In the present study, groundwater pollution in the central part of the Nile Delta is investigated. Natural chemical constituents and some contaminants of shallow groundwater and their distribution through the whole region of the studied area are investigated. A combination study of laboratory and numerical modeling are utilized. Numerical modeling for governing equations describing advective-dispersive transport with multi rate mass transfer is utilized employing FDM. A three dimensional finite difference groundwater model MODFLOW is used to deal with the hydrodynamics of the flow through porous media. A groundwater solute transport simulator MT3DMS which can be communicated with MODFLOW through data files, is utilized to solve the problem of contaminants transport and the change of their concentration with time. Field measurements and experimental works were conducted on sixty surface and groundwater samples collected from the study region. The collected samples were analyzed in the Central Laboratory of Environmental Isotope Hydrology, ENRRA. Stable isotopic techniques (Oxygen-18, Deuterium) were used to investigate the recharge sources, and Nitrogen-15 technique was applied to help tracing sources and fate of nitrate contamination found in collected water samples. The analysis indicated that vulnerability of the water resources to pollution is mainly related to the use of excess fertilizers (NO$_3^-$), the growing industrial activities, and sewage effluents. The sources for the higher nitrate concentration appear to be mixing with sewage or manure and ammonium phosphate fertilizer. Scenarios for groundwater remediation in Birma village employing extraction wells are presented.

Keywords: Groundwater contamination, numerical modeling, field experimentation, hydrochemistry, environmental isotopes, $^{15}$N, MODFLOW, Nile Delta.

1 INTRODUCTION

The water resources in the Nile Delta region have experienced drastic events in the last four decades since the operation of the High Aswan Dam. Many activities have impact on eutrophication and contamination status, the ecological value and environmental condition of the Nile Delta region such as agriculture development, industrial activities within the catchments and inadequate rural sanitation. Excessive irrigation applications lead to water logging problems in vast areas of the region. Moreover, the domestic, industrial, sewage and agricultural drainage to surface and groundwater with all known effluents deteriorate the ecosystem in the Nile Delta. Recent increases in global population, together with enhanced standards of living, have created greater demand on water resources, requiring improved groundwater management. Understanding the groundwater recharge process is essential in protecting groundwater source quality. Short transit times associated with the recharge process can potentially adversely affect groundwater quality due to lack of attenuation time or contaminant decay. Residence time estimation offers benefits to evaluating recharge water flow through the subsurface to groundwater sources. In El-Gharbiya Governorate, central of Nile Delta, excessive use of sewage effluent and sludge, over-fertilization, over-use of manures for irrigation purposes cause hazardous effects on plants, animals and human health. In addition, discharge of liquid or solid wastes with different kinds of contaminants
into the geologic environment causes groundwater deterioration. Numerical modeling techniques have been successfully utilized for simulating groundwater movement and solute transport mechanism. The well-known finite difference groundwater model MODFLOW has been proved to be an efficient technique to simulate groundwater hydrodynamics and a solute transport model which can be communicated with MODFLOW through data files MT3DMS, is widely employed to solve the problem of contaminants transport and the change of their concentration with time. Nitrogen isotopic method has been developed and successfully used in numerous case studies to identify nitrogen compounds pollution sources in some countries. Nitrate derived from manure or sewage is usually characterized by δ¹⁵N values greater than +10‰. It is therefore isotopically distinct from N in most synthetic fertilizers (0 ± 4‰), from natural soil organic N (+4 to +9‰) and nitrate generated therein by microbial nitrification. The overall objective of this study is to discriminate between these different sources of nitrate pollution in groundwater using the hydro-chemical and isotopic approaches and simulate them numerically. The purpose of this paper is to identify problems, knowledge, gaps and needs that deemed important to improve water management in the Middle Delta as well as propose scenarios for groundwater remediation and mitigation. A proposed groundwater remediation schemes for Birma region was presented.

2 STATE OF ART

The modeling of groundwater flow and contamination in the Nile Delta has been reported in the literature by various researchers. Zaghloul, (1958) and (1984), proposed a new classification for Nile Delta aquifers and its sources of pollution. The storage possibilities in different types of aquifers are outlined. The transmitting capacity of the Delta aquifer is studied. The monthly discharges are computed at various zones and a balance is made for gains and losses. Farid (1980) and (1985), discussed a detailed description of the geological conditions of the Nile Delta aquifer and its management. The hydrogeological and hydrological characteristics of the Nile Delta aquifer were determined. The sea water wedge was described suggesting sea water intrusion of about 30 km far from shoreline whereas the points of interface at distance of 80 km far from shoreline. Goamea (2000), studied the behavior of the transition zone in the Nile Delta aquifer under different pumping schemes. The fresh groundwater thickness increases with time, most probably due to increasing surface water diversions and also as an effect of the construction of the High Aswan Dam. The most efficient scheme among many investigated schemes is fresh water withdrawal with abstraction barrier in the transition and at the coast. The idea of utilizing the scavenger well scheme in general has been examined as a tool for groundwater abstraction. It is concluded that the scavenger well is applied in case of two different groundwater qualities. A unique saline well could be used to control four or more fresh water wells at a certain distance (circle of influence). RIGW/IWACO, (1990), studied the development and management of groundwater resources in the Western Nile Delta Region. Groundwater development scenarios are evaluated with numerical groundwater flow simulation using (TRIWACO) package. The model covers the major part of the Western Nile Delta region and the adjacent desert. El Molla et al. (2005) developed data base and a three dimensional groundwater model to simulate the behavior of groundwater system and its interaction with surface water at western Nile Delta area. An overview of the Nile Delta and its water resources assessment is presented by Zeydan (2005). Bear (1987) presented the basic equations of contaminant transport in groundwater. He presented two component for hydrodynamic dispersion of the contaminant concentration; advective transport which expresses the flux carried by the water at the average velocity (as determined by Darcy’s Law) and dispersive transport. Dispersive flux is a macroscopic flux that expresses the effect of the microscopic variation of the velocity. Dispersion in porous media refers to the spreading of contaminants over a greater region than would be predicted solely from the average groundwater velocity vectors. Shamrukh (2001) investigated the contamination of groundwater by nitrogen and phosphate chemical fertilizers in the Tahta region of the Nile Valley Aquifer. The three-dimensional groundwater flow and contaminant transport models; (MODFLOW & MT3D) were used to predict the future concentration of NO₃⁻ and PO₄³⁻ in shallow and deep groundwater. The availability of groundwater for irrigation and public water supply for the present century were studied. An overview of
Advances in groundwater studies including modeling, tracing and management is presented by Zeidan (2004). Wang (2005) presented a numerical solution for governing equations describing advective-dispersive transport with multi rate mass transfer between mobile and immobile domains. The solutions of two illustrative examples obtained using the new approach agree with those obtained by existing semi-analytical and numerical solution obtained using the transport simulator MT3DMS. Atta et al. (2005) and Sharaky et al (2007) employed the hydrochemistry of major-ions (K+, Na+, Mg2+, Ca2+, Cl-, SO42-, HCO3-, CO32-) together with trace elements (Fe, Mn, Zn, Pb, Cd, Cr, Cu, Ni) to constrain the hydrochemical characteristics, source and salinization processes of the shallow coastal aquifer, northwestern Nile Delta. The study aimed to obtain additional information on the possible contamination with major elements, trace elements (heavy metals) and/or nutrients (NO3-, PO42-, NH4+). Salem (2006) investigated the chemical contamination of the groundwater and surface water at the west Nile Delta. The study revealed that the source of the contamination is mainly derived from either natural sources (drains and canals) or from man-made sources (agricultural, domestic and industrial sources). The vulnerability the water resources to the pollution is mainly related to the use of excess fertilizers (NO3) and due to the growing industrial activities and sewage effluent, in addition to the seepage of untreated wastes to the surface water network. El-Fakharany (2009) studied the impact of local hydrogeological conditions and human activities on water resources at the southeastern part of the Nile Delta (El Khanka area). Results indicate that both surface water and groundwater in the study area are suffering from quality problems related mainly to natural and human-related factors. High concentrations of salinity, major elements, nitrate, and trace elements are detected in the water samples. Ahmed et al. (2009) utilizing isotopic and hydro-chemical tracers to investigate nitrogen pollution sources of surface water and groundwater system for proper management and decreasing pollution of freshwater resources in the Middle Delta, Egypt. Results indicate that Rosetta Branch has higher $\text{NH}_4^+$ concentration and enriched $\delta^{15}\text{N}$-$\text{NH}_4^+$ and $\delta^{15}\text{N}$-$\text{NO}_3^-$ values than Damietta Branch due to disposal of Tala sewage drain, with highly enriched $\delta^{15}\text{N}$-$\text{NH}_4^+$ value, in it. Ghoraba (2009) and Ghoraba et al. (2012) studied the groundwater quality management in Middle Nile Delta through a combination of laboratory and numerical modeling works. Environmental isotopes techniques were used to investigate the recharge sources and the nitrogen compounds pollution sources. MODFLOW and MT3DMS were employed numerically by applying the method of finite differences for solving the three dimensional problem. The obtained results include the prediction of water levels and solute concentration values distribution in the area at different times. A scenario for remediation is proposed. Hussin and Mousa (2012) used environmental isotopes and geochemical data to improve the water management in the Nile river system. Lo Russo and Taddei (2012) developed an effective and economically-sustainable land management strategy to protect subsurface water resources from anthropogenic pollution in which combined general safeguards were applied to the whole aquifer recharge area with specific local land use restrictions in the proximity of the abstraction point (i.e. WHPAs).

3 PROBLEM STATEMENT

The chosen area to conduct the study is El-Gharbiya Governorate. It extends between latitudes 30° 36’ - 31° 09’ N and longitude 30° 45’ - 31° 15’ E. It includes more than 1943.51 km² in the central part of the Nile Delta. The area is bounded on the west by the left branch of the Nile River “Rosetta” and on the east by the right branch “Damietta”. The Governorate extends into Kafir El-Sheikh in the north and Monofeya Governorate in the south. The Governorate consists of eight centres with very dense population reaches about 4,011,921 inhabitants with only 30% of the governorate is served by sewage network. Septic tanks, rural latrines and injected wells are the means used for sewage disposal in the other parts of Governorate. The land area is a low elevation plain where sediment is deposited at the mouth of Nile River, it is the most suitable land for intensive agriculture. Excessive fertilizers and pesticides applications are required for plant growth. This leads to water quality problems in vast areas of the region. Significant proportions of chemicals used is leached into the water system. In EL-Gharbiya Governorate,
extensive man-made drainage systems are found which are particularly noticeable in traditionally cultivated land areas and have been extended to some of the newly reclaimed areas. Large volumes of domestic and untreated industrial effluent are still discharged into the water channels or directly to the river branches. Kafr El-Zyat city is considered as one of the most important industrial cities in Egypt. The most of industrial plants constructed at Kafr El-Zyat city on the banks of the Rosetta branch directly discharge their effluents into the Rosetta branch without any treatment. The estimated flow of industrial wastewater discharge to the Rosetta branch is about 0.05 million m$^3$/day, (Daifullah et al., 2003). These industries were identified as being the major source of water pollution in this area. The Quaternary and Pliocene water bearing formations in the central part of the Nile Delta comprise a leaky aquifer system intercalated by semi-pervious clay and silty layers acting as an aquitard. This Holocene aquitard caps the main aquifer that belongs to the Pleistocene which forms the groundwater reservoir in itself. The formations are underlain by an impermeable base of Pliocene clay deposits which act as an aquiclude. The two hydrological units forming the semi-confined aquifer are hydraulically connected with each of them having its own water level. The transmissivity of the aquifer varies from 3000 to 5000 m$^2$/day and the hydraulic conductivity ranges from 50 to 100 m/day. The effective porosity varies from 15 to 18% and the storage coefficient ranges between 0.01 and 0.001. The differences between the piezometric levels of the aquifer and the shallow water table levels in aquitard don’t exceed more than 2 m, (Abd El-bary, 2004). The soil and aquifer properties, the fluid flow conditions combined with the physical and chemical characteristics of the contaminant create a three phases problem of considerable complexity. The objective of the study is to evaluate the groundwater quality for different purposes and to determine the interaction between groundwater aquifers and man-made sources which produce hazardous fluid waste.

Figure 1. The groundwater aquifers in the studied area
4 THEORETICAL APPROACH

By combining continuity equation with Darcy’s velocities, the partial differential equation governing the unsteady flow of water in a compressible confined aquifer of uniform thickness b, for the anisotropic media the equation reads following Harr (1962):

$$\frac{\partial}{\partial x} (K_x \frac{\partial h}{\partial x}) + \frac{\partial}{\partial y} (K_y \frac{\partial h}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial h}{\partial z}) = \frac{S}{b} \frac{\partial h}{\partial t}$$ (1)

where $K_x$, $K_y$, and $K_z$ are the coefficients of permeability in x, y, z directions, $S$ is the aquifer storativity or the storage coefficient and h is the potential head.

Solute transport in groundwater aims at computing the concentration of a dissolved chemical species in an aquifer at any specified time and place. Changes in chemical concentration occur within a dynamic groundwater system primarily due to four distinct processes: advective transport; hydrodynamic dispersion; fluid sources; and reactions. From principal of mass conservation, the flux $q$ defined by following Bear (1987):

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} (\rho q)$$ (2)

Where; $C$ contaminant concentration; $\Theta$ water content in the porous media, and $q$ the mass flow rate in x direction. The flux $q$ consists of both advection and dispersion components. Advective flux expressing the flux carried by the water at the average velocity as determined by Darcy’s Law. Dispersive flux is a microscopic flux that expresses the effect of the microscopic variation of the velocity. Equation (2) can be written as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right] - [u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z}]$$ (3)

where: $\frac{\partial C}{\partial t}$ rate change in concentration of contaminant; $(u, v, w)$ Darcian velocities in x, y, z directions; and $(D_x, D_y, D_z)$ Dispersion coefficients in x, y, z directions. A generalized partial differential equation describing the fate and transport of contaminants of species $k$ in three-dimensional, transient groundwater flow systems can be formulated as follows, Bear (1987):

$$\frac{\partial (nC^k)}{\partial t} = \frac{\partial}{\partial x} \left( nD_{ij} \frac{\partial C^k}{\partial x_j} \right) - \frac{\partial}{\partial x} \left( n_{vsi} C^k \right) + q_s C^k + \sum R_n$$ (4)

where:
- $C^k$ dissolved concentration of species $k$, ML$^{-3}$;
- $n$ porosity of the subsurface medium, dimensionless;
- $t$ time, T;
- $x_i$ distance along the respective Cartesian coordinate axis, L;
- $D_{ij}$ hydrodynamic dispersion coefficient tensor, L$^2$T$^{-1}$;
- $v_{si}$ seepage or linear pore water velocity; LT$^{-1}$; it is related to the specific discharge or Darcy flux through the relationship, $v_{si} = q/n$;
- $q_s$ volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative), T$^{-1}$;
The left-hand-side of equation (4) can be expanded into two terms, i.e.,

$$\frac{\partial(nC)}{\partial t} = n\frac{\partial C}{\partial t} + C\frac{\partial n}{\partial t} = n\frac{\partial C}{\partial t} + \dot{q}_nC$$

(5)

where \( \dot{q}_n = \frac{\partial n}{\partial t} \) is the rate of change in transient groundwater storage, T\(^{-1}\). Considering only two basic types of chemical reactions, i.e., aqueous-solid surface reaction; sorption which refers to the mass transfer process between the contaminants dissolved in groundwater (aqueous phase) and the contaminants sorbed on the porous medium (solid phase) and first-order rate reaction, the chemical reaction term can be expressed as follows, Bear (1987):

$$\sum R_i = -\rho_b \frac{\partial C}{\partial t} - \lambda_1 nC - \lambda_2 \rho_b C$$

(6)

where:

- \( \rho_b \) is the bulk density of the subsurface medium, ML\(^{-1}\); it is the ratio of the mass of dried soil to total volume of soil.
- \( C^k \) is the concentration of species \( k \) sorbed on the subsurface solids, MM\(^{-1}\).
- \( \lambda_1 \) is the first-order reaction rate for the dissolved phase, T\(^{-1}\).
- \( \lambda_2 \) is the first-order reaction rate for the sorbed (solid) phase, T\(^{-1}\).

Substituting equations (6) and (5) into equation (4) and dropping the species index for simplicity of presentation, equation (4) can be rearranged and rewritten as, Bear (1987),

$$n\frac{\partial C}{\partial t} + \rho_b \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j} \left( nD_j \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( n\psi_i C \right) + q_b C - \dot{q}_nC$$

(7)

Equation (7) is essentially a mass balance statement, i.e., the change in the mass storage (both dissolved and sorbed phases) at any given time is equal to the difference in the mass inflow and outflow due to dispersion, advection, sink/source and chemical reactions. Local equilibrium is often assumed for the various sorption processes (i.e., sorption is sufficiently fast compared to transport time scale). When the local equilibrium assumption is invoked, it is customary to express equation (7) in the following form,

$$R n \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j} \left( nD_j \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( n\psi_i C \right) + q_b C - \dot{q}_nC$$

(8)

where \( R \) is referred to as the retardation factor, which is a dimensionless factor defined as:
\[ R = 1 + \frac{\rho_b}{n} \frac{\partial C}{\partial x} \]

(9)

The linear isotherm assumes that the sorbed concentration \( C \) is directly proportional to the dissolved concentration \( C \) and the retardation factor is independent of the concentration field;

\[ C = K_d C \]

(10)

\[ R = 1 + \frac{\rho_b}{n} K_d \]

(11)

where \( K_d \) is the distribution coefficient of the solute in the porous medium, \( L^3 M^{-1} \). It depends on the solute species, nature of the porous medium, and other conditions of the system, Bear (1987).

5 NUMERICAL MODELING

Because aquifers are heterogeneous and have complex boundary conditions, exact analytical solutions to the governing equations cannot be obtained directly. Instead, numerical methods are used, in which the continuous variables of the governing equations are replaced with discrete variables that are defined at grid blocks (or cells or nodes). Thus, the continuous differential equation, which defines hydraulic head or solute concentration everywhere in the system, is replaced by a finite number of algebraic equations that defines them at specific points. However, numerical methods yield only approximate solutions to the governing equation; they require discretization of space and time. The variable internal properties, boundaries, and stresses of the system are approximated within the discretized format. In general, the finer the discretization, the closer the numerical solution will be to the true solution. MODFLOW code is a commercial software designed to describe and predict the behavior of groundwater system, Chiang and Kinzelbach (1998). This model employed Finite Difference techniques to simulate the hydrodynamic of the groundwater flow under non-equilibrium conditions in a heterogeneous and anisotropic medium. This model is a well established computer code, which has been successfully used in variable groundwater flow studies. Many models or programs can be stand alone codes or can be integrated with MODFLOW. These programs communicate with MODFLOW through data files. In this work the further development solute transport model MT3DMS is chosen for the Modular 3-Dimensional Transport model. MT3DMS can be used to simulate changes in concentrations of miscible contaminants in groundwater considering advection, dispersion, diffusion and some basic chemical reactions, with various types of boundary conditions and external sources or sinks, Chunmiao and Patrick (1999). MT3DMS is designed for use with any block-centered finite-difference flow model, such as the modular finite-difference groundwater flow model, MODFLOW, under the assumption of constant fluid density and full saturation. It simulates solute transport by using the calculated hydraulic heads and various flow terms saved by MODFLOW. It is based on the assumption that changes in the concentration field will not affect the flow field significantly. The present codes are utilized in the present study for the following purposes: prepare through chemical analysis as well as collection from different sources the data needed for the model application; assign the proper flow and boundary conditions that represent the actual field conditions as close as possible; calibrate the models and check the compatibility of the input data and study and analyse the results.
6 MODEL VERIFICATION

The groundwater flow model MODFLOW was verified using two measured groundwater level contour maps of regions located in Egypt: case study no. 1: The central part of the Nile Delta aquifer (RIGW, 1990) and case study no. 2: The Southern part of Cairo studied by Saltout, (1996). In the central part of the Nile Delta, the water levels in the Nile Branches; Rosetta on the west and Demietta on the east, which are bounding the area, are considered as a fixed head boundary conditions. The southern boundary is a flux boundary with an inflow rate variables along the boundary. The groundwater inflow rate is calculated from the hydrogeological map of the region by applying Darcy's Law. Considering verification of case study no. 1, a good agreement between the MODFLOW results and the groundwater levels presented in the hydrogeological map is shown in Fig. (2). Considering verification of case study no. 2, a good comparison between the actual field results and those obtained from the MODFLOW model is noticed in Fig. (3a &b).

![Figure 2: Verification of MODFLOW Model, case study no. 1 The Southern part of Cairo](image1)

![Figure 3: Measured and Calculated groundwater level contour map, case study no. 2](image2)

The computer program of solute transport simulation MT3DMS paired with MODFLOW were verified using one of the test cases that was proposed by Oldenburg & Pruess, (1995). This test case is addressed to model groundwater flow over a hypothetical salt dome. After completing the flow simulation the finite difference transport model can be used. Fig. (4a &b) shows the results presented by Oldenburg, & Pruess, (1995) and the present numerical model MT3DMS respectively. A good agreement between the two results is noticed.
CASE OF STUDY: BIRMA VILLAGE

The chosen area to conduct the numerical work as micro-scale study is Birma village where the concentration values of ammonium contaminant are the up most according to hydro-chemical analysis results. It lies at the central part of El-Gharbiya Governorate and belongs to Tanta center. The region to conduct the study looks almost like square shape with length of 1.76 km and a width of 1.5 km. It is surrounded by Birma Drain at north, Omm Halaka Canal at south, Omm Abd-Alla Canal at east and Nashart Al-Aalla Drain at west. Lateral boundaries of the modeling area had been defined at constant-head boundary.

7.1 Hydrochemistry And Stable Isotopes

From the studied area, representative groundwater samples from the Quaternary aquifer were obtained from 34 wells selected on the basis of geographical distribution. Most of the selected wells are used for irrigation and domestic uses and their depths range from 13 to 60 m. Other samples were also collected from the drain and canals waters (Figs. 5,6). All the water samples were collected for chemical and isotope analyses. Electrical conductivity (EC), bicarbonate, dissolved oxygen (DO), temperature and pH measurements were measured in situ. Water samples were filtered using 0.45 μm pore-size papers for measuring major cations and anions using Dionex-DX600 Ion Chromatograph. Atomic absorption spectrometer was employed for the determination of the metals (Fe²⁺ and Mn²⁺). Delta O-18 was analyzed using the carbon dioxide equilibration technique and δD was analyzed using a hydrogen equilibration technique at 18°C. For nitrogen isotope analysis, modified diffusion method was used for triplicate determination of ammonium and nitrate in water. They were converted to N₂ gas by reacting with LiOBr, Ahmed et al. (2009). Nitrogen, oxygen, and hydrogen isotope ratios were obtained using isotope ratio mass spectrometer (Thermo Quest Delta+XL). All stable isotope ratios are expressed in per mil (‰) notation:

\[
\delta = \frac{R_{\text{sample}}-R_{\text{standard}}}{R_{\text{standard}}} \times 100\text{‰}
\]  

(12)
where R is the $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, or $^2$H/$^1$H ratio of the sample and the standard, respectively. Delta N-15 values are reported with respect to air, while $\delta^{18}$O and $\delta^2$H values with respect to Vienna Standard Mean Ocean Water (VSMOW). The analytical errors are ±0.5‰, ±0.1‰, and ±1‰, respectively. All the previous analyses were carried out in the Central Laboratory for Environmental Isotope Hydrology, Egyptian Nuclear and Radiological Regulatory Authority (ENRRA), Cairo, Egypt. A detailed description of the analysis procedure and results of hydrochemistry and isotopes is given by Ahmed et al. (2009).

7.2. Groundwater Flow Simulation

A three-dimensional grid is constructed to bound Birma sub-regional groundwater model. The grid cell size in the horizontal plan of the model is 20m by 20m, requiring the modeled area to be subdivided into 75 rows and 88 columns. Fig.(7) illustrates the location map of Birma region and the horizontal grid of the modeling area. The aquifer system has been subdivided into seven modeling layers in the vertical direction. MODFLOW uses the elevation of top and bottom of the aquifer layer to calculate the aquifer thickness for each cell node. The value of the first layer top has been changed according to the nature topography of the area by the grid SURFUR tool and saved as spreadsheet file accepted by MODFLOW package. The saturated part of the silt-clay cap layer was modeled as two layers of 7m constant thickness. Layers 3 through 7 were assigned a constant thickness for each layer; 6, 6, 5, 5 and 4 m respectively. This vertical discretization was chosen according to the depth and screen length of the production wells that the groundwater samples were collected from.
8. NUMERICAL RESULTS AND ANALYSIS

The chemical analysis of the groundwater samples show large variations of dissolved ions concentrations with high salinity in some samples. The salinity map drawn from a representative set of 34 groundwater samples is shown in Fig. (8). Total dissolved solids show large spatial variations between 320 and 6112 mg/L, while dissolved oxygen (DO) range between 0.85 and 4.89 mg/L with a mean value of 2.21 mg/L. Drains water samples have the highest DO, K⁺, HCO₃⁻ and SO₄²⁻ concentrations with mean values of 7.8, 11, 373 and 80 mg/L, respectively, Table 1. In comparison to canals water, drains show higher TDS, Na⁺, Ca²⁺, Mg²⁺ and Cl⁻ concentrations with mean
values of 839, 137, 59, 27 and 141 mg/L, respectively, which could be attributed to agricultural activities and discharge of industrial, domestic and sewage wastes in it. Zifta drain has the highest salinity which reached 1357 mg/L, Ahmed et al. (2009).


<table>
<thead>
<tr>
<th>Constituents</th>
<th>Groundwater</th>
<th>Drains</th>
<th>Canals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean ± SD</td>
<td>Range</td>
</tr>
<tr>
<td>pH</td>
<td>7.4 - 8.4</td>
<td>7.79 ± 0.25</td>
<td>7.3 - 9.5</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>320 - 6112</td>
<td>1050 ± 1242</td>
<td>397 - 1357</td>
</tr>
<tr>
<td>EC (μS/cm)</td>
<td>500 - 9550</td>
<td>1646 ± 1938</td>
<td>820 - 2120</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>0.85 - 4.89</td>
<td>2.21 ± 0.97</td>
<td>0.47 - 9.95</td>
</tr>
<tr>
<td>Na⁺(mg/L)</td>
<td>8 - 328</td>
<td>70 ± 54.7</td>
<td>27 - 83</td>
</tr>
<tr>
<td>K⁺(mg/L)</td>
<td>0.6 - 24.1</td>
<td>5.75 ± 4.7</td>
<td>3 - 36.7</td>
</tr>
<tr>
<td>Ca²⁺(mg/L)</td>
<td>8 - 328</td>
<td>70 ± 54.7</td>
<td>27 - 83</td>
</tr>
<tr>
<td>Mg²⁺(mg/L)</td>
<td>4 - 214</td>
<td>33 ± 41.6</td>
<td>14 - 37</td>
</tr>
<tr>
<td>HCO₃⁻(mg/L)</td>
<td>186 - 845</td>
<td>313 ± 137.5</td>
<td>157 - 641</td>
</tr>
<tr>
<td>Cl⁻(mg/L)</td>
<td>37 - 3499</td>
<td>365 ± 700</td>
<td>37 - 243</td>
</tr>
<tr>
<td>SO₄²⁻(mg/L)</td>
<td>1.2 - 539</td>
<td>41 ± 90.5</td>
<td>23 - 201</td>
</tr>
</tbody>
</table>

Figure 8: Areal distribution of total dissolved solids (TDS) in mg/L for groundwater samples

Stable isotopes of oxygen (δ¹⁸O) and hydrogen (δD) were used in this study to determine the origin of water and to characterize possible mixing of different water sources of water in the Quaternary aquifer. Results of oxygen and hydrogen isotope analyses (δ¹⁸O and δD) of the groundwater, representing the Quaternary aquifer in the middle Delta, Table 2, and drains and canals water samples, Table 3, are plotted with respect to GMWL, Fig. 9. Isotope data for precipitation and Nile River water before and after erection of the High Dam are also included in Fig. 9. The groundwater isotope data shows a range of variation from -1.58 ‰ to +2.8 ‰ and from -5.23 ‰ to +28.5 ‰ for δ¹⁸O and δD, respectively. The large amplitude of isotope variations indicates the complexity of its source. Most of the groundwater samples have isotopic contents which lie on a mixing line between the two signatures of Nile River.
Nitrogen concentrations and isotopic ratios of $\text{NH}_4^+$ and $\text{NO}_3^-$ were analysed in the collected canals, drains and groundwater samples (Tables 2 & 3) in order to evaluate the sources and migration process of nitrogen pollution. Ammonium concentrations of groundwater samples are less than 3.8 mg/L. About 38% of these samples showed values above the maximum drinking standards of World Health Organization (WHO, 2004) of 0.5 mg/L. Spatial distribution of ammonium ion in the groundwater is shown in Fig. (11) where the nitrate concentrations range from 0.06 to 7.35 mg/L, the spatial variability of these concentrations are shown by Fig. (10) while Fig. (11) shows the spatial patterns of $\delta^{15}\text{N}-\text{NH}_4^+$ values in the studied area. As can be seen from the map, relatively depleted $\delta^{15}\text{N}$ values of -2.84 to +2.43‰ are mainly found in the central and western part of the studied area. These areas are affected by the application of synthetic fertilizers. By contrast, the north and south-eastern areas have $\delta^{15}\text{N}$ values $>+4\%o$ indicating soil organic nitrogen or seepage of raw sewage (untreated domestic effluents) replenishing the aquifer, particularly in the populated zones. Therefore, the natural nitrogen isotopic composition of $\text{NH}_4^+$ in the Middle Delta depends on topographical variations, geology, groundwater flow direction, other sources of contamination and general proximity to the agricultural sources. Figure (12) plots $\delta^{15}\text{N}-\text{NH}_4^+$ values for the groundwater samples versus their concentrations.

Many other processes affect the concentration of $\text{NH}_4^+$ in the groundwater, such as plant uptake, immobilization by microbes, fixation in clay minerals, etc. Groundwater samples in the Quaternary aquifer have nitrate concentrations range from 0.06 to 7.35 mg/L, the spatial variability of these concentrations are shown by Fig. (13), (Ghoraba, 2009). Relationship between nitrate concentrations and iron and manganese levels are shown in Fig. (14). Denitrification is accompanied by the appearance in solution of Mn$^{2+}$ and Fe$^{2+}$ ions if the corresponding minerals occur in the aquifer. In these samples, the Mn$^{2+}$ and Fe$^{2+}$ concentrations are only high where the nitrate levels are lowest. Figure (15) shows how the lowering in nitrate values correlates with an exponential increase of $\delta^{15}\text{N}$, according to the relation: $\delta^{15}\text{N} = 24.9 – 2.56 \ln \text{NO}_3^-$ ($r^2 = 0.91$) with an enrichment factor equal to -2.56‰.

**Table 2: Stable Isotopes And Ammonium, Nitrate, Iron, And Manganese Concentrations of Groundwater Samples After Ahmed et al (2009).**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample Identity</th>
<th>$\delta^{15}\text{O} %$</th>
<th>$\delta^D %$</th>
<th>$\text{NH}_4^+$ mg/L</th>
<th>$\delta^{15}\text{N}-\text{NH}_4^+$ %o</th>
<th>$\text{NO}_3^-$ mg/L</th>
<th>$\delta^{15}\text{N}-\text{NO}_3^-$ %o</th>
<th>$\text{Fe}^{2+}$ mg/L</th>
<th>$\text{Mn}^{2+}$ mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>well (1)</td>
<td>1.06</td>
<td>12.4</td>
<td>0.44</td>
<td>-0.28 ± 0.11</td>
<td>0.31</td>
<td>---</td>
<td>2.12</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>well (2)</td>
<td>0.26</td>
<td>6.95</td>
<td>1.18</td>
<td>1.90 ± 0.21</td>
<td>0.59</td>
<td>---</td>
<td>1.32</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>well (3)</td>
<td>0.12</td>
<td>7.99</td>
<td>1.86</td>
<td>1.25 ± 0.06</td>
<td>0.94</td>
<td>---</td>
<td>1.00</td>
<td>0.61</td>
</tr>
<tr>
<td>4</td>
<td>well (4)</td>
<td>0.45</td>
<td>13.36</td>
<td>2.36</td>
<td>-2.51 ± 0.91</td>
<td>0.82</td>
<td>---</td>
<td>0.72</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>well (5)</td>
<td>0.83</td>
<td>11.53</td>
<td>0.14</td>
<td>---</td>
<td>0.45</td>
<td>---</td>
<td>0.74</td>
<td>0.39</td>
</tr>
<tr>
<td>6</td>
<td>well (6)</td>
<td>2.8</td>
<td>23.63</td>
<td>0.34</td>
<td>-1.50 ± 0.62</td>
<td>0.82</td>
<td>---</td>
<td>1.12</td>
<td>0.41</td>
</tr>
<tr>
<td>7</td>
<td>well (7)</td>
<td>1.2</td>
<td>13.99</td>
<td>0.10</td>
<td>---</td>
<td>0.06</td>
<td>---</td>
<td>0.18</td>
<td>0.45</td>
</tr>
<tr>
<td>8</td>
<td>well (8)</td>
<td>-0.93</td>
<td>1.42</td>
<td>0.32</td>
<td>-2.54 ± 0.35</td>
<td>0.98</td>
<td>---</td>
<td>0.85</td>
<td>0.41</td>
</tr>
<tr>
<td>9</td>
<td>well (9)</td>
<td>-0.04</td>
<td>4.95</td>
<td>0.19</td>
<td>---</td>
<td>1.00</td>
<td>---</td>
<td>2.60</td>
<td>0.66</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Sample Name</td>
<td>δ¹⁵N-NH₄⁺</td>
<td>δ¹⁸O Water Samples</td>
<td>δD Water Samples</td>
<td>NH₄⁺ mg/L</td>
<td>δ¹⁵N-NO₃</td>
<td>NO₃ mg/L</td>
<td>δ¹⁵N-NO₃ %</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
<td>-----------</td>
<td>-------------------</td>
<td>------------------</td>
<td>----------</td>
<td>-----------</td>
<td>----------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Ganag Drain</td>
<td>1.63</td>
<td>16.72</td>
<td>1.61</td>
<td>9.44 ± 0.62</td>
<td>44.42</td>
<td>8.1 ± 0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Ebshway Drain</td>
<td>3.98</td>
<td>28.23</td>
<td>1.22</td>
<td>7.94 ± 0.32</td>
<td>23.96</td>
<td>9.25 ± 0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Tala Drain</td>
<td>3.61</td>
<td>28.59</td>
<td>2.46</td>
<td>11.84 ± 0.7</td>
<td>17.45</td>
<td>9.67 ± 0.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>Ebyar Drain</td>
<td>4.90</td>
<td>32.08</td>
<td>6.24</td>
<td>10.6 ± 0.63</td>
<td>2.30</td>
<td>16.38 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Qotor Big Drain</td>
<td>3.93</td>
<td>29.02</td>
<td>5.56</td>
<td>8.35 ± 0.25</td>
<td>8.87</td>
<td>13.5 ± 0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Seperpay Drain</td>
<td>2.19</td>
<td>23.39</td>
<td>35.01</td>
<td>5.48 ± 0.48</td>
<td>3.13</td>
<td>17.11 ± 0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>El-Gharbia Main Drain</td>
<td>5.66</td>
<td>35.90</td>
<td>17.48</td>
<td>5.54 ± 0.49</td>
<td>2.05</td>
<td>21.8 ± 0.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 10:** Areal distribution of NH₄⁺ conc. in mg/L for groundwater samples

**Figure 11:** Areal distribution of δ¹⁵N-NH₄⁺ values for groundwater samples

**Table 3:** Stable Isotopes and Ammonium and Nitrate Concentrations of Surface Water Samples
<table>
<thead>
<tr>
<th>No.</th>
<th>Drain Type</th>
<th>NH₄⁺ (mg/L)</th>
<th>NO₃ (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>No.5 Drain</td>
<td>4.15</td>
<td>36.40</td>
<td>6.86</td>
<td>4.8 ± 0.68</td>
</tr>
<tr>
<td>43</td>
<td>Tile Drain</td>
<td>3.54</td>
<td>29.09</td>
<td>0.66</td>
<td>---</td>
</tr>
<tr>
<td>44</td>
<td>Mehalat Roh Drain</td>
<td>3.30</td>
<td>25.69</td>
<td>7.53</td>
<td>6.62 ± 0.85</td>
</tr>
<tr>
<td>45</td>
<td>Zifta Drain</td>
<td>2.61</td>
<td>27.48</td>
<td>33.25</td>
<td>11.08 ± 0.9</td>
</tr>
<tr>
<td>46</td>
<td>Omar Beah Drain</td>
<td>3.73</td>
<td>33.34</td>
<td>7.02</td>
<td>5.8 ± 0.19</td>
</tr>
<tr>
<td>47</td>
<td>El-Khadrawia Drain</td>
<td>3.48</td>
<td>29.75</td>
<td>15.64</td>
<td>7.03 ± 0.83</td>
</tr>
<tr>
<td>48</td>
<td>Wasef Drain</td>
<td>3.58</td>
<td>31.45</td>
<td>1.55</td>
<td>6.43 ± 0.63</td>
</tr>
<tr>
<td>49</td>
<td>Rosetta Branch (1)</td>
<td>4.16</td>
<td>29.26</td>
<td>2.52</td>
<td>7.45 ± 0.09</td>
</tr>
<tr>
<td>50</td>
<td>Rosetta Branch (2)</td>
<td>3.82</td>
<td>30.36</td>
<td>2.62</td>
<td>7.53 ± 0.25</td>
</tr>
<tr>
<td>51</td>
<td>El-Qasid Canal</td>
<td>4.28</td>
<td>31.77</td>
<td>0.34</td>
<td>-0.32 ± 0.01</td>
</tr>
<tr>
<td>52</td>
<td>Bahr Seef</td>
<td>3.94</td>
<td>29.66</td>
<td>0.45</td>
<td>-0.42 ± 0.63</td>
</tr>
<tr>
<td>53</td>
<td>Bahr Shbin</td>
<td>3.74</td>
<td>31.14</td>
<td>0.83</td>
<td>5.0 ± 0.41</td>
</tr>
<tr>
<td>54</td>
<td>Damietta Branch (1)</td>
<td>3.89</td>
<td>29.45</td>
<td>0.70</td>
<td>1.0 ± 0.21</td>
</tr>
<tr>
<td>55</td>
<td>Mit Badr Canal</td>
<td>3.39</td>
<td>28.05</td>
<td>1.06</td>
<td>3.07 ± 0.06</td>
</tr>
<tr>
<td>56</td>
<td>EL-Rayah El-Abacy</td>
<td>3.37</td>
<td>29.17</td>
<td>0.63</td>
<td>5.79 ± 0.08</td>
</tr>
<tr>
<td>57</td>
<td>El-Qurashiya Canal</td>
<td>3.48</td>
<td>29.88</td>
<td>1.82</td>
<td>-0.38 ± 0.11</td>
</tr>
<tr>
<td>58</td>
<td>Damietta Branch (2)</td>
<td>3.41</td>
<td>28.22</td>
<td>0.41</td>
<td>0.95 ± 0.05</td>
</tr>
<tr>
<td>59</td>
<td>Tanta Navigation Canal</td>
<td>3.30</td>
<td>28.69</td>
<td>0.50</td>
<td>1.32 ± 0.25</td>
</tr>
</tbody>
</table>

**Figure 12:** Relation between δ¹⁵N-NH₄⁺ and ammonium concentrations for groundwater samples.  
**Figure 13:** Areal distribution of nitrate concentrations in mg/L for groundwater samples.  
**Figure 14:** Relation between nitrate concentration and (a) iron and (b) manganese contents for groundwater samples.
To investigate the direction of contaminant movement and its variation with time, a unit rate of ammonium concentration is assumed to be applied from a point. The injection is assumed to start at t=0 and continues indefinitely. The concentration of the contaminant at t=0 is assumed to be zero in the whole region. The simulated contaminant concentrations for the 5, 10, 15 and 20 years after injection in the fifth layer were calculated for six observation boreholes in the horizontal direction and other six boreholes in the vertical direction around the source Fig.(16). The distance between the source the boreholes in each direction are 50, 100, 150m respectively. The relations between relative concentration and time measured from boreholes are shown in Figs (17.a and b). The calculated concentration in boreholes no. 1 and 10 which lie only 50m west and north of the injection point increase to 7.66*10^{-3} and 7.07*10^{-3} respectively after 360 days, and reach the maximum relative concentration of 28*10^{-3} and 26.14*10^{-3} respectively after 2160 days (6 years). The analysis of the figures leads to the conclusion that most of the contaminant flows towards the northern-west direction. This results show that the hydraulic properties and gradient play the major role on the contaminant transport direction.

Figure 15: Relation between δ¹⁵N-NO₃ and (a) nitrate concentrations and (b) ln NO₃ for groundwater samples.

Figure 16: Variation of relative concentration around the source.

Figure 17: Positions of the unit source and the considered boreholes around it.
9 SCENARIOS FOR GROUNDWATER REMEDIATION

A management scenario is suggested to clean up the aquifer at Birma region from ammonium contamination. The suggested scenario is to use eight extraction wells to pump the contaminated groundwater out of the aquifer for treatment. The locations of wells are chosen as a diagonal shape toward the northern-west direction, as shown in Fig. (18), according to the flow direction of contaminant. The measured ammonium concentrations by hydrochemical analyses are used as the initial condition for the transport model. Prior to running the transport model, 25 observation boreholes are defined, for which the concentration-time relation can be calculated. The position of these boreholes are chosen irregularly to cover all Birma region. They are illustrated in Fig.(19). The proposed total extraction rate for the eight wells is 800 m$^3$/day (100 m$^3$/day for each well), all from layer five. The final groundwater levels after the simulation period of 7200 days (20 years) and the direction of flow are illustrated in Fig.(19). The transport model simulation results are presented in Figs.(20a, b, c and d), which illustrate the contour lines of ammonium concentrations obtained every five years through the simulation period of 20 years.
CONCLUSIONS

The groundwater in the studied area is quite vulnerable to pollution; deterioration of groundwater indicates clearly that the human activities caused serious pollution problems. The nitrate concentrations have clear mounts within the area except the north eastern part of the studied area. Ammonium concentrations of groundwater reached an alarming level and exceeded the drinking water standards (0.5 mg/L). The high concentrations are around Birma village at the central part of the studied area and at the north eastern region with concentration gradient increases toward the north boundary outside the area of study. The potential sources of nitrogen compound pollution are: water from sewage treatment plant used for irrigation, sludge and animal manure, septic tanks, soil nitrogen, and artificial fertilizers.

The analysis of the results leads to the conclusion that most of the contaminant flows towards the northern-west direction. The results assign that the hydraulic properties and gradient play the major role on the contaminant transport direction. Stable isotopes of oxygen ($\delta^{18}$O) and hydrogen ($\delta$D) were used in this study to determine the origin of water and to characterize possible mixing of different water sources of water in the Quaternary aquifer. Nitrogen-15 approach achieved the main goal of identifying the potential sources of nitrogen compound contamination at different locations in the studied area. In this respect, nitrogen isotope ratios ($\delta^{15}$N) in conjunction with hydrological data and water chemistry were used to help elucidate the sources and fate of ammonium (NH$_4^+$) and nitrate (NO$_3^-$) in the Middle Delta region, Egypt. MODFLOW and MT3DMS codes are employed for solving the 3-D polluted groundwater problem in the study area and for predicting the concentration of pollution at several time intervals. In the present study, MT3DMS was utilized to simulate ammonium contaminant variation in Birma region. Three verifications for modelling codes are performed and good agreements between results of present study and previous studies are attained. A unit rate of ammonium concentration is assumed to be applied from a point. The injection is assumed to start at $t=0$ and continues indefinitely. The concentration of the contaminant at $t=0$ is assumed to be zero in the whole region. The simulated contaminant concentrations for the 5, 10, 15 and 20 years after injection are presented.

The $\delta^{15}$N results indicated that the relatively depleted $\delta^{15}$N-NH$_4^+$ values ($\pm 2\%$) are mainly found in the central and western part of the studied area. These areas are affected by the application of synthetic fertilizers. By contrast, the north and south-eastern areas have $\delta^{15}$N-NH$_4^+$ values $>+4\%$ indicating soil organic nitrogen or mixing with raw sewage (untreated domestic effluents) injected in the aquifer, particularly in the populated zones. The inverse correlation between nitrate concentrations and $\delta^{15}$N-NO$_3^-$ values indicates that a clear redox barrier is present in the north-eastern area, accompanied by the appearance of Mn$^{2+}$ and Fe$^{2+}$ ions and disappearance of nitrate, with a very distinct enrichment in $\delta^{15}$N ($\delta^{15}$N-NO$_3^->+20\%$) of the remaining NO$_3^-$ (denitrification process).
A mitigation scenario is suggested to clean up the Birma region. The remediation scheme assumes dewatering system through eight extraction wells to pump the contaminated groundwater out of the aquifer for treatment. The locations of wells were chosen toward the flow direction of contaminant. The procedure of solution proved to be efficient in minimizing groundwater pollution. Moreover, it proved to be applicable and can be generalized for a wide class of regions that suffer from groundwater contamination phenomenon.

REFERENCES


RIGW/IWACO, (1990): "Development and Management of Groundwater Resources in
the Nile Valley and Delta: Assessment of Groundwater Pollution from Agricultural Activities". Research Institute for Groundwater, Kanater El-Khairia, Egypt.


