest sampling effort with 34,552 samples collected during the 10-year study period. The West Coast and San Fernando basins were second and third in terms of sample effort with 19,799 and 17,511 samples collected, respectively. The number of samples correlate to the size of the basins: the Central basin is the largest basin (177,000 acres), the San Fernando and West Coast are the third and fourth largest basins covering 145,000 and 91,300 acres, respectively. Additionally, the variations in sampling in each basin could also be attributed to the population distribution in the basin area. The higher volume of population would contribute to a larger number of underground storage tanks, site clean-ups and land disposal sites that would have been monitored and included in the Geotracker data set utilized in this thesis study. This additional analysis could provide insight to the potential relationship between the limited distribution of sampled sites in San Fernando, San Gabriel and Raymond groundwater basins and the distribution of the population across these basins.

The Geotracker database consists of data driven by types of land use (open and closed underground storage tanks, site clean-up programs and land disposal sites) and the related permits required for these uses. The primary purpose of each permit holder's monitoring requirements that are catalogued and reported in Geotracker is to help the Los Angeles Regional Water Quality Control Board discover and track substantial site specific groundwater quality problems as they develop. A secondary purpose of the Geotracker database may be to assist the Regional Board in monitoring the overall groundwater quality conditions across Los Angele's 10 groundwater basins. While the Geotracker database and permit holder monitoring program works well for the first priority, the results of this thesis study show that the database does not support the task of overall monitoring of groundwater quality across the county.

The results of the analysis show that it is difficult to clarify spatiotemporal trends given that individual samples at specific locations were collected at different time intervals and that the measurement locations are clustered around the permit holder sites. These two qualities of the data collection approach coupled with the high levels of variability in groundwater quality conditions that might be expected in space and time meant that the Geotracker database provides insufficient support to make wider use of the spatial interpolation and analysis tools available in ArcGIS and similar spatial analysis software. The results reported for the Central basin TDS spatiotemporal analysis showed that the varying spatial extent of sampling may be the reason for the identified decrease in TDS percentage of samples exceeding the respective Basin Plan limits rather than an actual decrease in the constituent that was measured. Meanwhile the figures and accompanying text discussing the Hollywood chloride spatiotemporal analysis and the San Gabriel spatiotemporal analysis show that while the limited spatial extent of the samples did not allow for a trend to be recognized across entire basins, the spatial distribution did allow for trends to be seen in certain portions of selected basins.

Overall, no overarching spatial or temporal trends were uncovered in this thesis study. Some basins were found to contain higher instances of constituents exceeding the limits, such as the San Gabriel basin, which has the highest percentage of samples exceeding the respective Basin Plan limits for both chloride and TDS and the second highest percentage of samples exceeding the Basin Plan limits for sulfate. However, the individual constituents varied from basin to basin in terms of their spatial and temporal patterns. The lack of spatial and temporal trends across the basins could be a result of the limitations of the dataset that was analyzed, or the need for additional analysis at different scales or utilizing different methods.

5.2 Limitations of the Spatiotemporal Analysis

The data set obtained from the California Water Quality Control Board's Geotracker site had certain limitations that may have affected the spatial and temporal patterns seen in this thesis study. First, the dataset does not contain samples that are collected in a dispersed pattern across each basin, nor are they collected at uniform depths, because the locations were limited by the locations of the permit holder sites. Therefore it can be difficult to determine spatial and temporal patterns when the sampling does not cover the entire basin and the same aquifers (i.e. depth). This was a notable limitation in the San Fernando, San Gabriel and Raymond basins. Similarly, the sampling in the dataset was not uniform over time and therefore it was difficult to characterize the temporal patterns.

In addition to the sampling pattern, errors in the Geotracker dataset could have stemmed from differences and mistakes in the collection and analysis protocols. The samples included in this dataset were all collected and analyzed by different contractors hired by the permit holders of the underground storage tanks, site clean-ups and land disposal sites. While the California Water Quality Control Board specifies to the level of accuracy to which the measurements must be completed, the sampling and analytical procedures and protocols likely varied both between different contractors and with time over the 10-year analysis period; these changes likely introduced different and untraceable sources of error. There errors may have affected the percentage of samples exceeding the respective Basin Plan limits, which would in turn affect the spatial and temporal patterns observed in this thesis study. The extent of such problems is unknown.

5.3 Recommendations for Future Research

Some additional analysis could still be completed on the Geotracker dataset utilized in this thesis study, from which it might be possible to uncover finer scale spatial and temporal trends. Since no county level trends were observed, the analysis might focus on the basin and sub-basin scales, and possibly specific clusters of samples sites. The Geotracker samples were often clustered in small areas that had multiple samples, so conducting analysis at this scale would allow for the utilization of every individual sample and therefore might help to uncover spatial and temporal trends for the salt and nutrient contamination.

Looking beyond these incremental steps, a more complete and thoughtful dataset would be needed to create a true understanding of the complex sources and pathways of the salt and nutrient constituents in Los Angeles County's groundwater basins. This dataset would contain uniformly collected data that was collected using a spatially distributed sampling frame across each of the groundwater basins, and contains samples taken at multiple groundwater depths. This dataset would allow for a better understanding of the spatial patterns across the San Fernando, San Gabriel and Raymond groundwater basins, for example, since they currently lack good spatial distribution of samples in the Geotracker dataset. Additionally, this dataset would allow for a better representation of the groundwater quality in each of the aquifers in each of the basins. This dataset would allow for more than just a spatial and temporal analysis but would be able to construct an interpolated surface for each aquifer that could be used to characterize the horizontal and vertical distributions of groundwater constituents in Los

Angeles County. Additional information that may advance our understanding of the complex sources and pathways of groundwater pollution include the locations of penetrable and impenetrable surfaces, the sewer systems, and groundwater flow models that account for the geology of the alluvium in each of the basins in Los Angeles County. These kinds of data might be combined in a variety of modeling frameworks and the monitoring data would be used to calibrate and validate the models with the overall goal of tracking the sources and best means of prevention and remediation of groundwater contamination in Los Angeles County over time.

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