Assessment and Modeling of Groundwater Flow and Nitrate Contamination within Coastal Karst Aquifer of Puerto Rico

A Thesis Presented

By

Kooshah Kalhor

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ABSTRACT

Karst aquifers, capable of store and transmit large amount of water, are the main source of drinking water in many regions worldwide. Their excessive permeability leads to enhanced vulnerability to contamination accordingly. In the first section of this study, a comprehensive overview of hydrological processes and concepts, assessment methods and governing equations regarding groundwater flow and contaminant transport in karst aquifers is presented. Moreover, surface water and groundwater interaction and recent groundwater remediation techniques in karst terrains are discussed. Due to the complexity of karst aquifers, different approaches are developed by researchers for investigating and predicting karst processes and groundwater behavior. Modeling techniques are among the most beneficial and powerful methods for assessing groundwater flow and contaminant transport in karst aquifers, as hydrogeological systems with complicated and unpredictable behavior. Hence, several modeling approaches, are reviewed and assessed. Moreover, associated research works conducted for northern Puerto Rico are discussed to complement ongoing hydrogeologic investigations in this island.

In the second section, groundwater Nitrate contamination, as a result of agricultural, industrial and urban development, is assessed for north-central part of Puerto Rico. Using collected field samples and historical data, a Nitrate fate and transport simulation was conducted using MODFLOW and MT3D models. The calculated results of the regional-scale simulation showed high correlation with observed values and hence, the calibrated model was used for prediction purposes. Using land cover data and by assessing agricultural development trend in the island, spatiotemporal pattern of groundwater Nitrate concentration was predicted for the next two decades. It was predicted that agricultural activities will rise dramatically after economic damages of Hurricane Maria and this will negatively impact the groundwater quality. Based on the model prediction results, recommended management plans for each municipality were presented for the use of policy makers and authorities.
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Chapter 1:

Overview

Sustainable water resources management is a crucial concern in most countries across the globe. Only 3% of total water on the Earth is considered as fresh water resources and approximately 30% of these are accessible as groundwater, which is vital for human health, ecosystem, energy industry and other water-dependent topics (Shiklomanov, 1993). Karst aquifers are responsible for providing potable water for 40% and 25% of the US and world’s population, respectively (Ghasemizadeh et al., 2012). The increasing demand by residential, industrial and agricultural uses have caused groundwater depletion and have affected water quality in many regions.

With particular reference to karst aquifers, the first part of this study (Chapter 2) provides a comprehensive review of hydrological concepts and novel investigation and modeling techniques followed by a short discussion of groundwater contamination and remediation techniques. It is tried to present and review the work of other researchers in the recent years (especially after 2010) and to discuss the improvements that have been occurred regarding groundwater quality and quantity assessment. In each section, the associated research work that has been done for Puerto Rico is presented to better understand what research works have been conducted and can be done in the island regarding karst groundwater.

Puerto Rico (8,937 km²), as the case study location, is considered a territory of the United States (US). The island is located in northeastern side of Caribbean Sea and has an estimated population of 3.6 million (Castro-Prieto et al., 2017). Several surface water and groundwater resources across the island provide residents with fresh water and are used for agricultural, industrial and energy-based purposes. Figure 1.1 exhibits the geographical location of Puerto Rico and its altitude range based on Digital Elevation Model (DEM) database of United Stated Geological Survey (USGS).
Due to the presence of karst aquifers with high level of heterogeneity and anisotropy in northern coast of the island, rainfall water can easily percolate into the ground and this rapid movement, makes karst aquifer ultimately vulnerable to contamination. Several sources of contamination such as agricultural and industrial activities in addition to proximity to urban areas are responsible for groundwater contamination in the region (Cherry, 2001). Moreover, highly heterogeneous and karstic aquifers with conduits can cause high rate of water level fluctuation even in small temporal scaling (Yu et al., 2016).

There are different types of GW pollutants, including inorganic contaminants such as heavy metals, Nitrate and chloride; organic contaminants such as volatile organic compounds (VOCs), pesticides, plasticizers, chlorinated solvents, pharmaceuticals and personal care products (PPCP); and microbial
contaminants such as Coliform bacteria (Galitskaya et al., 2017; Kaçaroğlu, 1999; Lapworth et al., 2012; Sui et al., 2015). High concentrations of Nitrate (NO₃) is one of the most common concerns regarding GW contamination worldwide. Industrial sites, landfills, agricultural activities, urban wastewater etc. are among major sources of GW Nitrate contamination (Almasri and Kaluarachchi, 2004; Eshtawi et al., 2016; Wang et al., 2016). In the second part of this study (Chapter 3), groundwater Nitrate contamination in North coast limestone aquifer of Puerto Rico is assessed. The scope of the research work in this part is to predict the spatiotemporal distribution of Nitrate within karst aquifers by developing a numerical model and by assessing agricultural development capacity of the region. In fact, groundwater flow and Nitrate transport simulations were done using MODFLOW and MT3D models, respectively using historical observations and field data. After successful calibration and validation of the transport model, it was used for prediction purposes for the years 2025 and 2035. Finally, recommended management actions, regarding sustainable agricultural development, were presented for different municipalities in the area.
Chapter 2:

Quantitative and Qualitative Assessment of Groundwater in Karst Aquifers: A Review

2.1. Karst Aquifers

Comprising of chemically soluble rocks with large passages or network of conduits and caves inside, karst aquifers are very permeable and capable of store and transmit large amount of water. Limestone, dolomite, gypsum and anhydrite are the most common materials that form karst aquifers and carbonate rocks. Similar to other groundwater resources, regions in which karst aquifers exist are very popular for people to reside in because of their potential of providing habitants with fresh water (Quinn et al., 2006). Millions of people live in areas where there karst aquifers exist and 20-25% of the world’s population depends on water supplies from karst aquifer directly or indirectly. Approximately 10% of the world’s land surface areas have karst aquifer beneath them. This percentage is higher in some areas such as in Europe where it is roughly 35% (Ford and Williams, 2007). Until recently, the boundaries of karst aquifers around the world were not recognized accurately. Hence, by taking advantage of GIS tools, recent exploration of karst aquifers, Global Lithological Map that was developed before, Chen et al. have almost completed the first World Karst Aquifer Map (WOKAM). Their map distinguishes continuous carbonate rocks and discontinuous carbonate rocks and include major karst springs, wells and caves (Chen et al., 2017). Figure 2.1 demonstrates the distribution of karst aquifers within the United States and its territories.
Karst aquifers are individually different with unique work-frame and characteristics and they should be studied case by case (Stevanović, 2015). Two important characteristics of karst aquifers are heterogeneity and anisotropy which make it hard for hydrogeologists and researchers to develop models using simplifying assumptions. Basically, they have the most complex system amongst karst terrains and this will cause a lot of uncertainties and errors in developed models for studying and predicting their behavior (Bakalowicz, 2005). Also, the recharge and discharge rate of karst springs can vary a lot due to several reasons such as fluctuations in water table level caused by hydrological events or seasonal variations (Gárfias-Soliz et al., 2009). Table 2.1 elaborates hydrogeological characteristics of three main aquifer types, porous media, fractured rock and karst system based on ASTM D 5717–95 Standard: Guide for Design of Ground-Water Monitoring Systems in Karst and Fractured Rock Aquifers.

Figure 2.1. Distribution of karst aquifers in the United States and its territories – Compiled from open files associated with the USGS report of (Weary and Doctor, 2014)
Table 2.1. Hydrogeological characteristics of three main aquifer types, porous media, fractured rock and karst system based on ASTM D 5717–95 Standard (Rosenberry and LaBaugh, 2008)

<table>
<thead>
<tr>
<th>Aquifer characteristics</th>
<th>Aquifer type</th>
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<td></td>
<td>Porous (Granular)</td>
</tr>
<tr>
<td>Effective porosity</td>
<td>Mostly primary,</td>
</tr>
<tr>
<td></td>
<td>through intergranular</td>
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<tr>
<td></td>
<td>pores</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Isotropy</td>
<td>More isotropic</td>
</tr>
<tr>
<td>Homogeneity</td>
<td>More homogeneous</td>
</tr>
<tr>
<td>Flow</td>
<td>Slow, laminar</td>
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<tr>
<td>Flow predictions</td>
<td>Darcy's law usually</td>
</tr>
<tr>
<td></td>
<td>applies</td>
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<tr>
<td>Storage</td>
<td>Within saturated zone</td>
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<td></td>
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<tr>
<td>Recharge</td>
<td>Dispersed</td>
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<tr>
<td>Temporal head variation</td>
<td>Low variation</td>
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<tr>
<td>Temporal water chemistry</td>
<td>Low variation</td>
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</tbody>
</table>

Based on the information in Table 2.1, a karst aquifer system comprises several elements such as caves, conduits, sinkholes and springs. Limestone karst aquifers are common in many areas around the world including Puerto Rico (Cherry, 2001; Rafael et al., 2016), Florida (Xu et al., 2016) Mexico (Bauer-Gottwein et al., 2011), China (Luo et al., 2016) etc. Basically, they usually are evolved from fractured or fractured-porous rock networks after several years and by carbonate dissolution, large passages and caves are created. It should be noted that several modeling methods have been employed to simulate the evolution of karst aquifers from fractured or porous-fractured rock systems (Kaufmann, 2003, 2016; Kiraly, 2003). Figure 2.2 depicts sinkhole plain in the Barceloneta municipality of PR with
an industrial facility in the background and surrounded by residual limestone hills (a) and a block of vuggy limestone from the north coast karst aquifer of PR (b). Industrial facilities in the area have faced with several issues due to frequent creation of new sinkholes (Field, 2017).

Figure 2.2. Sinkhole plain in the Barceloneta municipality of PR with an industrial facility in the background and surrounded by residual limestone hills (a) and a block of vuggy limestone from the north coast karst aquifer of PR (b) –(Field, 2017)

Figure 2.3, modified from iasmania.com/karst-topography-limestone-chalk, depicts a conceptual model of a limestone coastal aquifer in a karstic area. Several sources of contamination such as agricultural and industrial activities in addition to proximity to an urban area are responsible for groundwater contamination in the region. The graphics of urban and industrial areas have been captured from San Juan (Capital of Puerto Rico) area using Google Earth software.
Figure 2.3. Conceptual model of a limestone coastal aquifer in a karstic area being exposed to several sources of contamination

As it appears in Figure 2.3 and based on the information in Table 2.1, a karst aquifer system comprises several elements such as caves, conduits, sinkhole, spring etc. Limestone karst aquifers are common in many areas around the world including Puerto Rico (Cherry, 2001; Rafael et al., 2016; Zack, 1994), Florida (Dufresne and Drake, 1999; Xu et al., 2016), Mexico (Bauer-Gottwein et al., 2011), China (Luo et al., 2016) etc. Basically, they usually are evolved from fractured or fractured‐porous rock networks after several years and by carbonate dissolution, large passages and caves can be created. It should be noted that several modeling methods have been employed to simulate the evolution of karst aquifers from fractured or porous‐fractured rock systems (Kaufmann, 2003, 2016; Kiraly, 2003; Siemers and Dreybrodt, 1998).

In groundwater hydrology, hydraulic conductivity quantifies the ability of soil in transferring water. Based upon different types and properties of aquifer material, hydraulic conductivity can range from 10 cm/s for gravel to $10^{-10}$ cm/s for shale. Figure 2.4, modified from (Freeze and Cherry, 1979), demonstrates the range of hydraulic conductivity (K) for different types of rock.
Commonly, laboratory, field and numerical methods are 3 main methods for measuring hydraulic conductivity. Numerical and finite element-based methods are used for determining vertical and horizontal hydraulic conductivities (Kalbus et al., 2006; Smith et al., 2016). Usually, in karst aquifers where subsurface heterogeneity exists, determining hydraulic parameters such as K requires a complicated analysis because this parameter is spatially and temporally variable throughout the aquifer. Hydraulic tomography is a novel method that can be used for imaging the heterogeneity in karstic terrains (Illman et al., 2007). Moreover, in karst aquifers, the average range of K can vary depending on several factors such as geology, slope, level of heterogeneity and karstification. Angulu et al. studied hydraulic conductivity in karst areas by applying water injection tests and electrical resistivity logging (Angulo et al., 2011). Similarly, different researchers reported experimental values for hydraulic conductivity based on their research approach and case study area (Chen et al., 2011; Fu et al., 2015; Sudicky et al., 2010). As it is shown in Figure 2.4, K of limestone karst aquifer which is dominant in northern coast of Puerto Rico, can be assumed in the range of $10^{-4}$ to 5 cm/s which demonstrates high level of permeability in karst aquifers. The estimated values of K in different locations of north coast karst aquifer of Puerto Rico can be found in the water resources investigation reports (Rodriguez-Martinez, 1995) or similar sources for modeling purposes.

2.1.1. Means of Studying Karst Aquifers

Based on the complex characteristics of karst, several techniques and methods associated with modified and reformed conventional hydrogeological methods have been employed for understanding the behavior of karst aquifers. Hydrologic and hydraulic methods, geophysical and geological methods, modeling techniques and tracer tests are among the most common means of describing karstic systems (Goldscheider and Drew, 2007; Stevanović, 2015).
(Giudici et al., 2012; Hu et al., 2009) studied karst aquifers by taking advantage of modeling methods. In spite of their limitations (sufficient data requirement), advantages of using modeling techniques have made them popular. Variable parameters can be used and the model can be generalized for other aquifers. More importantly, other assessment methods such as remote sensing tools and geological methods can be coupled with modeling techniques for a better description of karst systems. Remote sensing tools, either coupled with modeling methods or be used separate, can be very beneficial because of their strong data analysis and management capability which allows assessment of several datasets and layers simultaneously. However, lack of high resolution data for local studies can be problematic in some cases (Manda and Gross, 2006; Theilen-Willige et al., 2014). In addition, taking advantage of geological methods, which help understanding the aquifer geometry and hydraulic properties such as permeability in addition to orientation and characteristics of potential flow paths, can boost the accuracy of modeling results (Goldscheider and Drew, 2007). Geophysical techniques can also be employed in conjunction with geological methods to understand geologic structures and overburden thickness of the aquifer (Chalikakis et al., 2011; Ford and Williams, 2007; Goldscheider and Drew, 2007).

Moreover, understanding karst aquifers can be achieved by using hydrological and hydraulic methods. By using these methods, water balance dynamics are assessed and spring hydrographs, hydraulic parameters, boundary conditions, flow directions and water table variations are identified to characterize karst behavior. Sometimes, because of unknown and complex catchment boundaries, water budgets are often problematic (Goldscheider and Drew, 2007; Hartmann et al., 2014; Kovács et al., 2005).

In many cases, isotropic techniques and artificial tracers are used for determining residence time and water age and understanding the movement of water through conduits. The main advantages of these techniques are determining linear flow velocities and information on contaminant transport and delineating catchment areas. Although obtained information and data from tracers are often reliable and unequivocal, limited applicability in large areas with long transit times and also change of color and toxicity concerns are some of the disadvantages of using isotropic techniques and artificial tracers (Goldscheider et al., 2008; Jones and Banner, 2003; Morales et al., 2017)

2.1.2. Governing Equations

Taking advantage of the general form of Darcy's velocity, Cheng and Chen described the governing equation of groundwater flow in conduits. The hydraulic conductivity of karst conduit flow under laminar and non-linear situation can be expressed as $K_{lc}$ and $K_{nc}$ respectively (Cheng and Chen, 2004).

$$K_{lc} = \frac{d^2 \gamma}{32 \mu}$$ (1)
\[ K_{nc} = 2gd/uf \]  

(2)

Where \( u \) is the mean velocity and \( f \) is friction factor that depends on Reynolds number and relative roughness of the karst conduit.

For describing steady flow in an open-channel and closed-channel, Mannings equation (eq. 3) and Darcy Weisbach equation (eq. 4) can be employed respectively (Ghasemizadeh et al., 2012).

\[ V = \frac{1}{n} R^{2/3} S^{1/2} \]  

(3)

\[ Q = \left( 2\pi g^{1/2} r^{5/2} / f^{0.5} \right) i^{1/2} \]  

(4)

Where \( n \) is Manning’s roughness factor \([T/L^{1/3}]\), \( R \) is hydraulic radius of the channel \([L]\), \( S \) is the channel slope \([L/L]\), \( f \) is the empirical Darcy-Weisbach friction factor, \( g \) is the gravitational acceleration \([LT^{-2}]\), \( r \) is the radius \([L]\), \( i \) is the hydraulic gradient \([L/L]\), \( A_c \) is the conduit cross sectional area \([L^2]\).

However, for the purpose of modeling unsteady and non-uniform flow in karst aquifers and discrete conduit systems, Reimann et al. presented related equations by considering groundwater flow as free-surface flow (open-channel) and pipe flow (flow in fully filled conduits). Hence, unsteady and non-uniform flow hydraulics in an open-channel situation can be expressed by equation of continuity (eq. 5) and equation of motion (eq. 6) (Reimann et al., 2011).

\[ \frac{\partial Q}{\partial x} + W \frac{\partial h_c}{\partial t} + q = 0 \]  

(5)

\[ \frac{\partial Q}{\partial t} + \frac{\partial}{\partial x} \left( \frac{Q^2}{A} \right) + gA \frac{\partial h_c}{\partial x} + gA(s_f - s_0) = 0 \]  

(6)

Where

\[ s_f = \frac{n^2 Q |Q|}{A^2 R^{4/3}} \]

and \( Q \) is discharge \([L^3/T]\), \( W \) is conduit width \([L]\), \( h_c \) is conduit head \([L]\), \( x \) is spatial coordinate in flow direction \([L]\), \( t \) is time \([T]\), \( q \) is lateral discharge per unit length of channel \([L^2/T]\), \( g \) is gravitational acceleration \([L/T^2]\), \( A \) is cross-sectional area \([L^2]\), \( s_0 \) is channel slope, \( s_f \) is the friction slope \([L]\), \( n \) is Manning coefficient \([T/L^{1/3}]\) and \( R \) is the hydraulic radius \([L]\).

Furthermore, Li mathematically described the 1D solute transport in conduits by introducing a formula which is displayed here as equation 7 (Li, 2009).

\[ \frac{\partial C}{\partial t} + \frac{\partial}{\partial x} \left( V_c C - D_c \frac{\partial C}{\partial x} \right) = \frac{2}{r_f} C_0 q \]  

(7)
Where \( C \) is the solute concentration in the conduit \([M/L^3]\), \( r \) is the conduit radius \([L]\), \( V_c \) is the mean speed of conduit flow \([L/T]\), \( D_c \) is the coefficient of dispersion in the conduit \([L^2/T]\), \( q \) is the Darcian flow from matrix into conduit \([L/T]\), \( C_0 \) is the solute concentration in the matrix \([M/L^3]\) and \( j \) is the specific flux of solute at the wall which is equal to 1 for contaminated water and 0 for non-contaminated water. Although this equation works for mean velocity of flow inside the conduits, variable velocity due to flow increase in the downstream direction can be expressed as:

\[
V_c(x) = V_c(0) + \frac{2xq}{r}
\]  

(8)

Where \( V_c(0) \) is the average speed at \( x=0 \).

2.2. Groundwater Contamination and Remediation Techniques

2.2.1. Contamination sources

Karst aquifers which are characterized with high permeability with many caves and fractures inside and also recharged by sinkholes, rivers etc., have shown high vulnerability to contamination (Kaçaroğlu, 1999). The formation of solution channels and sinkholes facilitates the intrusion of seawater and contaminated stormwater and wastewater into the aquifer. Coastal aquifers, such as north coast limestone aquifer of Puerto Rico, are susceptible to seawater intrusion which can increase the salinity of groundwater (Arfib et al., 2007). Having a hydraulic connection to the sea, karstic-coastal aquifers can be characterized by having groundwater flow in conduits, sub-marine freshwater springs and intrusion of seawater through the aquifer via conduit networks (Fleury et al., 2007) and are exposed to contamination by NaCl-based brackish water from the sea or the ocean nearby (Mongelli et al., 2013). It was found out that pharmaceutical and personal care products (PPCP), pesticides and a few more contaminants have caused groundwater contamination (Metcalfe et al., 2011). Hence, because coastal aquifers are susceptible to seawater intrusion and municipal wastewater-based contamination, developing a sustainable plan by using integrated models for managing and monitoring water resources is essential (Sreekanth and Datta, 2015).

Anthropogenic operations such as agricultural, industrial, residential, commercial and municipal activities have shown responsibility for groundwater resources pollution in recent decades (Fetter, 2001; Wakida and Lerner, 2005). Leakage of storage tanks, chemical spills, landfills, fertilizers and pesticides, sanitation systems, untreated waste discharge and sewage etc. are some of the main sources of contamination due to anthropogenic activities (El Alfy and Faraj, 2017). Generally, regardless of the cause of contamination, organic compounds (Lapworth et al., 2012), Metals (Yao et al., 2012), Pathogens and Chemical compounds and elements such as Nitrate, Chloride and Fluoride, are considered as four main categories of contamination source (Panagiotakis and Dermatas, 2017; Vidal Montes et al., 2016). Nowadays, new chemical compounds mainly originated from pharmaceutical and
personal care products (PPCP) are a big concern because treating water that contains these products is more difficult. Concentration of PPCPs such as Antibiotics, Anti-inflammatories, Lipid regulators, Psychiatric drugs, Stimulants, Insect Repellants, Sunscreen agents etc. was observed to be higher than regulatory criterion in some areas. Usually, Wastewater and contaminated surface water, Landfills, Septic systems and Sewer leakages are considered as common sources of PPCP contamination especially in karstic areas (Dodgen et al., 2017; Sui et al., 2015).

2.2.2. Remediation strategies in karst aquifers

Karst GW remediation technologies usually take advantage of a combined set of treatment mechanisms for achieving higher efficiency. As an example, Xanke et al. proposed a combined protection plan for a large-scale aquifer recharge into a karst aquifer system in Jordan. Their suggested combined set of action plans was not able to prevent contamination but it was able to abate the extent of pollution and lower the remediation costs (Xanke et al., 2017). Due to high level of contamination at superfund sites in proximity of karst aquifer, many remediation methods have been employed by agencies. Gaining more knowledge about efficacy of remediation techniques and behavior of contaminants and karst aquifers have led to variation in use of remedial technologies (Parise et al., 2015).

2.2.2.1. Remediation by addressing source zones

This strategy is used in order to decrease the mass flux into the aquifer. The most common remediation techniques associated with this strategy are soil excavation, mass reduction by NAPL and vapor removal, physical, chemical and hydraulic containment and in-situ remediation methods. In spite of their advantages, these techniques are associated with some challenges as well. For example, contaminant mass may remain in epikarst zones and consequently not accessible to excavation. Moreover, capture zones cannot be reliably simulated using pumping wells data and numerical models such as MODFLOW. These techniques are often expensive and tricky to build any hydrogeologic barriers in karst aquifers.

In-situ thermal treatment, in-situ chemical oxidation (ISCO), and in-situ bioremediation are three main in-situ remediation methods that have commonly been used at karst aquifers (Parise et al., 2015). However, there are some limitations that can decrease the efficiency of these treatment methods. As an example, in thermal treatment method, preferential pathways within karst aquifers that lead to high seepage velocity, can cause heat loss. Electrical resistance heating (ERH) has been used for thermal remediation of GW in a karst aquifer in Alabama. It was reported that this technique was successful in removing DNAPLs in the case study area (Hodges et al., 2014). The preferential flow pathways within karst system that can disperse injected materials, usually are problematic for other treatment methods such as ISCO and bioremediation as well. Hence, identifying the location of conduits and major fractures is necessary for an efficient remedial treatment.
Regarding ISCO remediation method, by assuming that the contaminated area is well identified and the injection fluid has the right dosage and residence time, the possibility of delivering injection fluid to the contaminated area with minimal error is the major challenge, similar to other fluid-based remediation methods in karst aquifers. Moreover, for achieving the highest efficiency in treating contaminants diffused into the rock matrix or moving with slow advective transport, oxidizing agents should remain in the contaminated area. However, rapid movement of water through preferential flow pathways dilutes the oxidizing agents. Thus, it can be asserted that application of ISCO in karst aquifers is limited. Furthermore, it was shown that persistent reducing conditions in high flow settings cannot be achieved due to GW and native electron acceptor flux. Hence, using bioremediation techniques for treating GW in karst aquifers may not lead to acceptable results. However, in some cases, using bioremediation is recommended if tracer studies and sample collection can be done diligently. Regardless of limitations in applying treatment methods for karst aquifers, Randrianarivelos et al. pointed out chemical oxidation as a beneficial techniques for GW remediation (Randrianarivelos et al., 2017). As it appears in Figure 2.5, source zone treatment at superfund sites were associated with inconsistent preference of using GW remedial technologies. Nevertheless, soil vapor extraction was remained as the most common remediation method during 2005-2011.

![Figure 2.5. Preferred in-situ remediation techniques for source zone treatment chosen at superfund sites – modified from (USEPA, 2013)](image)

2.2.2.2. Remediation by mitigating exposure pathways

Exposure pathways often play a crucial role in spreading the contamination through karst aquifers. Mainly, remediation by mitigating exposure pathways can be done by treating at the tap, replacing...
drinking water supplies, treating spring flow using active and passive methods, land cover control using fences, signage, deed restriction and local law enforcement. In spite of their high remedial capability, these techniques often require long-term operation and maintenance costs (Randrianarivelo et al., 2017).

### 2.2.2.3. Remediation by managing contaminated groundwater

Several methods for treating and managing contaminated karst GW are being used worldwide. Pump and treat, permeable reactive barriers, chemical oxidation, bioremediation and thermal remediation are among most common techniques for treating impacted GW.

The main challenge associated with these techniques is to identify the zone that requires treatment. Based on site conditions and the type of contaminants, the most effective technology should be employed. Assessment of remediation technique requires an appropriate monitoring approach (for locations consist of springs, streams, extraction systems, and previously tested wells) and comprehensive hydrogeological and water quality sampling data (Randrianarivelo et al., 2017).

### 2.2.3. Groundwater Contamination in Puerto Rico

Several researchers have assessed the GW contamination in north coast limestone karst aquifer of Puerto Rico and have suggested beneficial remediation techniques and groundwater modeling and management approaches (Biaggi, 1995). Historical studies since 1980 show that mainly, contaminants with chlorinated solvents including TCE, Dichloroethene, Chloroform, Carbon tetrachloride, Tetrachloroethene, Tetrachloroethane, Dichloroethane and methylene chloride, were found to have high concentrations causing public health concerns (Padilla et al., 2011). Several wells and sites (Figure 2.6) were considered as the National Priority List (NPL) Superfund Sites and remediation actions for treating water in these sites have begun. Regarding studying the groundwater pollution and understanding the potential exposure pathways of contaminants, some methods such as using tracers and GIS was employed (Steele-Valentín and Padilla, 2009). The abundancy of superfund sites and high concentration of contaminants in GW recourses of Puerto Rico have caused increasing rate of pre-term birth (highest amongst US states and territories) in the island (Mathews and MacDorman, 2011). However, since 2006, this rate has been declined from 20% to 11.4% due to remediation techniques that were employed and awareness of inhabitant that was enhanced regarding water-borne diseases (March of Dimes Website, 2016; Rutigliano, 2016).

Hydraulic and hydrogeological properties of the aquifer are important in studying contaminant transport. In karst aquifers analysis of contaminant transport requires more sophisticated approaches (Hu et al., 2009). Fate and transport of Non-aqueous Phase Liquids (NAPLs), chlorinated compounds such as CVOCs and Phthalates in karstic aquifers of Puerto Rico was studied recently. Yu et al. assessed
the concentration of CVOC in northern Puerto Rico based on historical data. They stated that the hydrogeological conditions of the karst aquifer were greatly associated with the spatiotemporal distribution patterns of the CVOCs. Water resources pollution in northern Puerto Rico has caused negative social, economic, and environmental impacts. Hence, long-term and consistent monitoring of water quality in the areas with high concentration of contaminants were suggested. (Yu et al., 2015).

Furthermore, Yu et al. studied the historical variations in concentration of CVOCs such as TCE, PCE, CT, TCM, and DCM in north coast karst aquifer of Puerto Rico. By developing a model and analyzing data, they reported that the aquifer is highly contaminated and further remediation processes should be undertaken. Figure 2.6 which is modified from their paper depicts the location of wells, Resource Conservation and Recovery Act (RCRA) and National Priority List (NPL) superfund sites. (Yu et al., 2015).

As it appears in Figure 2.6, there is abundance of superfund sites in northern Puerto Rico mainly due to industrial activities, improper management of landfills, accidental spills, unidentified waste disposals, or residential septic systems. Most of these sites are located in upper aquifer of North Coast...
Limestone aquifer system. On the border of Arecibo and Barceloneta, there are 3 superfund sites which indicated high level of contamination in groundwater of that area. The spatiotemporal distribution of the CVOCs in the karst aquifers were reported to be largely associated with hydrogeological conditions of the karst (intrinsic properties and the biological environment) in addition to the source origin.

2.3. Surface Water and Groundwater Interactions (SWGWI)

Interaction of surface water and groundwater plays a critical role in understanding hydrological behavior of a basin. This interconnectivity incorporates the topographical, geological and morphological characteristics of terrains. Generally, water recharge from inflow of GW into the riverbed, water discharge from river bed to aquifer and also losing and gaining water for both SW and GW in some river segments are three main processes that can occur in SWGWI.

2.3.1. SWGWI Assessment Methods

Hydrochemical methods such as environmental isotopes, hydrochemistry and tracers and numerical modeling are among common techniques that can be used to assess SWGWI (Fleckenstein et al., 2010). Also, field observations, seepage measurement and also hydrogeological, hydrographic, hydrometric and geophysical analysis are beneficial tools that can be used in describing SWGWI (González-Pinzón et al., 2015; Martinez et al., 2015). Temperature change analysis and water budget assessment can be coupled with other methods to achieve more accurate and validate results (Brodie et al., 2007). Despite the variety in SWGWI analysis tools, tracers have been widely used due to their capability of providing independent ways of validating or refuting conventional-traditional methods of analyzing data and describing SWGWI (Baskaran et al., 2009; Jankowski, 2007). A comprehensive assessment of different means and methods of describing SWGWI is presented in Table 2.2 (Brodie et al., 2007).
<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Ease of Use</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrographic Analysis</strong></td>
<td>Monitoring time-series stream flow define base flow (GW discharge) component</td>
<td>High</td>
<td>Uses existing flow monitoring data. Can be undertaken as a desktop study prior to detailed field investigations. Provides information of seepage changes through time</td>
<td>Applicable to gaining stream conditions only. Assumption that base flow is groundwater discharge may not be valid.</td>
<td>Commonly applied method for unregulated catchments</td>
</tr>
<tr>
<td><strong>Hydrogeological Mapping</strong></td>
<td>Mapping of GW systems including flowpaths, GW quality, aquifer properties and geomorphology.</td>
<td>Low to Medium</td>
<td>Provides comprehensive understanding of GW systems around stream and its related hydrogeological systems</td>
<td>Compiling and interpreting hydrogeological data can be time consuming and complex. Limited borehole data can lead to misinterpretation</td>
<td>Describing GW flow system, surface geological and hydrogeological properties at a coarse scale (Gleeson et al., 2014).</td>
</tr>
<tr>
<td><strong>Modeling</strong></td>
<td>Simulating water flow regime around stream using mathematical equations</td>
<td>Low to Medium</td>
<td>Predictive and useful tool for policy-makers. Transient 3-D models can spatiotemporally estimate seepage changes</td>
<td>Oversimplified models may not be valid enough. Over-complex models need more data and are costly and time-consuming</td>
<td>Easy simulation of SWGWI that can make predictions for a hydrological system (Guay et al., 2013).</td>
</tr>
<tr>
<td><strong>Field Tools</strong></td>
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<tr>
<td><strong>Field Indicators</strong></td>
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<tr>
<td><strong>Tools</strong></td>
<td><strong>Visual indications of seepage such as water clarity, springs, aquatic plant species and chemical precipitates</strong></td>
<td><strong>Medium</strong> to <strong>High</strong></td>
<td><strong>Can identify seepage hotspots quickly. Return visits can provide information on seasonal changes in seepage flux.</strong></td>
<td><strong>Limited in quantifying seepage flux. Effectiveness varies with observer’s knowledge of field indicators (e.g. plant or aquatic biota).</strong></td>
<td><strong>Used in specific settings such as acid groundwater (e.g. iron precipitates) and karstic streams (e.g. travertine deposits)</strong></td>
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<tr>
<td><strong>Tracers</strong></td>
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<tr>
<td><strong>Tools</strong></td>
<td><strong>Monitoring movement of introduced tracers such as fluorescent dye or chemical constituents of water (such as major ions, stable isotopes, radon) to track water flow</strong></td>
<td><strong>Medium</strong></td>
<td><strong>Can provide evidence of water flow from stream into aquifer. Aquifer parameters such as recharge and discharge and fluid transport properties can be quantified.</strong></td>
<td><strong>Tracer studies require careful planning including meeting environmental regulatory controls. Processes such as degradation, precipitation or sorption can affect tracer performance. There can be a time gap between sample collection and final results analysis.</strong></td>
<td><strong>Karstic aquifers or investigations of contaminated sites (Ward et al., 2013), Groundwater seepage to streams (Martinez et al., 2015).</strong></td>
</tr>
<tr>
<td><strong>Geophysics and Remote Sensing</strong></td>
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<tr>
<td><strong>Tools</strong></td>
<td><strong>Use of geophysics (e.g. resistivity, EM, radiometrics) or remote sensing (e.g. Landsat) to map landscape features that</strong></td>
<td><strong>Low</strong></td>
<td><strong>Allows rapid, non-invasive mapping of landscape parameters with good spatial resolution. Some techniques provide information at depth.</strong></td>
<td><strong>Requires specific equipment, technical expertise and logistical support. Can require complex data processing and calibration with other datasets. Ground opportunities exist to use geophysical data collected for other purposes e.g. Mineral exploration. Satellite imagery commercially</strong></td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Difficulty</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>Notes</td>
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<tr>
<td>Hydrometrics</td>
<td>Measurement of hydraulic gradient between aquifer and stream and the hydraulic conductivity of intervening aquifer material. Based on Darcy’s Law.</td>
<td>Medium to High</td>
<td>Comparison of stream and groundwater levels a simple guide to seepage direction. Installation of minipiezometers in stream bed allows direct local measurement of potential seepage direction.</td>
<td>Relies on reasonable estimate of hydraulic conductivity to quantify seepage flux. Assumption of simple groundwater flow conditions may not be valid. Point measurement. Need to correct for density effects.</td>
<td>Comparison of stream levels with nearby groundwater levels commonly used to define direction of potential seepage.</td>
</tr>
<tr>
<td>Water Budgets</td>
<td>Quantification of stream reach water balance to define seepage component</td>
<td>Medium to High</td>
<td>Simple water balances estimated rapidly using existing stream flow monitoring. Provides estimate of aggregate seepage along reach.</td>
<td>Measurement errors in stream flow data can be significant, hence more suited to long reaches. Can be misleading if water balance component (e.g. extraction) is not adequately accounted for.</td>
<td>Routinely applied, particularly for regulated rivers or irrigation channels (Gebreyohannes et al., 2013).</td>
</tr>
</tbody>
</table>
Due to complexity of describing SWGWI, numerous researchers have tried to use different types of techniques such as model development to understand the interconnectivity between surface water and groundwater. Using GSFLOW model, Wu et al. showed that for large river basins, a systematic uncertainty analysis is important in SWGWI modeling. They took advantage of a probabilistic collocation method or PCM-based approach and were able to improve the model accuracy by calibration. They also suggested using a stochastic simulation rather than a deterministic one in uncertainty analysis (Wu et al., 2014). Fleckenstein et al. discussed development of new approaches and models, including numerical methods to spatiotemporally quantify SWGW patterns (Fleckenstein et al., 2010). Sulis et al. compared two physical-based, spatially-distributed numerical models, ParFlow and CATHY that can be employed for SWGWI analysis. Despite some minor differences due to using different discretization schemes (finite difference and finite element), they found both models to be in good agreement with data (Sulis et al., 2010). Sutton and Screaton explained SWGWI of a karst aquifer basin in Florida by analyzing river discharge and a transient numerical groundwater flow modeling. Their modeling results highlight the prominence of spatiotemporal variations in head gradients that can affect streams and karst aquifers connections and aquifer martial dissolution (Sutton et al., 2014).

Taking advantage of a lumped hydrological model, Wanders et al. studied SWGWI in a catchment in Netherlands. They used Lowland Groundwater-Surface water Interaction model (LGSI-model) and came into conclusion that this model shows very promising results and can generate excellent simulations of discharge and groundwater depths in addition to describing SWGWIs in the case study area (Wanders et al., 2011).

Understanding the SWGWI in coastal aquifers is vital for water resources management; because SWGWI dynamically controls water regimes and salinity in coastal wetlands and aquifers. SWGWI in coastal wetlands is influenced by complexity of hydrological and ecological processes (Langevin et al., 2005). Researchers have developed physically-based and fully-integrated models such as hydrogeosphere (Brunner and Simmons, 2012), MIKE SHE (McMichael et al., 2006), InHM (VanderKwaak and Loague, 2001), MODHMS (Panday and Huyakorn, 2004) and some other methods that was reviewed and discussed by (Sebben et al., 2013). Most of the developed models are based on the assumption that density of fluid is constant. Nevertheless, in coastal wetlands, due to seawater intrusion, this assumption may not be completely true (Liu and Mou, 2014).

Despite the fact that numerous methods have been developed for describing SW-GW interrelationship, there are still uncertainties and lack of sufficient knowledge for fully understanding the time lag between GW pumping and its influence on SW, relationship between GW pumping and river losses and also exact recharge and discharge points in streams (Jankowski 2007). Wu et al. assessed uncertainties in SWGWI modeling and employing a probabilistic collection method, they evaluated the applicability of the frame-work through an integrated SW-GW model for a basin in China and asserted that in describing complex SWGWIs, modeling uncertainties depend on the output and have significant
spatiotemporal variability. Hence, employing a systematic uncertainty analysis can be extremely helpful in understanding SWGWI (Wu et al., 2014) and also in groundwater model development process (Engelhardt et al., 2014).

2.3.2. Surface Water-Groundwater Interaction in Karst

High permeability and low attenuation capacity of karst aquifers, make mixture of surface water and GW problematic for fresh water use in the karstic terrains. Usually, surface water refers to waste surface waters, sea and brackish water, lake waters and river waters which are already contaminated or untreated. Attempts can been made to minimize the interaction between polluted surface water and GW in karstic areas by placing an impermeable seal along canal bottoms or riverbeds, constructing small dams/weirs, building grouting curtains, changing the flow direction of surface waters, plunging ponors, creating reactive barriers by pumping freshwater into aquifer (Milanović et al., 2015).

Furthermore, many researchers have studied SWGWI particularly in karst aquifers (Chu et al., 2016; Katz et al., 1997; Rugel et al., 2016). For example, (Bailly-Comte et al., 2009) studied the hydrodynamic interactions between GW and surface water in a karst watershed in southern France. Their focus was on the effect of GW on the genesis and propagation of surface floods. They shown the role of initial water level in a karst aquifer in predicting the type of hydraulic connection between surface water and GW during flood events. Moreover, the analysis of surface water and karst GW interaction conducted by (Bayless et al., 2014) shows that analytical methods such as hydrograph separation and hysteretic loops can be used for identifying bounding conditions within the watershed. In north coast karst aquifer of Puerto Rico, where rivers, lagoons, intense precipitation and also seawater intrusion exists, SWGWI can have a major impact in the quality of fresh water in karst aquifers of the region. However, we failed in our attempts to find any detailed research works associated with SWGWI in karst aquifers of northern PR. Hence, collecting field data, doing research and developing models in order to fully understand the mechanism of SWGWI in north part of the island is strongly recommended.

2.4. Modeling Methods

In order to predict the behavior of an aquifer based on hydrological variations, groundwater models have been developed by hydrogeologists and water resources scientists. In addition, some models are developed to chemically analyze the water quality and to simulate fate and transport of contaminants. A groundwater flow model is able to exhibit precise representation of hydrological and geological systems and also it can give a real insight into relationship and interactions between system elements. Modeling using computer programs can be truly beneficial when there are karst aquifers in the case study location. This is mainly due to the fact that karst aquifers are very heterogeneous and anisotropic and have a complex structure. Ergo, developing a relatively sophisticated model is the best option for simulating these types of aquifers.
2.4.1. Model Parameters and Development

Depending on the soil type and water table level, the percolation rate regarding the movement of water from saturated zone to groundwater differs (Ritchey and Rumbaugh, 1996). Additionally, the impact of human interferences with natural water cycle which can be caused mostly by irrigation and pumping water from wells, should be taken into account. Actually, a groundwater model can determine how much it is perilous for an aquifer and also for the ecosystem if certain level of human interference exists. This can help developing water resources management plans that can not only help optimizing water extraction, but also can preserve the environment and natural resources (Drew and Hötzl, 1999). Other physical parameters such as topographical and geological information of the region that is going to be modeled should be given to the modeling platform (Peterson and Wicks, 2006).

Anisotropy of aquifers regarding hydraulic conductivity, which is a parameter that can have a dissimilar value in each direction, can only be considered in two or three-dimensional models. Nowadays, by developing computer programs and also due to the need of acquiring more valid result as the output of modeling, three-dimensional models are more acceptable despite the possible complex procedure of setting them up (Anderson et al., 2015). While one-dimensional models can be applied for vertical flow in multiple horizontal layers, two-dimensional models considers water flow in a vertical plain and this is repeated in multiple parallel vertical plains as well. Nevertheless, a three-dimensional model subdivides the flow region into smaller cells that each of them can have a different properties regarding aquifer condition, soil characteristics, water flow etc. (Ebrahim, 2014).

Mostly, numerical analysis and tools should be used to solve complex differential equations of groundwater flow. In fact, a mathematical groundwater flow model is able to represent conceptual model of an aquifer mathematically and this mathematical representation enables researchers to solve the governing equations numerically by computers (Ebrahim, 2014; World Meteorological Organization, 2009). Using numerical solutions for solving groundwater flow equations in a three-dimensional scale is beneficial for models that follow the flow domain discretization approach. Usually, in a groundwater flow model, hydraulic head at each cell center and groundwater flow rate between cells can be considered as outcomes. Moreover, impacts on streamflow because of pumping or long-term impacts of current pumping can be assessed. Additionally, checking the consistency of datasets and parameters and also defining framework for future studies related to groundwater and aquifer condition are two prominent products of a groundwater model (Hartmann et al., 2014; Ritchey and Rumbaugh, 1996).

Researchers and hydrogeologists have tried to develop groundwater models that can predict and simulate the groundwater flow in the karst aquifers in a regional or local scale. Regional groundwater modeling are usually large-scale transient groundwater models capable of optimizing groundwater
resources development plans, analyzing water budget of aquifers and assessing regional flow systems. Zhou and Li published a review paper regarding regional groundwater modeling and discussed their characteristics and associates drawbacks (Zhou and Li, 2011). Moreover, regional groundwater modeling was studied by a few researchers. Sauter assessed the quantification and prediction of regional groundwater flow and transport in a karst aquifer in Germany. He discussed how the most appropriate modeling tool can be selected and how it can be used for simulation for a specific case study location. By analyzing spring flow, spatiotemporal variations of groundwater levels, hydraulic parameters etc., his model was able to successfully describe the karst aquifer system in the studied location (Sauter, 1992). Figure 2.7 depicts the schematic diagram of the process of developing a groundwater model.

![Schematic diagram representing the process of developing a groundwater model](Modified from (World Meteorological Organization, 2009))

**2.4.2. Spatially lumped models and distributed parameter models**

Ghasemizadeh et al. categorized groundwater models into different groups based on their capabilities and characteristics. Due to high level of heterogeneity and anisotropy in karst aquifers, accurately understanding of their behavior and distribution has always been challenging. This has forced
modelers to employ approximate-based approaches and consequently consider the impact of the uncertainties caused by these approaches in their models. Hence, Spatially Lumped Models (SLM) and Distributed Models (DM) or Spatiotemporal Distributed Models (SDM) were introduced as two general approaches in modeling karst aquifers (Ghasemizadeh et al., 2012; World Meteorological Organization, 2009).

Spatially lumped models comprises of concentrated elements at spatially singular points; whereas, the elements are spatially distributed in distributed models. Hence, in distributed systems, physical quantities are spatially and temporally dependent. Spatially lumped (or global) models do not consider spatial alternation of flow patterns and are supposed to simulate a global chemical-hydrological response at the aquifer output point (for example spring discharge point) with regard to inputs of the aquifer (e.g. rivers, groundwater recharge points, net runoff etc.) (Ghasemizadeh et al., 2012; Singh, 2014). Assessing temporal alternations is an approach that spatially lumped models take to describe the global water balance and hydrological behavior of an aquifer. Moreover, in spatially lumped models, some factors that cause complexity in calculations and simulating are neglected due to simplifying assumptions and hence, using only the global parameters in simple ordinary linear differential equations and also low data requirements, are some of their properties that can be considered when trying to select the best modeling approach for groundwater flow and transport simulation. Although these models cannot produce accurate results, especially in karstic areas, they have been widely used by researchers in the areas that less data is available or only the prediction of groundwater flow, spring discharge and groundwater levels is necessary (Long, 2015; Panagopoulos, 2012). Hydrograph-Chemograph Analysis (Dewandel et al., 2003), Linear Storage Models (or Rainfall-Discharge Models) (Butscher and Huggenberger, 2008) and Soft Computing Techniques such as Fuzzy Logic (Mohd Adnan et al., 2013; Rezaei et al., 2013), Genetic Algorithm (McKinney and Lin, 1994; Nicklow et al., 2010) and Artificial Neural Network (ANN) (Hu et al., 2008), are three main approaches with regard to spatially lumped models that have been adopted by hydrological modelers.

In contrast, distributed models take complex parameters involved in groundwater flow and transport into account. In these models, dependent hydrological parameters and boundary conditions can be spatiotemporally variable and this will require the equations to be solved numerically and based on partial differential equations (Asher et al., 2015; Kuniansky, 2016). Also, due to the fact that all variables should be defined to the system, collecting more data and paying careful attention to details in this type of modeling is demanded which can make it more challenging. (Dong et al., 2012; Long and Gilcrease, 2009). For karst aquifer modeling, different type of distributed models based on the level of simplified assumptions have been used. Several methods have been developed that each of them treats complexity of karst aquifer differently and simulates groundwater flow based on its own logic and assumptions. Equivalent Porous Medium (EPM), Double Porosity (or Continuum) Method (DPM), Discrete Fracture Network (DFN), Discrete Channel (or Conduit) Network (DCN) and Hybrid Models
(HM) are five common modeling approaches in distributed systems that have their own characteristics which will be discussed shortly in the following (Ghasemizadeh et al., 2012). DFN can be subcategorized into Discrete singular fracture set approach (DSFS) and Discrete multiple fracture set (DMFS) approaches. Sometimes, EPM and DPM are also mentioned as Single continuum porous equivalent approach (SCPE) and Double Continuum porous equivalent approach (DCPE) respectively in the literature. It is worth mentioning that employing Hybrid Models, which are the result of integrating discrete models and EPM approach and are also called coupled continuum pipe flow models, can be beneficial in many cases regarding modeling complex hydrological systems such as karst aquifers (Kiraly, 1998; Liedl et al., 2003). Figure 2.8 demonstrated schematic configuration of the aforementioned distributed modeling approaches.

Figure 2.8. Distributed parameter modeling methods for karst aquifers – Modified from (Kuniansky, 2016)

Bauer et al. developed a numerical model to describe the influence of exchange flow between conduits and fissured system. They found out that under conditions of early karst evolution, conduit development is faster. Hence, exchange flow plays an important role in developing early karst evolution in limestone aquifers (Bauer et al., 2003). Also, some researchers employed numerical modeling approaches to describe groundwater flow and transport in rough fractures (Briggs et al., 2014) and karst aquifers (Faulkner et al., 2009). However, modeling karst aquifers cannot only be carried out by numerical approaches (Barrett and Charbeneau, 1998). Furthermore, for simulating the genesis of karst aquifer systems, a numerical couple reactive network model, comprising of a 2D porous continuum flow module, a discrete pipe network for modelling flow and transport in the conduits and a carbonate dissolution module was developed by (Clemens T., 1997).

2.4.3. Computer Models and Programs

MODFLOW is the most common groundwater modeling code that has been used due to its capability of simulating complex groundwater flows in a three-dimensional scale. Working based on finite
difference method and block-centered approach, MODFLOW simulates the groundwater within the aquifer by considering different type of layers underground (i.e. confined, unconfined or both) and also different recharge or discharge sources such as areal recharge, groundwater flow to wells, runoff caused by rainfall, flow to riverbeds, spring flow etc. (Harbaugh, 2005). The initial version of MODFLOW (MODFLOW-2000) was released in the year 2000 and five years later, the updated version (MODFLOW-2005) started gaining attentions from groundwater modelers and hydrogeologists. To enhance the application of MODFLOW-2000, two models were introduced by USGS which are VSF and MF2K-GWT. Basically, VSF is a version of MODFLOW-2000 that in addition to the ability of MODFLOW-2000 to model groundwater flow using a finite-difference method in a 3-D scale, can be applicable for variably saturated flow (VSF) (Thoms et al., 2006). Furthermore, MF2K-GWT is an integrated model with MODFLOW-2000 that have the ability to simulate groundwater flow and solute transport (U.S. Geological Survey Website, 2012). Nevertheless, some programs that were independent to MODFLOW but developed by USGS were released as well such as HST3D (3-D Heat and Solute Transport Model) that is able to simulate ground-water flow and associated heat and solute transport in a 3D scale. Its capabilities can be used in analyzing problems associates with landfill leaching, seawater intrusion, hot-water geothermal systems etc. (Kipp, 1997).

The most updated version of MODFLOW program (MODFLOW 6) was released recently. In this program, any number of models can be used for simulation. These models can have inter-connection with each other and this can help solving complex hydrogeological problems in many cases such as the conditions in karst aquifers. Also, within this framework, multiple local GW models can be coupled with regional scale models (Langevin et al., 2017). Moreover, Conduit Flow Package (CFP), which can be coupled with MODFLOW-2005, can facilitate simulation of karstic geometry and GW movement and consequently, increase the accuracy of GW flow modeling in conduits (Shoemaker et al., 2007).

After releasing MODFLOW-2005, several associated models and packages were introduced and released based on numerous approaches and techniques. As an example, MT3D model, which is a modular, comprehensive, numerical three-dimensional solute transport model, was developed by USGS. This model is designed to work very well regarding simulation of solute transport and reactive solute transport in complex hydrological systems. Being connected to MODFLOW, which is the USGS groundwater flow simulator, MT3D is able to simulate and analyze advection-dominated transport, especially solute transport, without refining new models (Bedekar et al., 2016). Lautz and Siegel used MT3D and MODFLOW to simulate groundwater and surface water mixing in the hyporheic zone. They took advantage of this model due to its ability to simulate advective transport and source and sink mixing of solutes (Lautz and Siegel, 2006).

Taking advantage of the features in MODFLOW and MT3D, a new computer program, SEAWAT, was released to assist hydrogeologists in simulating three-dimensional, variable-density and transient
groundwater flow that can be coupled with solute transport. In the last version of SEAWAT (version 4), the effect of fluid viscosity and density fluctuations can be considered in simulation of groundwater flow and solute transport. This will allow the users to recognize this model as a tool that can be used in a wide range of simulation practices including seawater intrusion in coastal aquifers (Langevin, 2009; Langevin et al., 2008). Xu employed SEAWAT in his dissertation to study seawater intrusion into a coastal karstic aquifer in Florida. It is worth mentioning that seawater intrusion can be considered as a substantial source of brackish water in coastal aquifers such as karst aquifer in north coast of Puerto Rico (Xu, 2016).

In addition, FEFLOW (Finite Element Subsurface Flow System) is a finite-element package for simulating 3D and 2D fluid density-coupled flow, contaminant mass (salinity) and heat transport in the subsurface. It has several applications including regional groundwater management, saltwater intrusion, seepage through dams and levees, land use and climate change scenarios, groundwater remediation and natural attenuation and also groundwater-surface water interaction. As an example, a study was conducted to simulate groundwater dynamics in an irrigation and drainage network in Uzbekistan using FEFLOW. After model calibration and validation, the results show high level of accuracy and can be used for hydrogeological management plans (Diersch, 2014; Khalid Awan et al., 2015).

SUTRA is another model that was released for simulating 2-D saturated-unsaturated, fluid-density-dependent flow with energy transport or chemically-reactive single-species solute transport capable of analyzing saltwater intrusion and energy transport. It uses a 2D hybrid finite-element and integrated finite-difference approach to approximate the governing flow and transport equations that explain the two interdependent processes. It should be noted that the 3D version of this model was also released recently. In SUTRA’s Version 2.2 specification of time-dependent boundary conditions can be identified without programming FORTRAN code. SUTRA, can also describe chemical species transport including absorption, production and decay processes and assess well performance and pumping test data (Voss and Provost, 2002). For instance, Hussain et al. used SUTRA in their paper to study coastal aquifer systems that are subjected to seawater intrusion (Hussain et al., 2015).

Furthermore, Visual MODFLOW Flex model, an integrated modeling environment that connects MODFLOW and MT3D, is able to simulate complex 3D groundwater flow and contaminant transport. Its graphical user interface and 3D visualization capabilities in addition to its ability to simulate groundwater flow and contaminant transport can gain attention of hydrological and groundwater modelers. As an example of work, Varghese, Raikar and Purandara successfully developed a Visual MODFLOW Flex model for simulation of groundwater flow in a region in India (Kumar and Singh, 2015; Varghese et al., 2015).
CHEMFLO-2000, which is interactive software for simulating water and chemical movement in unsaturated soils, enables users to simulate groundwater flow and chemical fate and transport in vadose zones. The model can be used as a tool that can enhance the understanding of unsaturated flow and transport processes. In this model, water movement and chemical transport are modeled using the Richards and the convection-dispersion equations, respectively. The equations are solved numerically using the finite differences approach (Nofziger and Wu, 2003).

Another 3D finite-element based model for simulating flow and transport is 3DFEMFAT. This model works for saturated/unsaturated heterogeneous and anisotropic media. Its typical applications include infiltration, agriculture pesticides, sanitary landfill, hazardous waste disposal sites, density-induced flow and transport, saltwater intrusion, etc. Its flexibility and feasibility in simulating a wide range of practical problems especially by employing its transport module, has made it valuable software for researchers and transport modelers. Also its application in studying seawater intrusion in coastal aquifer was verified by some scientists (Lathashri and Mahesha, 2016; Park et al., 2012).

Regarding surface water and groundwater interaction which was discussed in the previous sections in detail, GSFLOW (Groundwater and Surface-water FLOW) was released by USGS in 2008 as an integrated tool that is able to couple groundwater and surface water flow models by taking advantage of the approaches used in USGS Precipitation-Runoff Modeling System (PRMS) and the USGS Modular Groundwater Flow Model (MODFLOW and MODFLOW-NWT). Meteorological and hydrological data such as rainfall, sunny hours and temperature in addition to groundwater stresses and initial/boundary conditions are involved as inputs for the process of simulation in this model. GSFLOW can also take into account the impact of land cover change, climate change and groundwater extraction on surface water and groundwater flow for spatiotemporally variable situations (Markstrom et al., 2008). However, regarding its limitations, it was asserted by researchers that its ability to simulate surface water and groundwater in karst aquifers with high level of heterogeneity is not guaranteed (Fulton et al., 2015).

By taking advantage of a control volume finite-difference method, MODFLOW-USG (Un-Saturated Grid version of MODFLOW) is able to simulate groundwater flow and its related processes. This version of MODFLOW supports different types of structured and unstructured grids. This capability is extremely useful when high resolution along rivers and around wells is needed. In addition, MODFLOW-USG couples Connected Linear Network (CLN) process to Groundwater Flow (GWF) process, which was introduced in MODFLOW-2005, to analyze and simulate the influence of karst conduits and multi-node wells. Hence, this version can help modelers to gain a deeper understanding about karst systems and conduit networks (Panday et al., 2013). Moreover, for the purpose of generating layered quadtree grids that can be used in MODFLOW-USG or other similar numerical models, a new computer program, GRIDGEN, was developed by Lien et al. in 2015. After reading a 3-D base grid, GRIDGEN will continue
dividing into refinement features, which is provided by user, until reaching the desired refinement level. After finishing the process of gridding, a tree structure file will be created and can be used in numerical models such as MODFLOW-USG. This model was used for assessing the Biscayne aquifer in southern Florida in which karst aquifers are abundant (Lien et al., 2014).

Developing a Newton-Raphson Formulation for MODFLOW-2005 for offering an enhanced solution for problems related to groundwater flow in unconfined aquifers, MODFLOW-NWT was introduced and developed by Niswonger et al. Its main application in addition to Surface-Water Routing (Hughes et al., 2012) and Seawater Intrusion (Bakker et al., 2013) can be described as its ability to solve problems that are coupled with drying and rewetting nonlinearities in equations that govern groundwater flow in unconfined aquifers.

A recently developed model similar to MODFLOW but with a wider range of applicability in describing hydrological systems is Rainfall-Response Aquifer and Watershed Flow Model (RRAWFLOW). This lumped-parameter model receives hydrological inputs such as rainfall, recharge and discharge etc. and is able to simulate groundwater level, streamflow and spring flow. It also can be used for modeling solute transport in aquifers and assessing system response to hydrological events (Long, 2015). For classification of karst aquifers and characterizing time-variant systems, Long and Mahler developed and used this model in 2013. This model was used to predict and classify hydraulic responses to recharge in two karst aquifers in Texas and South Dakota, USA (Long and Mahler, 2013).

Usually, groundwater flow and contaminant transport models are used simultaneously using software platforms such as GMS. Several researchers conducted flow and transport analysis (e.g. using MODFLOW and MT3D) and achieved accurate and valid results (Abdalla and Khalaf, 2015; Bora and Borah, 2016). Also, few scientists studied the groundwater flow and contaminant transport in karstic aquifer of northern Puerto Rico using GMS and their modeling results show its capability in analyzing and describing hydrological systems with complex properties such as high level of heterogeneity and anisotropy (Ghasemizadeh, 2015; Ghasemizadeh et al., 2016; Maihemuti et al., 2015). Table 2.3 elaborates the characteristics and application of aforementioned most commonly used groundwater modeling codes.
Table 2.3. Prevalent groundwater models that were used for simulating groundwater flow and contaminant transport. FE and FD represent Finite Element and Finite Difference respectively.

<table>
<thead>
<tr>
<th>Model/Software</th>
<th>Modeling technique</th>
<th>Focus</th>
<th>Application and Advantages / Reference</th>
<th>Ease of Use and Accuracy for Karst Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DFEMFAT</td>
<td>FE</td>
<td>GW Flow</td>
<td>*</td>
<td>GW modeling in saturated/unsaturated heterogeneous and anisotropic media, simulation of infiltration, agriculture pesticides, sanitary landfill, hazardous waste disposal sites, density-induced flow and transport, seawater intrusion etc. (Lathashri and Mahesha, 2016; Park et al., 2012)</td>
</tr>
<tr>
<td>AQUA3D</td>
<td>FE</td>
<td>GW Flow</td>
<td>Solute Transport</td>
<td>3D groundwater flow and transport simulation for homogeneous and anisotropic flow conditions, simulation of heat and contaminant transport by taking into account the effect of dispersion</td>
</tr>
<tr>
<td>CHEMFLO</td>
<td>FD</td>
<td>GW Flow</td>
<td>Solute Transport</td>
<td>Simulation of water movement and chemical fate and transport in vadose zones and layered soil by employing improved numerical methods (Nofziger and Wu, 2003)</td>
</tr>
<tr>
<td>FEFLOW</td>
<td>FE</td>
<td>GW Flow</td>
<td>Solute Transport, Heat Transport</td>
<td>Regional groundwater management, saltwater intrusion, seepage through dams and levees, land use and climate change scenarios, groundwater remediation and natural</td>
</tr>
<tr>
<td>Model</td>
<td>Method</td>
<td>Rank</td>
<td>Features</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>--------</td>
<td>------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>GSFLOW</td>
<td>FD</td>
<td>Medium</td>
<td>Attenuation, groundwater-surface water interaction (Diersch, 2014; Khalid Awan et al., 2015)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*</td>
<td></td>
<td>Coupled Groundwater and surface water model which can assess the hydrological behavior based on land use change, climate variability and groundwater withdrawals (Markstrom et al., 2008)</td>
<td></td>
</tr>
<tr>
<td>HST3D</td>
<td>FD</td>
<td>Medium</td>
<td>Sub-surface waste injection, landfill leaching, saltwater intrusion, freshwater recharge and recovery, radioactive waste disposal, hot water geothermal systems, and subsurface-energy storage (Kipp, 1997)</td>
<td></td>
</tr>
<tr>
<td>MODFLOW</td>
<td>FD</td>
<td>High</td>
<td>Simulation of steady or unsteady flow in complex flow system with irregular geometry, Simulation of flow from external stresses in a confined or unconfined aquifer (Harbaugh, 2005), High applicability for karst aquifers if it couples with CFP package</td>
<td></td>
</tr>
<tr>
<td>MODFLOW-NWT</td>
<td>FD</td>
<td>Medium</td>
<td>Surface water and groundwater interactions, seawater intrusion and solving problems related to drying and rewetting nonlinearities of the unconfined GW flow equation (Niswonger et al., 2011)</td>
<td></td>
</tr>
<tr>
<td>MODFLOW-OWHM</td>
<td>FD</td>
<td>Low to Medium</td>
<td>Simulation, analysis, and management of human and natural water movement within a physically-based supply-and-demand framework, seawater intrusion, conjunctive use of groundwater and surface water (Hanson et al., 2014)</td>
<td></td>
</tr>
<tr>
<td>MODFLOW-USG</td>
<td>FD</td>
<td>*</td>
<td>Unstructured grid version of MODFLOW for simulating GW flow and other related processes, simulation of the effects of multi-node wells, karst conduits and tile drains (Panday et al., 2013)</td>
<td>High</td>
</tr>
<tr>
<td>-------------</td>
<td>----</td>
<td>---</td>
<td>----------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>MT3D</td>
<td>FD</td>
<td>*</td>
<td>simulation of solute transport and reactive solute transport in complex hydrological systems and analyzing advection-dominated solute transport (Bedekar et al., 2016)</td>
<td>High</td>
</tr>
<tr>
<td>SEAWAT</td>
<td>FD</td>
<td>*</td>
<td>* 3D simulation of variable density, transient groundwater flow in porous media coupled with multi-species solute and heat transport, seawater intrusion in coastal aquifers (Langevin, 2009; Langevin et al., 2008; Post, 2011)</td>
<td>High</td>
</tr>
<tr>
<td>SURTA</td>
<td>FE</td>
<td>*</td>
<td>* Simulation of saturated-unsaturated, fluid-density-dependent groundwater flow with energy transport or chemically-reactive single-species solute transport (Voss and Provost, 2002)</td>
<td>Medium</td>
</tr>
</tbody>
</table>
2.4.4. Equivalent Porous Media (EPM) method

Several approaches have been followed to achieve accurate and valid results with acceptable efficiency at the same time. For some cases, simulation of groundwater hydraulic and contaminant transport in karst aquifers is carried out by employing Equivalent Porous Media (EPM) method (Scanlon et al., 2003). Basically, using EPM approach for modeling a karst aquifer means considering simplifying assumptions in order to make the model more practical and applicable. Ghasemizadeh et al. developed their model based in EPM approach and found out that its result is acceptable for predicting water table fluctuations. Although their EMP-based model was not supposed to be accurate enough for contaminant transport, they found good agreement between their model output and actual data regarding spreading TCE (Ghasemizadeh et al., 2015). Furthermore, in another study, by employing drainage features in regional groundwater flow modeling in karstic aquifer of northern Puerto Rico, Ghasemizadeh et al. asserted that they were able to improve their simulation by assigning arrays of adjacent model cells with drains to simulate conduits. They suggested that using this feature can be truly helpful especially when there is not sufficient data for conduit characteristics. Similarly, Maihemuti et al. developed a regional model for assessing karst aquifer system and groundwater resources for a case study location in northern Puerto Rico. They came into conclusion that although there is high potential of conduit dominated flow, the result of their EPM-based approach is reliable in representing the hydrodynamics of the karst aquifer in their case study location (Maihemuti et al., 2015). Moreover, Maihemuti et al. simulated a regional karst aquifer system to evaluate groundwater system in northern Puerto Rico. They developed this model using EPM approach to predict the karst system response to rainfall events and high pumping demands and also to describe the hydrological behavior of the aquifer. They asserted that this model can be used for prediction of groundwater level fluctuations under various exploitation scenarios (Maihemuti et al., 2015).

2.4.5. How Remote Sensing Can Improve Karst GW Assessment and Modeling?

Using Geographic Information System (GIS) as a tool in groundwater modeling procedure, is truly beneficial; because all parameters such as distribution of rainfall, groundwater recharge and discharge, land cover etc. are defined within a spatial context (Singh and Fiorentino, 1996). Several researchers took advantage of this powerful tool directly or as a parallel method in integrated approaches (Dar et al., 2010; Nampak et al., 2014). (Alonso-Contes, 2011) used remote sensing and advanced digital image processing techniques to delineate karst features which can enhance the understanding with regard to hydrogeology of the Tanamá River and Rio Grande de Arecibo catchments located in the north coast tertiary basin of Puerto Rico. Basically, remote sensing tools assisted the author in lineament mapping for GW exploration.
Also, Manda and Gross employed GIS analysis to characterize solution conduits in karstic areas. Based on their study, they showed that GIS-based methods can be used for determining depths, dimensions, shapes, apertures and connectivity of potential conduits and also for describing physical characteristics that have an effect on the groundwater flow in karst aquifers (Manda and Gross, 2006). In addition, Theilen-Willige et al. employed GIS and remote sensing methods by analyzing satellite data in order to detect of near-surface faults and fracture zones that can lead to dissolution processes in conduits of karst aquifers (Theilen-Willige et al., 2014).

Numerous researchers took advantage of this to improve their models and solve some un-answered and complex problems by increasing the accuracy of prediction and also by taking into account other hydrological phenomena (Ashraf and Ahmad, 2012; Machiwal et al., 2012; Thakur et al., 2016; Xu et al., 2011). Table 2.4 elaborates the application of GIS and remote sensing in different phases of groundwater modeling.

Table 2.4. The potential role of GIS and remote sensing in different steps of groundwater modeling procedure – Modified from (Ashraf and Ahmad, 2012)

<table>
<thead>
<tr>
<th>Phase</th>
<th>GIS functions</th>
<th>Modeling Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Collection and Analysis</td>
<td>Data input, Digitization, Data conversion (import/export, Coordinate transformation, Map retrieval)</td>
<td>Groundwater and hydrological data collection</td>
</tr>
<tr>
<td>Developing Conceptual Model</td>
<td>Conversion of vector and raster layers, Data integration, Image processing, buffering, Surface generation, Linking of spatial and attribute data</td>
<td>Developing conceptual model</td>
</tr>
<tr>
<td>Model Design</td>
<td>Map calculations, Neighborhood operations, Interpolation, Theissen polygons, buffering, Surface generation</td>
<td>Delineating boundary conditions, Mesh generation, 3D layering of the aquifer</td>
</tr>
<tr>
<td>Model Calibration</td>
<td>Data layers integration</td>
<td>Parameter zonation, Recharge estimation, Water balance</td>
</tr>
<tr>
<td></td>
<td>Overlay analysis</td>
<td>Steady-state and Transient-state simulations</td>
</tr>
<tr>
<td></td>
<td>Statistical analysis</td>
<td>Parameters estimation</td>
</tr>
</tbody>
</table>
2.5. Conclusion

Employing a comprehensive and efficient approach for managing water resources in regions where groundwater is the key source of water supply and vulnerable to contamination (e.g. karst aquifers) is vital. Limestone karstic aquifer of northern Puerto Rico has been experiencing high level of contamination and this has resulted in accelerating rate of preterm births in the island in addition to other human health related disorders. In PR, several wells and sites were considered as the National Priority List (NPL) Superfund Sites and remediation action for treating water in these sites are in process. By considering northern part of the island as the case study location and also by focusing on karst aquifers with conduit network as the most complicated and hard-to-analyze forms of aquifers, a review study to assess GW resources was presented. After a short explanation of karst systems and their associated study methods, a brief review discussion on groundwater contamination and risk assessment was carried out. Potential contamination threats in karst aquifers were discussed and different remediation techniques were evaluated.

Surface water and GW interaction (SWGWI), as a major source of GW contamination and water level fluctuation, was also reviewed. Desktop and field tools associated with SWGWI were introduced and assessed as key approaches for understanding interconnectivity between GW and surface water. Despite the fact that numerous methods have been developed for describing SWGWI, there are still uncertainties and lack of sufficient knowledge for fully understanding the time lag between GW pumping and its influence on SW, relationship between GW pumping and river losses and also exact recharge and discharge points in streams (Jankowski, 2007). Multiple features and software packages for simulating SWGWI can be employed; however, a systematic uncertainty analysis is essential for achieving valid and reliable results.

Furthermore, a comprehensive discussion on existing groundwater modeling methods with regard to their application, advantages and disadvantages was presented. Mostly, numerical modeling approaches are taken by modelers to simulate complex groundwater systems. Numerical modeling tools often take advantage of finite-difference and finite-element techniques to solve complicated
equations that governs hydrological system dynamics in an aquifer. For karst aquifers, lumped models and spatially distributed models are considered as two general modeling approaches that can be used for certain conditions. Spatially lumped models can be used even when heterogeneous structure of karst aquifers is unknown and hydraulic data is not sufficient. These models are usually used for regional groundwater quality predictions. On the other hand, spatially distributed models are often used when spatially assessment of groundwater quality and quantity is the purpose. Obviously, these models, require more data as input, have more accuracy and are capable of simulating fine-scale local groundwater flow. In addition, various computer-based models have been explained and evaluated. MODFLOW, as the most popular groundwater flow modeling code in addition to FEFLOW, HST3D, SEAWAT and AQUA3D have been introduced in this study as powerful tools for groundwater flow simulation. For solute and contaminant transport, usually, MT3D code is used. Also, using HST3D, SEAWAT, SUTRA and other similar codes, researchers have successfully developed contaminant and solute transport models. A combination of the aforementioned models can be used to simulate groundwater flow and contaminant transport either in steady state or transient form.
Chapter 3:

Assessment and Modeling of Groundwater Nitrate Contamination within a Coastal Karst Aquifer

3.1. Introduction

There are several approaches for assessment of contaminant fate and transport in GW. Modeling methods offer valuable capability of for accurate simulation and assessment of GW flow and contaminants transport in aquifers (Conan et al., 2003; Molénat and Gascuel-Odoux, 2002). These methods, however, are challenging to implement in aquifers within karst regions because of the significant heterogeneity of such aquifers. The scope of this work is to study GW Nitrate contamination in karst aquifer of North Coast Limestone aquifer of Puerto Rico by employing a numerical models. The applicability of modeling tools in quantitative and qualitative evaluation of complex hydrogeological systems in karst is examined. Also, prediction of spatiotemporal distribution of Nitrate contamination in addition to implications and recommendation are presented.

3.1.1. Site Description

3.1.1.1. Geographical Location

Puerto Rico island (8937 km²), a territory of the United States (US), is located in northeastern side of Caribbean Sea and have an estimated population of 3.7 million (Castro-Prieto et al., 2017). There are many surface water and GW resources across the island that provide fresh water and also are used for agricultural and industrial development. The case study location is in northern part of Puerto Rico (PR), comprising Arecibo, Barceloneta, Manati, Vega Baja, Vega Alta, Dorado and small portion of Florida and Toa Baja municipalities. Figure 3.1 exhibits the geographical location and elevation range (Based on online Digital Elevation Model or DEM data) of the case study area.
3.1.1.2. Geology

Along the northern coast of PR, widespread solution-based activities have influenced the limestone and this has led to karst topography formation in the area. Karst terrains are the most important physiographic features in Northern PR (NPR). These terrains consist of common solution feature landforms (e.g. sinkholes and cockpit) and residual tower karst features (i.e. landforms which have elongated plains surrounded by steep hills) (Gómez-Gómez et al., 2014).

There are 2 major aquifers (Figure 3.2) in north coast limestone aquifer of PR: 1- The upper aquifer which has connection to the surface throughout most of its outcrop area and is associated with Aymamón and Aguada limestone and alluvial deposits along the coastal areas and 2- The lower aquifer which is associated with various locations of the Cibao formation and Lares limestone and also is confined toward the coastal zone and outcrops to the south of the upper aquifer, where it is recharged (Maihemuti et al., 2015; Renken et al., 2002).
Figure 3.2. Generalized surficial geology of the North Coast Limestone aquifer of Puerto Rico (Vertical scale in the lower picture is exaggerated) – Modified from (Gómez-Gómez et al., 2014)

In northern PR (NPR), GW flows through a network of preferential flow-paths such as closely-spaced conduits and faults due to existence of many major springs and limestone rocks containing water (Giusti, 1978). Due to presence of limestone karst aquifers with high level of heterogeneity and anisotropy in this area, rainfall water can easily percolate into the ground and this rapid movement, makes karst aquifer vulnerable to contamination. In fact, limestone aquifers in humid areas (similar to PR) have been reported to be more vulnerable compared to other aquifers in sub-humid areas (Kreitler and Browning, 1983). Moreover, highly heterogeneous and karstic aquifers with conduits can cause high rate of water level fluctuation even in small temporal scaling (Yu et al., 2016). Behavior of karst conduit system plays a more important role than hydraulic conductivity of matrix in assessing contaminant transport within karst aquifers (Ghasemizadeh et al., 2016). Hence, more complex approaches should be employed for quantitative and qualitative assessment of GW in karst aquifers.

Based on hydrogeological studies, in northwestern PR, between Aguadilla and Rio Camuy area, water-containing conduits are present. There are 3 major springs between Rio Grande de Manati and Rio
Indio area which are categorized as conduit type springs by Rodríguez-Martínez. This confirms that intense fluctuations in transmissivity data is probably because of fracture zones and dissolution channels in that area (Ghasemizadeh et al., 2016; Rodríguez-Martínez, 1997).

3.1.1.3. Climate

The air temperature in the island falls within a relatively short range due to constant solar radiation and seawater temperature. August and February are the hottest and coolest months, respectively. In the central north coast, on average, maximum and minimum temperatures were recorded as approximately 30 and 21 °C (86 and 70 °F), respectively, based on three decades of National Oceanic and Atmospheric Administration (NOAA) data from 1981 to 2010 (Figure 3.3 shows temperature trend since 1995). Because of the existence of Cordillera Central and Sierra de Cayey mountains, the upper two third of the island (including our case study location) has a humid climate while the lower one third is semi-arid. Along the north coast, prevailing winds blow from the northeastern side (Gómez-Gómez et al., 2014).

3.1.1.4. Hydrology

Historical rainfall data from National Oceanography and Atmospheric Administration (NOAA) demonstrates that NPR has relatively dry and wet seasons in December to April and May to November periods, respectively. In particular, based on monthly precipitation data, May and February are wettest and driest months, respectively. Hurricanes in the region occur mostly in the wet season. According to the scientific investigations and historical data, infiltration due to precipitation is considered the main source of aquifer recharge while there are several streams in the area. The infiltration and percolation occur through the limestone outcrops via runoff to sinkholes and existing depressions associated with topography (Maihemuti et al., 2015). On average, the amount of precipitation and evapotranspiration in the island are roughly 1,825 and 1,189 mm/y respectively. From the remaining 636 mm/y of water on/in the ground, the portions of streamflow and GW are 583 mm (161 m³/s) and 53 mm (14.6 m³/s) annually, respectively (Gómez-Gómez et al., 2014). Major streams in the study area are Rio de la Plata (the longest river with the largest watershed area in the island), Rio Cibuco, Rio Grande de Manati and Rio Grande de Arecibo from East to West (Figure 3.8). Figure 3.3 shows rainfall and temperature trends in Manati (NOAA MANATI 2 E (66-5807) station, Elevation: 250 ft, Latitude: 18.43° N, Longitude: 66.45° W) and also depth to water table from ground surface (USGS 182549066304300 USGS 166 Observation Well, Latitude: 18.43° N, Longitude: 66.51° W)
Figure 3.3. Rainfall, Temperature range and depth to GW level from ground surface for 1995 - 2015 in Manati, PR

3.1.1.5. Land Cover

Puerto Rico has been subjected to urban, industrial and agricultural development for a few decades. This has been the result of population growth and its consequences such as demand for food, jobs etc. (Castro-Prieto et al., 2017; Martinuzzi et al., 2007). PR is a tropical island with extensive rainfall and green areas (i.e. forest, shrublands, grasslands and vegetated fields). The main urban developed area is in the San Juan city (the Capital). Along the study area in NPR, extensive agricultural development and industrial activities during past decades have resulted in deterioration of GW quality (Yu et al,
Figure 3.4, created from Land Cover National Dataset, depicts land cover map of north-central municipalities of the island.

Moreover, Figure 3.5, demonstrates agricultural capacity of soil in municipalities of north-central part of PR. This map was generated using Soil Survey Geographic (SSURGO) Database, prepared by Natural Resources Conservation Service at United States Department of Agriculture.

Figure 3.5. Agricultural capability of soil in municipalities of north-central part of PR

### 3.1.2. Occurrence of Nitrate in GW

The concentration of Nitrate (NO₃), Nitrite (NO₂) and Ammonia (NH₃⁺), as common forms of Nitrogen, are typically measured in GW (Almasri, 2007). Since Nitrite exists in a much smaller concentration that
Nitrate due to its instability, the combination of these two is sometimes reported as the concentration of Nitrate. It was reported that the presence of Ammonia and organic Nitrogen in GW is rare because of the low level of demanded biological activities in aquifers that result in their production (Burkartaus and Stoner, 2008). Moreover, Nitrous Oxide (N₂O), which is a major greenhouse gas, is another form of Nitrogen in GW and is accumulated within the aquifer mostly because of denitrification (Jurado et al., 2017). Additionally, different isotopes of Nitrate in GW systems have been discussed by (Kendall and Aravena, 2000).

Because of its solubility and negative charge, Nitrate is very mobile and can easily leach from ground surface and unsaturated zone. High concentration of Nitrate in drinking water can potentially cause health problems such as methemoglobinemia (a decrease in the capacity of the blood to transport oxygen, also known as "blue baby syndrome") in infants and stomach cancer in adults (Hall et al., 2001; Wolfe and Patz, 2002). Moreover, (Galaviz-Villa et al., 2010) and (Majumdar and Gupta, 2000) reported other health problems such as the dysfunction of the thyroid gland, production of nitrosamines (which commonly leads to cancer), gastric cancer, goiter and hypertension. Consequently, the US Environmental Protection Agency (USEPA) has determined 10 mg/l NO₃-N as the maximum contaminant level (MCL) of Nitrate in drinking water. (Almasri, 2007; Kendall and Aravena, 2000)

Spatiotemporal changes in Nitrate leaching from the unsaturated zone ties with uncertainties and also complex interactions and parameters. Land cover, point sources of Nitrogen, rainfall and infiltration, behavior of N is soil, geological setting and water table level are among most significant factors that contribute to occurrence of Nitrate in GW. (Almasri, 2007). Moreover, uncertainties such as presence of multiple Nitrogen loading sources in a certain area, point and non-point Nitrogen source overlapping and occurrence of biogeochemical processes within the soil (Kendall and Aravena, 2000) increase the complexity level of Nitrogen-GW interconnectivity. Hence, thorough understanding of the relationship between the amount of on-ground Nitrogen loading and Nitrate concentration in GW systems requires complicated analysis and careful consideration. As presented in Figure 3.6, spatiotemporal occurrence of Nitrate in GW depends on on-ground Nitrogen loading, soil characteristics/behavior and GW properties. It can also be asserted that Nitrate follows an advective and dispersive movement within the aquifer.
Figure 3.6. Schematic diagram of on-ground Nitrogen loading sources and possible interaction of Nitrogen-based compounds in unsaturated and saturated zones (Almasri, 2007)

Often, land cover can be a good indicator and predictor of Nitrate concentration in the aquifers (Gardner and Vogel, 2005). However, there are several uncertainties and factors such as rainfall, temperature, and soil properties in each region that can undermine the prediction of Nitrate contamination merely based on land cover data (McLay et al., 2001; Wick et al., 2012). Keeler and Polasky have estimated that the increased cost for addressing GW Nitrate contamination due to land cover change and agricultural development in Southeastern Minnesota can be up to $12 million for a 20-year period (Keeler and Polasky, 2014). Urban and rural aquifers can have a different response to climatic variations with regard to Nitrate concentration and studying the response of an aquifer to Nitrate dynamics (especially in karst aquifers) requires more in-depth understanding and analysis due to several complex conditions (Opsahl et al., 2017). It was also reported that GW Nitrate contamination can be affected adversely by climate change (Stuart et al., 2011).
In many geographical locations, elevated concentrations of Nitrate mainly due to human activities have been reported (Buvaneshwari et al., 2017; Elisante and Muzuka, 2015). Point sources of Nitrogen/Nitrate leachate such as old septic systems, landfills, wastewater holding ponds and leaks from cracks in sewer pipelines can cause GW Nitrate contamination (Almasri, 2007; Kendall and Aravena, 2000; Wakida and Lerner, 2005). Additionally, non-point sources of N leaching, such as fertilizer use in agricultural areas, play a very significant role in increasing GW Nitrate contamination. Strong correlation between agricultural activities (use of fertilizers and manure) and GW Nitrate contamination was reported (Babiker, 2004; Burkartaus and Stoner, 2008; Carey and Cummings, 2013). Gu et al. assessed sources of GW contamination Nitrate in China and asserted that agricultural activities followed by landfill leachate are two main sources of Nitrate pollution (Gu et al., 2013). In a USGS report with focus on Manati and Vega Baja municipalities in NPR, Nitrate occurrence and contamination were assessed. It was identified that the major sources of Nitrate contamination in the karst aquifer of the region are use of fertilizers for cultivation of pineapples and also septic tank effluent in rural and un-sewered (no sewer system) areas (Conde-Costas and Gómez-Gómez, 1999).

Although Puerto Rico is located in a humid and hot region which intensifies denitrification in soil as a natural contaminant attenuation process, elevated levels of Nitrate have been constantly reported due to excessive agricultural activities (Spalding and Exner, 1972). It is reported that the use of fertilizers for agricultural activities is increasing every year in the US. Hence, based on the fact that large amount of fertilizers has a strong correlation with elevated Nitrate concentration in GW, usage of fertilizers should be limited at least in the regions with highly permeable and vulnerable aquifers (Kumarasamy, 2007). It was shown by (Kurtzman et al., 2013) that 50% reduction in use of nitrogen fertilizer added to the irrigation water in Israel, results in 70% mitigation of average NO$_3$-N flux to GW in addition to 20% reduction in root N uptake and a significant decrease in concentration of NO$_3$-N in pore water within vadose zone. A comprehensive study by Burow et al. implies that GW Nitrate concentration in the US is higher in shallow and oxic aquifers especially beneath the areas with intense agricultural activities, high soil permeability and oxic geochemical conditions. It was asserted that the existence of dissolved Iron followed by manganese, calcium, farm N fertilizer inputs, percentage of highly permeable soil and dissolved oxygen (DO), is able to justify the fluctuations in Nitrate concentration. Additionally, the most important factors influencing GW Nitrate concentrations were identified as redox conditions, non-point N loadings, other water quality indexes and physical variables (Burow et al., 2010).

### 3.1.3. GW Nitrate modeling and prediction

Several researchers have developed accurate and valid models to assess GW Nitrate contamination in many geographical locations. For instance, using ordinary and indicator kriging techniques, Arslan et al. assessed spatiotemporal distribution and variation of GW Nitrate (Arslan et al., 2016). Akhavan et
al. used Soil and Water Assessment Tool (SWAT) to assess Nitrate leaching and pollution in a watershed in Iran (Akhavan et al., 2010). Lake et al. developed series of models by merging spatial data of on-ground loading, soil properties, drift cover and aquifer type to evaluate factors affecting vulnerability of GW in aquifers of England and Wales to Nitrate contamination (Lake et al., 2003).

Moreover, by analyzing the Nitrogen inputs and dynamics in an area, an approximate prediction of Nitrate concentration can be achieved by assuming that N in inputs is equal to N in output plus variations in the N contents of the soil, livestock and other elements (Goss and Goorahoo, 1995). Maintaining soil fertility while minimizing environmental contamination with regard to the amount of N input and output depends on several factors. It was determined by Ju et al. that 100 kg ha⁻¹y⁻¹ of excess N is the baseline of leaching NO₃ into GW on a regional scale (Ju et al., 2006).

Using a modular neural network approach, Almasri and Kaluarachchi developed a model to predict the concentration of Nitrate in an agricultural-based terrain and aquifer (Almasri and Kaluarachchi, 2005). Kotir et al. developed a system dynamic simulation model to assess the influence of agricultural activities and population growth on surface water and GW resources quality and quantity in a region in Ghana. Upon successful model development with high level of accuracy and validity, they considered a few more scenarios (development of the water infrastructure, cropland expansion and dry conditions) and predicted the future behavior of water resources systems (Kotir et al., 2016).

Furthermore, by employing MODFLOW and MT3D models for GW flow and contaminant transport simulations respectively, Almasri et al. assessed the Nitrate contamination in an aquifer in Washington state (Almasri and Kaluarachchi, 2007). Using the same approach, Lasserrea et al. developed a “GIS-transport” model to assess the Nitrate contamination in a watershed in France using minimal data (Lasserrea et al., 1999). Levy et al. and Eshtawi et al. assessed the Nitrate contamination by developing an integrated MODFLOW-MT3D model in Israel and Ghaza Strip respectively (as Mediterranean regions) and made predictions based on different scenarios (Eshtawi et al., 2016; Levy et al., 2017). Likewise, Conan et al. employed MODFLOW, MT3D and SWAT models for a Nitrate fate analysis in France (Conan et al., 2003). By studying the literature, it was realized that integration of MODFLOW and MT3D models is the most popular and common method that were used by researchers for assessment of GW Nitrate contamination (Baalousha, 2010; Guse et al., 2015; Lam et al., 2010; Narula and Gosain, 2013; Prommer et al., 2003; Zhang and Hiscock, 2016). Table 3.1 tabulates the most common GW flow and contaminant transport models for simulating Nitrate concentration.
Table 3.1. Summary of other research works regarding GW Nitrate contamination modeling

<table>
<thead>
<tr>
<th>Source</th>
<th>Models</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Jiang and Somers, 2008)</td>
<td>MODFLOW</td>
<td>MT3D</td>
</tr>
<tr>
<td>(Karatzas and Psarropoulou, 2014)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Molénat and Gascuel-Odoux, 2002)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Pisciotta et al., 2015)</td>
<td>DRASTIC; SINTACS</td>
<td></td>
</tr>
<tr>
<td>(Roelsma and Hendriks, 2014)</td>
<td>ANIMO</td>
<td></td>
</tr>
<tr>
<td>(Wheeler et al., 2015)</td>
<td>Random forest</td>
<td>Iowa, USA</td>
</tr>
<tr>
<td>(Almasri and Kaluarachchi, 2007)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Levy et al., 2017)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Eshtawi et al., 2016)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Lasserrea et al., 1999)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Conan et al., 2003)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Guse et al., 2015)</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>(Baalousha, 2010)</td>
<td>PMPATH; DRASTIC</td>
<td></td>
</tr>
<tr>
<td>(Prommer et al., 2003)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Lam et al., 2010)</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>(Narula and Gosain, 2013)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(Zhang and Hiscock, 2016)</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>
3.2. Materials and Methods

3.2.1. Model Setup

3.2.1.1. GW Flow Model

GW flow in the region was simulated using MODFLOW model within GMS software interface. This model is based on a previous model developed by (Ghasemizadeh et al., 2016). Upon accurate result of that model, in this study, some minor changes and improvements (e.g. adding data, adjusting parameters etc.) were implemented to make regional GW flow model for the case study area even more accurate and valid. Due to complexity of conduit network within karst aquifers, usually Equivalent Porous Medium (EPM) approach, as a simplifying method, is used for GW flow model development in karstic terrains (Ghasemizadeh et al., 2015). In current study, using Drainage feature, more complexity was brought into the modeling scheme in order to simulate karst system of NPR in more detail.

Data, used for model development, calibration and validation, was collected from literature, historical studies and USGS database. Model boundaries extend 10.9 and 54.9 km in the north/south and east/west directions respectively with a total area of 545.6 km². The developed model comprises of 30 rows and 151 columns, making a uniformly-spaced block-centered grid network with cell size of 358.9 x 363.3 m. Aquifer recharge, as an input parameter, varies throughout the aquifer based on areal topography and hydrogeological conditions. The spatiotemporal values of recharge were estimated based on rainfall data of a station in Manati municipality and by assuming an evapotranspiration of approximately 60%. This water recharge comes from streams, limestone outcrops, sinkholes and enclosed topographic depressions. Moreover, Laguna Tortuguero, which is a coastal lagoon located in northern side of Manati/Vega Baja boundary, is considered as a regional drainage feature in NPR. Figure 3.7, demonstrates modeling steps followed in current study for GW flow and contaminant transport model.
Figure 3.7. Schematic diagram of GW flow and Nitrate transport modeling process using MODFLOW and MT3D codes in current study.
Springs, sinkholes, dip directions, dry valleys, strikes, and partially mapped surface lineaments were initially considered as drainage features that can contribute to regional groundwater flow. However, only drain lines connecting sinkholes to springs were identified to have a significant impact and hence, were added to the model (Figure 3.8 – brown lines). Additionally, Rio Santiago, Rio Tanama, Rio Grande de Arecibo, Rio Grande de Manati, Rio Indio, Rio Cibuco, and Rio de la Plata streams were added to the model as a transfer boundary condition with constant water level and riverbed conductance values. Finally, the model was calibrated using parameter estimation tool (PEST) and during calibration process, parameter values were adjusted within predefined ranges until the simulated head values matched the observed data. Because of data limitation and regional scale of the model, uniform values for the effective porosity (0.3), specific yield (0.05), and storage coefficient (10⁻⁵ m⁻¹) were defined in the transient calibration. Furthermore, automatically calibrated hydraulic conductivities of discrete zones were used to increase the accuracy of modeling. It should be noted that drain properties herein do not represent the actual locations, roughness, diameter, tortuosity, and lumped matrix conduit exchange coefficients of the conduits. They basically simulate the drainage effect of conduits on the regional GW flow to enhance the accuracy of the EPM method (Ghasemizadeh et al., 2016). Figure 3.8 depicts the model boundary, location of streams, drain features, conduits, observation wells and springs that were defined in the GW flow model.

![Figure 3.8. Location of streams, drain features, conduits, observation wells, pumping wells and springs in GW flow model](image)

### 3.2.1.2. Contaminant Transport Model

After successful development of GW flow model using MODFLOW code for both steady-state and transient conditions, Nitrate transport model was developed using MT3D code within GMS software interface and was linked to the flow model. MT3DMS is a modular three-dimensional transport model for the simulation of advection, dispersion, and chemical reactions of dissolved constituents in
groundwater systems (Zheng et al., 2012). This model uses a modular structure similar to the structure utilized by MODFLOW, and is used in conjunction with MODFLOW in a two-step flow and transport simulation. In this process, the heads and cell-by-cell flux terms initially computed by MODFLOW during the flow simulations were used as the flow input for the transport portion of the simulation. Stress periods and time steps for the transport model were considered as the same as those used for the flow model. The initial Nitrate concentration and other input parameters such as transient recharge concentration of Nitrate based on land cover type and field data were given to the transport model. In advection package of MT3D model, Third order TVD scheme (ULTIMATE) was chosen as solution scheme. For calibration of the transport model, Nitrate concentration data of certain wells in NPR since 1992 was used. Data collection in the study area (2000-2016) was carried out at different locations and dates. Nitrate sampling data, USGS data and other historical observations were used to setup transient observation points in the model.

In a study conducted by (Conde-Costas and Gómez-Gómez, 1999), Nitrate loading in a small area within Manati and Vega Baja municipalities was determined based on land cover type. In fact, Agricultural areas (use of manure and fertilizers) and un-sewered rural communities (effluent of septic tanks) were known as the main sources of Nitrate leachate into the karst aquifer of the region for each of them transient recharge concentration was specified. Rural communities without sewer service were responsible for an estimated nitrogen loading of approximately 200 Kg per hectare per year (kgN/ha.y). This estimation was based on the following assumptions: 1- total nitrogen excreted by human is 17 g/d per capita, 2- there are 36 persons per 10 housing units (hu) on average in PR and 3- an average rural housing density is 9 hu/ha. By applying an estimated domestic wastewater discharge onto the subsurface of about 0.71 m$^3$/d per housing units or about 0.20 m$^3$/d per person, this load translated to an approximate effluent nitrogen concentration of 85 mg/L/ha over rural community areas not having sewer system. Domestic wastewater discharge from un-sewered rural communities was estimated based on water-use data of 1982 which indicates 4,160 m$^3$/d of water supply to 5,852 households through the un-sewered public water supply distribution system.

The potential Nitrate loading coming from agricultural lands varies throughout the year because of the variability in rainfall, runoff and fertilizer use rates. Nitrate load based on fertilizer use rate in agricultural areas of NPR was estimated as 760 kg-N/ha.y between 1992 to 1995. However, only 550 kg/ha.y of Nitrogen may be available for leaching or volatilization due to incorporation by plants or mineralization in soil. For Manati, it was calculated that Nitrate load from agricultural areas to the upper aquifer is 45 kg-N/ha.y. Finally, diluted Nitrate concentration caused by aquifer recharge yields a recharge concentration of approximately 110 mg/L. It should be noted that during 1992 to 1995, relatively high concentration of Nitrate (above 10 mg/L as MCL) was observed in the selected wells.
Nitrate recharge rate calculation was repeated for other municipalities and for different years based on variations in Nitrate concentration at different observation wells. This was mainly because after 2000, agricultural activities in a few areas were reduced or ceased according to local farmers and unofficial sources. In fact, it was observed that GW Nitrate contamination has been mitigated during last 15 years. Accordingly, different amounts of Nitrate recharge concentration associated with agricultural areas were given to the model as input. Figure 3.9 shows land cover types associated with GW Nitrate contamination and location of sampling wells where data collection was conducted.

Figure 3.9. Selected land cover types and location of Nitrate sampling wells in NPR

Table 3.2 elaborates the annual maximum GW Nitrate concentration in mg/l for municipalities of north-central PR based on field data collection. In addition, Figure 3.10 depicts spatiotemporal distribution of Nitrate sampling sites and amount of Nitrate concentration using gradual symbols.

Table 3.2. Annual maximum GW Nitrate concentration (mg/l) for municipalities of NPR – Data of 1992-1995 was derived from a USGS study (Conde-Costas and Gómez-Gómez, 1999)

<table>
<thead>
<tr>
<th>Year</th>
<th>Arecibo</th>
<th>Barceloneta</th>
<th>Manati</th>
<th>Vega Baja</th>
<th>Vega Alta</th>
<th>Dorado</th>
<th>Toa Baja</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992-1995</td>
<td>-</td>
<td>-</td>
<td><strong>18</strong></td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2005</td>
<td>4.64</td>
<td>3.6</td>
<td>7.55</td>
<td>9.04</td>
<td>6.11</td>
<td>4.85</td>
<td>-</td>
</tr>
<tr>
<td>2006</td>
<td>4.49</td>
<td>3.05</td>
<td>6.73</td>
<td>8.24</td>
<td>4.11</td>
<td>4.31</td>
<td>3.84</td>
</tr>
<tr>
<td>2007</td>
<td>5.19</td>
<td>3.66</td>
<td>8.65</td>
<td>8.95</td>
<td>2.94</td>
<td>6.87</td>
<td>2.84</td>
</tr>
<tr>
<td>2008</td>
<td>4.11</td>
<td>3.57</td>
<td>5.35</td>
<td>9.23</td>
<td>2.48</td>
<td>3.45</td>
<td>-</td>
</tr>
<tr>
<td>2009</td>
<td>5.02</td>
<td>2.81</td>
<td>5.41</td>
<td>8.26</td>
<td>2.96</td>
<td>4.43</td>
<td>-</td>
</tr>
<tr>
<td>Year</td>
<td>2010</td>
<td>5.64</td>
<td>2.74</td>
<td>7.05</td>
<td>8.64</td>
<td>5.97</td>
<td>4.22</td>
</tr>
<tr>
<td>------</td>
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<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>2011</td>
<td>5.07</td>
<td><strong>10.6</strong></td>
<td>4.99</td>
<td>7.52</td>
<td>4.95</td>
<td><strong>10.7</strong></td>
<td>3.38</td>
</tr>
<tr>
<td>2012</td>
<td>4.69</td>
<td>9.13</td>
<td>4.25</td>
<td>6.84</td>
<td>6.53</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>2013</td>
<td>4.51</td>
<td>3.9</td>
<td>2.04</td>
<td>7.91</td>
<td>5.7</td>
<td>3.06</td>
<td>-</td>
</tr>
<tr>
<td>2014</td>
<td>4.04</td>
<td>2.85</td>
<td>3.63</td>
<td>7</td>
<td>5.05</td>
<td>3.19</td>
<td>-</td>
</tr>
<tr>
<td>2015</td>
<td>3.86</td>
<td>2.94</td>
<td>3.51</td>
<td>7.17</td>
<td>5.3</td>
<td>3.14</td>
<td>-</td>
</tr>
<tr>
<td>2016</td>
<td>3.95</td>
<td>2.79</td>
<td>3.18</td>
<td>6.92</td>
<td>4.75</td>
<td>2.23</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.10. Spatiotemporal distribution of Nitrate sampling sites and amount of Nitrate concentration
3.2.2. Prediction of Nitrate Concentration

Nitrate transport model can be used for prediction of Nitrate concentration based on hydrological and meteorological conditions and also by considering urban, industrial and agricultural development in NPR for the next 20 years. This helps authorities to make policies accordingly to minimize the environmental impacts of economic and agricultural growth and move toward sustainable development.

In order to predict the GW Nitrate concentration in NPR, the same model developed for the period of 1983-2015 was employed for the period of 2015-2035 based on a few assumption. First, precipitation data was assumed as the average rainfall data of 2005-2015 period. This rainfall variation was repeated for every year of the 2015-2035 period. This assumption may not be accurate enough because of many uncertainties such as occurring major hurricanes or the impact of climate change. However, because the goal of this study is to predict the GW Nitrate concentration for the years 2025 and 2035, neglecting those uncertainties seems to be acceptable. Moreover, although GW Nitrate concentration was observed to be mitigated in the past years due to reduced agricultural activities and proper management of landfills, it is predicted that after hitting Hurricane Maria in 2017 and its negative economic consequences, agricultural activities intensify. Agricultural development is one of the possible ways of economic growth within the island. Thus, if this assumption is correct, it is expected that using fertilizers in existing agricultural lands will exacerbate GW Nitrate concentration again. Moreover, it was assumed that some areas that have not been used for agricultural activities yet but have the potential to grow cultivated crops, will also be used for agricultural activities. These areas are identified as Hay/Pasture in Figure 3.4. Using the land cover data of Figure 3.4 (cultivated crops and hay/pasture) and also the data in Figure 3.5 regarding agricultural capability of soil, areas with high potential of becoming cultivated lands in the future were identified and used in modeling process.

3.3. Results and Discussion

3.3.1. GW Flow Model

After successful calibration and validation of transient MODFLOW model, calculated GW head levels were compared to observed head levels. The results led to $R^2$ value of 0.97 and Root Mean Square Error (RMSE) of 1.3 m (Figure 3.11).
Figure 3.11. Scatter diagram depicting simulated versus observed hydraulic head values for steady-state calibration of the flow model

It was found out that the presence of conduits can affect the GW flow of the region significantly. A novel method for simulating the heterogeneities in karst aquifers by assigning arrays of adjacent cells as conduits was introduced. Moreover, precipitation followed by river leakage through streambeds and from unconfined parts of the lower aquifer in the south were identified as the main sources of GW recharge in the region. Model outflows are spring discharges, discharge to the ocean and discharge into wetland areas. Major sinks in the mode are groundwater withdrawals in wells. The water budget of the model shows that approximately 11% of the GW recharge ties with conduits or diffuse flow at the springs. The steady-state GW budget for the year 1992 and surface water-GW interconnectivity is tabulated in Table 3.3 (Ghasemizadeh et al., 2016).
Table 3.3. Steady-state groundwater budgets for 1992 hydrologic conditions in the central NPR
(Ghasemizadeh et al., 2016)

<table>
<thead>
<tr>
<th>Source/Sink</th>
<th>Discharge (m³/d)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inflows</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recharge</td>
<td>270,650</td>
<td>76.8</td>
</tr>
<tr>
<td>River leakage</td>
<td>62,090</td>
<td>17.6</td>
</tr>
<tr>
<td>Subsurface contributions</td>
<td>19,600</td>
<td>5.6</td>
</tr>
<tr>
<td>Total inflows</td>
<td>352,340</td>
<td>100</td>
</tr>
<tr>
<td><strong>Outflows</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Withdrawals</td>
<td>149,500</td>
<td>42.4</td>
</tr>
<tr>
<td>Springs</td>
<td>30,120</td>
<td>8.6</td>
</tr>
<tr>
<td>Ocean discharge</td>
<td>72,030</td>
<td>20.4</td>
</tr>
<tr>
<td>Wetland drainage</td>
<td>93,700</td>
<td>26.6</td>
</tr>
<tr>
<td>Lake</td>
<td>6,990</td>
<td>2.0</td>
</tr>
<tr>
<td>Total outflows</td>
<td>352,340</td>
<td>100</td>
</tr>
</tbody>
</table>

3.3.2. Nitrate Transport Model

After calibration process of the transport model and minimizing the errors by adjusting the input parameters, the output of the model was compared to the observed values. The simulated Nitrate concentration values were observed to have high correlation with observed values. For each municipality, 3 statistical indexes namely, mean absolute error (MAE), root mean squared error (RMSE) and coefficient of determination (R²) were calculated. On average, the values of MAE, RMSE and R² were calculated as 0.92 mg/L, 0.89 mg/L and 91.4% respectively.

Although the statistical indexes prove satisfactory results of our modeling, the error values can be decreased even more if more data and information are available. The main source of GW Nitrate contamination was identified as agricultural activities and effluent of septic tanks in un-sewered rural communities. However, it was observed that in some areas where the dominant land cover is “Evergreen Forest” or “Herbaceous”, GW Nitrate concentration is relatively high in some years compared to other locations. This can be due to presence of abandoned landfills in those fields. Not much data was available for presence or status of the landfills in NPR; hence, this can be considered as a weakness in our modeling. Moreover, animal waste on the ground surface (mixed with storm runoff or rainfall) can be considered as a source of Nitrate recharge in those areas. On the other hand, for some areas with agricultural land use, the value for GW Nitrate concentration was observed to be lower than expected. This is mainly because of the following reasons: 1- Agricultural activities in those
areas are limited or less intense compared to other cultivated fields. 2- Use of fertilizers and manure is limited in those areas. 3- Soil permeability is less than other areas. For example in Arecibo, agricultural fields are mainly located in areas with lower hydraulic conductivity and as it can be observed in Figure 3.10, GW Nitrate concentrations in Arecibo are generally lower compared to areas with higher hydraulic conductivity such as Vega Baja and Vega Alta.

3.3.3. Prediction of GW Nitrate contamination

The model was expanded to predict the GW Nitrate concentration in NPR for the years 2025 and 2035 based on estimated use of fertilizers and manure application in cultivated areas. Although during last years, agricultural activities were reduced and many cultivated croplands were abandoned, it is predicted that agricultural industry will rise again and the use of fertilizers and manure will be escalated which is mainly because of the unacceptable economic status of the island. This prediction became more valid after hitting Hurricane Maria, a category 4 hurricane, in September 2017. The hurricane has devastated farmlands of PR and has resulted in $780 million of crop losses (80% of the value of the crops in a matter of hours). This financial damage is approximately $45 million for Hurricane Irma that hit the island a few weeks before Maria. Before these hurricanes, the island used to import 85% of its food. This import rate is predicted to become even higher for the next 1-2 years. Hence, agricultural development and growth seems to be a priority for policy makers and authorities of the island (Abbott, 2017; Perroni, 2017). Flores Ortega, secretary of agriculture in PR, said that agriculture, as one of the major economic sectors of PR, will be recuperated in a near future (McGrory, 2017). Additionally, Ricardo L. Fernández, President and CEO of Puerto Rico Farm Credit, said that the island is planning to have bigger farms in the future (Fernández, 2017).

Accordingly, our model predicted the GW Nitrate concentration in a regional scale for north-central part of PR. The predicted results show that areas with existing high Nitrate concentration (such as Vega Baja and Vega Alta) will remain vulnerable to contamination in the next 2 decades; but agricultural development in Arecibo will not lead to intense GW Nitrate contamination compared to other locations. Hence, for Arecibo, focusing on existing cultivated fields and also areas with high potential of agricultural development in their proximity (i.e. land cover of hay/pasture) is recommended. Moreover, our prediction results indicates GW Nitrate concentration of less than 10 mg/L (Recommended MCL of EPA) throughout the north-central part of the island for the next 20 years. This prediction is tied with a lot of uncertainties and unknown factors and may not be accurate enough. However, it gives an overall understanding of the spatiotemporal trends of Nitrate contamination within karst aquifer of NPR. Figure 3.12 illustrates the prediction results of our modeling for the next 2 decades. It is worth mentioning that the output result from GMS software was imported into ArcGIS for interpolation and for depicting a smoother transition between counters.
Figure 3.12. Spatial distribution of simulated GW Nitrate concentration (mg/L) for the years 2015, 2025 and 2035 in north-central part of Puerto Rico

In addition, using our collected data and historical observations, Nitrate concentration variation trend since 2005 was assessed for different locations throughout NPR (Figure 3.13). As it appears from this figure, a generally declining trend can be observed for all sampling locations. The average Nitrate concentration in some areas such as Vega Baja and Vega Alta seems to be higher than other municipalities. However, this high concentration has always been less or slightly higher than MCL of 10 mg/L.
Figure 3.13. GW Nitrate concentration trend for sampling sites in each municipality with highest observed Nitrate concentration since 2005

Based on the available data, information and historical trend of GW Nitrate concentration and also our prediction result, recommended water resources management actions for different municipalities of NPR are tabulated in Table 3.4. In addition to these recommended actions, there are some methods (such as biogeochemical controlling processes) that can be used to mitigate Nitrate contamination in GW (Rivett et al., 2008; Thayalakumaran et al., 2008).
Table 3.4. Recommended management actions for controlling GW Nitrate contamination in municipalities of NPR

<table>
<thead>
<tr>
<th>Municipality</th>
<th>Protection Priority and Vulnerability to contamination</th>
<th>Recommended Management Action</th>
<th>Data Collection Priority</th>
<th>Recommended Monitoring Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arecibo</td>
<td>Low</td>
<td>Use modern agricultural equipment and technology for new farms</td>
<td>Medium – but more data is needed for agricultural areas in northwestern side</td>
<td>Yearly</td>
</tr>
<tr>
<td>Barceloneta</td>
<td>Low</td>
<td>Use modern agricultural equipment, Collect Nitrate samples at wells every 3 months</td>
<td>Low – But more data is needed for the northern side</td>
<td>Seasonal</td>
</tr>
<tr>
<td>Manati</td>
<td>Medium to High</td>
<td>Use modern agricultural equipment and technology, Reduce the use of fertilizer and manure, Collect Nitrate samples at wells every month</td>
<td>High – Compared to the area of the municipality, more data points especially for agricultural lands are needed</td>
<td>Monthly</td>
</tr>
<tr>
<td>Vega Baja</td>
<td>High</td>
<td>Use modern agricultural equipment and technology, Reduce the use of fertilizer and manure, Collect Nitrate samples at wells every month</td>
<td>High – More data for northeastern and western side is needed</td>
<td>Weekly to Monthly</td>
</tr>
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</tr>
<tr>
<td>Vega Alta</td>
<td>Medium to High</td>
<td>Use modern agricultural equipment and technology, Reduce the use of fertilizer and manure, Collect Nitrate samples at wells every month</td>
<td>Medium</td>
<td>Monthly</td>
</tr>
<tr>
<td>Dorado</td>
<td>Medium</td>
<td>Use modern agricultural equipment; Collect Nitrate samples at wells every 3 months</td>
<td>Low to Medium</td>
<td>Seasonal</td>
</tr>
</tbody>
</table>
3.4. Conclusion

In northern Puerto Rico, high permeability of soil/rock in karstic aquifers, as one of the most accessible and productive fresh water resources, has increased their vulnerability to contamination. In this study, groundwater Nitrate contamination, as a result of agricultural, industrial and urban development, was assessed and simulated for north-central part of the island. Using collected field samples (since 2005) and historical data (since 1992), a Nitrate fate and transport simulation was done using MODFLOW and MT3D models within GMS software interface. The calculated results of the regional-scale simulation showed relatively high correlation with observed values and hence, the calibrated transport model was used for prediction purposes. Using soil type data (agricultural capability of soil), land cover data, and by assessing agricultural and economic development trend in the island especially after hitting Hurricane Maria, spatiotemporal distribution of groundwater Nitrate concentration was projected for the next two decades. It was predicted that although groundwater Nitrate concentration has been reduced generally during last decade due to mitigated use of fertilizers or cultivation, agricultural activities will rise again dramatically after economic damages of Hurricane Maria. This agricultural development, if not managed properly, will negatively impact the groundwater quality and quantity especially in Manati, Vega Baja and Vega Alta municipalities. Hence, based on the model prediction results, recommended management plans for controlling groundwater Nitrate contamination in each municipality were presented for the use of policy makers and authorities.
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