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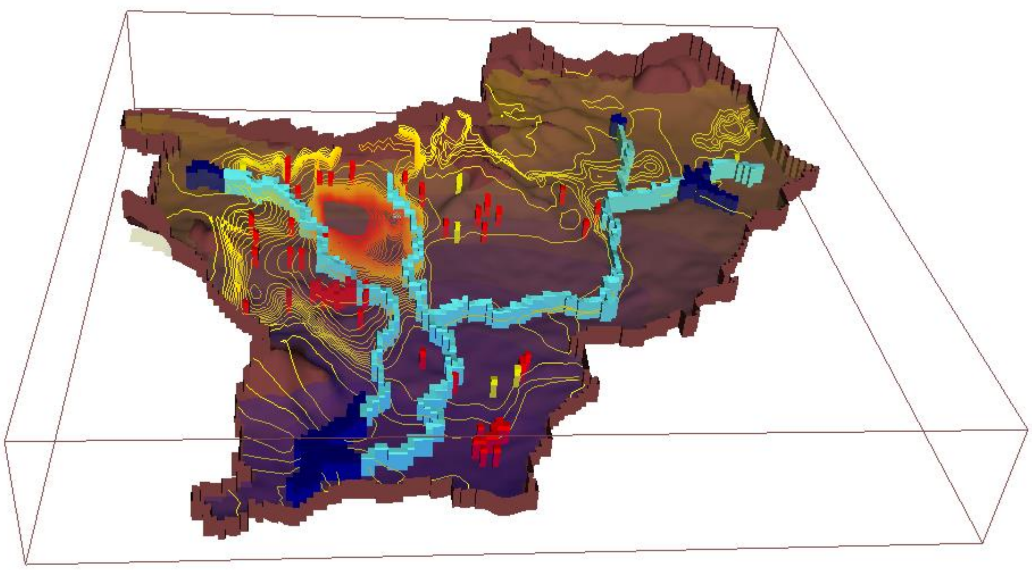
Numerical Groundwater Flow and Nitrate Transport Modeling for the Prediction of Impacts of Land Use Changes on Water Quality in Akaki Catchment



A Thesis Submitted to the School of Earth Sciences of Addis Ababa University in Partial Fulfilment of the Requirements for the Degree of Master of Science in Environmental Geology

By:
Kassa Aynalem
Advisor: Seifu K. (PhD)

June, 2015
Ethiopia

ADDIS ABABA UNIVERSITY

SCHOOL OF EARTH SCIENCES

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By:

Kassa Aynalem

Approved by Board of Examiners:

Seifu Kebede (PhD) ______________________________________

Chairman, School of Earth Sciences

Advisor:

Seifu Kebede (PhD) ______________________________________

School of Earth Sciences

Examiners:

Dessie Nadew (PhD) ______________________________________

School of Earth Sciences

Worash Getaneh (PhD) ______________________________________

School of Earth Sciences

June, 2015

Ethiopia

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Let glory and thanks be to God for He has always been with me and has removed all my sicknesses in all my days! I got no words to thank you Mom. You are the best of a woman. Thank you!!

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Finally, I want to tell my friends Yehualshet Tadesse, Gebru Hadush and Lamesgin Melese my feelings of blessedness to have you all. Thank you for sharing my load in all the study time.

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Acronyms and Abbreviations

AAWSA:	Addis Ababa Water Sewerage Authority
ADE:	Advective Dispersive Equation
AME:	Absolute Mean Error
CSA:	Central Statistical Agency
DEM:	Digital Elevation Model
EC:	Electrical Conductivity
Fig. :	Figure
ITCZ:	Inter-Tropical Convergence Zone
LULC:	Land Use/Land Cover
m, mm:	Meter, Milimeter
m.a.s.l.:	Meters Above Sea Level
m^3/l:	meter cube per Liter
ME:	Mean Error
MER:	Main Ethiopian Rift
mg/l:	milligram/Liter
MT3DMS:	Multi Species Three Dimensional Mass Transport
NE, NW, SE, SW:	North-East, North-West, South-East, South-West
OC:	Organic Carbon
RMSE:	Root -Mean-Squared Error
TDS:	Total Dissolved Solute
USGS:	United States Geological Survey
UTME:	Universal Transverse Mercator East
UTMN:	Universal Transverse Mercator North
WHO:	World Heath Organizations

Abstract

Water is one of the most valuable resources that mankind needs for survival. One source of this precious resource is the groundwater, water beneath the surface. This resource is being contaminated by numerous organic and inorganic pollutants in the current study area. Thus, there is an urgent need to intensive investigations. Groundwater and contaminant transport modeling practices are one of the most powerful tools in groundwater studies. The present study has mainly performed a numerical advective-dispersive-reactive phenomenon of nitrate transport modeling to showing the effect of land use types and changes on groundwater quality by using a software called MODFLOW/MT3DMS. Primary and secondary data were collected from different sources. This modeling process has two independent but complementary modeling activities; the groundwater and contaminant transport process, the former being a precondition for the latter. Accordingly, the groundwater calibration process has produced a very cloth values between the observed and calculated values and statistically the ME, AME, and RMSE were found to be 7.6, 11.01 and 12.7 respectively. The groundwater modeling results shows that the maximum and minimum head values were 2729 and 1970 m.a.s.l. in the north and south ends respectively. Thus, groundwater flows north–south direction. The water balance of the model shows that a total volume of 665280 m^3 water flows in the groundwater system in a day. Moreover, a very high groundwater-surfacewater interaction was observed. The model was very sensitive for hydraulic conductivity and recharge values.

The calibration process for the contaminant transport process was done in two fold; one calibration for time series data and calibration for 10 and 20 mg/l observed and calculated contour comparison. The former was done for 5 wells of 5 year time series data. Accordingly, the ME, AME, RMSE of the differences of these wells in the whole calibration time (5 years) was found to be 0.019, 0.6833 and 0.8760 respectively. The 10 and 20 mg/l contours produced for model simulated and observed nitrate concentration map has found to be visually similar; and the difference between areas covered with these contours of simulated and observed concentrations were very minimal. The general contaminant transport model result shows that the highly polluted areas were very populated built areas (from pit latrine and poor sewerage system) and these points were able to generate a huge mass of nitrate plume. There were 4 hotspot areas identified where nitrates migrates from. Nitrate migrates in all directions from these hotspots and advective transport mechanism were found to be the dominant one while dispersive and diffusive type migration were very significant. The temporal aspect of this model shows that more wells will be polluted as time increases even future nitrate loading is stopped. Spatially, Wells towards Gefersa were found to be very susceptible due to their proximity to the main plume center from the diffusive migration of nitrate. Wells towards Legedadi were the less vulnerable one due to their distance from the main plume center and relative position. But, these wells were endangered due to the new habilitation activities. Wells towards Akaki were found to be safe in the short term but very extremely vulnerable in the future. The scenario analysis part shows that about 9, 16 and 18 wells (out of 45 major wells) will exceed the WHO drinking water standard limit of nitrate concentration (50 mg/l) in the coming 25, 37 and 50 year if everything is kept constant. Further population increment with in the current land use will force other wells to exceed the drinking water standard. Distributing the upcoming population increment to the whole catchment will minimize the effect on the currently susceptible wells. There is less option of reducing the imminent impacts caused by the already contaminated water. In recommendation, it would be possible to minimize future nitrate loading by upgrading these infrastructures for already built area and setting a very tight structures to newly emerging villages.

Key Words: MODFLOWMT3DMS, Contaminant transport, Flow Modeling, Groundwater Contamination, Effect of Population, Addis Ababa

1. Introduction

1.1. Background

Water, the color less liquid made of Hydrogen and Oxygen atoms, is a very precious resource that enables the earth to support life that in turn makes the earth to be unique of all other planet. The use and value of water could simply be recognized by everyone and this has been summarized in many instances by saying 'water is life'. Derived from its physicochemical properties, the role of water in many human activities including agriculture, industry, domestic uses, power generation, transport and recreation makes it priceless commodity (Shilima Abebe, 2011).

Proper utilization of the groundwater, the water beneath the surface of the earth, becomes increasingly more important all over the world as a sustainable method managing water resources (Foster et al., 2003) and it is important source of water for over 25 cities in Ethiopia including the present study area Addis Ababa (Jemal Seid, 2009). This shift to groundwater resource, specific to the current study area, emanates from the rapid population growth and urbanization and their associated demand for domestic and industrial activities leading to the shortage of water from surface fresh water sources (Alema Tesfaye, 2009).

The capital of Ethiopia, the city of Addis Ababa, depends on the Akaki catchment for its entire water supply to its dwellers; tapping both surface and groundwater sources (Demlie and Wohnlich, 2006) and the groundwater contributes beyond 30% of the total (AAWSA, 2000). Very importantly than other cities of the country, due to the exponential population growth, urbanization (Alemayehu et.al., 2009) and the associated industrialization without adequate water supply and waste disposal facilities (Gizaw, 2002 in Demlie and Wohnlich, 2006) both the surface and subsurface water resources have been severely polluted with organic and inorganic contaminants.

The contamination of groundwater is very complex and it arises from the use of chemical products like detergents, fertilizers, pesticides, herbicides etc., improper disposal of large volume of liquid and solid wastes and limitedly from the natural geology of the site. In every study being conducted in Akaki catchment new sort of pollution are being recognized. Contaminants, being knowingly disposed or accidentally spilled or of also applied to agricultural purpose, are gradually reaching the groundwater table. This contamination poses a serious health problem to the community (Jemal Seid, 2009). Thus, the need for better management of the groundwater resource is crucial.

The wise management of groundwater resources contamination requires an understanding of the subsurface components and their interaction with each other i.e. the geology, the liquid (water in case), the contaminant and the physio-biogeochemical processes taking place in the system.

Numerical groundwater flow (Ayenew et.al., 2008; Jemal Seid, 2009) and contaminants transport (Alema Tesfaye, 2009; Jemal Seid, 2009; Gudissa, 2010) has played an important role in managing groundwater resources by predicting changes and indicating alternative means and remedial measures. This would help in sustaining the resource and keeping the community health safe (Gudissa, 2010).

MODFLOW with its groundwater and contaminant transport modeling package could effectively simulate the groundwater movement and contaminant transport process both in space and time (Zheng and Wang, 1999; Zheng et.al., 2010; Harbaugh et.al., 2000).

1.2. Statement of the Problem

Everyone would approve the importance of water. One of the sources of this vital resource is the groundwater. In the study area, groundwater is being contaminated by numerous organic and inorganic pollutants and the availability of new contaminants or increasing in concentration of the already determined ones has found to be decisive, as discussed above. Future population growth and industrialization would make the case more pressing (Alema Tesfaye, 2009).

Nitrate is the most common form of inorganic nitrogen and it is also the most dominant substance in our environment. It usually enters the groundwater from various point and non-point sources such as sewage, industry, animal waste and fertilizers. Due to these facts groundwater contamination with nitrate is most studied phenomenon worldwide (Ahmed, 2004) and in the study area (e.g. Ferezer Eshetu, 2012). Yet nitrate is important for plant growth and human health (Addiscot, 2005), the excessive presence of this compound in groundwater has the reverse sever health problem (Ferezer Eshetu, 2012) including blue baby syndrome (Avery, 1999), chronic toxicity and cancer (Kensington et.al. 2003). The concentration of nitrate ranges from 0.04-241 mg/l which could possibly considered as sever and determined to exceed its World Heath Organizations (WHO) maximum limit of 50mg/l in some parts of the catchment (Girmay Kahssay et.al, 2010). Now, it is clear that management is critical. To manage these like problems, the understanding of primarily the groundwater movement and then the contaminant transport process is very important. Different methods are available to do so. Numerical groundwater and contaminant transport modeling have been utilized as a popular methods of determination of head of groundwater and fate of contaminants worldwide (Batu, 2005; Bear and Cheng, 2010). Such few modeling efforts have been done for conservative (chloride and fluoride) using MATLAB by Jemal (2009); particle tracking using PMPATH (a MODFLOW package) by Alema Tesfaye (2009) and Gudissa, (2010). Further, more general aquifer vulnerability assessment has been made by AAWSA et.al. (2000), Tenalem Ayenew et.al. (2001) and Dereje Nigussa (2003) and only groundwater flow modeling by Ayenew et.al. (2008). In the study area, yet there has been identified significant nitrate contamination, the transport process has never been modeled in the level needed. Previous works have modeled only the advective aspect of contaminant transport which could only show the effect of moving water in the direction it flows under conservative condition. But, contaminant transport process are by far very complicated than such conceptualization. There are additional processes like dispersive and diffusive transport processes and complication through chemical reaction with available other chemical species. The representation of such phenomena of transport in modeling process will make the estimation more realistic and accurate. Thus, the present study has modeled an advective-dispersive-reactive phenomenon of nitrate transport in Akaki catchment with an intension of showing the effect of land use types and changes using MODFLOW/MT3DMS (a software developed by United States Geological Survey (USGS)), in a steady state groundwater flow condition. More to show the realistic conditions of contaminant migration in time and space, this work has also show the applicability of the numerical methods of contaminant transport computation which have been found less successful (Batu, 2005) in field conditions.

1.3. Objective

General objective:

The general objective of the study is to perform an advective-dispersive-reactive nitrate transport modeling in Akaki catchment using MODFLOW/MT3DMS.

Specific objectives:

The specific objectives are:

- To identify nitrate contamination sources, representing current nitrate distribution map and estimating the groundwater nitrate loading rate of the catchment,
- To develop a conceptual and then numerical model for the groundwater flow and nitrate transport processes in the groundwater system of Akaki catchment that enable the visualization of the effect of land use type and changes on groundwater quality; there by showing the relevance of numerical contaminant transport computational methods, and
- To predict movement and concentration of nitrate over time and space for different scenarios; thus, it would be possible to determine when the concentration will exceed drinking water quality standards, if not so far exceeding.

2. Literature Review

2.1. Transport Phenomena

2.1.1. Advection

Advection refers to the contaminant movement by the force of flowing water in which its movement is expressed by the Darcy's velocity (Fig. 1 (a)); thus, when only advection is considered, a contaminant moves as fast as groundwater and therefore there is no attenuation in the concentration of the solute considered (Jemal Seid, 2009). The mass flux equation is therefore (Batu, 2005):

$$\boldsymbol{F_{x_{adv}}} = \boldsymbol{v_x \varphi_e C} = \boldsymbol{q_s C} \quad \text{....... Equation 1}$$

Where:

$\boldsymbol{F_{x\ adv}}$ *is mass of solute per unit cross sectional area transported in the x direction perunit area*

$\boldsymbol{v_x}$ *is the Darcy velocity in the same direction*

$\boldsymbol{\varphi_e}$ *is effective porosity*

$\boldsymbol{C}$ *is the* initial concentration of the solute

$\boldsymbol{q_s}$ *the groundwater velocity or pore water velocity*

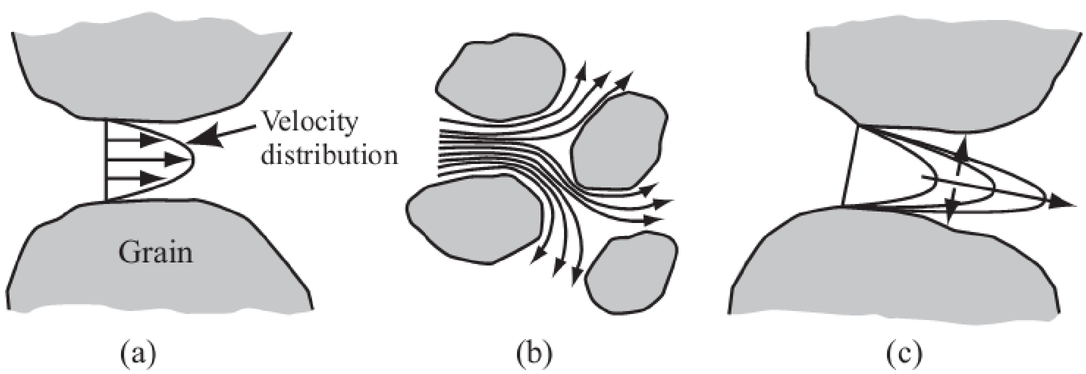

Fig. 1 **(a)** Advective migration **(b)** Dispersive **(c)** Diffusive migrations (From Bear and Cheng, 2010)

2.1.2. Diffusion

Diffusion expresses the migration of molecules from zones of high concentration to zones of lower concentration (Fig. 1 (c)), which is represented by Fick's law of diffusion (Equation 2, Fig. 2); which is modified for saturated porous media as in Equation 3 and it occurs even when the fluid is at rest (Fried and Combarnous, 1971-as cited in Batu, 2005).

$$F_{x_{diff}} = -D^* \frac{\partial C}{\partial x} \quad \text{................ Equation 2}$$

$$F_{x_{diff}} = -\varphi_e D^* \frac{\partial C}{\partial x} \quad \text{............... Equation 3}$$

Where:

$F_{x_{diff}}$ *is mass flux per unit time per unit area*
D^{*} *is the effective molecular diffusion coefficient*
$\frac{\partial C}{\partial s}$ *is concentration gradient*
x *is the distance*
φ_e *is the effective porosity*

The negative signs in the above equations indicate that solute migration is in the direction of decreasing concentration.

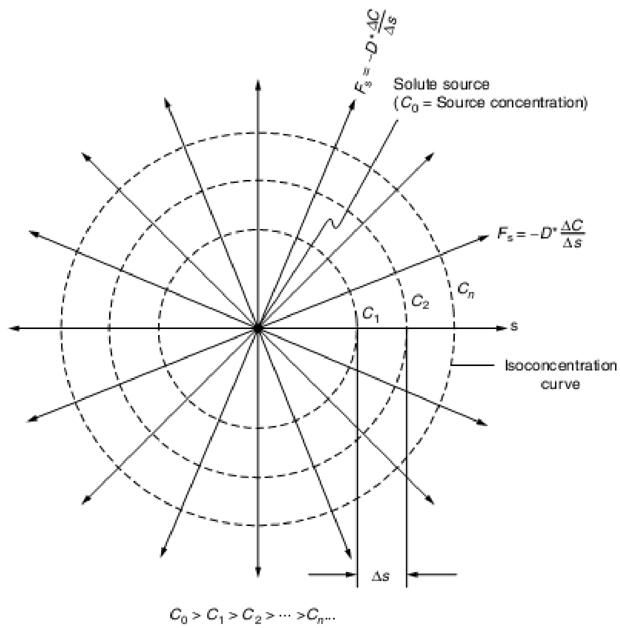

Fig. 2 Solute source in a stagnant liquid and schematic representation of Fick's first law (Adopted from Batu, 2005)

2.1.3. Dispersion

Dispersion is another term which tries to include the retarding effect of irregular shapes of grains and pores, local fluid velocities inside individual pores which in real situation make it to deviate from the average pore velocity (Fig. 1 (b)). These processes created a mixing process that is macroscopically similar to mixing caused by the diffusive transport (Equation 4).

$F_{x_{disp}} = -\varphi_e D_m{}^{*} \frac{\partial C}{\partial x}$, ……….. Equation 4

Where: Fs_{disp} *is mass flux per unit time per unit area and Dm is mechanical dispersion coefficient*

2.1.4. Reaction/Transformation

Sorption

Sorption, a term used to represent adsorption and desorption, refers to the exchange of molecules and ions between the liquid and solid phase of the groundwater system. The first represents to the transfer of solute constituent from the liquid to the solid matrix and it results an attenuation in solute concentration of the water; and, on the other hand, desorption expresses the reverse process in which solute molecules sorbed to a solid phase may be released back into solution as a result of changes in system conditions (Batu, 2005; Jemal Seid, 2009). To represent the amount of solute in the liquid and solid phase a graphical relationship is produced commonly stated as ***sorption isotherm*** which could be found by either of the following equations; Linear Sorption Isotherm assuming the sorbed concentration C is directly proportional to the dissolved concentration (equation 5), Freundlich isotherm (nonlinear equilibrium) (equation 6) and Langmuir isotherm (nonlinear, equilibrium) (equation 7) (Simcore Software, 2012; Batu, 2005; Bear and Cheng , 2010).

$$F = K_d C \qquad \text{……..equation 5}$$

$$F = bc^m \qquad \text{……..equation 6}$$

$$F = \frac{K_3 c}{1+K_4 c} \qquad \text{……..equation 7}$$

Where:

F is the concentration of the solute in the solid phase
C is the concentration of the solute in the liquid phase
Kd is distribution coefficient (the affinity of the species for the solid) in the linear isoterm
b, m are constant coefficients (functions of temperature) in the Freundlich isotherm
k3, k4, are constant coefficients in the Langmuir isotherm.

Decay/ Biological Degradation

Decay reactions of the contaminants that are relatively slow in comparison to the average travel time are able to induce a decrease over time in the solute mass. The reactions of the first-order kinetics due to radioactive decay or biodegradation follow the relationship (Spitz and Moreno, 1996; Ahmed, 2004; Bear and Cheng , 2010; Anserson and Woassner, 1992):

$$\frac{\partial c}{\partial t} = \lambda \boldsymbol{c} \qquad \text{……… Equation 8}$$

Where **λ** is the rate coefficient of biodegradation or decay and is defined by:

$$\lambda = \frac{ln2}{T_{1/2}} \qquad \text{……….. Equation 9}$$

Where **T** ½ is the half-life of the radioactive isotopes or the degraded contaminant.

2.2. Derivation of the Advective Dispersive Equation (ADE)

As per the mass balance rule,

$$I - O = \Delta \qquad \text{.......... Equation 10}$$

Where, I is the incoming flux, O is the outgoing flux and Δ is the change in storage.

Then,

$$\Delta = \frac{\partial C_T}{\partial t} \qquad \text{.......... Equation 11}$$

The three dimensional (in the x, y and z coordinates) mass flux could be expressed as

$$-\left(\frac{\partial F}{\partial x} + \frac{\partial F}{\partial y} + \frac{\partial F}{\partial z}\right) = \frac{\partial S}{\partial t} \qquad \text{.......... Equation 12}$$

(The minus sign indicates that mass moves from high to low concentration)

Where F is the total mass flux in each direction and S is the net mass storage in a unit volume of a porous medium.

Combining Equation 11 and Equation 12 we have Equation 13 for one dimensional migration:

$$\Delta = \frac{\partial C_T}{\partial t} = \frac{\partial F}{\partial x} \qquad \text{.......... Equation 13}$$

Where C_T is the total mass flux.

This total mass flux (F) is the sum of all transport phenomena, thus:

$$\boldsymbol{F} = F_{adv} + F_{diff} + F_{disp} = v_x \varphi_e C - \varphi_e D^* \frac{\partial C}{\partial x} - \varphi_e {D_m}^* \frac{\partial C}{\partial x} \qquad \text{.......... Equation 14}$$

By bringing the concept of hydrodynamic dispersion (D), which is the sum of diffusion and mechanical dispersion, we can rewrite equation 14 as:

$$\boldsymbol{F} = v_x \varphi_e C - \varphi_e D_H \frac{\partial C}{\partial x} \qquad \text{.......... Equation 16}$$

Substituting Equation *16 to Equation 11 we have:*

$$\frac{\partial C_T}{\partial t} = \frac{\partial}{\partial x}\left(\boldsymbol{v_x \varphi_e C - \varphi_e D_H \frac{\partial C}{\partial x}}\right) \qquad \text{.......... Equation17}$$

The total mass flux is the sum of the dissolved solute in the solvent and the solute adsorbed to the soil matrix, therefore we have:

$$\boldsymbol{C_T = \rho_b C_s + \varphi_e C_w} \qquad \text{.......... Equation 18}$$

, where C_s and C_w are the concentration in soil matrix and water respectively.

Substituting this in to equation 17 we have:

$$\frac{\partial}{\partial t}(\boldsymbol{\rho_b C_s + \varphi_e C_w}) = -\frac{\partial}{\partial x}\left(\boldsymbol{v_x \varphi_e C - \varphi_e D_H \frac{\partial C}{\partial x}}\right) \qquad \text{........... Equation 19}$$

And, $\boldsymbol{K_d = \frac{C_s}{C_w}}$, ... Equation 20

Where K_d is the sorption coefficient.

Then, $\boldsymbol{C_s = K_d * C_w}$ .... Equation 21

By assigning $\boldsymbol{C_w}$ to be simply C and calling the common C out of the bracket *Equation 19 will be:*

$$\frac{\partial C}{\partial t}(\rho_b K_d + \varphi_e) = -\frac{\partial}{\partial x}\left(v_x \varphi_e C - \varphi_e D_H \frac{\partial C}{\partial x}\right) \quad \text{........... Equation 22}$$

Divide both side by $\boldsymbol{\rho_b K_d + \varphi_e}$ *and simplified it we have:*

$$\frac{\partial C}{\partial t} = -\left(\frac{\partial C}{\partial x}\right)\frac{v_x}{\frac{\rho_b K_d + \varphi_e}{\varphi_e}} + \frac{D_H}{\frac{\rho_b K_d + \varphi_e}{\varphi_e}}\left(\frac{\partial^2 C}{\partial x^2}\right) \quad \text{........... Equation 23}$$

Then $\boldsymbol{R_d = \frac{\rho_b K_d + \varphi_e}{\varphi_e}}$ .... Equation 24

For 1 dimension transport, therefore we can have:

$$\frac{\partial C}{\partial t} = -\left(\frac{\partial C}{\partial x}\right)\frac{v_x}{R_d} + \frac{D_H}{R_d}\left(\frac{\partial^2 C}{\partial x^2}\right) \quad \text{........... Equation 25}$$

Then,

$$R_d \frac{\partial C}{\partial t} = -\left(\frac{\partial C}{\partial x}\right) v_x + D_H\left(\frac{\partial^2 C}{\partial x^2}\right) \quad \text{........... Equation 26}$$

The three dimensional expanded form of this equation in Cartesian notation for heterogonous anisotropic medium without sink and source terms is then:

$$\frac{\partial}{\partial x}\left(\varphi_e D_{H_{xx}}\frac{\partial C}{\partial x} + D_{H_{xy}}\frac{\partial C}{\partial y} + D_{H_{xz}}\frac{\partial C}{\partial z}\right) + \frac{\partial}{\partial y}\left(\varphi_e D_{H_{xx}}\frac{\partial C}{\partial x} + D_{H_{xy}}\frac{\partial C}{\partial y} + D_{H_{xz}}\frac{\partial C}{\partial z}\right) + \frac{\partial}{\partial z}\left(\varphi_e D_{H_{xx}}\frac{\partial C}{\partial x} + D_{H_{xy}}\frac{\partial C}{\partial y} + D_{H_{xz}}\frac{\partial C}{\partial z}\right) - \frac{\partial}{\partial x}\left(CK_{xx}\frac{\partial h}{\partial x}\right) - \frac{\partial}{\partial y}\left(CK_{yy}\frac{\partial h}{\partial y}\right) - \frac{\partial}{\partial z}\left(CK_{zz}\frac{\partial h}{\partial z}\right) = R_d\frac{\partial(C\varphi_e)}{\partial t}$$

.... Equation 27

Finally, the *governing contaminant transport equation* for heterogonous anisotropic media with sink and source terms is:

$$\frac{\partial}{\partial x}\left(\varphi_e D_{H_{xx}}\frac{\partial C}{\partial x} + D_{H_{xy}}\frac{\partial C}{\partial y} + D_{H_{xz}}\frac{\partial C}{\partial z}\right) + \frac{\partial}{\partial y}\left(\varphi_e D_{H_{xx}}\frac{\partial C}{\partial x} + D_{H_{xy}}\frac{\partial C}{\partial y} + D_{H_{xz}}\frac{\partial C}{\partial z}\right) + \frac{\partial}{\partial z}\left(\varphi_e D_{H_{xx}}\frac{\partial C}{\partial x} + D_{H_{xy}}\frac{\partial C}{\partial y} + D_{H_{xz}}\frac{\partial C}{\partial z}\right) - \frac{\partial}{\partial x}\left(CK_{xx}\frac{\partial h}{\partial x}\right) - \frac{\partial}{\partial y}\left(CK_{yy}\frac{\partial h}{\partial y}\right) - \frac{\partial}{\partial z}\left(CK_{zz}\frac{\partial h}{\partial z}\right) = R_d\frac{\partial(C\varphi_e)}{\partial t} - \varphi_e v R_d C + C'W^+ + CW^+$$

.... Equation 28

2.3. Possibilities of Groundwater Contamination in Akaki Catchment

Nitrate concentration in groundwater is a function of various interrelated and complex physical, chemical, and biological factors which their combination creates spatial and temporal variability; making modeling process quite difficult. Land use types, on-ground nitrogen loading, groundwater recharge, soil characteristics, transport processes in un-saturated and saturated zones, and bacterial effects are the important ones (Almasri and Ghabayen, 2008; Alagha and Mogheir, 2013).

Akaki catchment is an area where several land use types are found in which all area assumed to be potential sources of groundwater pollution. Here below, the possibilities in which Akaki catchment could be contaminated with pollutants, collected form the literature are discussed:

a. The weathered rocks of the area and associated structures and their orientation would facilitate contaminant migration (Gudissa, 2010).
b. Yet the black cotton soils are assumed to attenuate contaminant, contaminants may move down with infiltrating water during the rainy season through the cracks formed in the previous dry season. Specifically, nitrate could also not be sorbed to these black cotton soils (see part 3.3.4.4., sorption)
c. The pit latrine dug meters down to the ground may facilitate the movement of nitrate and other contaminants to join the groundwater, as in Girmay Kahssay et.al. (2010).
d. High recharge areas and areas with gentle slopes like the well field are highly vulnerable to groundwater contamination (Tenalem Ayenew, 2001; Dereje Nigussa, 2003; Gudissa, 2010).
e. Pollution from surface water bodies is significant. Akaki rivers (both little and great Akaki) have been reported to be severely polluted (Gebre and Van Rooijen, 2009; Demlie and Wohnlich, 2006); and these water bodies have found to be hydrologically connected to the groundwater (Ayenew et.al., 2008; Tenalem Ayenew, 2001; AAWSA, 2000).

Thus, pollution of surface water can cause degradation of groundwater quality and conversely pollution of groundwater can degrade surface water. This type of pollution could be explained by the following scenarios:

☞ **When water bodies become loosing stream**

Surface water bodies, for example, Akaki River may temporarily become a losing stream, in time when there is increased pumping rate on the groundwater. Here, water could directly move to the groundwater due to the reversed groundwater table, even at present pumping rate (Demlie et.al. 2007b). Example, for Akaki river groundwater level is lower than the river bed level from Akaki Bridge up to Aba Samuel hydropower plant (AAWSA et. al. 2000).

☞ **When water bodies are neither loosing nor gaining streams**

In hydrologic terms, under this condition there will not be net flux of water to either of the components. But, due to the presence of diffusion under rest condition for contaminants (Batu, 2005), a net movement of contaminants is expected. Example, water table and the surface water coincide around Kality (Berhanu Gizaw, 2002).

- **When water bodies are gaining streams**
  Under this condition there is a net gain of water to surface water bodies but the migration of contaminant due to the scientific fact that diffusion will happen even in the opposite direction of flow direction at the top and transverse (vertical and horizontal) at the bottom of the water bodies.

Validating the above possibilities, the level of nitrate contamination in minor aquifers (Fig. 7) is observed to be above permissible limits; as high as 112 mg/L have been observed for minor and values as high as 24 mg/L have been observed for major aquifers (Fig. 7) (Girmay Kahssay et.al., 2010). High pH, EC, TDS, and total coliform concentration in the groundwater was listed as reflectors of the influence imposed by polluted surface water seepage to the groundwater system (Gudissa, 2010). Demlie and Wohnlich (2006), have presented the presence of significant nitrate and chloride concentration as an indicator for anthropogenic pollution in Akaki catchment. Tamiru et.al. (2005) the excessive presence of abundant chloride levels in groundwater was proposed to be used as indicators of sewage contamination of the sub-surface water. Molla, (2007), WWDSE (2007), Yirga (2008) and Birhanu (2002)-as cited in Girmay Kahssay et.al., (2010), has also magnified the possibilities in which Akaki catchment water bodies could be contaminated from wastes of the town.

Keeping the above points as means in which nitrate could contaminate the groundwater, here below, sources of nitrate pollution for an aquifer viewed from the point of the study area are discussed briefly.

2.4. Source of Nitrate Contamination in Akaki Catchment

The possible sources of contamination (any contaminant) for the study area have been listed by Gudissa, (2010) as steel, pulp, paper, pigments, caustic soda paint, pump, brewing, textile, food processing, and meat packing factories; dairy farms, open - air slaughtering, quarries, agricultural plots, grave yards, dense settlements, and open market areas.

Specific for sources of nitrate contamination the following potential sources from the literature are compared to the real site condition.

2.4.1. Geological Nitrate

The aquifer geological formation can be one of the significant sources of nitrate to groundwater. But this type of contamination happens to specific types of geologic formations. Usually, the presence of nitrogen in geology is associated with presence of organic matter in sedimentary rocks. Rodvang and Simpkins, (2001)-cited in Buss et.al (2005), have found that organic matter-rich sediments contain relatively high concentrations of organically bound nitrogen, which is mineralized to ammonium as the sediment undergoes diagenesis to form a sedimentary rock. As have been discussed earlier the geologic formation of Akaki catchment has defined to be volcanic and no report has stated the presence of geologic nitrate in this catchment. In this circumstance it would not be sound to consider nitrogen loading in groundwater from the geology.

2.4.2. Atmospheric Deposition

In the atmosphere, nitrogen originates from a variety of natural and anthropogenic sources. HNO_3 created from nitrogen gas and water vapor by lightning, and natural ammonia emissions from rotting vegetation and manure have been mentioned to be among the natural sources of atmospheric nitrogen while the anthropogenic sources include nitrogen oxides (NOX) from the combustion of fossil fuels, industrial emissions and ammonia volatilization from manure stores (ITRC, 2000).

Regardless of the possibilities, in the study area the measured nitrate values shows 0.00 mg/l. Thus, the concentration of recharge water was taken to be 0.00.

2.4.3. Fertilizers

Nitrogen is the most common element used as a fertilizer supplement for agricultural and other related activities (ITRC, 2000). Nearly 55% of the study area is covered by cropland and open (grazing) lands (Fig. 5). This class of the land use in the study area receives nitrogen from commercial and homemade fertilizers. The rich source of nitrogen from the commercial fertilizers is UREA and animal manure is commonly used as homemade fertilizer. This part of the nitrate sources is expected to be the very significant source of nitrate for the groundwater and its modeling process is described in part **3.3.4.1.**

2.4.4. Settlement and Industries

The main sources of pollutants that deteriorate the quality of water in the study area are wastes generated from households, industries, domestic activities, garages, health centers and fuel stations (Shilima Abebe, 2011).

Waste produced by humans and animals are important sources of nitrate in any area characterized by significant human or animal populations. Nitrate from human waste originates mostly from individual septic systems or municipal wastewater treatment facilities. Septic tanks, waste drainage systems, treatment sites and effluent storage areas are areas where main nitrate plume occurs (ITRC, 2000). Addis Ababa is the biggest city of the country in which over four million people are expected to be within the city daily. It is very vivid that this much population can seriously pollute the environment unless and otherwise wise decisions have been taken over. Pit latrine has been identified to be the most significant anthropogenic source of groundwater contamination by Girmay Kahssay et.al. (2010). From this result, it has been mentioned due to poor cost sanitation problems including on site sanitation and the use of unhygienic pit latrine that both of infectious disease and chemicals originating from anthropogenic activities particularly from human waste could potentially be sources of serious risks (Girmay Kahssay et.al., 2010). Moreover, Gudissa (2010), in his source of contaminant identification for travel time calculation Kality treatment plant and Mesfin Zelelew dairy farm were selected as among the main sources contaminants because of they are areas where highly polluted rivers, most sewerage lines, and sanitation systems are directed into and presence of potential leakage of pollutants from the farm like bacteria and animal waste, respectively.

Therefore, this will be considered as an important source of nitrate pollution in this study process and its modeling process is described in part 3.3.4.1.

3. Methodology

3.1. Study Area

3.1.1. Location, Topography, Climate and Land Use

Location and Topography

Akaki catchment is located in the northwestern Awash River basin between $8^0$45'20'' to 9^0 13'17'' N and 38^0 34' 30''to 39^0 4'10''E. The catchment covers an area of 1462 km^2 and a perimeter of 216 Km (Ayenew et.al., 2008). The Intoto ridge system to the north, Mt. Menagesha and the Wechecha volcanic range to the west, Mt Furi to the southwest, Mt Bilbilo and Mt Guji to the south, Gara Bushu hills to the southeast and the Mt Yerer volcanic centre are the highly elevated area making the boundary of the catchment (Demlie et.al., 2007b).

The elevation generally decreases from north, being the highest elevation in Intoto mountain range i.e. 3200 m.a.s.l., toward the south, Aba-Samuel reservoir being the lowest elevation measured to be 2060 m.a.s.l. (Fig. 3). The fall in elevation from the north to south is nearly 1000 m in 30 km. This makes the catchment to grade enabling springs to emerge in the way (Ayenew et.al., 2008).

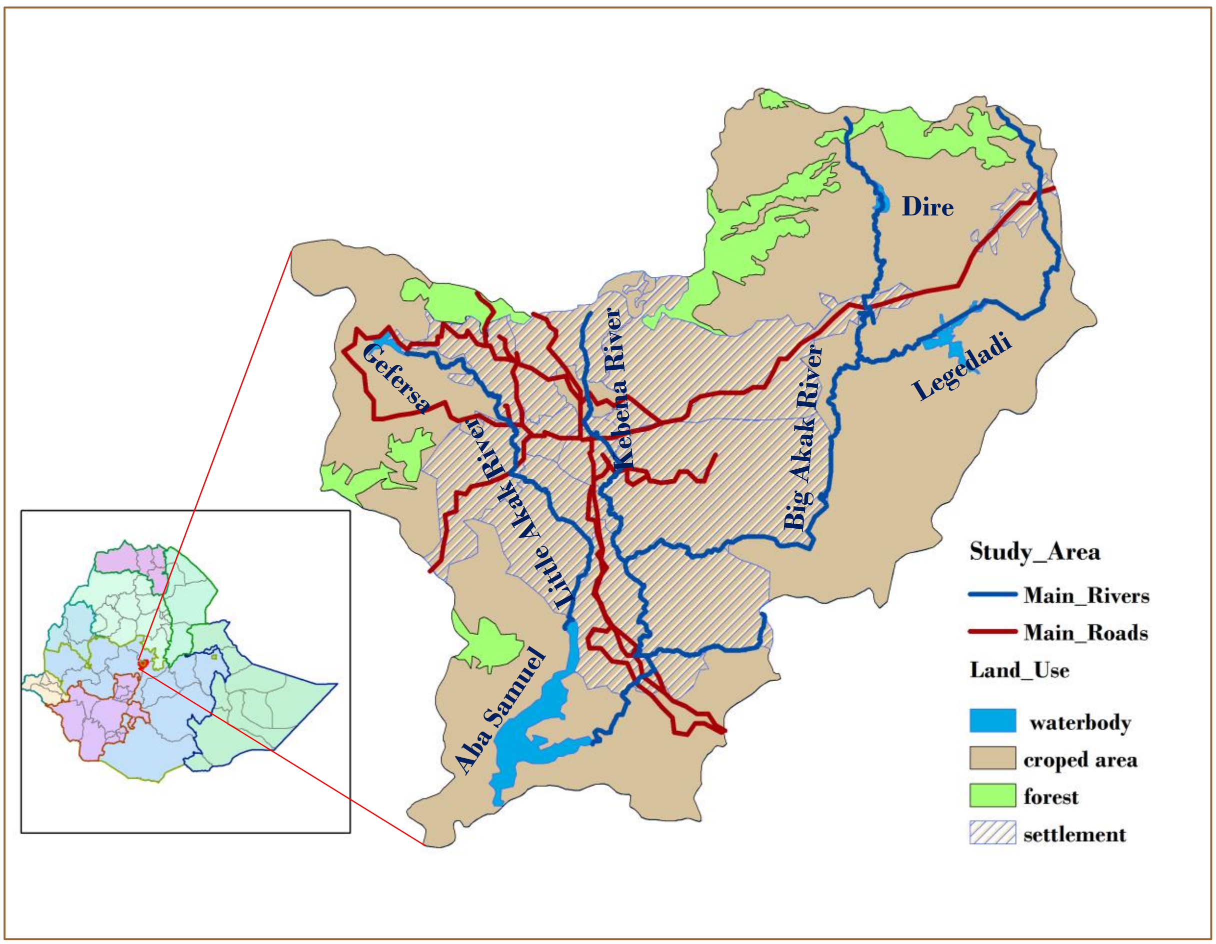

Fig. 3 Location map of the study area

Climate and Land Use

Climate

The catchment climatic condition could be categorized as afro-Alpine temperate type. It has two distinct seasonal weather patterns. Locally called 'Kiremt' is the main wet season extending from June to September and contributing for about 70% of the total annual rainfall. Known to fail in past few decades, a minor rainy season, locally known as Belg, which starts on mid-February and ceases on mid-May contributes the rest of the moisture to the catchment (Demlie et.al. 2007a). Referring to Daniel (1977), the variation in the seasonal distribution of rainfall in the region, in general, can be attributed by to the position of the Inter-Tropical Convergence Zone (ITCZ), the relationship of between upper and lower air circulation, the effects of topography and the role of local convection currents and the amount of rainfall. As measured from Addis Ababa Observatory, lowest and the highest annual average temperatures are 9.9 and 24.6°C, respectively, and the average annual rainfall is 1,254 mm (Demlie et.al. 2007a) making its minimum 970 and maximum 1705 (Alema Tesfaye, 2009). A summary of these all meteorological data has been put in table 1.

The rainfall increases with elevation in the catchment and the relationship has been summarized by Alema Tesfaye (2009) in the following Figure.

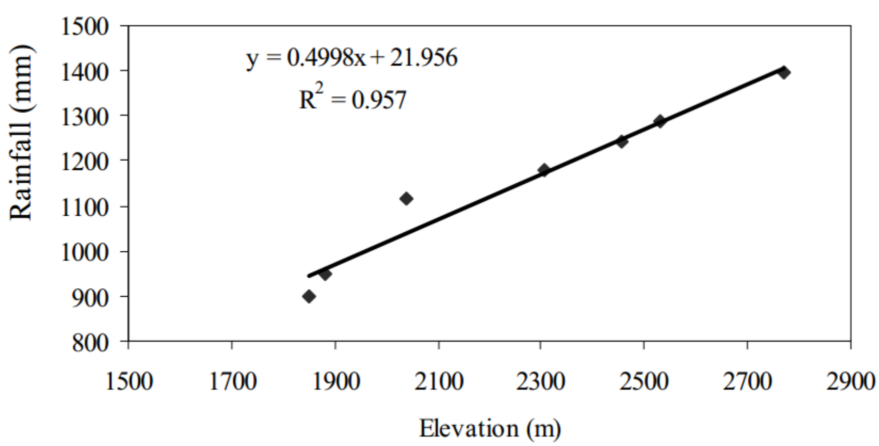

Fig. 4 Variation of annual rainfall with elevation in Akaki catchment (Alema Tesfaye, 2009)

Table 1: Summary of meteorological data for the study area (National Meteorological Agency)

Parameter	Station(periods)	Month												Total
		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	
Rainfall, mm	Intoto(1989-2009)	14.74	33.43	57.55	84.375	68.07	143.375	309.715	339.66	136.105	26.52	13.145	8.19	**1234.77**
	Akaki(1975-2009)	15.7	27.77	69.92	86.64	68.34	114.74	254.288	258.12	122.08	24.27	5.45	3.33	**1050.67**
	AABole(1980-2009)	13.88	31.47	66.33	93.14	77.49	125.7	246.225	256.01	136.476	32.23	5.01	4.896	**1088.43**
	AA Obs (1980-2009)	16.8	38.42	70.32	94.3724	89.31	137.63	277.62	293.53	177.81	38.38	8.055	11.94	**807.36**
Mean		**15.28**	**32.77**	**66.03**	**89.63**	**75.8**	**130.36**	**272**	**286.83**	**143.11**	**30.35**	**7.915**	**7.089**	**1157.23**
Temp oc	Entoto (1989-2009)	19.9	21.1	20.6	20	19.7	17.8	16.2	16.4	16.7	18.2	19.4	18.8	**242.5**
	AA Obs (1980-2009)	24.3	25	25.7	24.9	25.3	23.6	21.2	21	22	23.1	23.3	23.1	**282.4**
	AA Bole(1980-2008)	23.85	24.775	26	25.1	25.1	23.2	21.1	21	21.7	23.15	23	23	**281.05**
	Akaki (1997-2009)	26.5	27.6	28	27.8	28.2	25.9	24.2	24	25.15	26	25.8	25.9	**314.65**
Mean		**23.63**	**24.61**	**25**	**24.45**	**24.57**	**23.7**	**20.67**	**20.6**	**21.4**	**22.61**	**22.9**	**22.7**	**256.34**
Pan Evap. mm	AA Bole(1987-2004)	186.1	190	190.8	177.4	202	106.2	62.3	60.6	99.5	287	189	171	**1921.8**
	AA Obs (1992-2004)	131.7	141	145	117.6	138.3	84.2	52.7	50.2	73	121	137	127	**1318.5**
Mean		**158.9**	**165.5**	**167.9**	**147.5**	**170.15**	**95.2**	**57.5**	**55.4**	**86.25**	**204**	**163**	**149**	**1620.15**
Sunshine Hr	AA Obs (1964-1993)	8.6	8.1	7.2	6.5	6.8	5.1	3	3.5	5	8.1	9	9.1	**80**
Mean		**8.6**	**8.1**	**7.2**	**6.5**	**6.8**	**5.1**	**3**	**3.5**	**5**	**8.1**	**9**	**9.1**	**80**
Wind speed	AA Obs (1982-2005)	0.6	0.6	0.65	0.65	0.65	0.4	0.3	0.25	0.45	0.65	0.7	0.65	**5.9**
Mean		**0.6**	**0.6**	**0.65**	**0.65**	**0.65**	**0.4**	**0.3**	**0.25**	**0.45**	**0.65**	**0.7**	**0.65**	**5.9**
R. H in%	AA Obs (1979-2009)	49	45	46	47	47	58	70	72	64	48	43	45	**634**
	AA Bole(1964-2005)	49	41	47	54	59	65	79	77	72	52	50	48	**693**
Mean		**49**	**43**	**46.5**	**50.5**	**53**	**61.5**	**74.5**	**74.5**	**68**	**50**	**46.5**	**46.5**	**663.5**

Land use/ Land Cover

Akaki catchment has a variety of land use/land cover (LULC) systems. According to AAWSA et.al. (2000), the land use land cover in Akaki catchment could generally be classified in to four categories saying forest, urban area, agricultural or open areas and water bodies by grouping related land use systems in to one (Fig. 5).

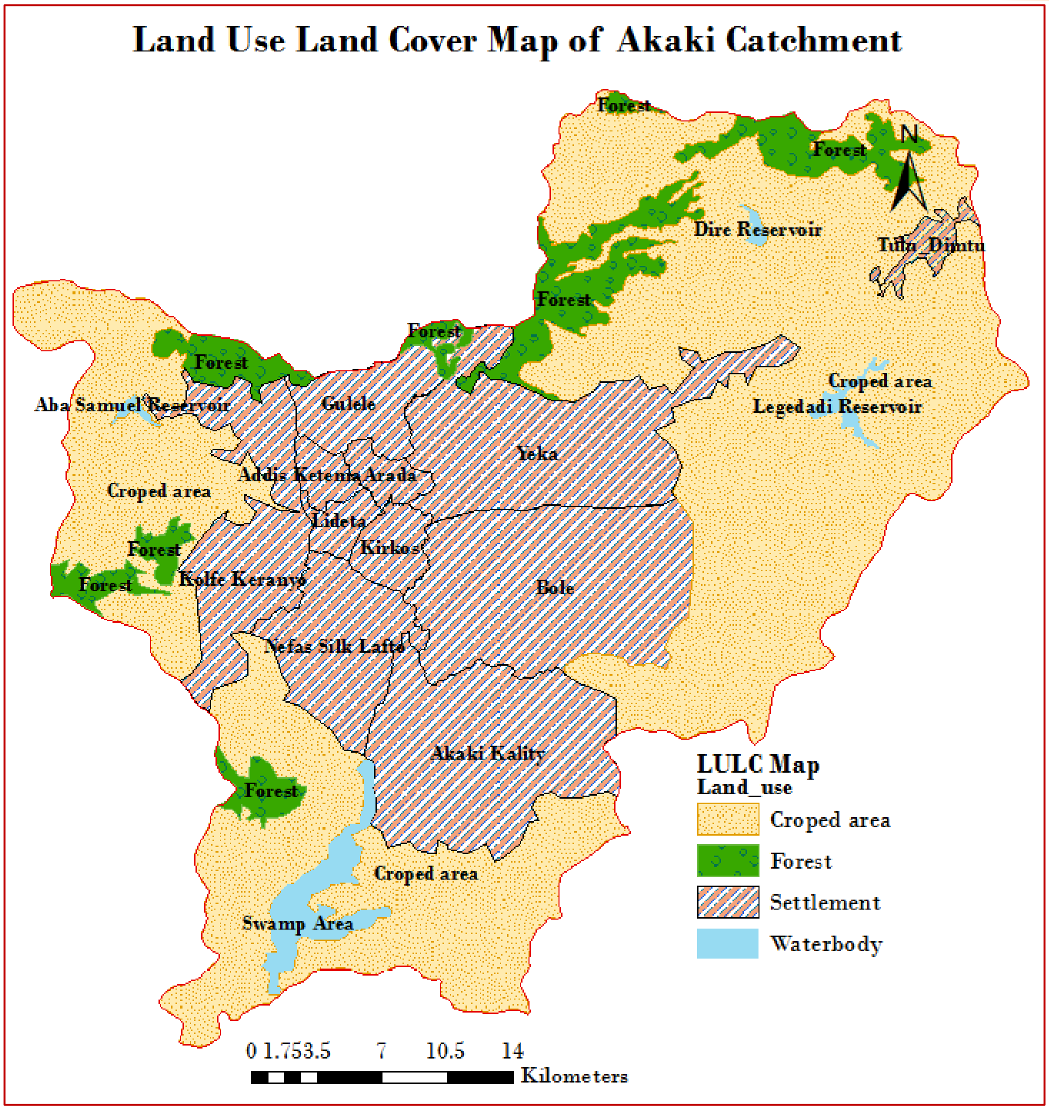

Fig. 5 Land Use/Cover Map of the Akaki River Catchment (Modified from OWWSE, 2012)

As per this land use-land cover classification, the forest land use land cover system includes northern part of the catchment on Intoto Mountain in which eucalyptus trees dominate. This is the non-human intervened part. The other land use system stated is the urban one. This covers the whole Addis Ababa town/city and villages or as sparse settlements of household including central Addis Ababa, Sendafa, Akaki, Burayu and other moderately populated rural settlement villages. This is characterized by paved surfaces or built up area. Due to the presence of pavements for infrastructure and built up areas, the amount of infiltration in this part is small. Around the city and following the mountainous in east, south and southwest part an agricultural or of open area occur contributing for the largest portion of the surface cover. Lastly, about 6 water bodies namely Gefersa I, II and III, Lega Dadi, Dire and Abba Samuel Lake exist. Most of these water bodies are serving for drinking water supply (Ebasa Oljira, 2006). Considering conceptualization the land use map developed by OWWSE (2012), have been modified as in Fig. 5.

3.1.2. Geology and Hydrogeology

3.1.2.1. Geology

The geological formation of Akaki catchment is categorized as Miocene–Pleistocene volcanic successions in which basaltic lava flows, acidic and intermediate lava flows, and pyroclastic flows interlayered and frequently intersected by Quaternary normal faults (Alemayehu et.al., 2009).

The study area being part of the Main Ethiopian Rift (MER) its geological setup arises from the evolution and development history of the Ethiopian Plateau and the Rift system. Thus, the catchment is covered by range of volcanic rocks overlain by fluvial and residual soils varying in thickness from a few cm to about 19 m in which black cotton soil being the predominant type. The volcanic formation includes mainly basalts, rhyolites, trachytes, scoria, trachybasalts, ignimbrites and tuff belonging to wide range ages most of which are highly weathered and fractured (Demlie et.al. 2007a).

Stating different sources, the summary made by Ayenew et.al. (2008) about the lithostratigraphy of the study area was as follows:

Generally the lithostratigraphy was classified in to four groups saying Alaji Formation, Addis ababa basalts, younger volcanic and rent deposits. The Alaji Formation group includes the rhyolites, trachytes, tuff, agglomerate, and aphanitic basalt dominating the northern and central part. These were also further extended into Alaji rhyolites and Intoto Silicics in which the Intoto Silicics represents massive Oligocene fissure-basalt, rhyolites, and trachytes with minor welded tuff and obsidian. The second groups, the Addis Ababa basalts, overlay the Intoto Silicics and cover the central and southern part of Addis Ababa. Paleosoils and scoraceous horizons are common and Olivine porphyritic basalt outcrop in central Addis Ababa with a thickness varying from 1 m in the foothills of Intoto to more than 130 meters in central Addis Ababa. Third ones, the Younger Volcanics, include the Nazareth Group and Bishoftu Formations. The Nazareth Group contains aphanitic basalts, welded tuffs, ignimbrites, trachytes, and rhyolites being the aphanitic at the top and porphyritic at the bottom. These rocks found dominantly south of the Filwuha Fault. On the other, the Bishoftu Formations consists of olivine porphyritic basalt, scoria, vesicular and scoraceous basalt, and locally trachy-basalt lava flows overlaid by scoria, tuff, sand, and gravel. These are dominant in the southern part in which Akaki well field is found forming the major aquifers. Their thickness varies from 20-40 m in the well field. The last group, Recent Deposits, includes alluvial, residual, and lacustrine deposits. Overlaid by dark younger black cotton clayey soils in some parts, their thickness of these deposits varies from 5 m to 50 m and are dominant in the southern part. Further, Alluvial deposits are found along the Little- and Big-Akaki rivers and in most flat plains.

Moreover, Akaki catchment being near the MER, rocks were subjected to rift tectonics that is manifested by a number of fault systems having a general trend of the rift system NE and some are also oriented in EW, NW and NS (Ebasa Oljira, 2006).

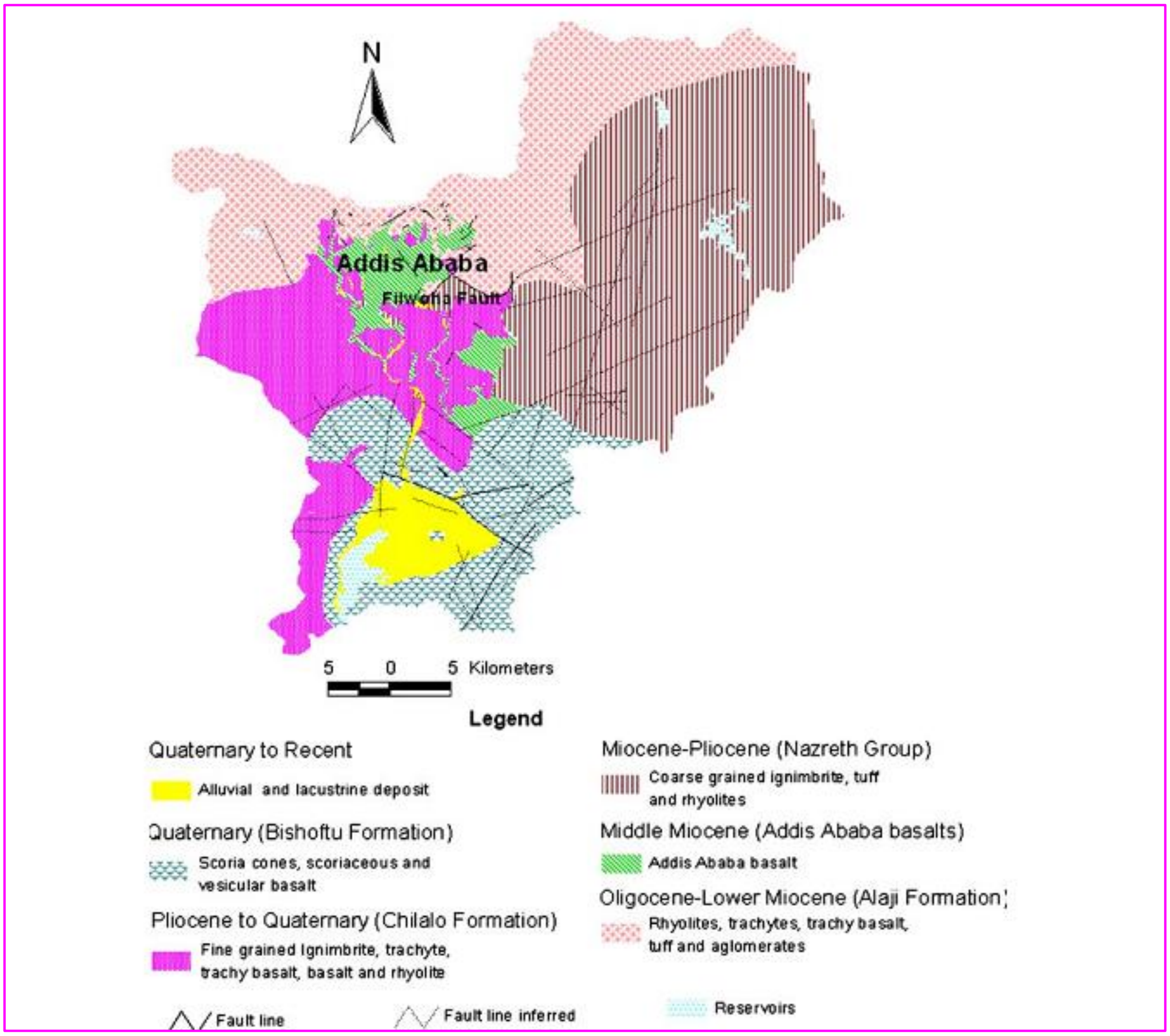

Fig. 6 Simplified geological map of the Akaki catchment (Demlie et.al., 2007a)

3.1.2.2. Hydrogeology

With this intricate lithostratigraphy, varying spatio-temporal distribution, different reciprocal stratigraphic relationships, contacts with ancient and recent rocks, their great compositional, structural and complex textural variability, and their different level of tectonization and weathering (Davis and DeWiest 1966; Vernier 1993-as cited in Demlie et.al. 2007a), the hydraulic characteristics of the study were found to be complex.

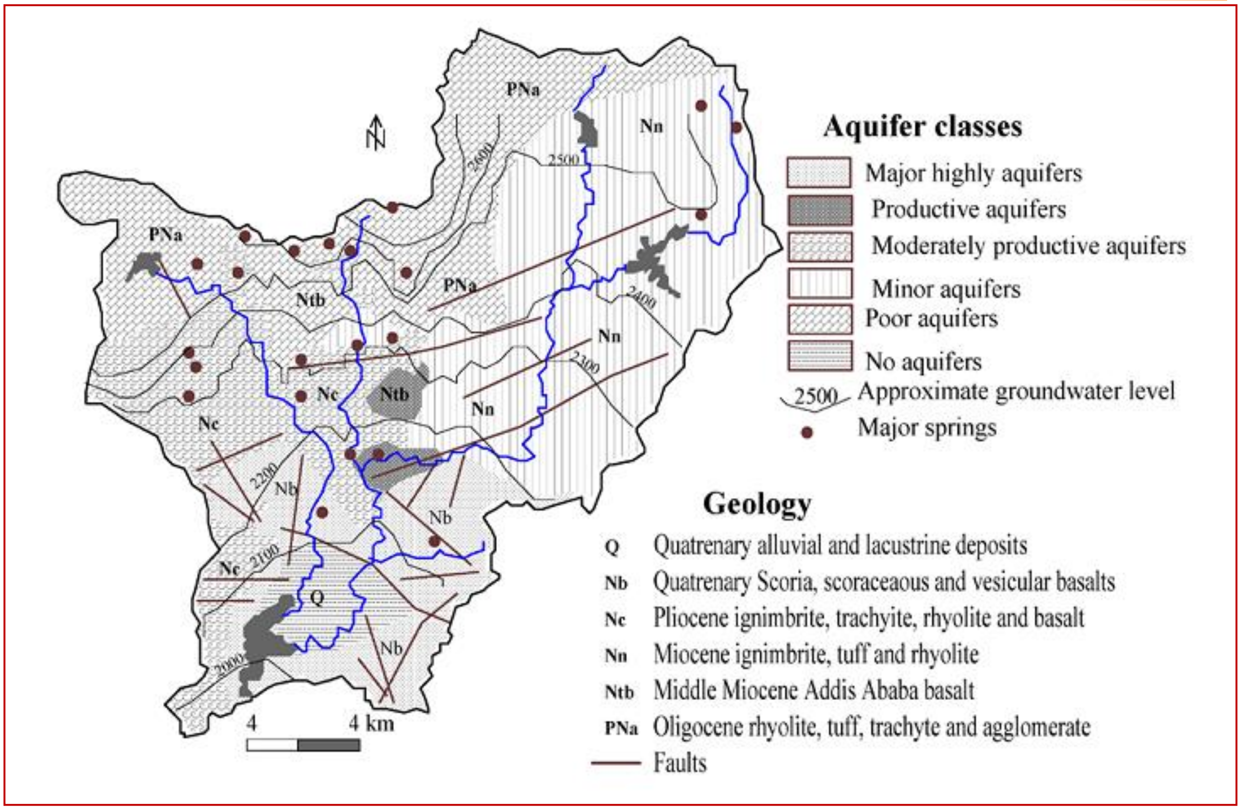

Fig. 7 Simplified hydrogeological map of Akaki catchment (Ayenew et.al, 2008)

Generally, Scoria, scoraceous, vesicular and fractured basalt of the Bishoftu Group located in the southern part of the catchment including the Akaki well- field are judged to be highly productive, fractured and weathered Addis Ababa basalt aquifer with some inter-volcanic coarse sediment, located in central, western and northern Addis Ababa are considered to be moderately productive; the young fractured ignimbrite of the Yerer volcano covering the eastern part of the catchment and young fractured trachyte of the Wechecha volcano covering the western part as low productive aquifers and the Weathered and fractured rhyolites and trachyte of the Intoto silicics covering the Intoto Mountain Range could be considered as non-aquifer. A summary is in table 2 taken from Demlie et.al. (2007a).

Table 2: A broad classification of aquifers in the Akaki catchment (From Demlie et.al. 2007a)

Aquifer unit	Average yield of water wells (l/s)	Transmissivity range (m^2/day)	Storativity range	Remark
Scoria, scoriaceous, vesicular and fractured basalt of the Bishoftu Group located in the southern part of the catchment including the Akaki well-field	3– 87 l/s	1,833 – 105,410	0.0065 – 0.016	Highly productive aquifer
Fractured and weathered Addis Ababa basalt aquifer with some inter-volcanic coarse sediment. It is located in central, western and northern Addis Ababa	0.5– 20 l/s	2–5,929	-	Moderately productive aquifer
Young fractured ignimbrite of the Yerer volcano covering the eastern part of the catchment, and young fractured trachyte of the Wechecha volcano covering the western part	0.4– 15 l/s	15 –110	0.0001 – 0.003	Low productive aquifer
Weathered and fractured rhyolites and trachyte of the Intoto silicics covering the Intoto Mountain Range	-	Non-aquifer. Fractured and weathered zones in this region are important recharge zones and shallow circulating groundwater could be tapped through hand-dug wells		

3.1.2.3. Hydrochemistry

Being a very heterogeneous aquifer the chemical properties of the groundwater varies spatially. Generally more fresh water is available on the elevated northern parts of the aquifer and the concentration of nearly all contaminants increased down to the southern part. This is due to the fact that the northern part (Intoto) being the major recharge area, water flows down (southwards) creating more rock-water interaction. Additionally, introduction of anthropogenic effluent to the groundwater from more populated area of the catchment (Addis Ababa City) upturn concentration of some contaminants like Cl and NO_3.

TDS is generally less than 500 mg/l for most non-thermal waters. The lowest was recorded in the northern part to be 50 and highest was 2070 mg/l. The general pattern shows increasing TDS measurement form north to the south ends. PH value ranges from 6.1 to 8.6, being the lesser in the north recharge area. In the same fashion temperature ranging from 17 to 25.

Confirming earlier studies made in this catchment, high Na (64 mg/l) and Ca (55 mg/l) concentration were observed in most wells. The cause for elevated concentration of Na could be the natural processes undertaking in the groundwater system like weathering of plagioclase feldspar and may additionally be from anthropogenic effluent. Weathering of rock forming minerals of various rocks like plagioclase feldspar were mentioned as a reason for the high concentration of Ca by Ebasa Oljira (2006).

As per the varying spatial distribution of species three groups of aquifer with having different types of water have been identified by Demlie et.al. (2007). The first group is much diluted Ca-HCO_3, Ca-Na-HCO_3 type in the northern recharge are. Second, Ca-Mg-HCO_3, Mg-Ca-HCO_3-type water found in the Addis Ababa basalt in the central parts of catchment and Bishoftu basalt aquifer in the south (Fig. 6). Considered to be anthropogenic impact a Ca-NO_3 and Ca-Cl-type water have been identified in central parts of the catchment, being the third group.

3.2. General Research Method

Both primary and secondary data sources have been utilized in this work. The primary data collection was mainly perfumed in order to know the nitrate concentration values of the wells in the catchment. Totally of 80 wells (each one times) were sampled and the samples were analyzed for nitrate concentration in AAWSA’s water chemistry laboratory. Secondary data utilized in this paper includes previously collected nitrate concentration measurements, different meteorological, geological, hydrogeological and geochemical maps, land use land cover maps, population number, and fertilizer application rate of local farmers (Fig. 8). Information from formal and informal discussion have been included in the conceptualizations and outcomes of the models. Moreover, the researcher has conducted field visits in each and every instance of the paper to understand field conditions and crosscheck model outputs and real site condition.

All the collected data were carefully encoded in to Microsoft Excel and Access data bases and exported to several formats to enable the use of automatically generated model parameter. The main programs used to analyze (build the models) the data was MODFLOW and MT3DMS. These programs uses numerical codes named Groundwater flow and Advective Dispersive Equation. Other programs including ArcGIS 10.2, Surfer 10, Global Mapper 12, Seer3D, 3D Master 1.0, Adobe Photoshop 7, Erdas Imagine 2010, Aquachem 4.0, and Microsoft Office 2013 were intensively utilized. Finally the results are presented using maps, graphs and tables.

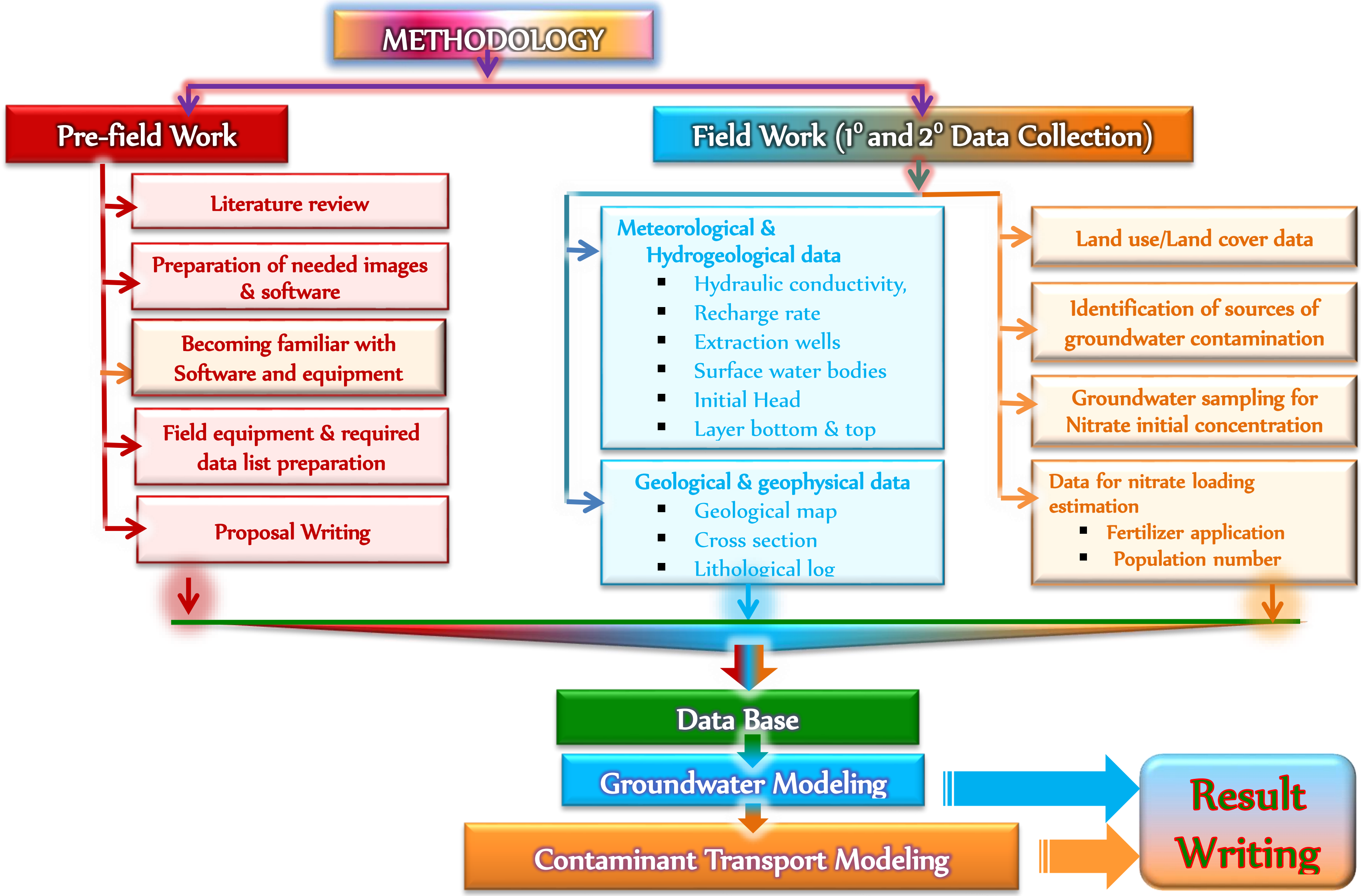

Fig. 8 Methodology flowchart

3.3. Groundwater Flow Modeling

3.3.1. Introduction

A model is a mimicked picture representing a real environmental system. These models could develop to solve different problems in different disciplines and their complication depends on the nature of the environment being modeled and objective of modeling. The aim of groundwater flow modeling is to simulate head over space and time (Fetter, 2004; Anderson and Woessner, 1992). This modeling process requires a due understanding of the geologic, hydrologic and hydrogeologic in addition to the acquainted-ness of the subject hydrogeology as a tool.

In the process of modeling an aquifer system there are main steps that refer as the modeling protocols (Fig. 9). The first step is the process of setting the purpose by which the modeler identify for what the model is intended to be developed. According to Anderson and Woessner (1992), a model could be developed mainly for three purpose; (1) Predictive – used to predict certain hydrological processes: for example water level decline for a certain pumping rate as a decision support tools, (2) Interpretative – used to interpret hydrological processes for a changing stress conditions. For example the roles of river in the groundwater recharge process, and (3) Generic – simple models used for teaching purposes. Calibration may not be required.

Secondly, the process of developing a conceptual model comes. In this, a real environmental systems is defined well in pictorial terms and always it is important to include all information determine groundwater flow. Type and extent of water bearing zones, aquifer hydraulic parameters, system boundary, flow system (groundwater levels), fluxes (recharge), sources (addition) and sinks (abstraction), initial conditions i.e. water levels for understanding the flow system and calibrating the model are most important information required in the conceptual model development. Next, after conceptual model has been developed, a mathematical model that could best explain the model is selected and this depends up on the data availability and objective of modeling. For this mathematical representation a numerical or analytical solutions are developed as a next step, i.e. as the explanation of the governing equation best fit the model. Then a model is designed by which spatial and temporal discretization is done followed by the execution of the available input data; thus a model should run. Now a model has been developed (Anderson and woassner, 1992; Batu, 2005).

After this, it is not considered everything is over. The model has to be calibrated to fit the real field condition under the model calibration process and the sensitivity of the model output to changing input parameters has to be tested. On this step a model can be used to predict future changes based on some changing parameters. The presentation of results may be done for the model users and some other scholars followed by post auditing processes with the ever changing environmental parameters like land use changes including construction of dams in the area, expansion of urban areas, irrigation development, and additional pumping etc. (Anderson and woassner, 1992; Batu, 2005; Fetter, 2000).

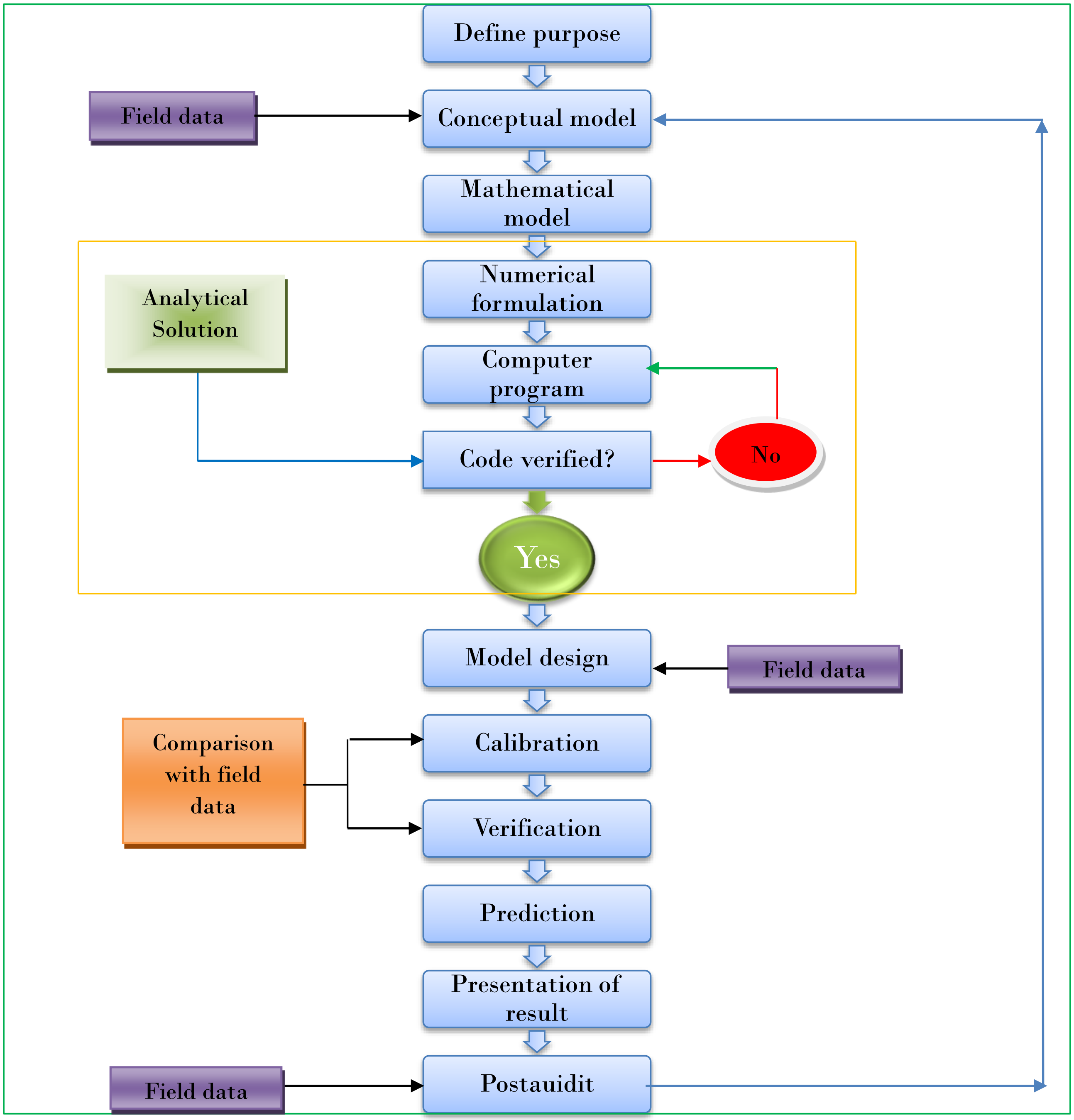

Fig. 9 Steps in a protocol for model application (Anderson and Woassner, 1992)

3.3.2. Groundwater Flow Model of Akaki Catchment

3.3.2.1. Conceptual Modeling

Conceptual modeling refers to the process of representing the groundwater system in a way that anyone could visualize the real field conditions. This stage is most important one in the groundwater flow modeling because of that it simplifies complicated field condition and could effectively show the organization and use of the field data in the modeling process (Ebasa Oljira, 2006). In this process having a good database takes the great role (Fetter, 2000) and these all field data could organize to correctly represent a groundwater system (Ebasa Oljira, 2006).

Aquifer types in Akaki catchment consists of confined, semi-confined, unconfined and perched aquifers, but most of the aquifers are hydraulically interconnected for the reason that the high permeability the different hydrostratigraphic units (Ayenew et.al., 2008) and the presence of continuous piezometric surface that follows approximately the topographic surface (Ebasa Oljira, 2006). Yet the borehole logs show variable lithology and degrees of fracturing the pumping test data indicates that the catchment could be considered as unconfined aquifer with varying specific yield (Ayenew et.al., 2008), up to the depth of 250m. Being nitrate transport modeling the main objective of this work, the first most upper aquifer was the area of interest for this work. This is because the most upper aquifer is the most susceptible aquifer for area with direct recharge from precipitation inside the catchment. Accordingly, Akaki catchment was modeled as single layered unconfined aquifer.

3.3.2.2. Boundary Conditions

In its physical boundaries, the catchment is bounded by central volcanic hills and mountains which are free of crossing fault systems (Ayenew et.al., 2008) described in Ebasa Oljira (2006) as; the northern and northeastern boundaries are closed by Intoto Mountain ranges, in the southwestern it coincides with the Wechecha range and Furi Mountain, in the northeastern side the Bereh Mountain and in the eastern boundary Mt Yerer makes the periphery. Thus, these stated boundaries of the study area could be treated as no flow boundaries. On the other hand, coming from hydrogeological observations, hydrochemical and isotopic studies, it has been stated in many works (eg. Ayenew et.al., 2008, Ebasa Oljira, 2006) that there is an out flow in the southern part of the catchment. This edge was considered as general head boundaries in which its extent was determined based on a field visit and existing works.

As per the protocol of MODFLOW, big rivers (little and great Akaki and Kebena), and reservoirs (Gefersa, Aba-Samuel and Legedadi) was modeled as constant head condition. Small reservoirs and springs was simulated using drain package.

3.3.2.3. Model Parameters

Initial and Prescribed Hydraulic Head

Initial and prescribed hydraulic head refer to the hydraulic head distribution in the aquifer at a time the area is going to be modeled (Anderson and Woessner, 1992). This could be worked out using different methods. In this study areal distribution of head was interpolated from point data that are available in the well database of the study area using Kriging method in Surfer 10 (Fig. 10).

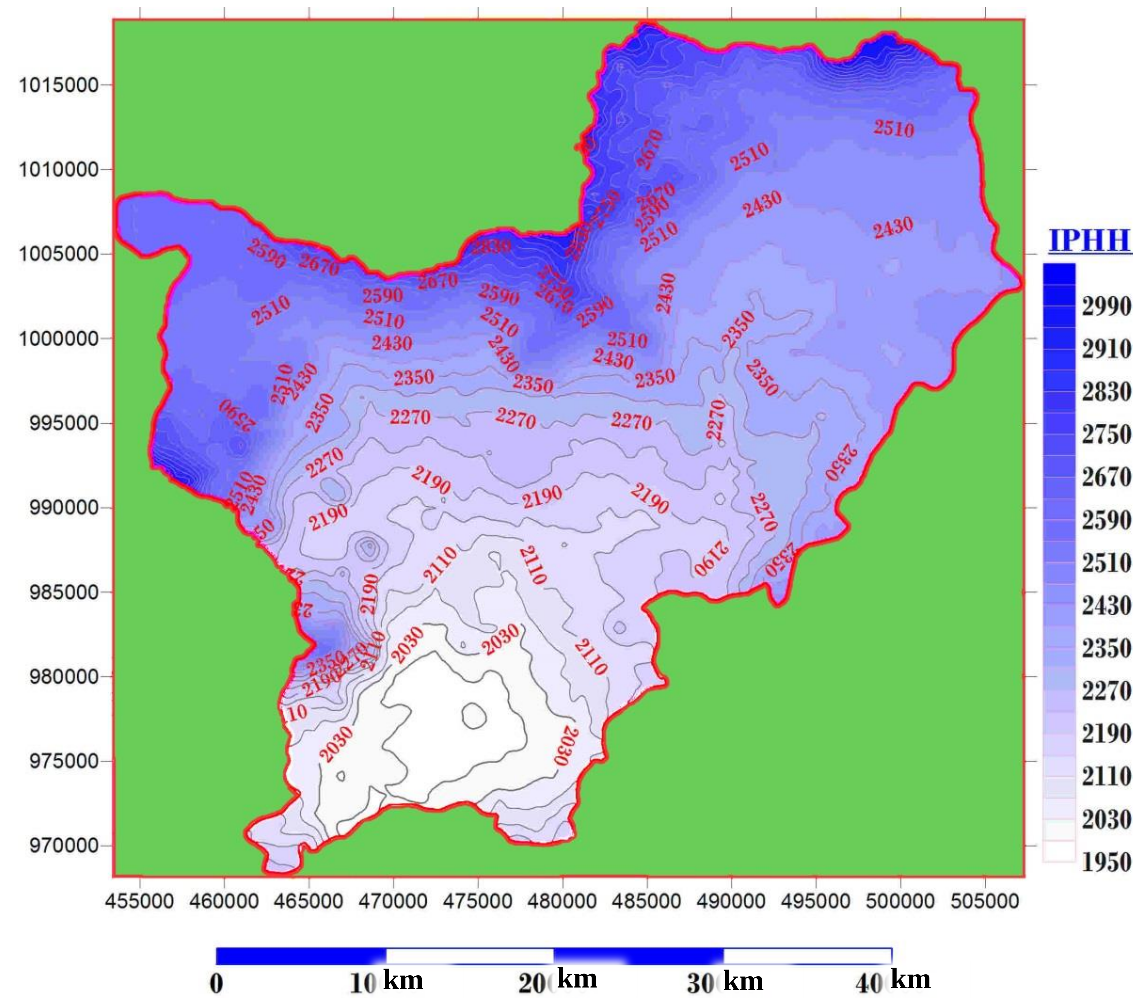

Fig. 10 Initial and Prescribed Hydraulic Head (m.a.s.l.)

Hydraulic Conductivity

Since the geology of Akaki catchment is very complex it could simply be expected that there will be very diverse hydrogeological characteristics. In relation to hydraulic conductivity, different works has been conducted. Ayinalem Ali (1999) has estimated the hydraulic conductivity of the Akaki well field aquifers to be in the range of 7.4 and 674.8m/day. In modeling groundwater flow for the same area, Alema Tesfaye (2009) has used the hydraulic conductivity to be between 1 and

26 m/day. According to Ayenew et.al. (2008), hydraulic conductivity was extended to be 0.09 m/day in the homogeneous less fractured highland volcanics and nearly 50 m/day in the highly fractured volcanics and permeable alluvial and lacustrine deposits. Other works conducted by AAWSA, BCEOM – Seureca and other studies are available. Thus, hydraulic conductivity values were taken from Ayenew et.al. (2008) and these values was modified in the calibration process with values ranges of Ebasa Oljira (2006). These two works were considered due to the reason that they are detail and a full catchment map is available for both studies. In the modeling process, the same values was taken for horizontal and vertical hydraulic conductivity for a cell and horizontal anisotropy with in a cell was defined to be 1, mean all hydraulic conductivities along the X(Easting) Y (Northing) and Z (Down vertically) for a cell were the same. Therefore, no anisotropy was simulated. The following map was used as a hydraulic conductivity value for the model.

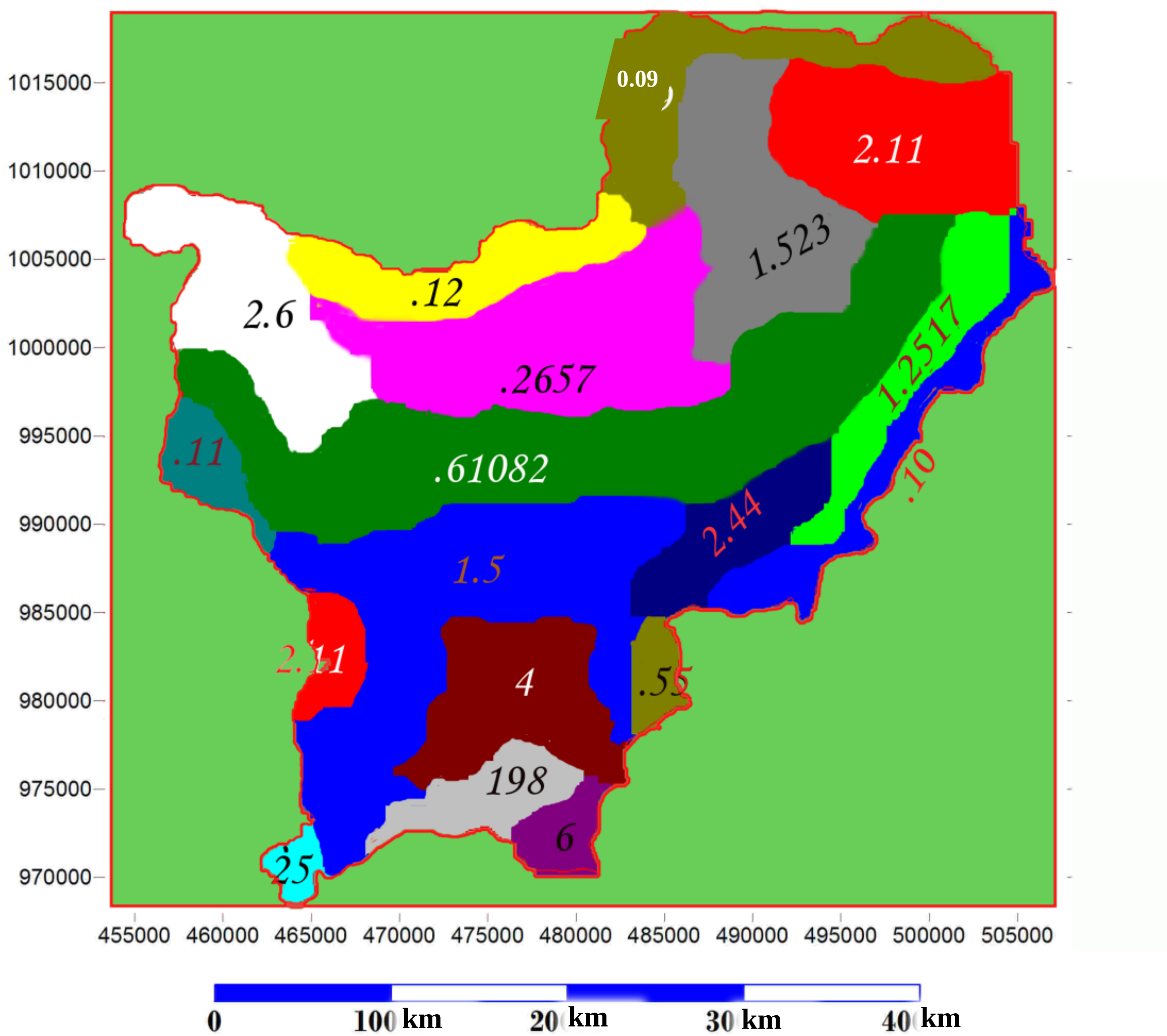

Fig. 11 Hydraulic conductivity map of Akaki catchment in m/day (from Ayenew et.al. (2008) and Ebasa Oljira (2006))

Aquifer Geometry and Extent

The aquifer is irregular shaped in it horizontal surface (Fig. 12). The boundaries have been identified by different studies. The top of the aquifer was derived from SRTM of the area. The aquifer's bottom elevation have not been known , since drilling activities were mainly for water tapping purpose in which all stop in the water baring zone.

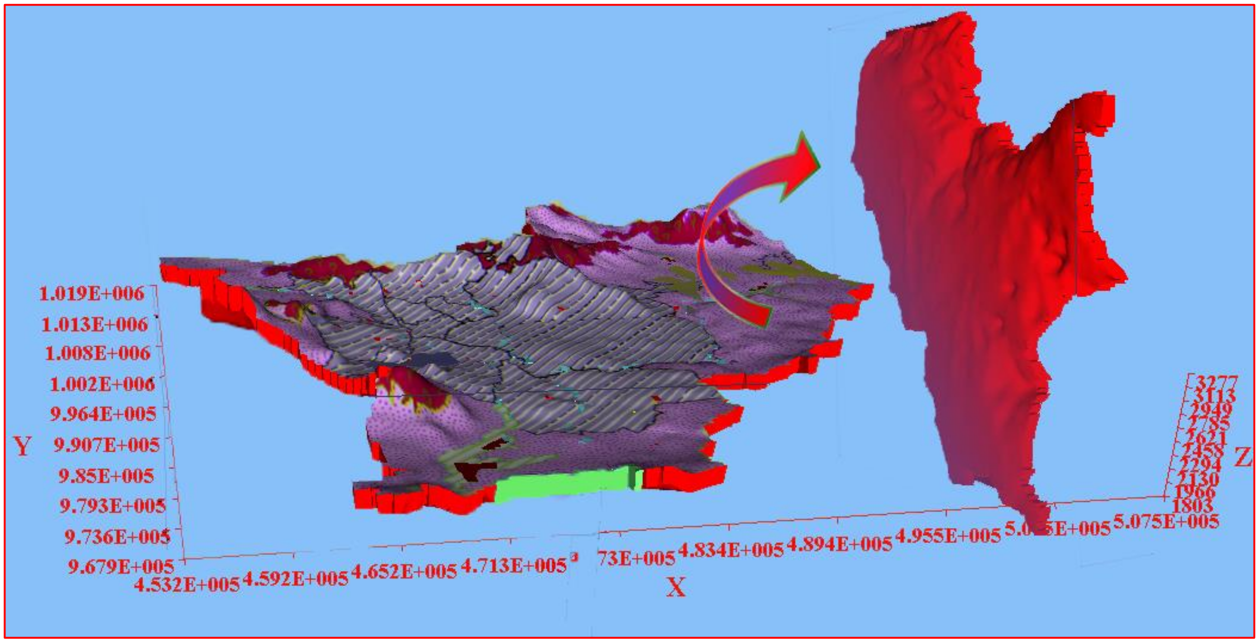

Fig. 12 3D conceptualization of Akaki catchment's aquifer geometry

Ayenew et.al. (2008) have considered depth of 300 m as bottom of aquifer for dual layer modeling, and it has been stated that only a little is known about the aquifer layering below 250m; suggesting additional investigations. In recent times, drilling has been done up to 500m and the results are being analyzed. In the preliminary works it is believed that the first aquifer ends in between 300 to 350m. Here, more or less accurate information is available on the other parameters than bottom elevation. Consequently, the bottom elevation was taken to be a parameter that was tested in the calibration process. Here, since aquifer thickness determines the amount of water stored in an aquifer other than parameters like storativity, it is worth mentioning to tell the possibility in which layer bottom elevation would be one of the most sensitive parameters.

For this model, the aquifer thickness was taken to be 250m (because of presence of detail information). Then in the calibration process it was found important to give more value in the highly elevation area of the catchment to remove dry cells. Finally, the following elevation map was developed for the bottom elevation input parameter of the catchment.

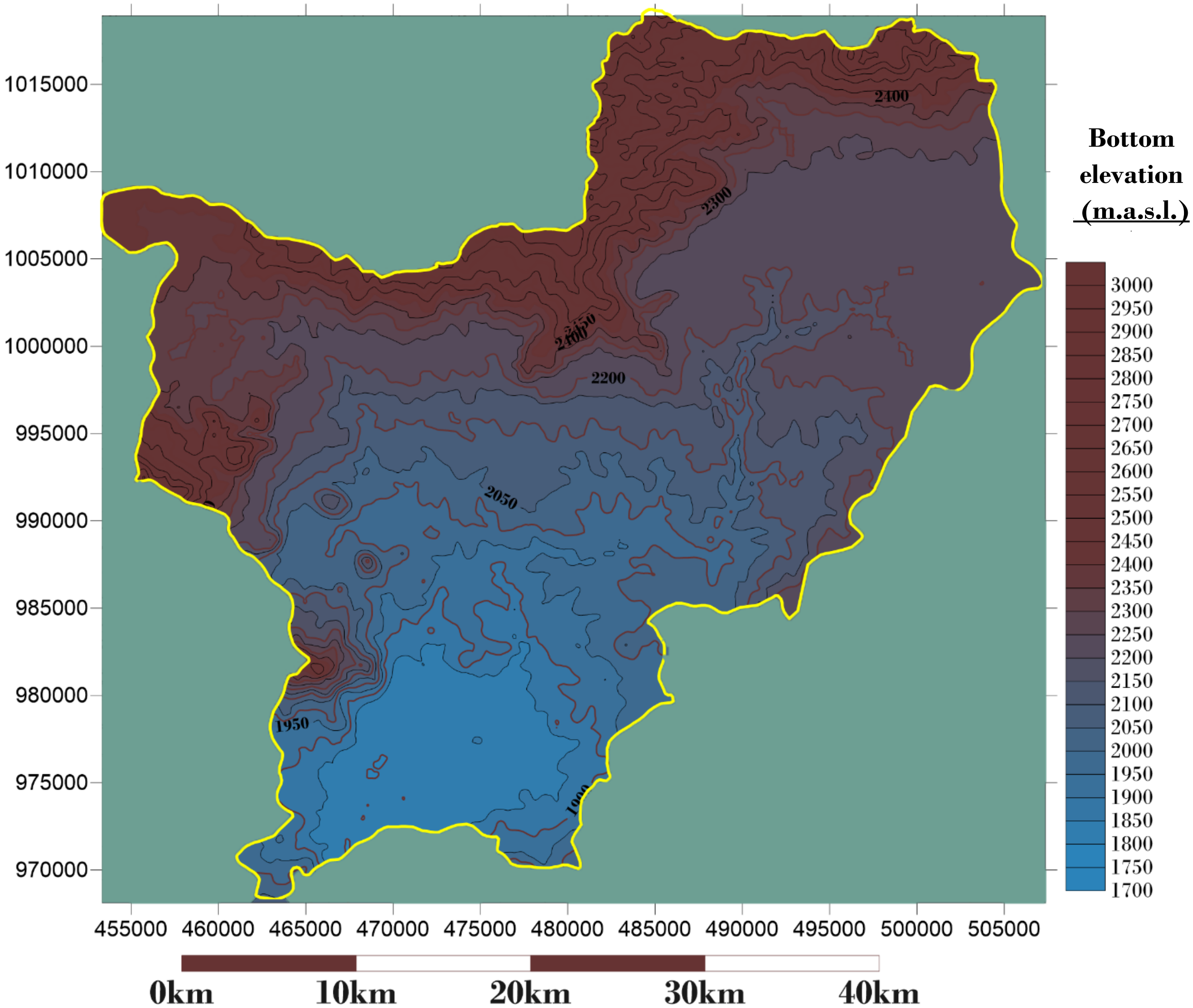

Fig. 13 Contour map of the catchment's bottom layer

Effective Porosity

Previous works has used the effective porosity values varying from 0.3 to 0.35. Most importantly, Ayenew et.al., (2008) has determined the representative value of the effective porosity of the catchment, which was expressed as the percentage of the volume of the voids to the total volume. Accordingly, the effective porosity was determined to be 32 %for medium gravel and 39 % for medium sand. Thus, some value in between 0.32 and 0.39 was considered to be logical.

Pumping/Injection and Observation Wells

In the catchment there are numerous boreholes mainly drilled for water supply purpose. Some are private others are managed by the Addis Ababa Water and Sewage Authority (AAWSA). There are no injection wells. The wells are either pumping or monitoring wells. Therefore, in this modeling process it was tried to include all pumping wells and conditionally most of the monitoring (observation wells) and no injection wells were used.

Recharge

Recharge is the main source of water for the catchment. In the study area recharge have been studied by different authors for different purpose including AAWSA in different years, Ayenew et.al, 2008, Jemal Seid , 2009, Demlie et.al. 2007b, Dereje Nugussa (2003). Those all works has more or less similar results and it has been identified that the elevated areas i.e. Northern and northwestern Intoto, Wechecha range and Bereh mountain ranges are the main recharge zones. Next, the areas covered with relatively thin clay cover at lower elevation than the previous zone with land use/cover of agriculture or open field and southern and southwestern tips of the catchment take the second rank. The built areas, Addis Ababa city, were with relatively lower amount of recharge preceded by the catchment southern and western peripheries. Thus, recharge was taken from the existing works and after the calibration processes the following map was produced.

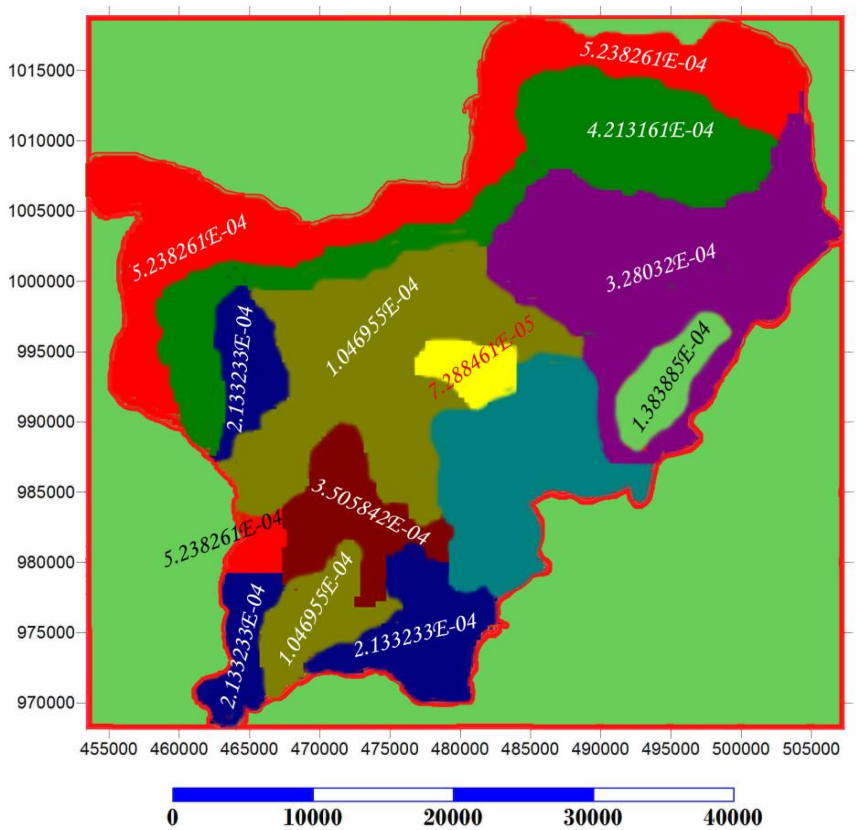

Fig. 14 Recharge map of Akaki catchment as a depth in m/day (Alema Tesfaye, 2009)

3.3.3. Overview of Flow Packages

Drain Package

This package is used to simulate effects of features that remove groundwater from aquifer at a rate proportional to the head difference between the aquifer and the drain; thus, the water that is sewer to the drain will be removed from the groundwater system model. In this model this package was used to simulate the discharge form springs. In the modeling process all major springs were included.

Evapotranspiration Package

This package tried to account for the effects of plant transpiration and direct evaporation in removing water from the saturated groundwater zone and the rate of evapotranspiration depends on the depth of the groundwater table from the surface; less evaporation when groundwater table is deep. Under this, there is a term called 'depth of extinction' measured from the surface, below which evapotranspiration is assumed zero (Simcore Software, 2012). The depth of extinction mostly is taken to be 50m.

For Akaki catchment, evapotranspiration was not modeled because of (1) the groundwater level is far from the surface (Ayenew et.al., 2008) and (2) the climatic condition is afro-alpine type and deep rotted trees capable of abstracting large amount of groundwater (e.g. eucalyptus) have been cut in the past decades (Alema Tesfaye, 2009).

General Head Boundary Package

The general head boundary package is used when it is assumed that flow into or out of a cell from an external source is a function of the head difference between the head in the cell and the head assigned to the external, used to simulate head-dependent flow boundaries.

This package was applied in Akaki catchment groundwater model for the southern edge of the groundwater system, in case believed to be the head inside is greater than outside. Thus, an out flow will occur under this condition.

Horizontal Flow Barrier Package

This is used to model low-permeability geologic features, such as vertical faults or slurry walls, which impede the horizontal flow of groundwater (Simcore Software, 2012). This in Akaki catchment this package was not used because of (1) there is no complete data on it and (2) from previous works, for example Ayenew et.al. (2008), shows continuity of flow in the north-south direction both aerial and cross-sectional simulation.

Recharge, Reservoir and river packages

These all three are packages described in different parts above. Referring to their details above, all was included in Akaki catchment groundwater flow modeling process.

As it has been stated in part 3.1.1.2., there are 6 major water bodies which all will be modeled as Head dependent cells that use the water flux between groundwater aquifer and surface reservoirs. Rivers including little and great Akaki and Kebena were modeled in the river package and recharge has been estimated by previous works.

Interbed Storage

When poorly permeable bed occurs within a relatively permeable aquifer groundwater is released from less permeable storage e.g. (highly compressible clay) to the more permeable aquifer part (e.g. adjacent coarse-grained beds) under conditions of decreasing hydraulic head. This is because of that the more permeable aquifer releases water faster than the less permeable one; thus, water flows in to the more permeable one in the process of water abstraction form an aquifer a stress happens for the matrices of the aquifer leading it to be compressed because reduction of the hydraulic head results in a decrement of the water pressure in the pore. Thus, the released water volume is proportional to the compressibility of the soil matrix and water. The package that helps to calculate the water volume released from storage and simulates elastic and inelastic compaction of compressible fine-grained beds in an aquifer due to groundwater extraction is Interbed Storage package (Simcore Software, 2012).

Due to the reason that there is no clear evidence and data for this type of formation in Akaki catchment groundwater system Interbed Storage Package was not included in the modeling process.

Streamflow-Routing

According to Prudic (1998) cited in Simcore Software (2012), the Streamflow-Routing is designed to account for the amount of flow in streams and to simulate the interaction between surface streams and groundwater. In this model the big rivers will be modeled using the river package. However, for small rivers due to the complexity of the surface and technical problems small streams were not included in the modeling.

3.3.4. General Assumptions

Since the real field situation is quite complex, every modeling activity involves the use of certain assumptions. In modeling groundwater flow of Akaki catchment, the following assumptions are considered which are either developed for the sake of simplifying the complexities of the natural environment or are assumptions considered while the simulating software were developed.

- Fractures and weathered zones through which water flows was considered as porous medium to which Darcy's Law can be applied.
- Since hydraulic parameters (recharge, hydraulic conductivity, and effective porosity) are very dynamic in space due to the aquifer heterogeneity, presence of fractures and faults, variable rainfall etc… to simplify this variation a zonation approach was adopted where similar hydraulic parameter values will be assigned to specific regions. This is the same as saying the values are approximation of the real field condition.
- Being a single layer model; one, vertical flow through the bottom of the layer was neglected and the geology below bottom elevation was considered as impermeable material by MODFLOW.
- The calibration process (described below) was based on trial and error calibration procedures. This doesn't produce unique solutions and are expected to introduce uncertainties in model results.

3.2.4. Governing Groundwater Flow Equation

Groundwater flow meet the terms of the equation of continuity; which expresses the principle of conservation of mass, i.e. the net inward flux through an elemental volume of an aquifer in the flow field must be equal to the rate at which matter is accumulating within the element. The Darcy's low of groundwater flow in its Three-Dimensional (3D) for anisotropy medium combined with the equation of continuity for steady (equation 29) and unsteady (equation 30) can be used as general governing equation of flow modeling (Anderson and Woassner, 19992; Batu, 2005; Singhal and Gupta, 2010).

$$\frac{\partial}{\partial X}\left(K_x\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_y\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_z\frac{\partial h}{\partial z}\right)-W=0 \qquad \text{………… Equation 29}$$

$$\frac{\partial}{\partial X}\left(K_x\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_y\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_z\frac{\partial h}{\partial z}\right)-W=S_s\frac{\partial h}{\partial t} \qquad \text{………… Equation 30}$$

Where:

- **H** is Potentiometeric head (L);
- **W** is Volumetric flux per unit volume and represents sources and/or sinks of water (T-1);
- **Ss** is Specific storage of the porous material (L-1);
- **T** is Time (T).
- $\mathbf{k_x}$, $\mathbf{k_y}$, and $\mathbf{k_z}$ are values of hydraulic conductivity along the x, y, and z coordinate axis, which are assumed to be parallel to the major, axes of hydraulic conductivity (LT^{-1})

3.2.5. Spatial Discretization of the Model Grids

Grid discritization in modeling transport requires some further consideration than only modeling flow. These additional considerations arise from the difficulties of solving transport equations than flow equations. When hydrodynamic dispersion coefficient is greater than zero, there is probability of occurrence of numerical oscillations may occur depending on the grid dimensions. To include such effects the grid size has to be based on a criteria name *Peclet Number (Pe)* which is defined as (Perkins and Johnston, 1963):

$$\boldsymbol{Pe} = \frac{\Delta \boldsymbol{l}}{\boldsymbol{\alpha_L}} \qquad \text{........... Equation 31}$$

Where:

- $\Delta \boldsymbol{l}\ (\boldsymbol{L}) is\ characteristic\ length\ in\ the\ ground\ water\ flow\ direction$
- $\boldsymbol{\alpha_L}(\boldsymbol{L})\ is\ the\ longitudinal\ dispersion\ coefficient$

Accordingly, that grid spacing should be selected such that the local Peclet number does not exceed 2. Thus, the grid spacing was based on this concept which could be calculated as:

$$\Delta \boldsymbol{l} = \boldsymbol{\alpha_L} * \boldsymbol{Pe} \qquad \text{........... Equation 32}$$

This is the same as saying:

$$\Delta \boldsymbol{l} \leq (\boldsymbol{\alpha_L} * \mathbf{2}) \qquad \text{OR} \qquad \mathbf{2} \geq \frac{\Delta \boldsymbol{l}}{\boldsymbol{\alpha_L}}$$

★ The grid spacing shouldn't exceed two times than that of the longitudinal dispersivity!

The longitudinal dispersivity value was taken to be 1150m (see part 3.3.4.2). Thus, any value below twice of this value could be considered as appropriate; the much lower values giving the accurate one. For this, the grid spacing 400m for Akaki catchment could be considered very reasonable.

3.2.6. Modeling Approach

To effectively execute the above stated ideal representation of the catchment's aquifer system a numerical computer program named MODFLOW was used. MODFLOW is a modular three-dimensional finite-difference groundwater model published by the United States Geological Survey (USGS). The first public version of MODFLOW i.e. MODFLOW-88 was released in 1988. MODFLOW-88 and the later version of MODFLOW-96 (Harbaugh and McDonald, 1996) were originally designed to simulate saturated three-dimensional groundwater flow through porous media. The later versions including MODFLOW-2000 and MODFLOW2005 attempts to incorporate the solution of multiple related equations into a single code and enable parameter estimation (PEST), Observation Process (OBS), sensitivity process (SEN).

This three-dimensional finite-difference grid system is formed by parallelepipeds or rectangular blocks in which it follows the Block-centered grid system grid discretization system of Finite difference node locating methods (Batu, 2005). In this method the grids are formed by the sets of parallel planes and the nodes are located at the center of the blocks.

3.3. Contaminant Transport Modeling

3.3.1. Introduction

Concept

In recent years, the interest in understanding the mechanisms and prediction of contaminant transport through soils has increased dramatically because of growing evidence and public concern that the quality of the subsurface environment is being adversely affected by industrial, municipal and agricultural activities. Transport phenomena are encountered in almost every aspect of environmental engineering science (Javadi et.al. 2008). Agriculture is generally recognized as the leading nonpoint source of water pollutants, such as sediments, nutrients, and pesticides (Liu et.al., 1997).

The aim of contaminant transport modeling is to determine the distribution of contaminants over time and space (Anderson and Woessner, 1992). The temporal aspect helped the groundwater resource managers in predicting future conditions under certain scenarios by looking for the past and prevailing conditions and future expected changes. Thus, from a model developed with a good understanding of the needed parameters, it would be possible to compare concentration values of specific areas of interest of an aquifer with different standards. With the second aspect, the spatial one, it is possible to look for where the concentrations are and/or will be higher in different parts of the aquifer thereby tracing for the sources of contamination, in the present and future. By Integrating the two i.e. knowing the sources, concentration, travel time and path it would be possible to demarcate aquifer protection zones for better management.

Technically, the definition and concept of the term 'transport' refers to the movement, storage, and transformations of contaminant in aquifers. With the term transformations it is to mean changes in concentrations of dissolved chemical species due to chemical reactions, and interphase transfers, such as dissolution of the solid matrix, and precipitation of the solute (Bear and Cheng, 2010).

Modeling contaminant transport is much far difficult than modeling the groundwater flow, due to the presence of additional assumptions and factors (input parameters) governing the output (Batu, 2005). In modeling contaminant transport, the aquifer properties, fluid type (water in this case), and the solute characteristics determines the fate of the contaminant. In general, these factors determining the contaminant migration are modeled as Advection, Diffusion, Dispersion and Reaction (chemical or biochemical) terms (Batu, 2005, Dominico, 2005; Bear and Cheng , 2010). A deatail of these processes is presented in part 2.1.

3.3.2. Conceptual Modeling

The general nitrogen cycle involves the process of mineralization, immobilization, nitrogen fixation, ammonification, nitrification, and denitrification (Addiscot, 2005; ITRC, 2000). Immobilization refers to the conversion of mobile nitrogen species to some organic through microbial and plant assimilation. Mineralization is the conversion of complex organic nitrogen to more simplified inorganic forms. Nitrification is the biochemical oxidation of ammonia to nitrate;

while Denitrification is the biochemical reduction of nitrate-nitrogen to nitrogen gas in the absence of oxygen.

For example, nitrogen may be found as ammonia (NH^{4+}) in the soil; Ammonia may be metabolized by organisms, assimilated by plants, adsorbed by clay minerals and/or organic matter, and oxidized to nitrate (NO^{3-}) and in the presence of specific bacteria and oxygen, ammonia is enzymatically oxidized to nitrite (NO^{2-}) then to nitrate, in an oxidizing environments. Taking it again to the cycle, nitrate follow the reverse process (nitrate-nitrite-nitrogen) in shortage of oxygen to be converted in to nitrogen, mean it denitrifies. Generally, temperature, moisture content, bacterial population of nitrifiers and denitrifiers, and pH are parameters controlling the speed of nitrogen cycle (ITRC, 2000).

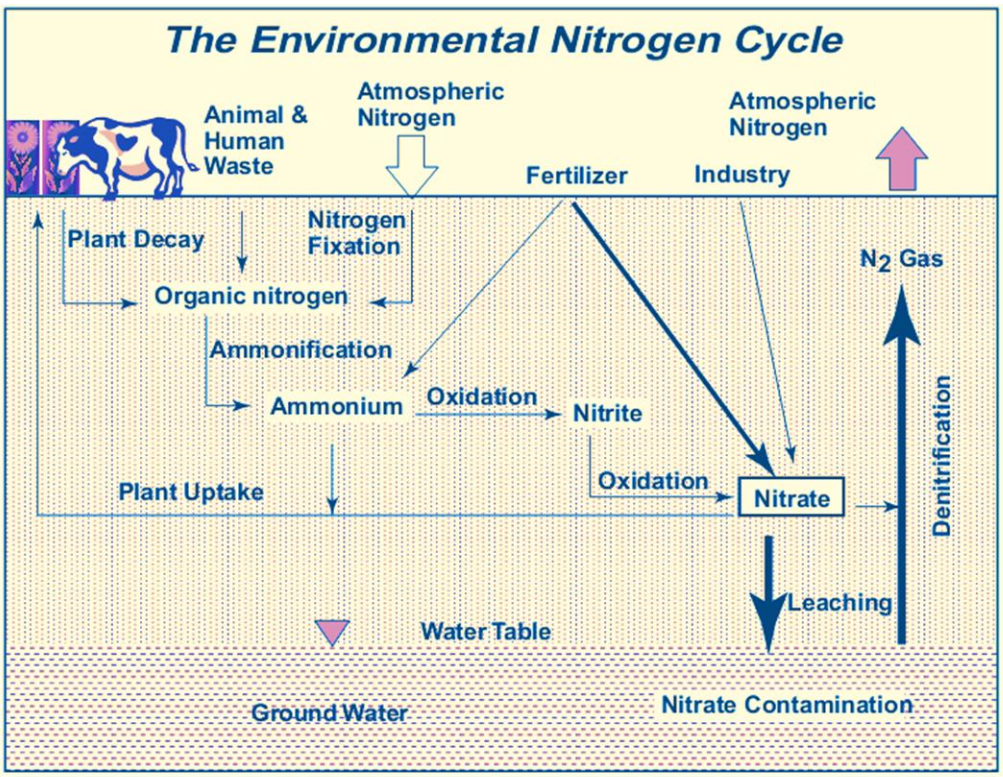

Fig. 15 The environmental nitrogen cycle (Deng, 1998)

As being observed from the above Fig., leaching from the unsaturated zone is the source for nitrogen loading to the groundwater and the only sink is the denitrification process (see sink/source below).

3.3.3. Boundary Conditions

In reference to the working area, as being noted from above, sources of nitrate for the catchment can generally be considered as diffused source of pollution (Kahssay et.al, 2010). The main transport agent for those diffused type of contaminant migration is recharge from the rainfall to the groundwater. Any where there is recharge means there is input of nitrogen to the groundwater, big or small depending on the site condition. In the same sense, when water leave the aquifer it will be considered as it is taking some sort of nitrogen with it. In this concept, taking the aquifer system as single layer aquifer, the boundary conditions will be identical as the groundwater flow boundary conditions. Accordingly, all boundaries except the southern end were simulated as no-solute flux boundary; while the southern tip of the catchment which it is believed water to flow out of the catchment was simulated as general flux boundary. In the same fashion, water bodies big rivers (Little and Great Akaki and Kebena), and reservoirs (Gefersa, Aba-Samuel and Legedadi) were simulated as constant concentration boundaries.

3.3.4. Parameters

3.3.4.1. Initial Concentration (C_o)

The presence of nitrogen in the groundwater has been reported by for example Ferezer Eshetu (2012), Shilima Abebe (2011), and AAWSA (2000). The responsible body of wells in the study area (AAWSA) periodically conducts physico-chemical analysis for several chemical species. From this record, point concentration map was prepared. These point concentration values were then interpolated ArcMap 10.1 with Spline with barrier technique to obtain the spatial distribution of nitrate concentration for the year 2012/2013 (Fig. 16). Then this interpolated map was imported to MODFLOW/MT3DMS as BMP image to set cell by cell initial concentration values.

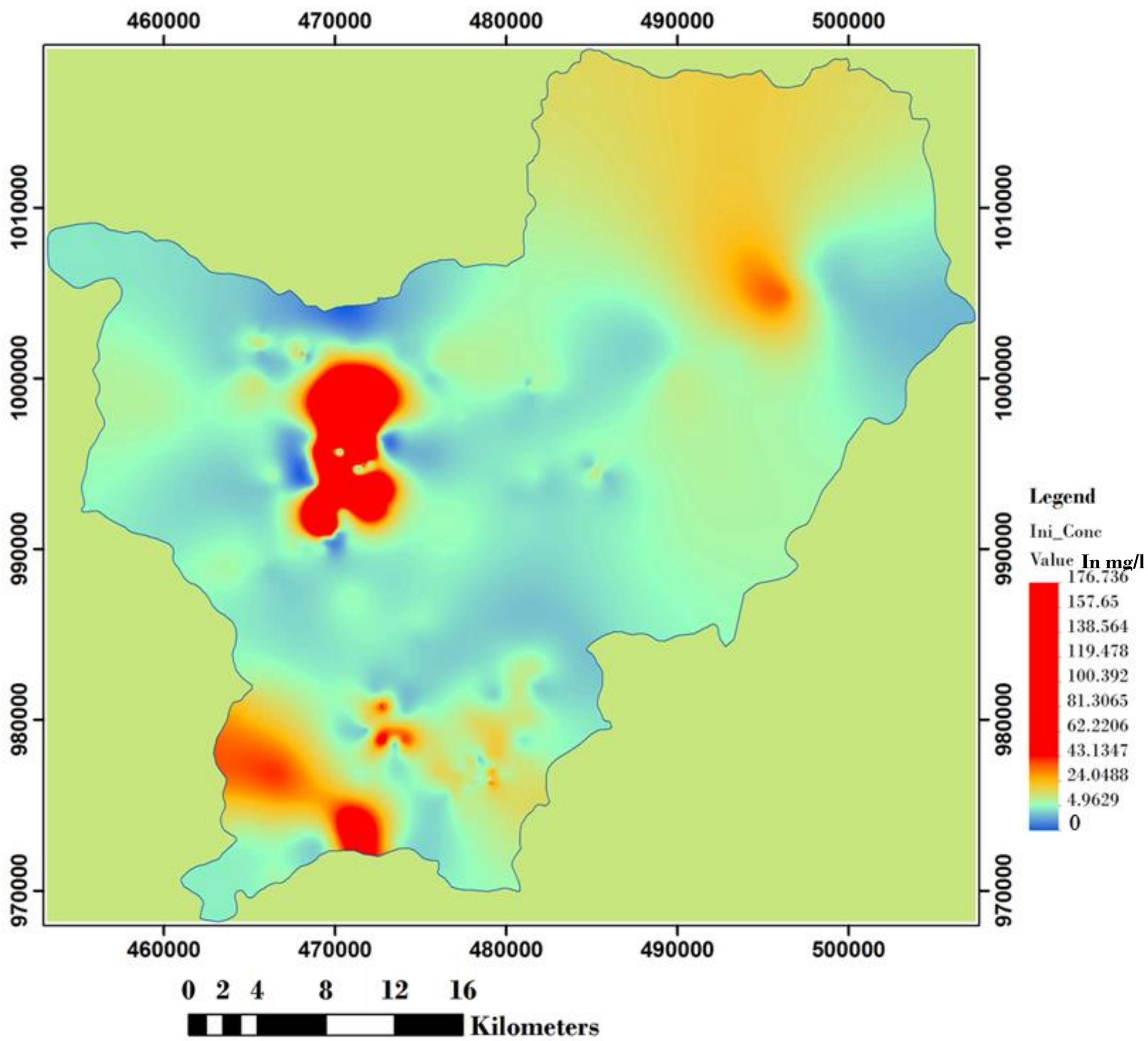

Fig. 16 Initial Concentration Map in mg/l (Year of 2012)

3.3.4.2. Longitudinal/ Transverse Horizontal and Vertical Dispersivity (A_l/A_t)

When a contaminant is added to flowing water it will migrate in the same direction to the water flow direction due to the mass movement effect of the flowing water and expands perpendicular to the flow direction due to the molecular and mechanical dispersion effects (Batu, 2005). In technical terms, longitudinal dispersivity is a term used to denote the process of mixing of a solute with the fluid medium along fluid flow direction (Fetter, 2000) and is expressed as the mathematical product of the longitudinal dispersivity value (α_L) and the average fluid velocity in the same direction. On the other hand, the spreading in the direction perpendicular to the flow is known as transverse dispersion. Seeing the water flow direction is the x-direction, the transverse dispersion will have two components; one, to the y-direction called the horizontal transverse dispersion (α_H) and second in the z-direction, the vertical transverse dispersion (α_T) (Appelo and Postma, 2005; Bear and Cheng, 2010).

In the study area there have not been any research conducted on the estimation of dispersivity parameters and the estimation of these parameters are costly, time consuming and are beyond the scope of the present study. As an alternative, there are effective means in which these values could reasonably be taken from existing literatures. Gelhar et.al., (1992) have worked out an effective means to use dispersivity values developed from 59 different site investigations and produces a sketch (Fig. 17) to be used based on different field conditions. This Figure correlates the scale of modeling with the dispersivity values from the concept of scale effect where by dispersivity tends to increase with the size of contaminant plume moving a longer distance downstream (Gelhar et.al., 1992; Anderson and Woesssner, 1992).

By modifying and further analysis of the Galhar's and some other 3 authors' data, Neuman (1990) has produced a universal correlation between dispersivity values and scale of measurement describes by Equation 33 and 34 and depicted in Fig. 18.

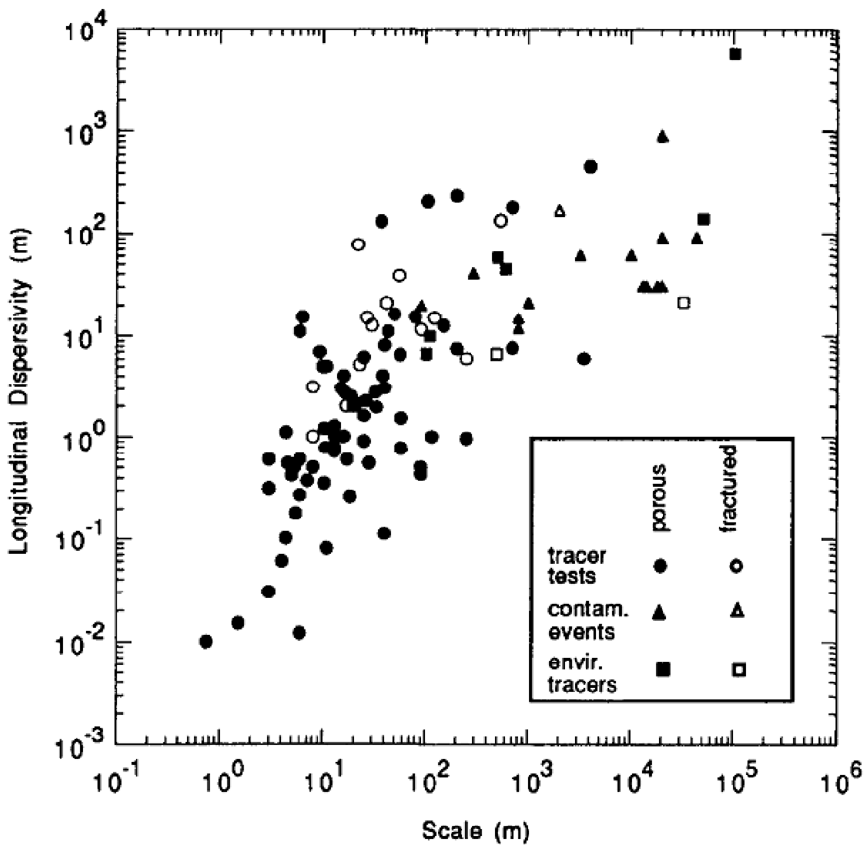

Fig. 17 Longitudinal dispersivity verse scale of observation (Gelhar et.al., 1992)

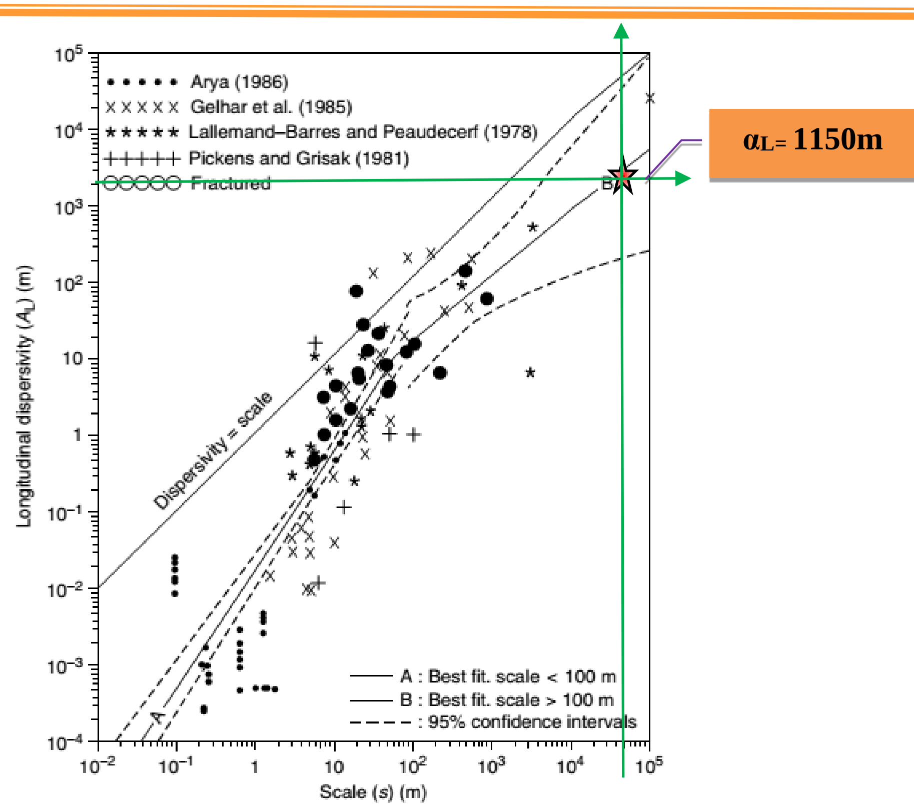

Fig. 18 Longitudinal dispersivity verse scale of observation (Neuman, 1993)

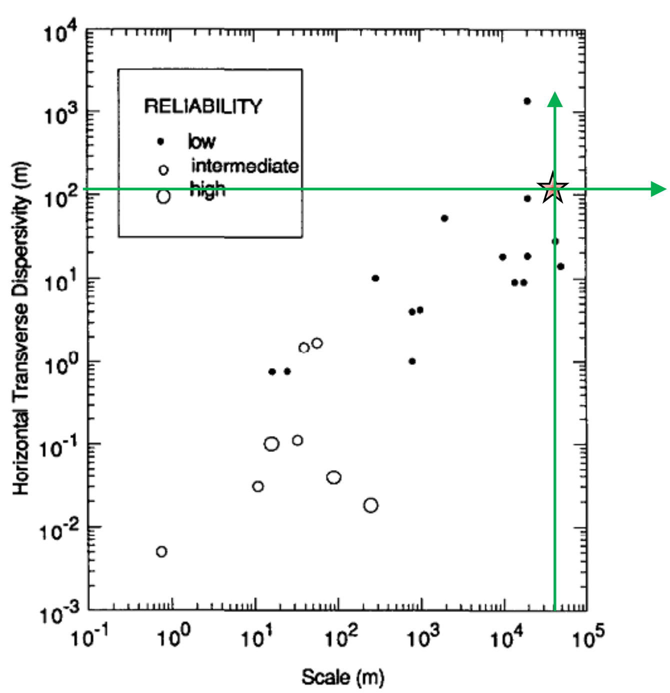

Fig. 19 Horizontal dispersivity verse scale of observation; is a function of scale (Gelhar et.al., 1992)

$$A_L = 0.0017s^{1.5}\ , for\ s \leq 3460m$$ …….. Equation 33

$$A_L = 0.32s^{1.83}\ , for\ s \geq 100m$$ …….. Equation 34

Accordingly, scale of modeling for Akaki catchment lies between the 10^4 and 10^5m with value of approximately 40,000m (green lines with star in Fig. 19). The corresponding value of longitudinal dispersivity for this scale was taken as 1150m. For the transverse dispersivity, it has been stated in many literatures (for example, Ahmed, 2004; Gelhar et.al., 1992; Batu, 2005) that taking the transverse dispersivity to be 10% of the longitudinal dispersivity is appropriate for most cases. Thus, horizontal transverse dispersivity for Akaki catchment was taken to be 115m.This could be supported also by the slope of the line formed between the longitudinal and horizontal transverse dispersivity, is 0.1(in Fig. 18); tells the longitudinal dispersivity is 10 times of the horizontal transverse dispersivity value. As have been justified in the groundwater flow model, vertical anisotropy was not considered in this study. Thus, the vertical transverse dispersivity will equal to horizontal transverse dispersivity i.e. 115m. Moreover, similar results to Gelhar et.al. (1992) have been reported also by Anderson (1984), Carrera (1993), and Schulze-Makuch (2005).

3.3.4.3. Effective Molecular Diffusion Coefficient (D*)

Molecular diffusion (D), the random Brownian movement of molecules, in water is dependent of the molecule type. Different molecules have different molecular diffusion. For nitrate the molecular diffusion has been found to be **$1.7X10^{-9}$ m^2/s** in water (Westrin and Axelsson, 1991; Picioreanu et.al, 1997). This is a case in water, much more different for molecules in porous media. In porous media molecules will travel longer distance; thus, the coefficient (termed effective molecular diffusion (D*), has to account for this travel and this extra distance. The tortuosity factor (τ) which is a ratio of the actual distance to the strait line distance traveled (L_a/L) is used to account for the extra distance. From this, the effective molecular diffusion is defined by: (Appelo and Postma, 2005; Batu, 2005; Bear and Cheng, 2010)

$$D^* = D\ x\ \tau$$ ………. Equation 35

This tortuosity factor is also dependent of the material and it ranges from 0.3 to 0.7. As presented in Gillham and Cherry (1982) - as cited in Batu (2005), Perkins and Johnston (1963) suggested that the value of τ is approximately 0.707 for most media from a review of data on unconsolidated granular media obtained by several investigators. Bear (1972) has also suggested the tortuosity factor to be 0.67 for the same media. Therefore, any value in between 0.67 and 0.7 will be appropriate to use for Akaki catchment tortuosity factor.

Therefore, taking the intermediate value for tortuosity factor between 0.67 and 0.7 the effective molecular diffusion for nitrate will be:

$D^{*} = \left(\frac{0.67+0.7}{2}\right) * 1.7 \times 10^{-9} = \mathbf{1.1645^{-9}} \, m^2/_{s}$ ………. Equation 36

3.3.4.4. Sorption coefficient (K_d)

In most attempts, it has been found that nitrate is highly soluble anion and not sorbed to any matrices in a significant extent (Loreti, 1988; Ahmed, 2004). Another, Calling to Stumm (1992) Buss et.al (2005) has put the following statement; "Sorption of anions (negatively-charged ions) under typical groundwater conditions is more complex and tends to only occur to specific species (such as phosphate and to a lesser extent, sulphate) and is therefore less commonly observed in groundwater".

A book that entirely written on nitrogen and its relation with other components of the environment by Addsicott (2005), has put the following explanation to show when nitrate will be sorbed to soils and solid matrices in groundwater.

"Clays can adsorb some substances strongly, but what they adsorb depends on the acidity or alkalinity of the soil as well as the properties of the clay. Clays may Bear and Cheng either a permanent charge (usually negative) or a pH-dependent charge, which arises from the reversible dissociation of hydrogen ions from sites at the edges of the clays, from metal oxide surfaces, or from the phenolic or carboxylic groups of organic matter. Most agricultural soils in the developed world are maintained at pH values of 5.5 to 8.0 by applying lime. This means slightly acid to slightly alkaline, pH 7.0 being neutral. At these pH values, clays carry an overall negative charge. With electric charges, like repels like; so cations such as potassium and calcium are attracted to the surface of the clay, while anions like nitrate and chloride are not only not adsorbed by the clay but actually repelled by it. This rises to an electrical double layer comprising a layer of cations held tightly at the surface (the Stern layer) and a diffuse layer in which cations outnumber anions but to a decreasing extent as we move away from the surface. …. ***In the absence of clear evidence that the soil is positively charged, it will be advisable to assume that sorption, like solubility, does nothing to limit nitrate concentrations in groundwater***." (Addiscott, 2005); **17 pp**.

In the study area the pH of soil and the groundwater are 7.45 (Agaje Mekonnen, 2007)) and 6 .5 to 8.6 (Shilima Abebe, 2011), respectively. As a result, sorption of nitrate in the groundwater system of Akaki catchment is unlikely, therefore it was not modeled.

3.3.4.5. Sink/source

The concentration of sources of water (constant head cell reverse, reservoirs and head dependent boundaries) were specified manually all over the simulation time while sink terms (Wells) were set at that groundwater timely concentration by giving active cells very high number (like $10x10^{-30}$). When such numbers in MT3DMS exists for sink terms it automatically set the concentration to the groundwater concentration.

3.3.4.6. Decay/Biological Degradation (Λ)

Nitrate is the most stable and end product of nitrogen transformation, before the cycle has restarted by the means of denitrification. When nitrate joins the groundwater, it does not form insoluble minerals that precipitate nor does it go other complexities (Ahmed, 2004). But, there is a probability of nitrate to be degraded under some complex requirements; the presence of absolute anoxic condition, presence of electron donors (organic carbon, pyrite), and denitrifying bacteria species. In this model, this process will not be incorporated because of the following points presenting and comparing the scientific findings and actual study site condition:

- There will no denitrification of groundwater if the concentration of nitrates electron acceptors is higher than the one of organic carbon electron donor (Korom, 1992)-as cited in Debernardi et.al., 2008**;** thus available source of carbon is required. Akaki catchment being an area with volcanic successions it is not expected to have any sources of available carbon, mostly this is applicable for sedimentary depositions.
- To denitrify, the concentrations of soluble organic carbon (OC) must be greater than 2 mg/l and dissolved oxygen (O_2) must be lower than 2 mg/l (Debernardi et.al. 2008). But, for Akaki catchment the average dissolved oxygen level is 6.5 mg/l. In the year of modelling, eight well samples suspected to be contaminated with OC were tested for OC content. Out of the eight six samples were with trace amount (< 0.0002mg/l) and only 2 samples were with OC content of 0.0002 and 0.00126 mg/l. This all shows that there is no room to denitrification in the groundwater system of Akaki catchment.
- Denitrification occurs in an anoxic condition with the help of heterotrophic organisms (Paracoccus, Pseudomonas) following the path NO_3 to NO_2 then to N_2 (equation 37) and the process could turn reverse if there is any residual oxygen in groundwater (Debernardi et.al., 2008; Liu et.al., 1997).

$$\underset{Nitrate\ ion(+5)}{2NO_3^-} \xLeftrightarrow{-2[O]} \underset{Nitrate\ ion(+3)}{2NO_2^-} \xLeftrightarrow{-2[O]} \underset{Nitric\ oxide(+2)}{2NO} \xLeftrightarrow{-[O]} \underset{Nitrous\ oxide(+1)}{N_2O} \xLeftrightarrow{-[O]} \underset{Dinitrogen\ gas\ (0)}{N_2}$$

…………… equation 37 (Process of denitrification, from Buss et.al, 2005)

3.3.4.7. Nitrogen Loading Rate to Groundwater through Recharge

The loading rate of nitrogen can be estimated using different techniques. Of all the methods, mass balance approach has been widely used to know fate of nitrogen input to land use. This loading rate of nitrogen to groundwater is dependent of land use/land cover (LULC) type in a given area. Then different approaches are followed for each LULC type to estimate loading rate to groundwater. This is because of the way nitrogen could join the groundwater in spatial and temporal terms is different for different LULC classes.

It has been specified above that, the source of nitrate contamination in Akaki catchment is a diffused (non-point) source type. Thus, it could be modeled by adding the loading rate to recharge water concentration or alternatively by using the Mass loading package. But, in the study area there is no complete work done to estimate groundwater nitrate loading rate. An attempt has been made by Girmay Kahssay et.al. (2010) to estimate the amount of nitrogen loaded to groundwater from pit latrine. In this study it has been suggested that, using the population number to estimate the loading of nitrogen is more appropriate. It has been also found that, about 10953 tons of N in a year will be loaded as nitrate in to the groundwater. Moreover, it has been noted that also the indicated loading amount was calculated for only 75% of the population which was considered to use latrines. The amount of nitrogen loading to the groundwater from the remaining 25%, portion not having latrine, was also believed to be higher because of that this people will use many forms of sanitation including to defecating on edges of rivers and sewage.

For this study the means to estimate the loading rate of nitrogen to the groundwater was based on the existing land use/ land cover (calculations on Appendix-A). In the study area four land use types have been identified before by BCEOM- Seureca (2000).

A more detail LULC map has been produced by OWW (2012). Accordingly nearly 10 land use types have been identified named bare land, bush shrub land, cultivated, flower farm, inundated open grass, plantation, settlement, water bodies and woodlots. For this work, these all land uses were reclassified in to 4 land use types as follows (Fig. 5 in part 3.1.1.2):

- ✓ Urban area
- ✓ Agricultural/open areas
- ✓ Forest,
- ✓ Water bodies

With no modification from its source, this land use/land cover has been conceptualized for this study as follows. The urban area category represents the built areas of Addis Ababa city including the settlements, city infrastructures and industrial area. Generally, this class is delineated to be the current Addis Ababa city boundary and some part in Sandafa. The second group, agricultural/open areas, represents the cultivated, bare, flower farms and open grass land, left as open area for grazing and rural settlement purpose. It is very clear that the proportion of rural residential area quite small in proportion to the arable and grazing lands; thus, it can be considered that this class consists of arable and grazing lands. The forest land use includes plantations and woodlots. Lastly, the water bodies were representing the areas stated as dam and the inundated lands. Taking this in mind, nitrogen loading rates were estimated for each land use types (Fig. 20) as follows.

- ✪ **Urban area**

  To estimate the loading rate from urban area the approach followed by Girmay Kahssay et.al. (2010) was used with a little modification; in which loading rate solely depends on population number. In Girmay Kahssay et.al. (2010), the nitrogen loading was calculated for 75% of the population which was considered to have a latrine and the rest 25% was with no latrine but believed to contribute much more than the per capita nitrogen loading used i.e. 4kg/person/year. In this paper the loading was calculated for whole population (100%) with a per capita loading of 4kg/year. As a result, the amount of nitrogen loading in a year from this class will be the product of the population number and the per capita loading rate

4kg/person/year. This result was distributed to the area covered by this class to know spatial distribution of nitrogen loading.

✪ Agricultural/Open areas

The sources of nitrogen input to this category mainly come from addition of fertilizer (commercial or non-commercial) while the removal is through denitrification, plant uptake (harvest), runoff loss and leaching to the groundwater. The amount of nitrate leaching to the groundwater is the needed parameter for this modeling purpose. This case has been treated by the mass balance approach effectively in different study area in the literature. For Akaki catchment this value has not been computed. Therefore, literature based estimation techniques were followed.

Taking fertilizer application as only input to the arable land surface, the literature shows that the amount of nitrogen leached to the groundwater from the total fertilizer applied ranges from 10 to 50% (Böhlke, 2002). The average 30% have been suggested by many authors to be used as nitrate leaching percentage in the absence of concrete study (Barry et al. 1993; Puckett et. al. 1999).

From the above, nitrate loading rate from land use for this modeling purpose could be calculated by taking the 30% of nitrogen application in the study area. Nitrogen Fertilizer application rate were also considered to be the national application rate if N-fertilizer for the major crop or a weighted average of major crops; which was 100 Kg/ha.

✪ Forests

Leaching from forest lands ranges from 2-8 mg/l of concentration on recharging water, and under natural condition the natural nitrate content of groundwater doesn't exceed 3 mg/l. The higher values are applied to thick, high litter-fall, high decomposition and moist warm conditioned forests. But, in actual site condition, being near the city of Addis Ababa, the forests are scattered due to deforestation and the probability of having decomposed litter-fall and remaining parts of plants is lower because of collection of litter and other plant parts for fire-wood purpose. Therefore, in this modeling process, the lower limits of this range were used, 3mg/l of concentration in recharging water.

✪ Water bodies

Different water bodies exist in the study area mainly of rivers and reservoirs. These parts were modeled as constant concentration boundaries in which concentration remain the same over simulation period. These an averaged NO_3 concentration was used to include the nitrate loading from water bodies. From the data collected by AAWSA for monitoring purpose the nitrate concentration value ranges between 2.7 and 4. The average value for the observation was nearly 3 mg/l. Related water chemistry of these water bodies studies have been conducted (for e.g. Demlie et.al. 2007a). Same values were reported in these studies.

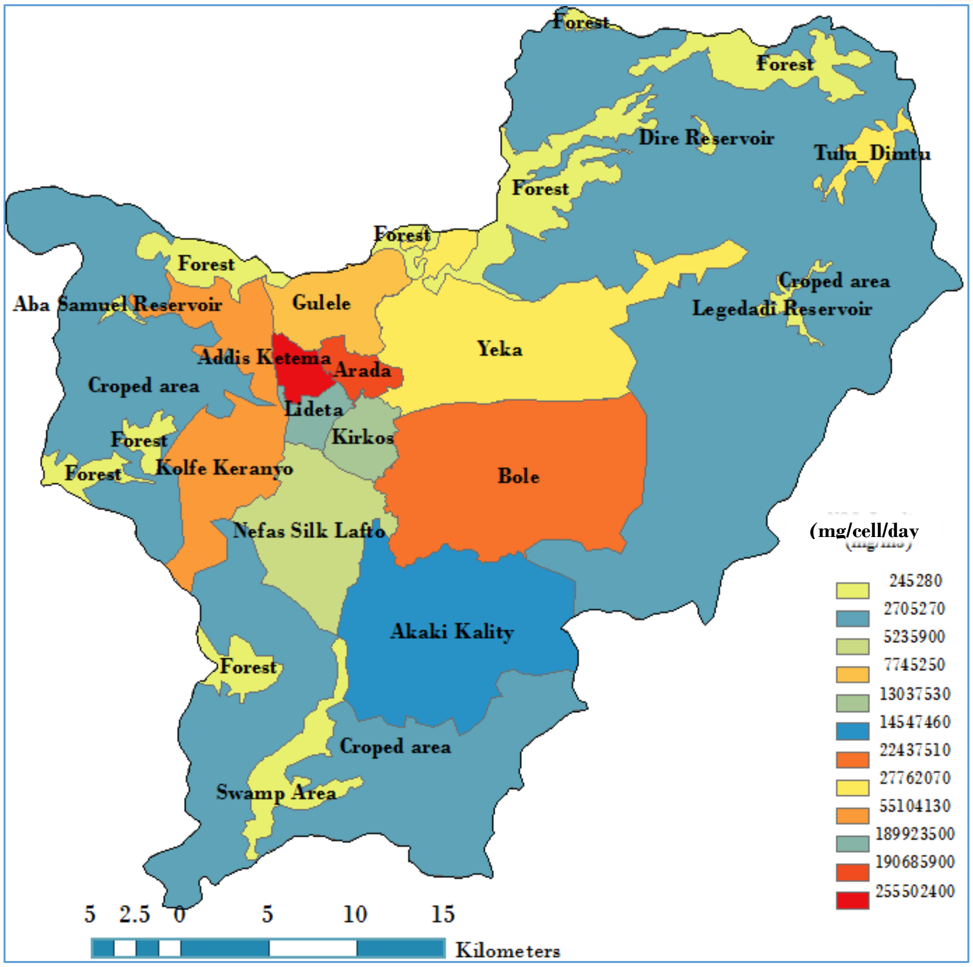

Fig. 20 Nitrogen loading map in mg/cell/day

3.3.5. General Assumptions and Limitations

The general assumptions in the conceptual modeling of transport modeling of Akaki catchment are:

- From the assumption taken for flow modeling, the medium was taken to be equivalent porous medium. For this reason, the complications emanating from quantification of dispersion caused by channeling of contaminant along path of high hydraulic conductivity i.e. the preferential flow was assumed negligible.
- Yet the patches of other land uses exist in each land use type (e.g. patches of settlement in cultivated areas), it was assumed to be the same for that specific land use system. This may create some problem in the estimation of nitrogen loading rate to the groundwater system.
- Emanating from absence of data and studies, many variable including longitudinal and transverse dispersivity, effective diffusion coefficient (tortuosity) and nitrogen loading estimation methods were taken from the literature. This may introduce errors in the modeling process.

3.3.6. The Advective Dispersive Equation (ADE)

The determination of contaminant distribution from a give source merely tries to quantify factors that determine contaminant migration. As have been mentioned in part 3.2.1.1., the factors are related to the nature of the transporting fluid in which the solute is in, the characteristics of the solute itself and the aquifer system formation and availability of other reactive component. The advective, dispersive and reactive terms in equation 39 denotes all the stated factors. The derivation of this equation is based on the concept that the flux of a given solute fulfills the requirements of mass balance approach. Taking this as a basic, the contaminant mass flux equation has been derived from Darcy's law (a detail is presented in part 2.1).

The governing equation for transport of contaminant, called the Advective Dispersive Equation (ADE), for homogeneous three dimensional (3D) anisotropic medium including sink and source terms is (Batu, 2005; Anderson and Woassner, 1992):

$$\boldsymbol{\varphi_e R_d \frac{\partial C}{\partial t}} = \frac{\partial}{\partial x}\left(\varphi_e D_{xx}\frac{\partial C}{\partial x} + \varphi_e D_{xy}\frac{\partial C}{\partial y} + \varphi_e D_{xz}\frac{\partial C}{\partial z}\right) + \frac{\partial}{\partial y}\left(\varphi_e D_{yx}\frac{\partial C}{\partial x} + \varphi_e D_{yy}\frac{\partial C}{\partial y} + \varphi_e D_{yz}\frac{\partial C}{\partial z}\right) + \frac{\partial}{\partial z}\left(\varphi_e D_{zx}\frac{\partial C}{\partial x} + \varphi_e D_{zy}\frac{\partial C}{\partial y} + \varphi_e D_{zz}\frac{\partial C}{\partial z}\right) - \frac{\partial}{\partial x}\left(CK_{xx}\frac{\partial h}{\partial x}\right) - \frac{\partial}{\partial y}\left(CK_{yy}\frac{\partial h}{\partial y}\right) - \frac{\partial}{\partial z}\left(CK_{zz}\frac{\partial h}{\partial z}\right) - \varphi_e v R_d C + C'W^+ + CW^+$$

…………… equation 39

In which,

$$\boldsymbol{R_d = 1 + \left(\frac{\rho_d}{\varphi}\right) K_d}$$

……………equation 40

Where:

$\boldsymbol{\varphi_e}$ *is effective porosity*
$\boldsymbol{R_d}$ *is retardation factor*
$\boldsymbol{\rho_d}$ *is aquifer matrix bulk density*
$\boldsymbol{\frac{\partial C}{\partial t}}$ *is change in concentration with resprct to time*
$\boldsymbol{\frac{\partial h}{\partial t}}$ *is hydraulic gradient*
$\boldsymbol{\frac{\partial C}{\partial x}}$ *is change in concetration with resprct to space*
$\boldsymbol{D_{xx}, D_{xy}, D_{xz}}$ …..*and* $\boldsymbol{D_x, D_y, D_z}$ *are the Hydrodynamic dispersion tensors*
$\boldsymbol{K_{xx}, K_{yy}, K_{zz}}$ *are hudraulic conductivity tensors as in Darcy′equation*
$\boldsymbol{v}$ *is the first − order decay or degradation constant*
$\boldsymbol{C}$ *is the concentration solute in the groundwater*
$\boldsymbol{C^-}$ *is the concentration of a source of water*
$\boldsymbol{W^+}$ *the volumetric flux per unit volume of a source of water*
$\boldsymbol{W^-}$ *the volumetric flux per unit volume of a sink of water*

3.3.7. Concentration Observation Wells

In the catchment there are both monitoring and pumping wells. The objectives of the study include observing the concentration of nitrate in selected areas of interest. From the view of keeping water quality safe and ensuring people welfare, these areas of interest were the water pumping wells for the water supply purpose of the catchment. Therefore, all major water pumping wells (Q>500 m^3/day) for water supply purpose and some other wells put for analysis purpose were used as concentration observation wells. Additionally, in order to understand contaminant movement directional effect 15 wells in 3 groups (4, 5, and 6) were projected in three directions (part 4.2.3. Fig. 29).

4. Result and Discussion

4.1. Groundwater Flow Model

4.1.1. Model Calibration

Errors in modeling process are common and their common sources are inaccuracy in field measurement of hydrogeologic conditions, errors related to estimation of parameters and complexities of the system (Alema Tesfaye, 2009). In definition, calibration refers to the process of adjusting selected model parameters within an expected range until the differences between model-predicted heads and field-observed heads are within the selected criteria of performance (Batu, 2005; Anderson and Woessner, 1992).

Calibration in modeling practices is done by comparing model simulated results with the real environmental conditions. Calibration of groundwater flow model are done by comparing the real field observation of water levels (head) and model output head for specific different points of the groundwater aquifer system.

For Akaki catchment groundwater flow modeling, a trial and error calibration method was used by which model parameters are adjusted manually within reasonable limits of the existing data and field hydrogeological observations . To measure the fitness of the model, statistical tools of measuring central tendency named Mean Error (ME), Absolute Mean Error (AME), Root -Mean-Squared Error (RMSE) were used, expressed as in equation 32a, 32b, 32c respectively (Anderson and Woessner, 1992; Alema Tesfaye, 2009).

$$\textit{Mean Error} = \frac{1}{n}\left(\sum_{i=1}^{n}(\mathbf{h_m} - \mathbf{h_s})_\mathbf{i}\right) \quad \text{........... Equation 41a}$$

$$\textit{Absolute Mean Error} = \frac{1}{n}\left(\sum_{i=1}^{n}|\mathbf{h_m} - \mathbf{h_s}|_\mathbf{i}\right) \quad \text{........... Equation 41b}$$

$$\textit{Root Mean Squared Error} = \left[\frac{1}{n}\sum_{i=1}^{n}(\mathbf{h_m} - \mathbf{h_s})_\mathbf{i}^{2}\right]^{1/2} \quad \text{........... Equation 41c}$$

Where:

- **n** is the number of points where comparisons are made,
- $\mathbf{h_m}$ is the observed hydraulic head at some point i, and
- $\mathbf{h_s}$ is the computed hydraulic head at the same point.

For the calibration process of the current model a total of 45 control points distributed over the whole catchment were used. After several trials it was possible to bring a good agreement between the observed and calculated values of the model Fig. 21 the reslting shows the graphical representation the comparison of observed and calculated values. Note, in this figure, a point more nearer to the diagonal line is the more accurate one.

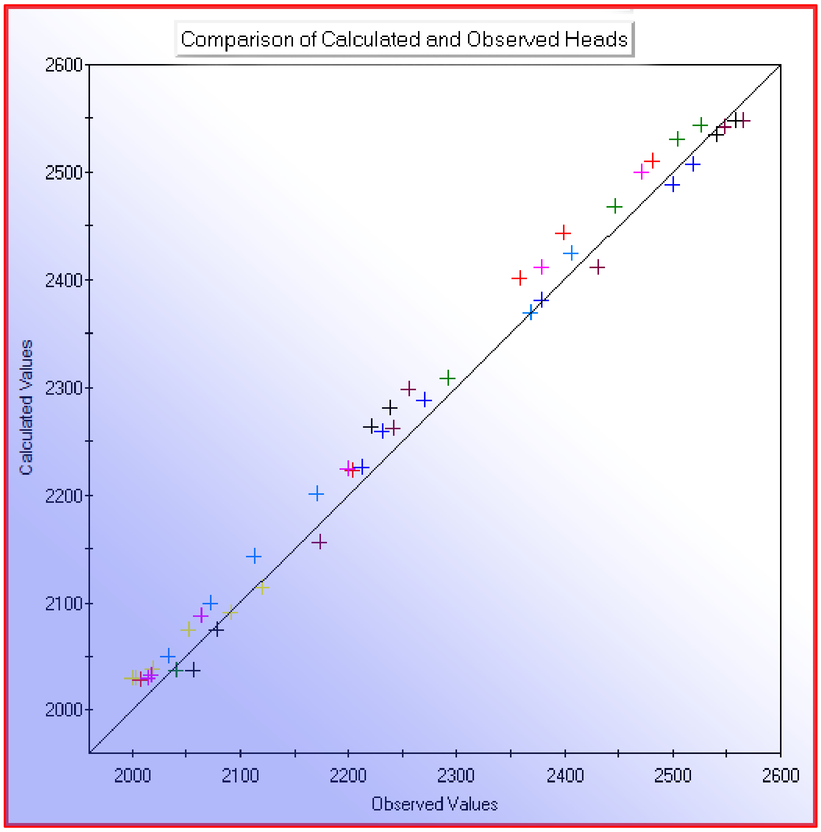

Fig. 21 Observed verse Calculated Head Scatter Diagram

Further, ME, AME and RMSE result of the observed and calculated values of the model calibration control points were found to be 7.6, 11.01 and 12.7 respectively, which was with acceptable limit of 5% tolerance of the average aquifer depth i.e. 15m.

Generally, the difference between the observed and calculated value was increasing moving towards elevated area. The same trend was also observed by all the stated modeling works for the present study area and Molenat (2002).

4.1.2. Groundwater Model Outputs

4.1.2.1. Simulated Head and Flow Direction

As being depicted in Fig. 22 the head value drops from northern to the southern part of the catchment leading the water to flows north-south direction continually. This in concept means the whole aquifer is hydrologically connected. The highest head recorded was 2729 m.a.s.l. at Entoto Mountain in the north and the lowest simulated water level was 1970.5 m.a.s.l at the southern end of the catchment. Yet there is a catchment outlet in the southern most end, the flowing water generally concentrates in Akaki well field from which high amount of water is pumped out for city water supply purpose. Since the flow direction of the groundwater is towards the city's major well field, this may potentially be a treat for the healthiness of the well field. Thus, it has an implication on well head protection (Ayenew et.al., 2008). Every groundwater flow model that has been developed for this catchment has shown the same flow pattern of groundwater with this work.

The simulated groundwater level of this model shows more or less closer maximum and minimum values with Ayenew et.al. (2008) which were calculated to be 2700 and 2000 respectively. Ebasa Oljira, (2006) has also calculated the minimum water level to be 2010 m.a.s.l. which was the same closer to the value developed by this model and the maximum to be 2600 m.a.s.l. which was considered to be a minute lower.

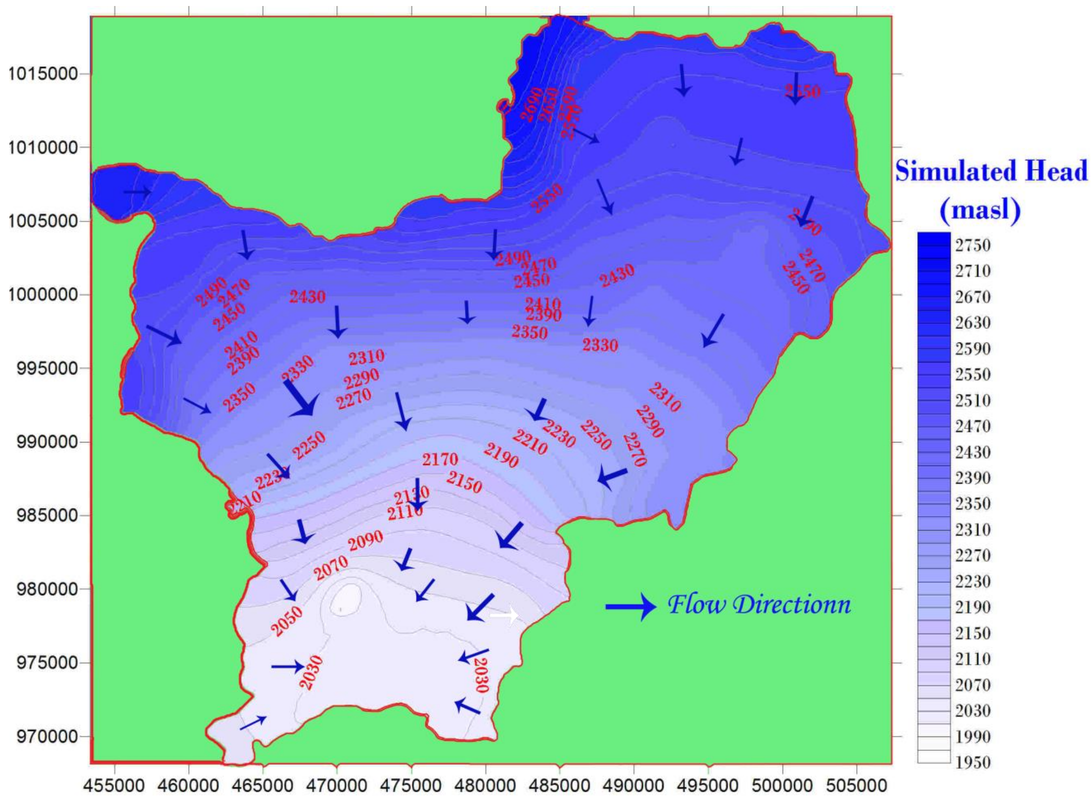

Fig. 22 Contour map of simulated head and its flow direction

4.1.2.2. Model Groundwater Balance

The quantification of the inflow and outflow terms in groundwater modeling, referred groundwater balance, should be done for parts or whole model under steady state condition (Anderson and Woessner, 1992). After calibrating the model, the water balance (Table 3) as per the input parameters shows that a total volume of 665280 m^3 water joins the groundwater system daily and being the model a steady state model the same amount of water leaves out of it. Thus, the total net effect (the sum of IN-OUT term) and the percent discrepancy results of the model are zero; showing the model is running under perfect steady state condition.

Table 3: Water balance of the model

FLOW TERM	IN (m^3)	OUT(m^3)	IN-OUT(m^3)
STORAGE	0.000000E+00	0.000000E+00	0.000000E+00
CONSTANT HEAD	1.927285E+05	3.324746E+05	-1.397461E+05
WELLS	0.000000E+00	7.452400E+04	-7.452400E+04
DRAINS	0.000000E+00	2.280097E+03	-2.280097E+03
RECHARGE	4.486094E+05	0.000000E+00	4.486094E+05
ET	0.000000E+00	0.000000E+00	0.000000E+00
RIVER LEAKAGE	2.386596E+04	2.318950E+05	-2.080291E+05
HEAD DEP BOUNDS	7.616672E+01	2.410631E+04	-2.403015E+04
STREAM LEAKAGE	0.000000E+00	0.000000E+00	0.000000E+00
INTERBED STORAGE	0.000000E+00	0.000000E+00	0.000000E+00
RESERV. LEAKAGE	0.000000E+00	0.000000E+00	0.000000E+00
SUM	6.652800E+05	6.652800E+05	0.00
DISCREPANCY[%]	0.00		

In this water balance, the very important input term is recharge contributing for 67.5% of the followed by inflows from constant head and river leakage with contributions of 29% and 3.5%. In the balancing output term constant head, river leakage and withdraw from wells take the first three ranks with a percentage contribution of 49.92%, 34.86% and 11.2 % of gross outgoing water respectively.

In general terms, this water balance shows that the inflow from the major input term, recharge, from the highly elevated areas joins the groundwater system through infiltration. This infiltrated water, is then stored in the groundwater system. The majority of this water (about 84.35% of the total inflow) leaves the groundwater system through constant head cells (49.98%) used to represent all surface water bodies and river leakage (34.86%) mainly from the two Akaki Rivers. This water again joins back as the remaining amount of the inflow water (about 32.56% i.e. 28.97% from constant head and 3.59% from river leakage). This all shows that there is a significant amount of groundwater-surfacewater interaction in Akaki catchment, which generates movement of contaminants with the exchange of water. Yet it is bidirectional, the model in its current condition shows that there is a net movement of groundwater to the surface water bodies due to relative higher groundwater levels emanating from continually falling topography; i.e. dropping topography has helped the groundwater to get higher elevation than the succeeding area (moving north-south direction in the catchment) that in effect helping springs to emerge here and there in the way (Ayenew et.al., 2008). Here, it is clear that any stress to the groundwater system from future utilization of the water resource would reverse this water balance leading to the reversal of the groundwater flow direction between surface and groundwater systems. This would aggravate groundwater contamination from contaminated surfacewater bodies

Comparing this work to previous works, it has fundamentally very similar groundwater flow direction and closer output values. Looking to output of the model made by Ayenew et.al., (2008), the same pattern of flow and closer values of input parameters were observed with a bit higher total inflow and out flow terms of water balance as compared to the stated work i.e. 605000 m^3/day of water.

Another modeling work was done by Alema Tesfaye (2009). As the above the same groundwater flow and proportion of input output terms were observed. Nevertheless, this work has higher input and output terms than the stated work which was 452455 m^3/day due to the slight higher estimation of parameters.

This work has much higher total inflow and out flow terms in its water balance as compared to the model developed by Ebasa Oljira (2006) estimating the terms to be 366674 m^3/day. This difference has raised from different conceptualization of the aquifer thickness and recharge amount. Aquifer thickness was used in the range of 150 to 250 in Ebasa Oljira (2006) while it was between 200 and 300m in this work. The maximum and minimum recharge for Ebasa Oljira (2006) was 0.0000822 and 0.000411 m3/day while it was 0.00010489 and 0.0005248 m3/day for this work. Note that this is the model with lowest input output terms in all the four models discussed here.

Generally, this model has reproduced the same groundwater flow direction and slight higher input output terms of water balance due to the use of higher aquifer thickness and a slight modifications made to the recharge values in the calibration process. This model has a very tiny amount of head calculation difference with the models developed earlier to this work.

4.1.3. Sensitivity Analysis

Sensitivity analysis is carried out in order to understand how the changes in some specific parameters affects the model output. A model is said highly sensitive for a parameter if a change in that specific parameters affects the model output significantly than other parameters. If a change in a parameter is not affecting the model output significantly it is said the model is less sensitive to that parameter. Thus, knowing how parameters affect a model outputs helps to take care of data collection, entry and processing in developing a model. Further, it is very helpful for users of the model to visualize possible upcoming model output patterns in relation to changing parameters. In this work, as have been identified by previous works, sensitivity analysis for two parameters, hydraulic conductivity and recharge was done.

4.1.3.1. Sensitivity Analysis of Hydraulic Conductivity:

To observe how the model is sensitive to hydraulic conductivity, hydraulic values of the whole model was decreased by 25 and 50% and increased by the same to look in to both sides of changes. 49 boreholes (Fig. 23) having water level between 2000m and 2600m were set to see the effect of changing hydraulic conductivity on different elevations.

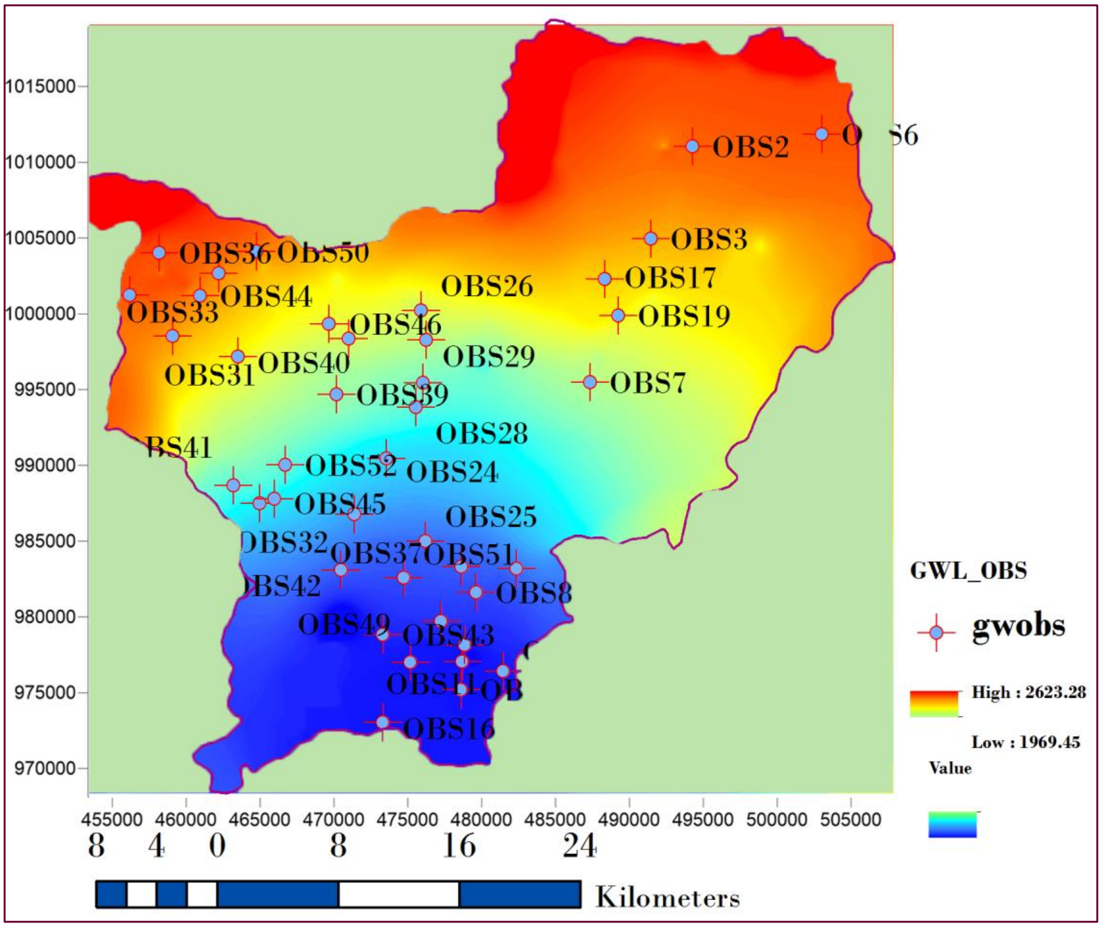

Fig. 23 Groundwater observation points

Table 4: Model sensitivity analysis of hydraulic conductivity

Water Level Range	Num_BH	50%_Dec	25%_Dec	25%_Inc	50%_Inc
2000-2300	27	5.0794444	1.92011111	-1.3172963	-2.2421852
2301-2600	22	31.451333	11.6162857	-7.96004762	-13.419095
Average	49	16.617146	6.1621875	-4.2235	-7.1320833

Accordingly, in average, a decrement of hydraulic conductivity value by 50 and 25% resulted a rise of 16.16 and 6.16m of water level and an increment of hydraulic conductivity value by the same has the effect of 4.22 and 7.13m decline in water level respectively (Table 4, Fig. 24). Note, the model is very sensitive to decreasing hydraulic conductivity values than increasing values. The model also returned very differently for different elevations. Elevated catchment parts (northern) replied very sensitively than the lower flat (southern) parts. Showing this, head observation points having elevation in between 2300 and 2600 m.a.s.l. has shown increment of 31.45 and 11.61m for decrement of hydraulic value by 50 and 25% respectively. Increasing hydraulic conductivity values by 50 and 25% has resulted lowering of head values by 7.26 and 13.41m respectively for the same area. On the other hand, observation points having elevation between 2000 and 2300 have 5.09 and 1.92m head decrement for increasing hydraulic values by 50 and 25% and there were 1.31 and 2.24m decrement of water level for 25 and 50% increment of hydraulic conductivity values.

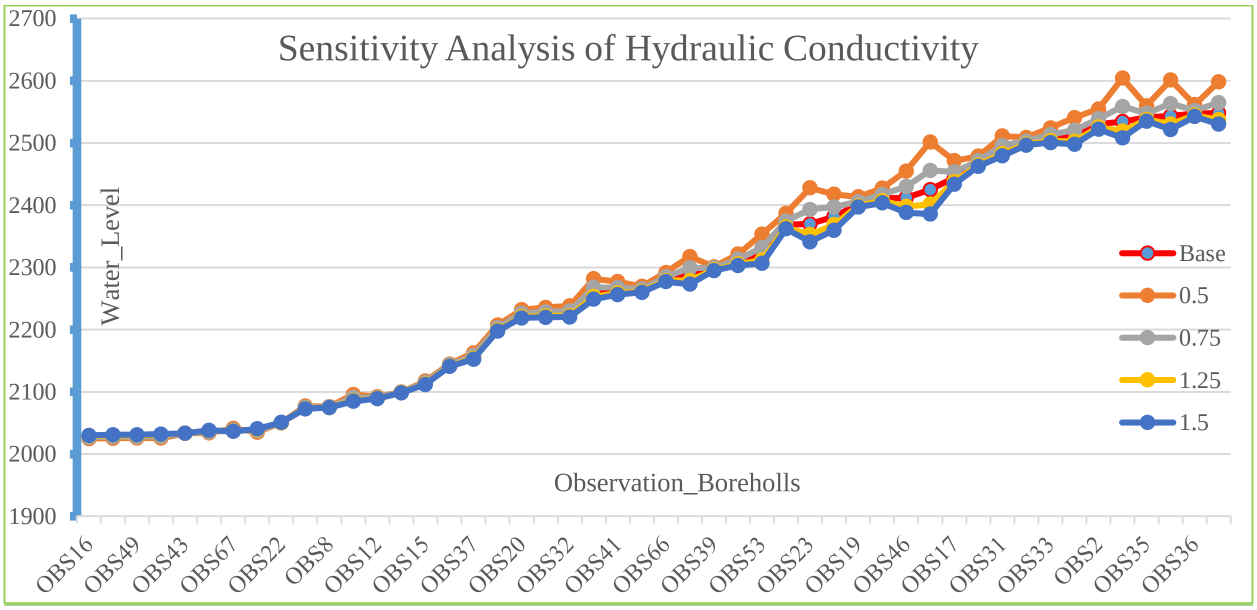

Fig. 24 Comparison of effect of different hydraulic conductivity value on model output

4.1.3.2. Sensitivity Analysis of Recharge

In the same fashion to the sensitivity analysis for hydraulic conductivity, to see the effects of changing recharge condition on the outputs of the model, the calibrated model was tested for increasing and decreasing recharge values of 25 and 50%.

For all observation wells (49), as have been summarized in table 5, the effect of increasing recharge value by 25 and 50% has raised the groundwater water level by 6.57 and 12.56m while decreasing the recharge by the same amounts has an effect of lowering the water table by 7.3 and 15.21m respectively. Both increasing and decreasing values have very significant effect on the highly elevated areas (Fig. 25). The elevated areas (northern parts), specifically, observation points having elevation between 2300 and 2600 m.a.s.l. has an average rise of groundwater table of 21.52 and 11.23m for 50 and 25% increment in recharge respectively. While the southern part having elevation between 2000 and 2300m have an average rise of groundwater level of 6.45 and 3.4m for the same level of increment in recharge. On the same but opposite fashion, the effect of decreasing recharge by 25 and 50% has cause fall of head values by 12.58 and 25.70m for northern elevated ones and 3.79 and 8.03m for southern lower elevated areas respectively.

Table 5: Model sensitivity analysis of recharge

Range	Num_BH	50%_Dec	25%_Dec	25%_Inc	50%_Inc
2000-2300	27	-8.02886	-3.78993	3.39525	6.447929
2301-2600	22	-25.6946	-12.5765	11.23932	21.52268
Average	49	-15.2072	-7.36065	6.577304	12.55654

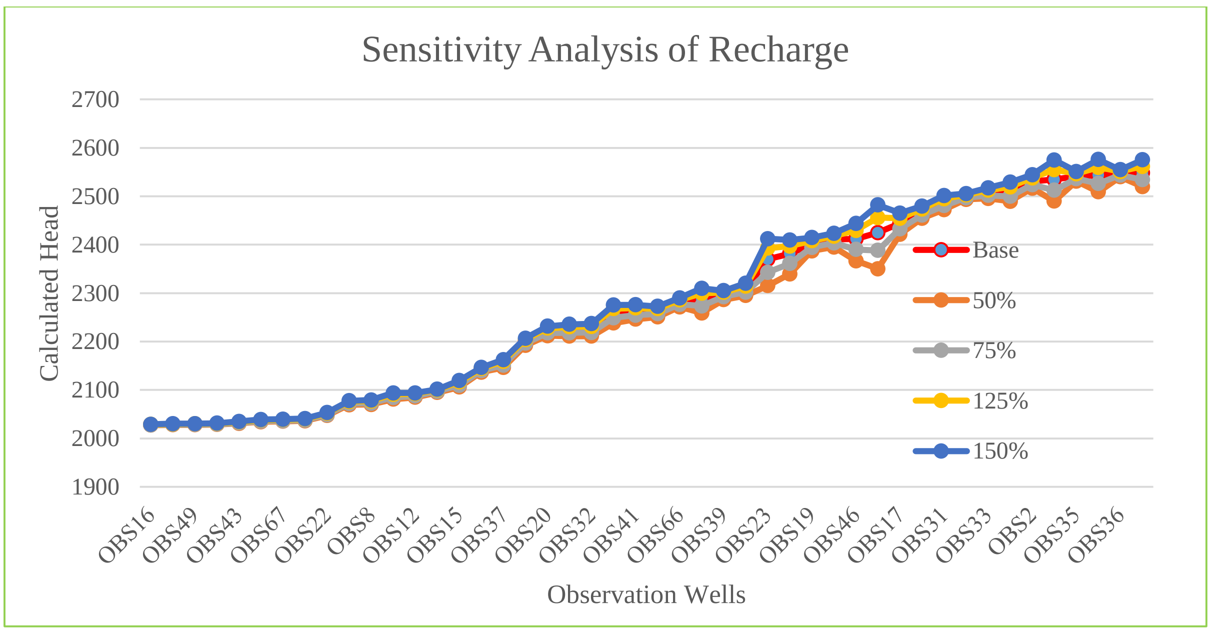

Fig. 25 Comparison of effect of different recharge value on model output

4.2. Contaminant Transport Model Calibration and Result

4.2.1. Contaminant Transport Model Calibration

The calibration process of contaminant transport was done in two folds. The first is calibrating the model with time serious data. Five boreholes with a record of 5 years back to the year of modeling were utilized. Accordingly, a very good agreement have been brought between time serious calculated and observed values by the calibration process of the contaminant transport model. The Mean Error (ME), Absolute Mean Error (AME) and Root Mean Square Error (RMSE) of the differences of all wells in the whole calibration time (5 years) was found to be 0.019, 0.6833 and 0.8760 respectively, which all were considered acceptable as compared to the maximum and minimum value of the range of data used to calibrate i.e. 5 and 15 mg/l concentration respectively (Fig. 26).

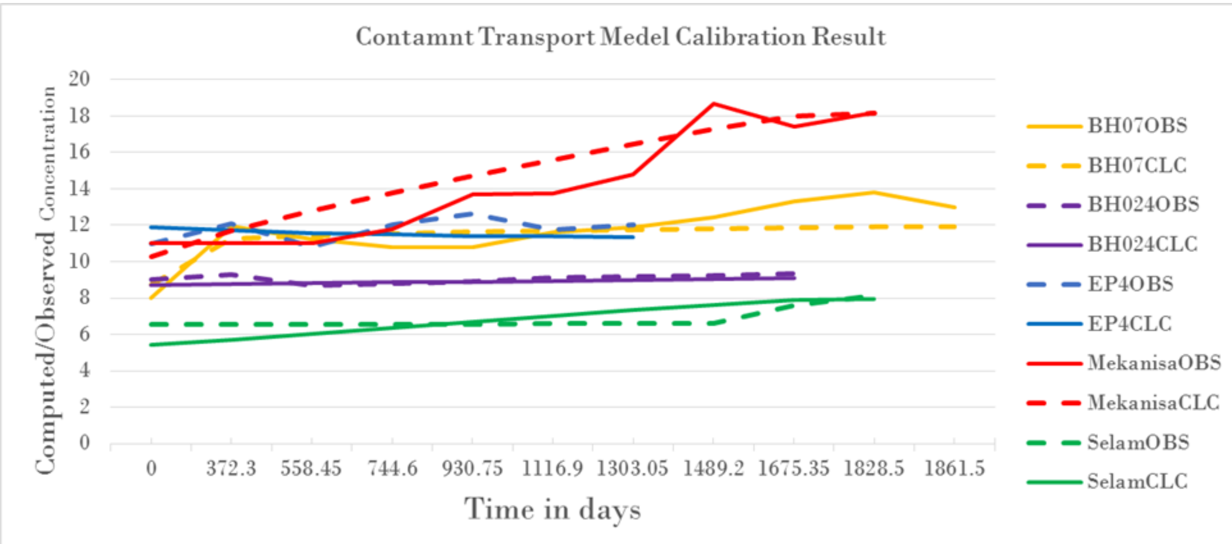

Fig. 26 Contaminant transport modeling calibration result (Note: the broken lines represent calculated while the unbroken ones denotes observed concentration in mg/l)

Compared to the large area coverage of the catchment the calibration process using only these points was not considered enough. Therefore, a second calibration process was used. In this method, the model was feed with parameter values of older data collected 5 years back to the modeling year. Then the model was run to simulate the catchment conditions to the modeling year in which all the necessary data need for calibration are available. Through this, it was possible to compare and calibrate concentration contour map of the catchment on the modeling year with the contour map predicted by the model by running it up to the modeling year. For this, contours of 10 and 20 mg/l concentration was used in the calibration process to bring visual similarities of the plume shape and reasonable closeness between areas covered by the contours of the simulated plume and actual concentration map of the modeling year. Accordingly, the model calculated concentration contours of 10 and 20 are very similar with the actual concentration map (Fig. 27) developed for the modeling year for the same concentration contours. It was also brought very close values in area coverage with 10 and 20 mg/l contours. The difference in area coverage for

10 mg contours by slight higher at the central parts of the main plume yet the differences were tolerable. The area coverage differences were totally negligible for 20 mg/l. Note that the tiny extra area (extra to their union) can be canceled each other.

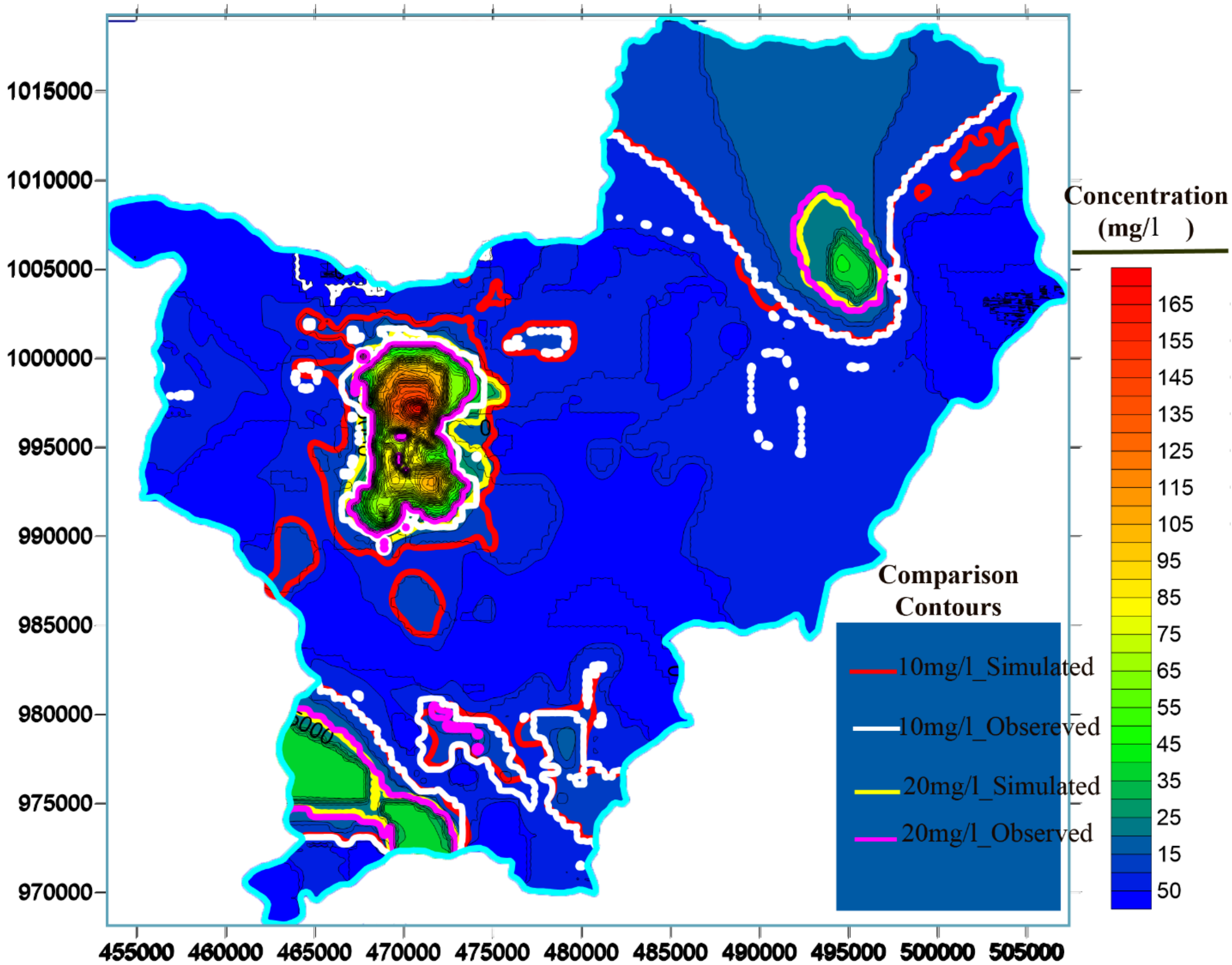

Fig. 27 Comparison between observed and calculated contours in the year 2012.

4.2.2. General Contaminant Transport Model Output

The main aim of developing this numerical finite difference model was to replicate the distribution and movement of nitrate in Akaki catchment. This would help in the creation of deeper understanding of nitrate contamination both in space (at every point of the catchment) and time i.e. the current distribution and prediction of future nitrate dynamics.

After calibrating the contaminant transport model, the general representation of catchment nitrate distribution was a function of land use land cover condition. Different land use systems has contributed different amount of nitrate for the groundwater. This can be shown by comparing land use land cover maps of the catchment and the groundwater nitrate concentration map at different time. Initially, the nitrate distribution of the catchment was only restricted to few boreholes restricted around central Addis Ababa. These places with higher nitrate concentration was relatively active and populous ones in time. As time goes the nitrate distribution expands with the growing population making its center Addis Ketema Sub-City located at 470530 UTME and 997815 UTMN. With further expansions of the city, new areas were being built and converted to inhabited ones which previously were cropped or forest area. Following that new hot spots of nitrate plumes were being formed. The model concentration-time contours (Fig. 28) has a good representation of these hot spots. Here, note that the population number was the most important factor making built areas to be the most polluted areas. This higher nitrate loading associated with the high population number is due to the poor sanitation system of sewerage and presence of unpaved pit latrine (Kahsay, 2010; Demlie and Wohnlich, 2006).

Due to the release of nitrate in fertilizer use, cropped areas has got the next rank in contribution nitrate to the groundwater following highly populated built areas. Water bodies and plantations (forests) was with the lesser contribution of nitrate to the groundwater. It is well known that the water bodies especially of rivers are well known to be polluted by different contaminants. But, different several measurements of nitrate on different parts of the rivers has shown concentration amount not greater than 3mg/l. This may be due to the high rate of conversion of nitrate to nitrogen i.e. via bacteria facilitated denitrification process.

In relation to the direction of contaminant movement, making the center of plume formation mainly central Addis Ababa Addis Ketema subcity (470530 UTME, 997815 UTMN), nitrate migrates in all direction (Fig. 28). As can be expected a very high amount of contaminants were migrating following the flow direction, southwards from the center of plume formation due to the high velocity of ground water facilitated by the elevation drop down of the catchment. On the other hand, wells closer to the plume center were highly affected by contamination due to diffusive migration, though they were located towards relatively higher elevation areas as compared to the center of plume (southern, southern-east and southern-west). Here we can see that nitrate is migrating even against the flow direction.

Though previous aquifer vulnerability maps (e.g. Dereje Nigussa, 2003; Tenalem Ayenew et. al., 2001) shows that the northern especially the highly elevated recharge zones were very susceptible to pollution the results of this model has determine a bit different concentration map. This wouldn't in fact contradict with the susceptibility maps but it signifies that even though these recharge zones are highly susceptible due to their aquifer characteristics and recharge condition the availability of source of contamination plays a very vital role in determining the risk of groundwater contamination. The major recharge zone of the catchment, Entoto, was determined to be extremely susceptible to pollution, but in land use type it was less populated built area and plantation forest. This helps the recharge zone to release nitrate contamination free water. This would have an implication on the groundwater contamination protection activities. In the future, any deforestation and building/populating the area would increase its riskiness to the groundwater unless and otherwise a very tight sanitation infrastructures are set. Some of the parts of this recharge zone were also found to be affected by diffusive migration from the main plume area.

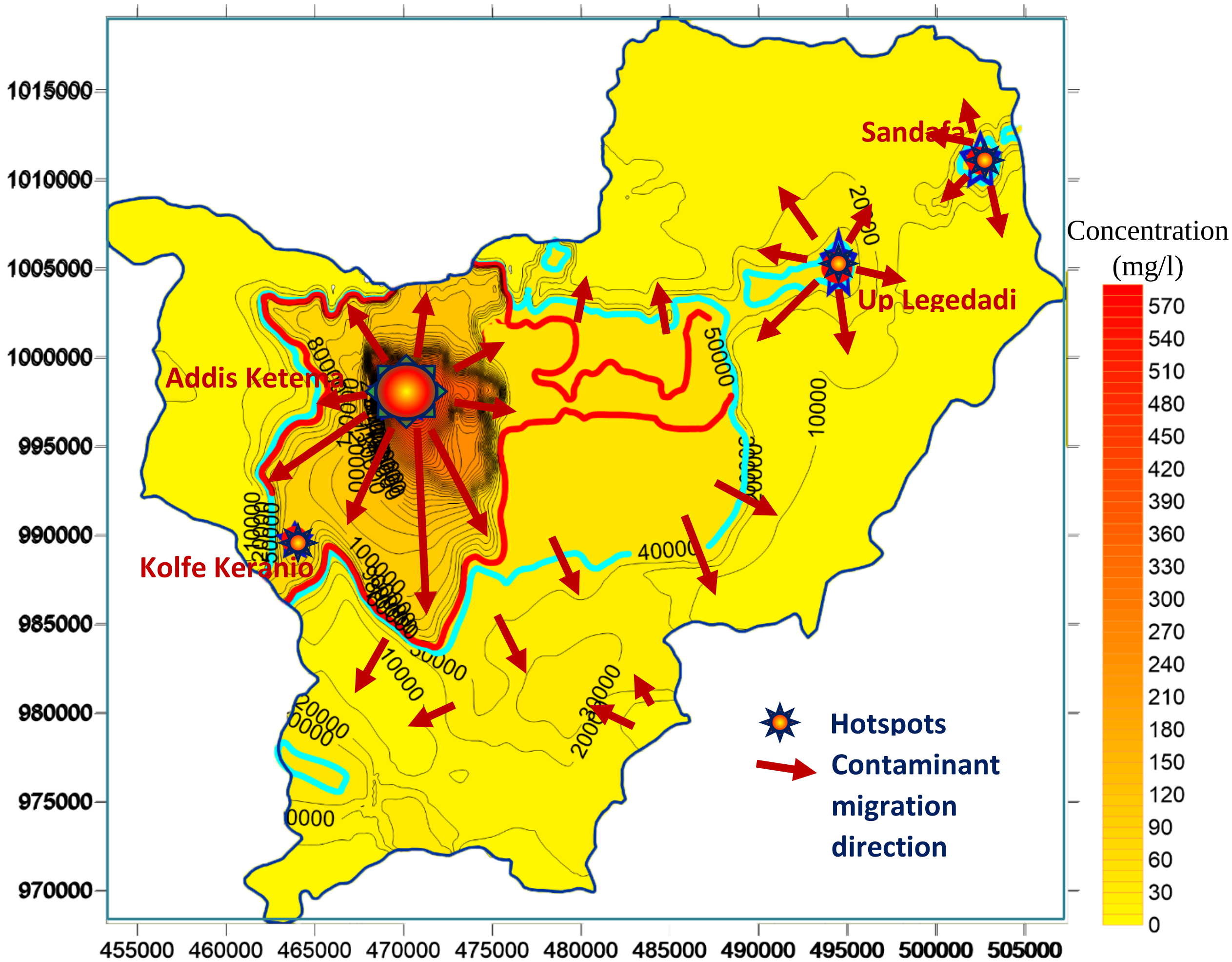

Fig. 28 Hotspot Identification (concentration-time contours at 50 year time)

Wells found below the center of the plume formation, even at longer distance are prone to pollution in the long run. The model run for 50 years shows that the major Akaki well field wells will be affected by pollution significantly in the coming years (see the scenarios). This is because of the very fast advective downward movement of groundwater that rolls down the contaminant particles.

In the essence of identifying the relatively high concentration areas, the model has identified 4 hot spots of nitrate contamination. These hot spots are Addis Ketema (470530 UTME, 997815 UTMN) Sandafa (502370UTME, 1011003UTMN), Legedadi (494394UTME, 1005122 UTMN) and Kolfe Keranye (463790 UTME, 989678 UTMN); Addis Ketema being by far the biggest (Fig. 28). These areas are points from which contaminants were migrating from. Looking for their land use, the areas were highly built areas i.e. greatly inhabited ones. These points are not necessarily places of peak concentration rather these are points of higher concentration relative to their surrounding area. This means, these points are either extremely inhabited old city areas like the major plume forming Addis Ketema area or they are newly emerging villages like the Legedadi and Sandafa areas. This relative high number of inhabitants has enable the places to develop by far the greatest nitrate concentration from which this contaminant migrates via any single or combination of the mechanisms of contaminant transport.

Here we can say that, the newly developed areas are a threat for the previously less polluted nearby aquifers. Some city expansion activities (for example, mountain parts of Yeka and Gullele sub-cities) were even on the main recharge zones of the catchment. This would impact both the quality and quantity of the groundwater. Thus, unless and otherwise a due attention is given for the construction of infrastructures future inhabitation and built up is in expense of groundwater quality. Emphasis has to be given for the coincidence between the fast growing city parts which potentially are source of nitrate pollution and the location of the major city water supply wells. High yielding wells are located around Gefersa, Legedadi and Akaki Well fields which in case have been detected to be either they are centers of plume formation or destinies of contaminant migration.

Generally, contaminants were moving in all directions from the centers of plume formation. Among the transport mechanisms, favored from the topographic condition of the catchment advective transport has played a major role although mechanical dispersion type migrations (diffusion and dispersion) have a very significant role in places where groundwater velocity is lower. According to Gillham and Cherry (1982), diffusion will become a dominant mechanism of contaminant transport for groundwater speed less than $1.6x10^{-10}$ m/s ($1.3824x10^{-5}$m/day). Since, the topographic condition is steeper (1Km drop down in 50 Km cross section) and the hydraulic conductivity values used were higher (min=0.09 and max=200), the aquifer will always be dominated by advective transport. Yet mechanical dispersion type migrations can't become the dominant mechanisms of contaminant transport we can understand that these were significant transport mechanism by comparing the result of this model with previous advective transport model developed for the catchment by for example Jemal (2009), Alema Tesfaye (2009) and Gudissa, (2010). We can notice the effects also by looking for the hill route movements (against the flow direction) of contaminant in for example towards Entoto ridge and lateral migration towards Gefersa and Legedadi reservoirs.

Beyond showing the general contaminant migration and center of plume formation such models enables the prediction of future changes. To show the existing nitrate distribution and possible dangers of future likely changes a detail scenario analysis is presented below.

4.2.3. Scenario Analysis

The purpose of modeling activity is always to represent a real environmental process. More to visualizing system overall component interaction, one of the most powerful advantage developing a model is to enables the prediction of future possible changes.

In order to create a brief and clear image of this contaminant transport model and show the effect of possible changes in the future, three different scenarios were developed. The first scenario (Sceinario-1) is a base condition for this analysis in which all its parameters are fixed to the year of modeling. In other words, scenario one will try to show model outputs under the assumption that every parameter will kept constant as the values of its modeling year i.e. 2012. This is used as a base condition to show the effect of other scenarios, else it can't be imagined that everything will keep unchanged for the coming years. The second scenario (Sceinario-2) tries to show the effect of population change and agricultural intensification under the existing land use system. This scenario keeps the current land use land cover condition and simulates the effect of the increasing population and usage of fertilizer in the coming 50 years. This is from the possible consideration that the city Addis Ababa would stop expanding sidewise rather it grows upward and/or it tries to use the vacant space available; as this is one of the best recommended management practice for growing cities. This can be shown by the current vast rebuilding activities in the city. The third scenario (Sceinario-3) seems very expectable. It tries to consider the both the population increment and land use changes. On one hand, as have been estimated by the Central Statistical Agency (CSA), the city population grows 2.1 % annually and it doubles every 35 years (Fig. 29).

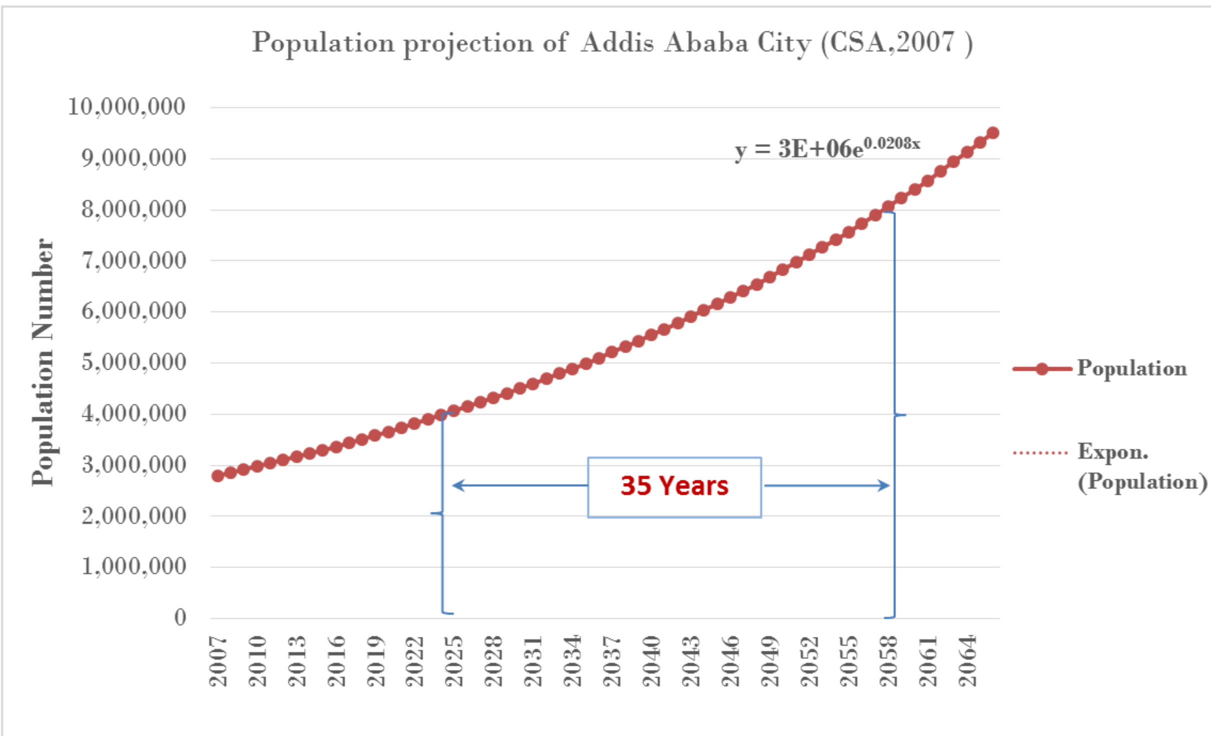

Fig. 29 Population Projection of Addis Ababa City (CSA, 2007)

On the other hand, as have been proposed by the City Administration of Addis Ababa in the master plan work of 2012, different rural parts of the catchment will become part of the city. This makes the whole catchment to be part of the city administration in which future development activities are planned for. Further, more pollution to water bodies would be expected. From this, scenario-3 tries to show model output under the assumption that the whole catchment will be built and new coming inhabitants (additional population) would be distributed to the whole catchment (Appendix A).

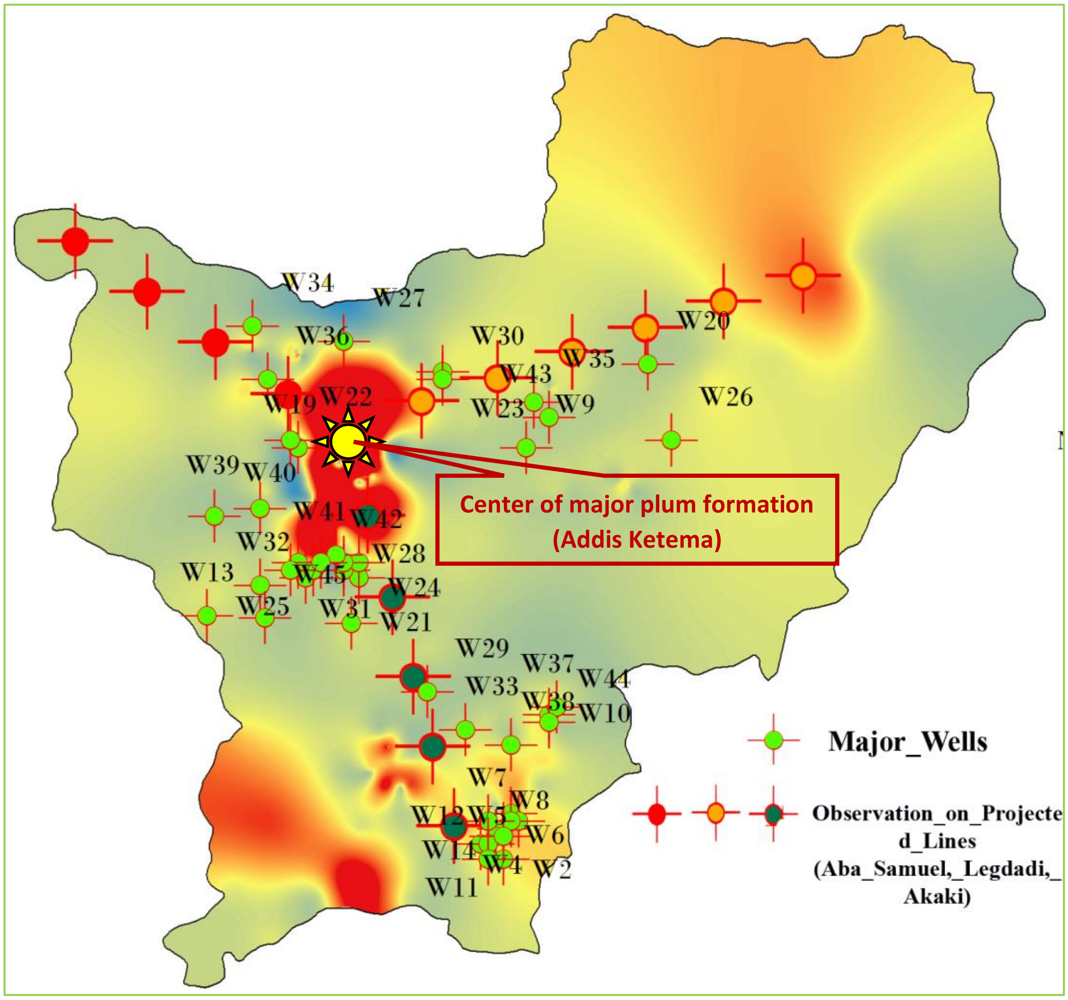

Fig. 30 Concentration Observation Points for Scenario Analysis

For all those scenarios, the results are presented in perspective of showing the effects of future changes on water supply and spatial migration of contaminant over time. To show the effect of changing conditions on city water supply, 45 major wells (wells having pumping rate ≥ 500 m^3/day) were selected which are distributed over all the catchment (Light green points in Fig. 30). Then the effect of future changes on these water wells by comparing with WHO drinking water standard are seen. On the other side, to show plume movement and spatial effect, making their center the major plume forming point central Addis Ababa (470530 UTME, 997815 UTMN), three observation lines were projected. The first was projected towards Gefersa reservoir (North-west), the second towards Legedadi reservoir (North-east) and the third shows the cases towards Akaki well filed (South) (Red, Yellow & Green points in Fig. 30 respectively). Here it is the outcome of all the three scenarios.

4.2.3.1. **Result of Scenario One (Scienario-1)**

Now, this is a base condition for all the scenarios and every parameter is kept constant to its modeling year. Parameter estimations are based on the detail above (Section 3.3.4). This model is then run for the coming 50 years and the resulted concentration map is presented in Fig. 31.

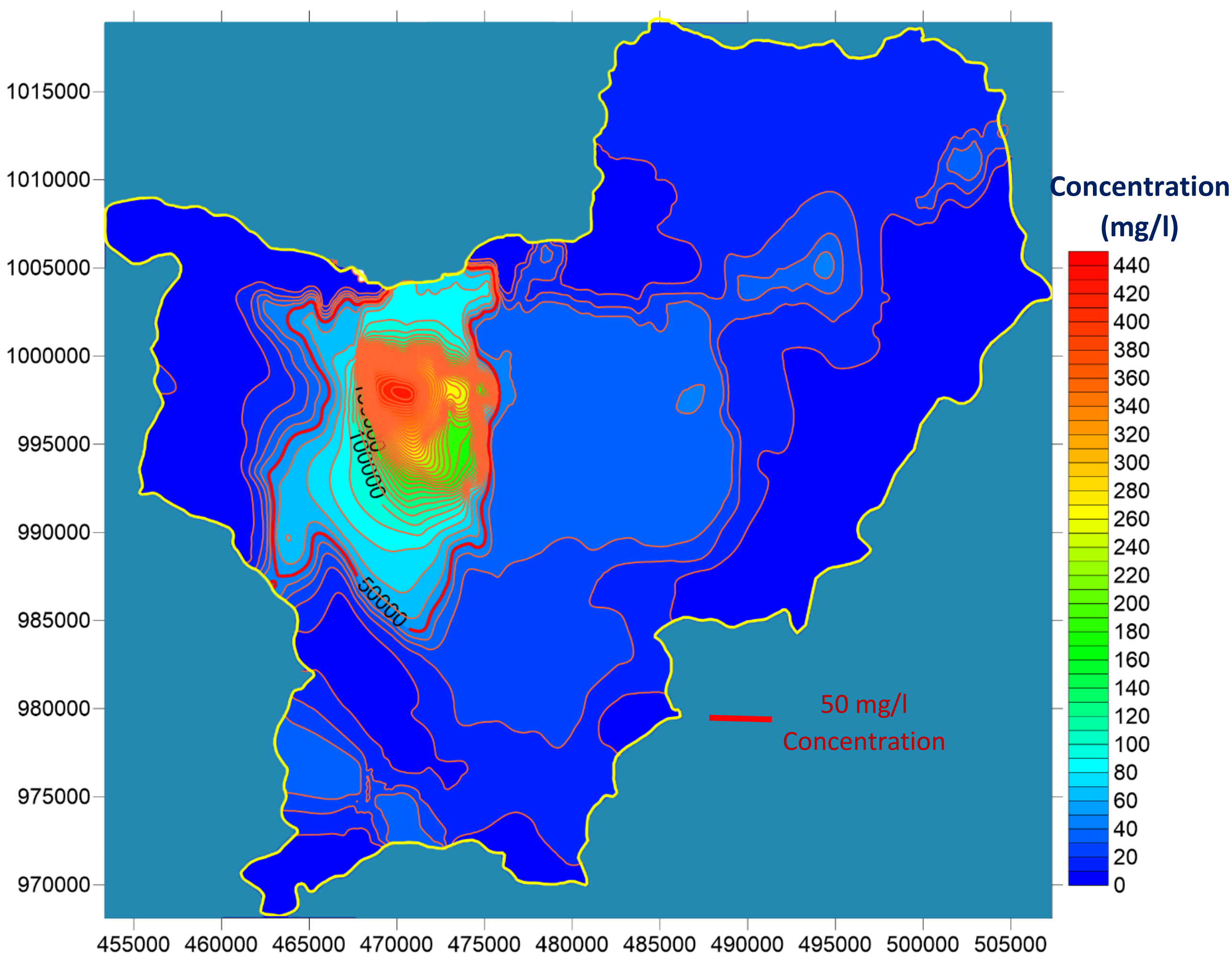

Fig. 31 Concentration Contour in 50 years for Scenario-1

Accordingly, the result of this scenario shows that 9, 16 and 18 wells will exceed the WHO drinking water standard limit of nitrate concentration (50 mg/l) in the coming 25, 37 and 50 year (Fig. 32) (Their list is put in Appendix-D). Major tapping wells located in the center of the city were very susceptible. Spatially, yet wells towards Gefersa reservoir are located above the center of major plume (opposite to the groundwater movement direction), they were found to be very vulnerable due to their proximity and diffusive migration of contaminants. Wells towards Legedadi reservoir are the less susceptible wells due to their long distance from the center of the plume and their relative position (elevation). The very bothering thing about these wells is the expected future development activities. Yet, there would not be advective transport rolling to this places, loading of nitrate from the increasing inhabitants in the area will put the aquifer in danger. This can be shown from LG5 and LG6 of Fig. 33 and 36. All were initially less polluted wells then two borehole become continually polluted with nitrate. It show that newly emerging built up areas could possibly endanger the aquifer wellbeing.

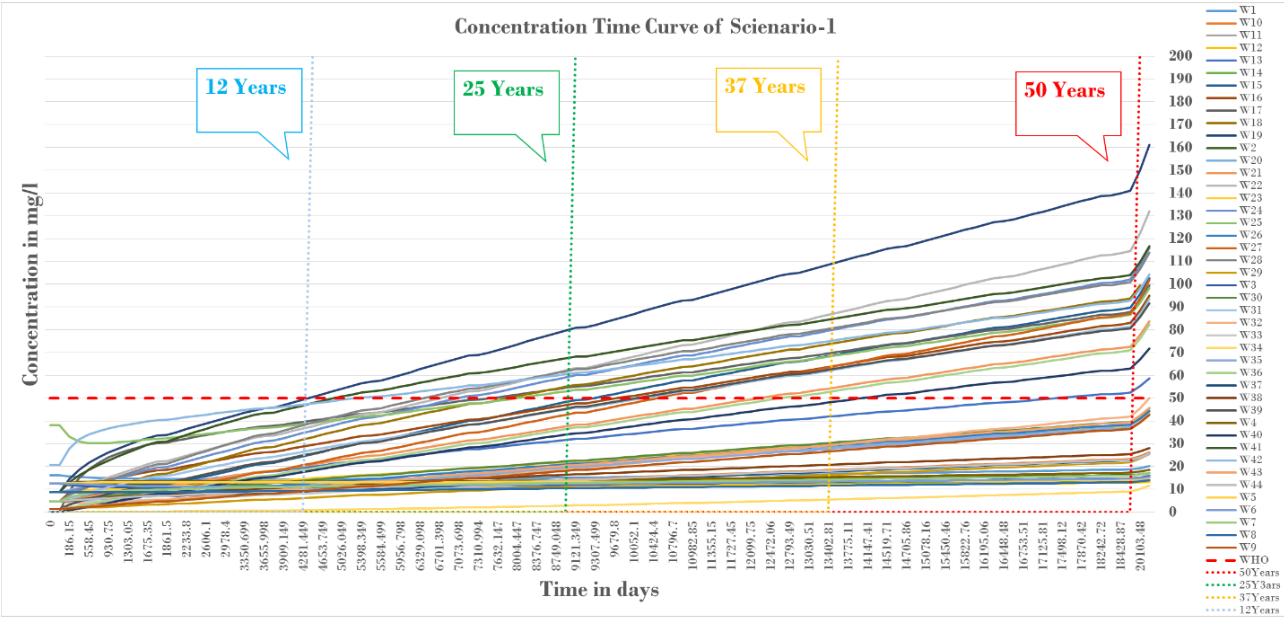

Fig. 32 Concentration-Time curve of Scenario-1for major wells

The third group of wells, wells on the projected line towards Akaki well field are lesser polluted ones as far as we use distant points. But, the nitrate migration from high speed advective movement will put the wells in risk. As time goes more wells will exceed the drinking water standard in respect of their distance, the more nearer being polluted faster. The mass of nitrate moving to the well fields is also extremely tremendous. Even it can leak down for hundreds of years in assumption that we have stopped further pollution after some years of the modelling year, leading the wells to exceed the drinking water standards limit. The high transmissivity values of the aquifers (aggravating further advective passage) as one approaches the well field makes these well extremely prone to danger. Here, there is a need to have urgent well head protection activities. As can be seen from the next scenario, further city inhabitation makes the situation even worse.

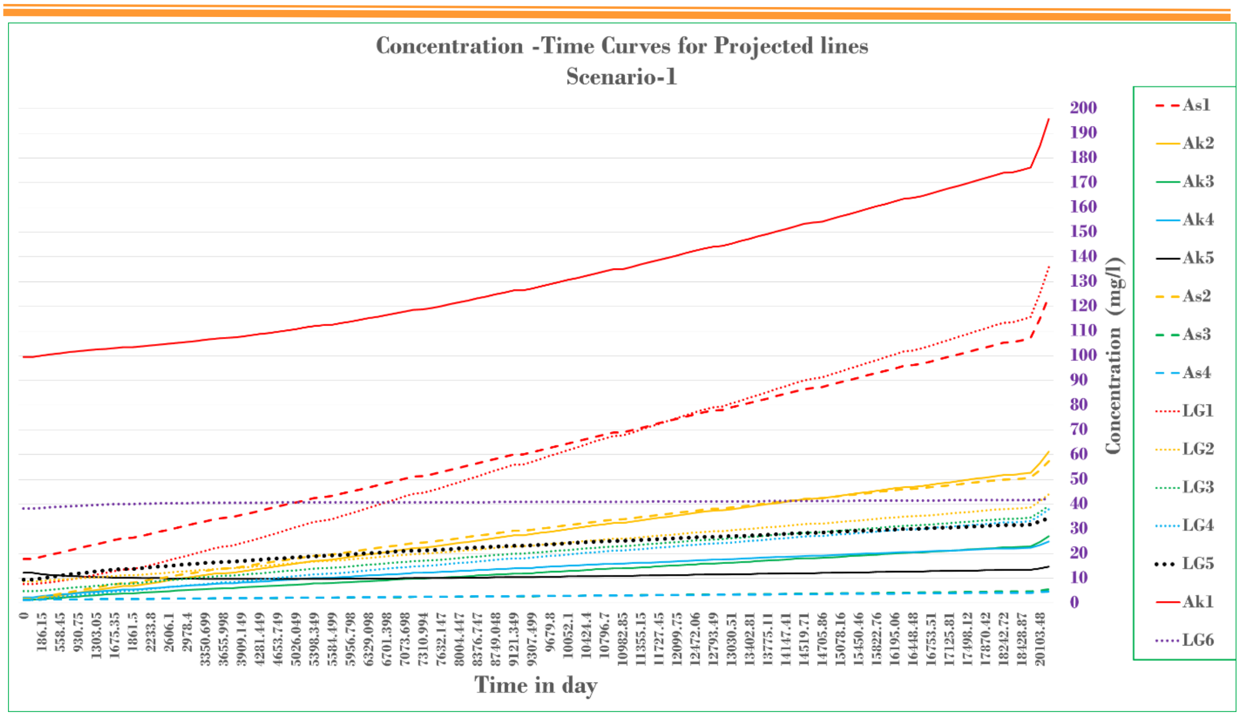

Fig. 33 Concentration -Time Curves for Projected lines, Scenario-1. (Note the red, yellow, Green and blue lines shows the respective distance of the observation points of 4, 8, 16 and 20 km from the main plum center)

4.2.3.2. Results of Scenario Two (Scenario-2)

In this scenario by keeping the current land use land cover conditions, future population and fertilizer use changes are considered. For the population increment, the population growth rate of Addis Ababa city projected by CSA for the next 50 years is utilized. For fertilized, the survey for fertilizer usage shows that the farmers' fertilizer usage rate is increasing by 5% every year nationwide by making 200kg Urea the limit for the maximum nitrate loading. This is because the rate is the worldwide optimal usage of urea.

Accordingly, out of 45 major wells 14, 18 and 26 wells were exceeding the WHO limit in 25, 37 and 50 years respectively. Note that, additional 5, 2 and 8 wells were influenced to exceed the drinking water standard as compared to scenario-1 in the stated years respectively, due to the effect of increasing population and higher fertilizer use (Fig. 34).

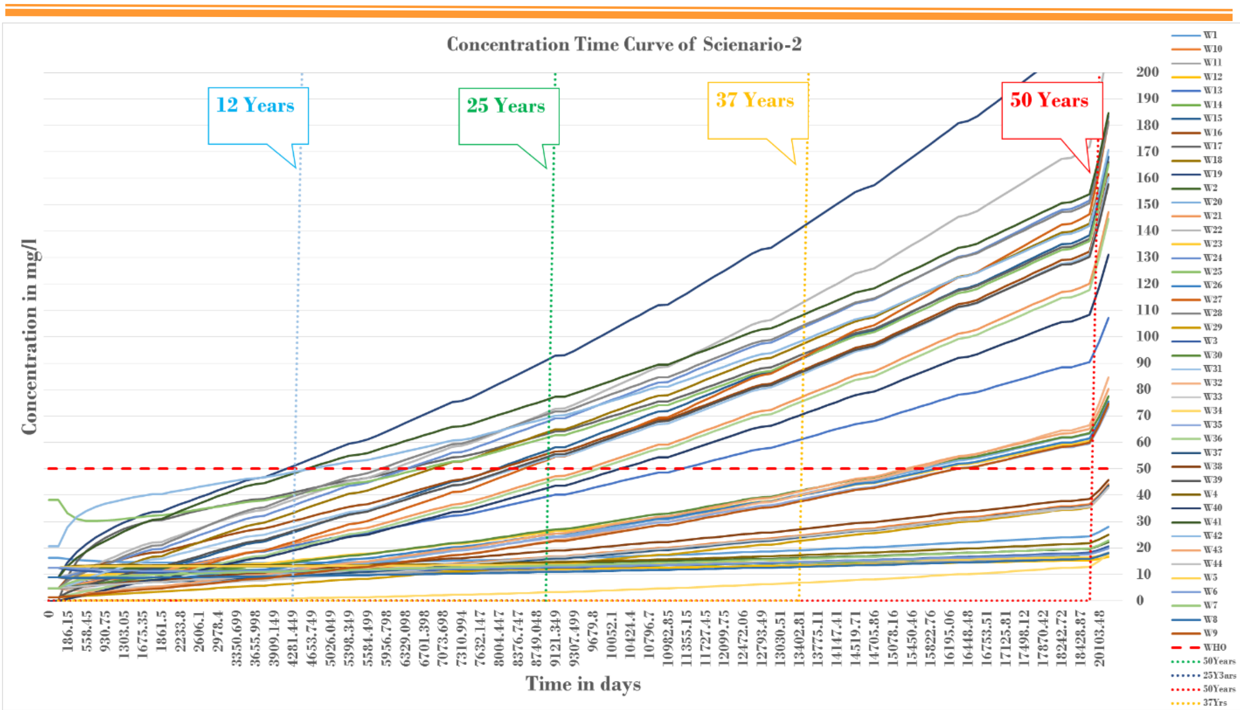

Fig. 34 Concentration-Time curve of Scenario-2 for major wells

In the aspect of spatial migration, the effect of this increasing loading was very significant in the downward movement of the major plume to the Akaki well field and diffusion of contaminants against the flow direction. Accordingly, it have been seen that the wells on the line towards Gefersa (even to Entoto Mountain) were found to be by far affected. Concentration contours as high as 150 mg/l were able to reach edge of Entoto ridge and the aquifers beneath Gefersa reservoir in 50 years (Fig. 35). Legedadi wells located at 20 and 24 Km (LG5 and LG6) from the main plume area will reach as high as 65 mg/l and Akaki well field wells were on the margin of exceeding the drinking water standard in the 50th year. These Legedadi wells are rising not because of the pollution from the main plume area but from the new inhabitation activities around Legedadi reservoir on the way to Sandafa and Sandafa area itself.

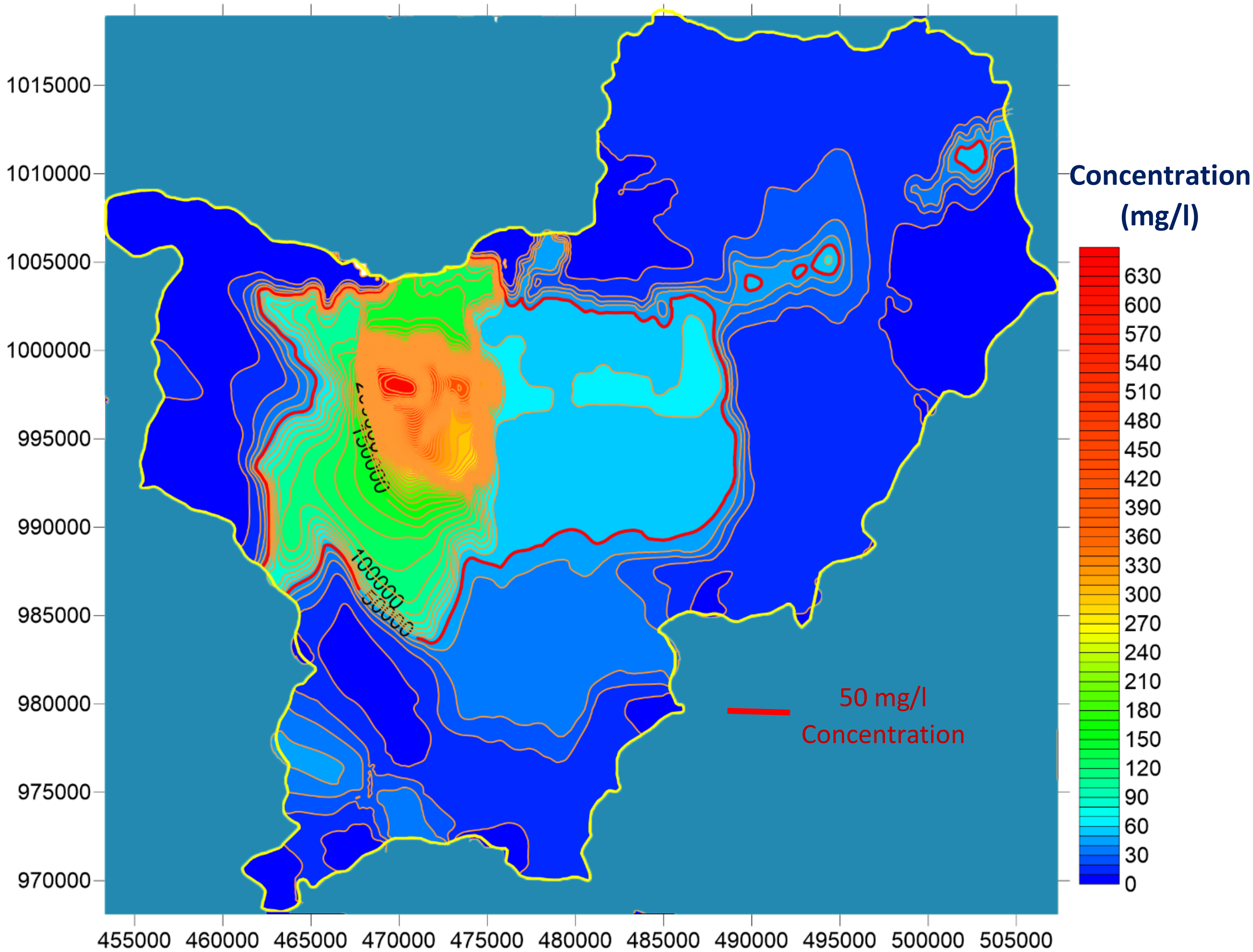

Fig. 35 Concentration Contour in 50 years for Scenario-2

For Akaki well field, at the 50th year a contour of nearly 50 mg/l has reached the high yielding wells. Being the aquifers around this area very transmissive (e.g. 4m/day), these wells will rise all at once after this time of tapping ground water with current discharge rate. Thus, in respect to the drinking water standard these wells will be of no use after 50 to 60 years of time from now. This is worse for the well field because of the increased loading rate of nitrate to the groundwater from the area the well field receives inflow. If we consider the exceptional growing up of Akaki Sub City (being center of industry) the contamination level will further be triggered and the time that the wells will exceed the standard limit could be shorten significantly. This would give a good implication for well head protection activities.

Comparing this scenario's contaminant spatial distribution with scienario-1, points in 4km radius of the main plume were affected by net average addition of nitrate concentration of 70 mg/l in 50 years while points at 8, 12 and 16 km radius were affected by an average addition of 33, 21 and 10 mg of nitrate concentration respectively. Exceptionally, a point set at 24 km towards Legedadi has raised by a concentration 20 mg/l than its value of scienario-1 (LG6 of Fig. 36). As have been said, this from the influence of the newly emerging villages in the way to Sandafa.

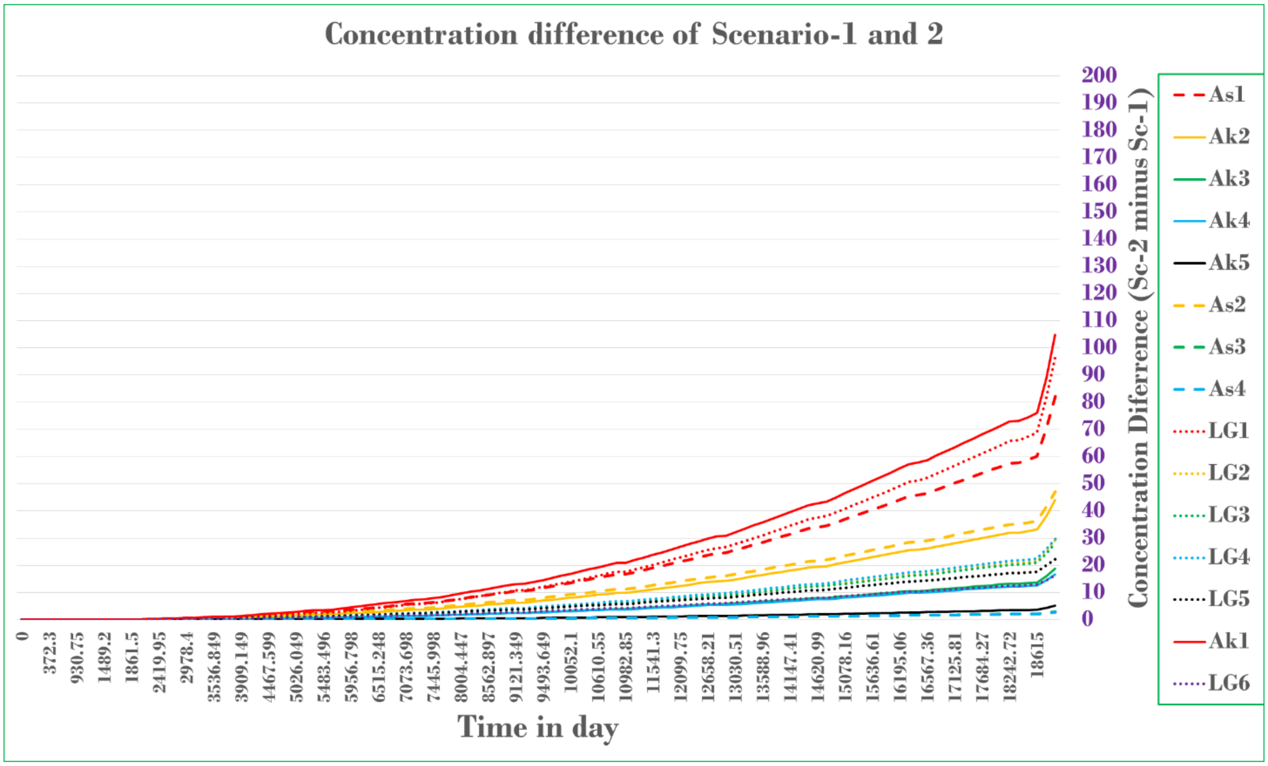

Fig. 36 Concentration difference between scenario-1 and scienario-2 for projected lines. Note the red, yellow Green and blue lines shows the respective distance of the observation points of 4, 8, 16 and 20 km from the main plum center respectively .

4.2.3.3. Results of Scenario Three (Scenario-3)

The estimation of groundwater nitrogen loading was based on the idea that the new city plan has been launched five years late to the modeling year. The new master plan map will change the whole catchment parts to inhabited area. City development activities will be started here and there then further upcoming population will be distributed all over the catchment and the previously inhabited dwellers will be kept in their places. Land use like cropped areas and forests diminishes through time, as parts will be converted to build areas. The nitrate loading estimation methods are the same to previous scenarios and only how it is distributed is the difference here.

Accordingly, this scenario was found to be very important from the view of saving the water resource of the whole catchment. Extra to scienario-1, a maximum of 4 mg/l increment in nitrate concentration was observed in the catchment in 50 years (Fig. 39).

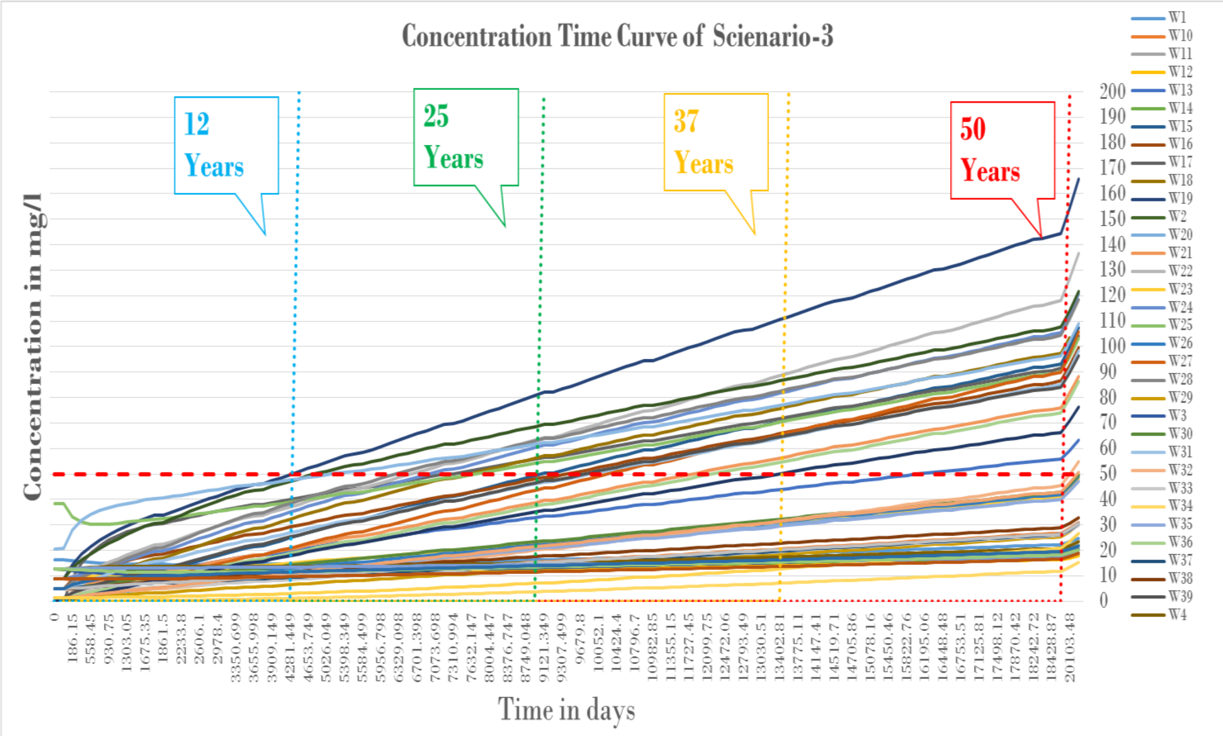

Fig. 37 Concentration-Time curve of Scenario-3 for major wells

This is because of the reason that the additional population influence was distributed to the whole catchment's aquifers that contains a very huge amount of diluting water. Comparing this scenario and scenario-2, the excessively migrating plume boosting was able to be tackled. Thus, keeping in mind the initial population of Addis Ababa city is contributing as its inhabitation rate of the modeling year, the effect from the additional population has been reduced significantly. Consequently, this scenario has lower concentration value than scenario-2 (Fig. 38) but a very little higher value than scenario-1(Fig. 39) in its catchment level concentration values. The concentration observation points of 4, 8, 12 and 16 km radius were able to decrease with an average of 64.5, 32.2, 15 and 5.2 mg/l of concentration than scenario-2 respectively. This scenario was with an average increment of concentration of 3.8, 3.2, 3 and 3.3 mg/l at radiuses stated respectively than scenario-1.

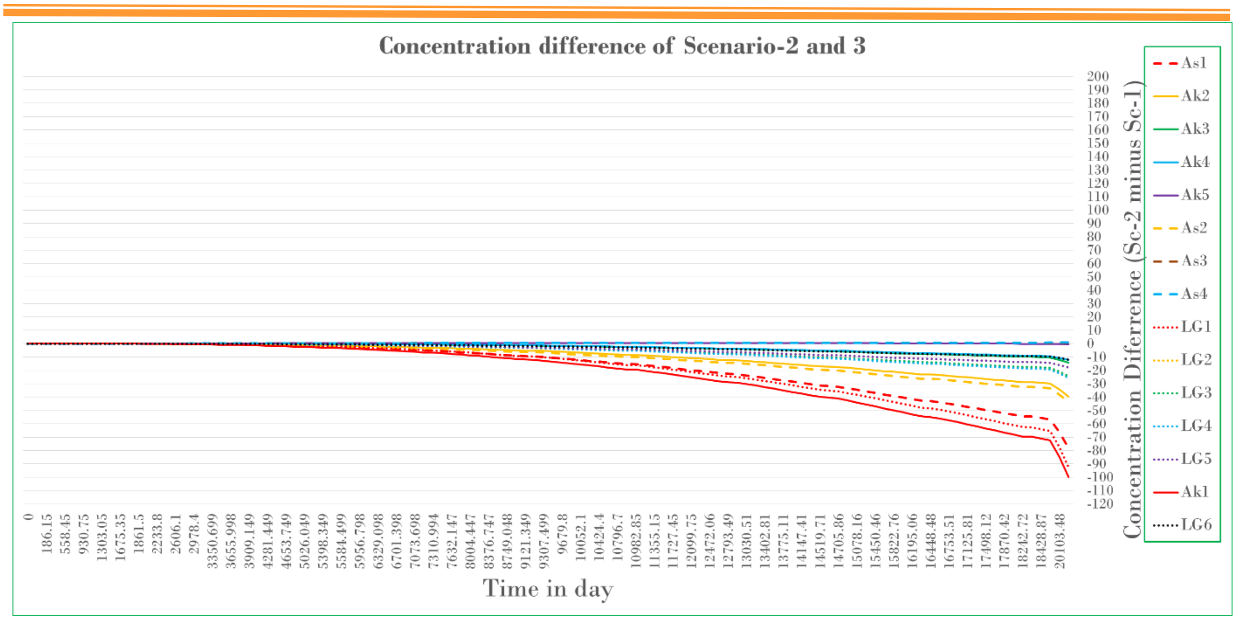

Fig. 38 Concentration difference between scenario-2 and scienario-3. Note the red, yellow Green and blue lines shows the respective distance of the observation points of 4, 8, 16 and 20 km from the main plum center.

In relation to the water supply wells 10, 17 and 18 wells will top the WHO drinking water standard in 25, 37 and 50 years respectively. There are 1, 1 and 0 additional boreholes exceeding the standard as compared to scenario-1 in the stated years respectively. Comparing this with scenario-2, there is a reduction of 4, 1, and 6 wells exceeding the standard in 25, 37 and 50 years respectively (Fig. 37).

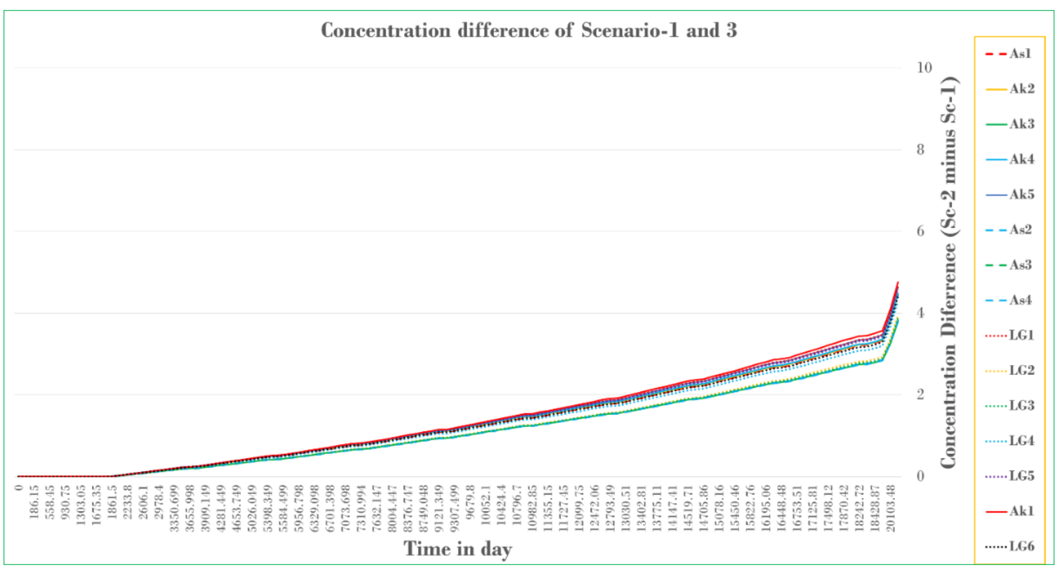

Fig. 39 Concentration difference between scenario-1 and scienario-3. Note the red, yellow Green and blue lines shows the respective distance of the observation points of 4, 8, 16 and 20 km from the main plum center.

5. Conclusion and Recommendations

In conclusion, this work explains the advective dispersive reactive contaminant transport process in Akaki catchment. This modeling process was able to simulate the groundwater movement and contaminant transport process and has shown mainly the effect of land use/land cover conditions on groundwater quality. In the calibration process, it was possible to bring a good agreement between the observed and calculated head and concentration values in groundwater and contaminant transport models respectively. After calibrating the models, the groundwater model was able to compute groundwater head and flow direction. The head was in between 2729(North) and 1970 (South) m.a.s.l. and flows North-South direction. The water balance of this model shows that there is high groundwater-surfacewater interaction; recharge and river leakage playing the major role for the input and output terms respectively. This have been presented as a mean for groundwater contamination from surface water bodies. The sensitivity analysis of this work has shown that the model is very sensitive to changes in hydraulic conductivity and recharge values. Spatially it was also found that the highly elevated areas very sensitive for changing values of hydraulic conductivity and recharge values.

An attempt made to identify major contributors nitrate to the groundwater the loading from the pit latrines were very extremely high which always are associated to highly populated build areas. It have been repeatedly reported that the groundwater of Akaki catchment is very vulnerable for pollution from the highly polluted rivers of the catchment. But, several repeated measurement for nitrate concentration for the rivers have shown very minimum values; mostly lower than the groundwater they interact with. In this, yet it is possible to say that the groundwater could be polluted from the contaminated surfacewater sources, this doesn't have any effect on the nitrate concentrations. The model shows that the effect from the rivers is very minimal yet there is high level of interaction between the groundwater and the surfacewater sources.

The contaminant transport model has presented the nitrate contaminant distribution in space and time. The temporal aspect of this model shows that more wells will be polluted as time increases. Wells towards Gefersa was found to be very susceptible due to their proximity to the main plume center from the diffusive migration of nitrate. Wells towards Legedadi were the less vulnerable one due to their distance from the main plume center and relative position. But these wells were endangered due to the new inhabitation activities. Wells towards Akaki were found to be safe in the short term but very extremely vulnerable in the future. Since they are located in areas where every drop of water concentrates, they are very prone to pollution from the high speed advective transport of nitrate. Demonstrating this, Akakai well field wells were in the boundary of exceeding the WHO drinking water standard in 50 years.

Of all the transport mechanisms advective transport has found to be the dominant mechanism in all over the catchment parts favored from the high topographic dropdown of the catchment as one move from north to the south, though the mechanical dispersion mechanisms were very significant.

From this all, one can note that there is a need for groundwater management activities. Since the model main sources of nitrate loading were the unpaved pit latrines from built areas and poor sewerage systems, it would be possible to minimize future loading by upgrading these infrastructures for already built area and setting a very tight structures to newly emerging villages. The latter would potentially reduce the effect of future loading on the lesser polluted aquifers. Moreover, there is already a huge volume of nitrate contaminated water beneath the built areas of the catchment. This in time will move to the high yielding Akaki well fields. It is estimated the time this plume will reach the well field to be around 60 years from the modeling year in this model. Accordingly, the city will face a nitrate contaminated groundwater after this time. There are remedial activities like pumping and using the contaminated water for other purpose, different methods of pump and treat techniques and reactive barriers. The bad lack here is, it is always difficult and/or expensive to treat groundwater. Unless and otherwise future water purifying technologies solve both the technical and financial aspects of the problem, it will be urgent to work hard on delaying the time the wells become beyond the drinking water standard by reducing future loading as in scenario-3 and developing a new water sources. Finally, the city expansion activities for example in mountain parts of Yeka and Gullele sub-cities will pose a very serious problem both on the groundwater quantity and quality. Inhabiting these areas will decrease the input to the groundwater because these areas have been identified to be top recharge area; and possibly would endangers the quality because these areas are going to be areas from were contaminated water flows down to the rest parts of the catchment areas. Thus, if situations continue as they are today, every stakeholder has to merely understand that every city development activity is in expense of the groundwater safety.

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Appendix-A: Nitrate Loading Calculations

Nitrogen Loading Calculation for Addis Ababa City

Sub-city	Population Projected (2012)	Nitrogen loading estimation (4kg N/person/year)	Nitrogen loading estimation for 2012 in mg N in sub-city in a year	Nitrate loading estimation in mg NO_3 in a year	Area of Sub-cities in m^2	Nitrate loading ($mg/m^2/day$)
AKAKI KALITY	201628.70	806514.80	806514800680.84	3572860567016.12	107513131.00	91.05
NEFAS SILK-LAFTO	351805.21	1407220.83	1407220834687.14	6233988297664.05	52120323.00	327.69
KOLFE KERANIYO	477064.83	1908259.31	1908259311733.93	8453588750981.31	67156731.00	344.87
GULELE	297681.24	1190724.98	1190724979408.67	5274911658780.41	29813455.00	484.74
LIDETA	224367.68	897470.73	897470734207.18	3975795352537.78	9163848.00	1188.65
KIRKOS	246081.12	984324.46	984324463032.08	4360557371232.12	14641283.00	815.96
ARADA	235254.99	941019.95	941019952881.33	4168718391264.29	9570103.00	1193.42
ADDIS KETEMA	284053.20	1136212.82	1136212818886.01	5033422787665.04	8623848.00	1599.08
YEKA	385598.34	1542393.37	1542393373769.64	6832802645799.52	107740661.00	173.75
BOLE	343698.68	1374794.73	1374794730713.17	6090340657059.35	118822738.00	140.43
Total (in AA)	**3047234.00**	**12188936.00**	**12188936000000.00**	**53996986480000.00**	**525166121.00**	**281.70**

Nitrogen Loading Calculation for Cropped Areas

Major crop type	Applicatuion rate per ha of UREA in kg	% of Nitrogen in UREA	Nitrogen loading per ha in Kg per year	Amount of N leaching in kg/ha/year (30% & 10%)	NO3 leading rate per ha in mg in a year	NO3 loading rate per m2 in a year (mg/m2)	NO3 loading rate per m2 in a day (mg/m2/day)
Teff/Wheat	100	0.465	46.5	13.95	61798500	6179.85	16.90793434
				4.65	20599500	2059.95	5.635978112

Nitrogen Loading Calculation for Forests and Water Bodies

Recharge rate (m/day)	Volume (m³/d/m²)	m³/day/cell	Concentration (mg/m³)	Mass of Nitrate Loading (mg/m²/day
0.000511	0.000511	81.760000	2,000.000000	1.022000
			8,000.000000	4.088000
			3,000.000000	1.533000
			100,000.00	51.100000
0.0002081000	0.000208	33.296000	2,000.000000	0.416200
			8,000.000000	1.664800
			3,000.000000	0.624300
			100,000.00	20.810000
0.0004110000	0.000411	65.760000	2,000.000000	0.822000
			8,000.000000	3.288000
			3,000.000000	1.233000
			100,000.00	41.100000
0.0003420000	0.000342	54.720000	2,000.000000	0.684000
			8,000.000000	2.736000
			3,000.000000	1.026000
			100,000.00	34.200000
0.0000711000	0.000071	11.376000	2,000.000000	0.142200
			8,000.000000	0.568800
			3,000.000000	0.213300
			100,000.00	7.110000
0.0002420000	0.000242	38.720000	2,000.000000	0.484000
			8,000.000000	1.936000
			3,000.000000	0.726000
			100,000.00	24.200000
0.0003200000	0.000320	51.200000	2,000.000000	0.640000

			8,000.000000	2.560000
			3,000.000000	0.960000
			100,000.00	32.000000
0.0001021320	0.000102	16.341120	2,000.000000	0.204264
			8,000.000000	0.817056
			3,000.000000	0.306396
			100,000.00	10.213200
0.000135	0.000135	21.600000	2,000.000000	0.270000
			8,000.000000	1.080000
			3,000.000000	0.405000
			100,000.00	13.500000

Appendix-B: Nitrate Concentration Measurements

Wells Managed by AAWSA (2012)

Locality	IDSource	UTME	UTMN	T_NO3	Locality	IDSource	UTME	UTMN	T_NO3
Lebu mekanisa	AA002	469191	989547	**0**	**Akaki**	AA051	478130	982300	3.815
AA-Repi Enyi General Business Group	AdBh0994	464538	991302	**0.003**	**AA-Water lll Borehole BH17**	AdBh0787	478199	976361	4.05
Sheromeda Kidanemihret	AA022	474238	1002370	**0.015**	**Akaki BH16**	AA092	478347	976752	4.05
AA-Water lll Testwell-B11	AdBh0759	466200	988800	**0.03**	**AA-Water lll Borehole BH11**	AdBh0782	478780	977307	4.05
Asko BH	AA010	465578	999808	**0.04**	**Salo Gora**	WF01 PW1	473595	981135	4.1
AA-Gulele Misionery of Charity No.1	AdBh0946	465651	1001575	**0.05**	**Summit, Michael**	AA068	481681	994296	4.11
AA-Beverage CorpGasv& Crate factory	AdBh0715	478462	977721	**0.05**	**WF02-pw10**	BHT-124	469239	972866	4.2
AA-Hillton Hotel	AdBh0919	474175	996550	**0.09**	**AA-Mekanisa-99**	AdBh1113	467135	989840	4.66
Militatry Food Kichin	AdBh0650	466050	993650	**0.1**	**Mekanisa BH 16**	AA014	469360	990078	4.66
AA-Water lll Testwekk-T2	AdBh0765	479400	981400	**0.11**	**Salo Gora**	WF01-PW3	474918	980496	4.7
Legatefo	AA055	486738	1001391	**0.12**	**Ferensay,Ras Kasa**	AA057	475165	1001449	4.81
AA-Burayu-99	AdBh1106	464031	1002909	**0.13**	**Akaki BH20**	AA0101	477945	976985	4.91
Legadadi	AMW8	493518	1004421	**0.145**	**Ayat-1**	AA017	487268	995400	5.01
Ankorcha-2	AA019	481462	998906	**0.17**	**Akaki**	AA052	470888	987426	5.015
CMC	AMW15	484821	994284	**0.18**	**Salayish**	AA005	480999	999648	5.015
Legetafo	AA047	486723	1000881	**0.2**	**Fire hiwo-salayish**	BHT-123	480999	999648	5.015
Ministry of defence	AdBh0706	472700	996500	**0.21**	**Total Belay Zeleke-1**	AA023	470504	1002135	5.41
French Embassy Abo Church-Abo Bridge	AA035	475638	999991	**0.21**	**Gerado**	WF02-PW10	469239	972866	5.8
Hana Mariam SANSUZI NEW	AA063	465729	1002755	**0.234**	**Hechu**	WF01-PW14	471521	976630	5.89
East bole,EBV 03	AA049	480717	993193	**0.25**	**Augusta**	AA036	468505	995156	6.115
AA-Glass and Bottle Factory	AdBh0509	467200	1001017	**0.27**	**Lafto BH 1**	AA007	471500	990500	6.215
CMC	AA060	482682	994124	**0.28**	**AA-Water lll Testwell-B3**	AdBh0751	463700	988500	6.52

ayat2	SANFTW 2	484094	987465	**0.28**	**AA-Watter lll Borehole BH22**	AdBh0792	477651	975923	6.61
New Kara Road WNDV-3	AA064	481368	997713	**0.301**	**Alem Bank,Kidane Mihiret**	AA069	466430	994219	6.81
Summit SMV- 13	AA054	484971	994879	**0.31**	**Chebe**	LLA-1	493247	1001478	6.91
kotabe	AA044	481462	998906	**0.32**	**Alem Gena-Dika**	AdBh0246	466662	970715	7.01
AA-Anbessa Transport Garage	AdBh0510	468400	1001016	**0.35**	**legedadi**	LLA6	497455	1006373	7.17
legedadi	LLA4	498961	1005177	**0.35**	**Akaki city**	SWAWF-2	475697	979915	7.21
BH 2	AA009	463972	1000788	**0.36**	**AA-Hagbes PLC., Bisrate Gabriel area**	AdBh0910	468875	993750	7.45
Summit,SMV-15	AA045	485733	994302	**0.37**	**Abo Church**	AA048	476078	1000763	7.49
Summit SMV 10	AA061	482163	993603	**0.4**	**Tatek Military Camp**	AdBh0158	459689	998340	7.51
Egzeabher Ab	AA033	471026	1002023	**0.405**	**kotcha**	WF01-PW13	472233	976508	8.5
ayat1	SANFTW1	477819	987018	**0.41**	**Alem Gena-Gombobdu**	AdBh0245	464607	973547	8.51
New Kara Road-Ararat	AA034	480321	997370	**0.41**	**Selam Technique**	AA029	481519	999648	8.51
Fanta valley III	AA058	481828	981943	**0.415**	**TW2 Test well No.2**	AdBh0965	473576	972821	8.85
Akaki	WF01-PW7	471909	979461	**0.42**	**Gewasa**	LLA-2	489927	1000153	9.15
AA-Burayu Simachew mekonen Borehole	AdBh0992	465161	1003103	**0.503**	**AA-Water lll Testwell-T5**	AdBh0762	481600	982900	9.62
Legadadi-NAS Food Factory BH No.2 Legetafo	AdBh1036	488150	1002300	**0.503**	**AA-Water lll Borehole BH14**	AdBh0785	478580	976051	9.69
MIKILILAND-3	AA013	466601	1001250	**0.53**	**Akaki BH12**	AA090	478808	976897	9.81
Galetti Project	AdBh0662	474800	984700	**0.53**	**kotcha**	WF01-PW12	471476	977396	10.3
Yeka-Ankorcha 1	AA003	477446	997611	**0.53**	**Akaki**	WF01-PW16	473386	980122	10.77
AA-Water lll Testwell-B4	AdBh0752	486200	1001042	**0.53**	**Fanta valley 1**	AA046	480847	981623	11.107
AA-Water lll testwell-B7	AdBh0755	43566	978610	**0.535**	**Akaki Koye Defence Gulele**	AdBh0660	465600	1001855	11.37
AA-Water lll Testwell-B12	AdBh0760	466400	987600	**0.57**	**AA-Water lll Testwell-T1**	AdBh0761	481200	980000	11.75
Hana Mariam,SHEGOLE NEW 2	AA065	468094	1001478	**0.57**	**Akaki BH26**	AA100	477086	975624	12.31
ayat3	SANFTW3	481012	984597	**0.57**	**Akaki Water Supply Well Ep-4**	AdBh0801	479942	977322	12.31

Salo Gora	WF01-PW2	474204	980459	**0.7**	**Akaki Beverly Internation**	AdBh1038	480895	977403	12.33
Hana Mariam AKV-2	AA038	477248	982879	**0.71**	**Mikliland**	AA043	485290	994522	12.605
AA-Kality Metal products Factory	AdBh0717	474225	982650	**0.78**	**Akaki BH 25-2**	AA099	477162	976038	13.6
legedadi	LLA5	501033	1006222	**0.97**	**AA-Water lll Borehole BH24**	AdBh0794	477330	976793	14.39
East Bole,EBV 24	AA053	480863	992647	**1.01**	**Akaki Water Supply Well EP-5**	AdBh0802	478450	979950	14.52
AA-Shegole Mesgid-99	AdBh1144	468295	1001339	**1.02**	**Hechu**	WF01-PW11	472245	977865	15.4
Bole Lemi,SMV 19	AA059	482757	990710	**1.03**	**Netherlands Embassy,Keranio area**	AdBh0904	468800	996600	15.42
Luke Stream	AA020	482994	998429	**1.14**	**Tulula**	WF01-PW6	472630	979912	15.6
Belay Zeleke-2	AA018	470218	1001886	**1.21**	**Akaki**	WF01-PW18	471918	979657	15.92
Akaki BH23	AA097	477477	977216	**1.46**	**Akaki Water Supply Well EP-8**	AdBh0805	478998	977937	16.42
Ketchene Meketeya	AA021	472608	1002066	**1.505**	**AkakiBH-9**	AA089	476246	977104	16.72
AA-Ato Tahas Burayo	AdBh0988	465410	1002944	**1.52**	**AA-Water lll Borehole BH10**	AdBh0781	479058	976020	16.72
East Bole EBV 22	AA067	481213	991853	**1.78**	**Kolfe Keraniyo-KOV3**	AA024	467830	998168	17.91
AA-Batu Tannery	AdBh1042	473466	987247	**1.8**	**AA-Water lll Borehole Bh07**	AdBh0778	479405	976735	18.62
AA-French Embassay	AdBh0507	474300	1001005	**2.23**	**AkakiBH06**	AA086	479714	978929	18.62
AA-Yekamichael-99	AdBh1105	477515	997474	**2.3**	**AA-Watet lll Testwell-T4**	AdBh0770	473108	979851	18.91
YeKA Mikayel Church	AA008	477715	997474	**2.31**	**Salo Gora**	SWAWF-04B	472836	980785	24.22
AA-American Embassy(Marine old)-1	AdBh0501	473900	1001050	**2.43**	**Akaki BH08**	AA088	479061	976370	25.71
Salogora	WF01-PW17	472460	981553	**2.68**	**AA-Water lll Borehole BH09**	AdBh0780	479246	977104	25.71
AA-Water lll Testwekk-B14	AdBh0764	480900	978800	**2.71**	**8.0**	WF01-PW8	473583	979260	28.6
AA-Water lll Testwell-B6	AdBh0754	470800	982900	**2.72**	**Akaki**	WF01-PW15	473944	978722	28.6
Repi-23	AA027	465741	989188	**2.74**	**LLA3**	BHT-121	496269	1004908	28.9
Korea Embassy, Ketena Hulet area	AdBh0908	468425	996350	**2.88**	**Alem Gena-Ilamu**	AdBh0244	466690	976790	32.51
AA-Water lll Testwell-B10	AdBh0758	461500	1001023	**3.01**	**Salo Gora**	SWAWF-04A	472826	980785	41.31

Akaki BH5b	AA085	476574	975607	**3.24**	**Hechu**	SWAWF-5	472779	978788	41.59
Mekanisa-19	AA015	468261	990357	**3.58**	**Roge**	SWAWF 3	471027	973709	52.6

Most Nitrate Polluted Wells (Private Wells)

Well name	X	Y	Well name	X	Y
Addis beer-2	471500	995900	**Alert**	470387	992150
Addis beer-3	471400	995800	**Bisrate Gebriel**	469280	993350
Addis beer-4	471400	996000	**Hagbez plc**	468875	993450
Addis beer-5	471500	996000	**Epharm**	469280	993350
Addis beer-6	471500	995950	**Old Airport**	469300	995500
Addis beer-7	471500	995800	**Lidate-2**	469800	991200
Addis beer-9	471400	995900	**Awash Winery**	469900	996000
Mexico-1	471550	995950	**Coca cola**	470000	996400
Mexico-2	471550	995950	**Building college**	470100	996100
SEDE-A-1	471700	995100	**Lidata-3**	470140	996150
SEDE-A-2	471700	995000	**Lideta-4**	470150	996125
SEDE-A-3	471700	994900	**Mekaneyesus**	470465	991100
Techinical School	471700	995900	**Building college -2**	470500	996000
African Hotel	471700	996300	**Old Airport-2**	470500	994500
Cambo Asmiye	471800	995200	**Sar Bet**	471200	993675
Ministry of Mine	471800	995500	**Tobaco company**	471300	994800
Genet Hotel	472000	995100	**Defence industry**	471300	995050
Kerra	472100	993300	**St. George**	471300	998200
Ministry of P. works	472500	996000	**Anuar Mosque**	471300	998200
Ras Hotel	472500	996300	**Merkato**	471350	998300
Pepsi	473000	992700	**Mexico-3**	471350	995890
Lideta	470387	995821	**Meskerem Soft**	471400	997400

Appendix-C: Concentration Effects of Increased Pumping

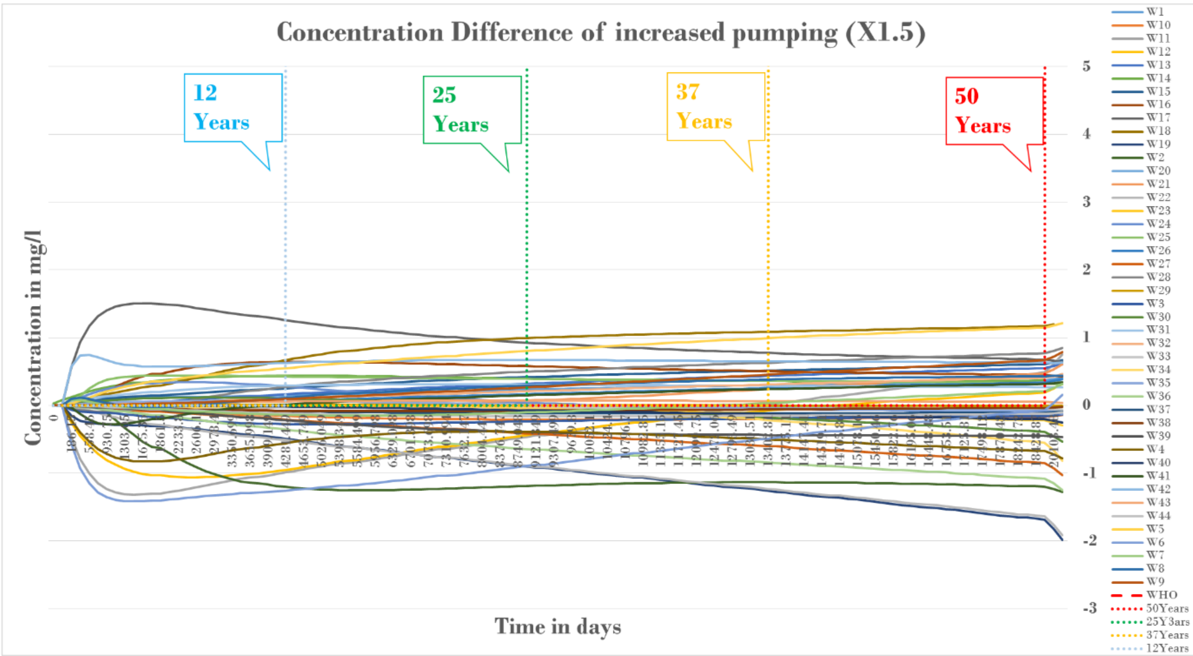

Fig. Concentration Difference of Increased Difference (50% increment)

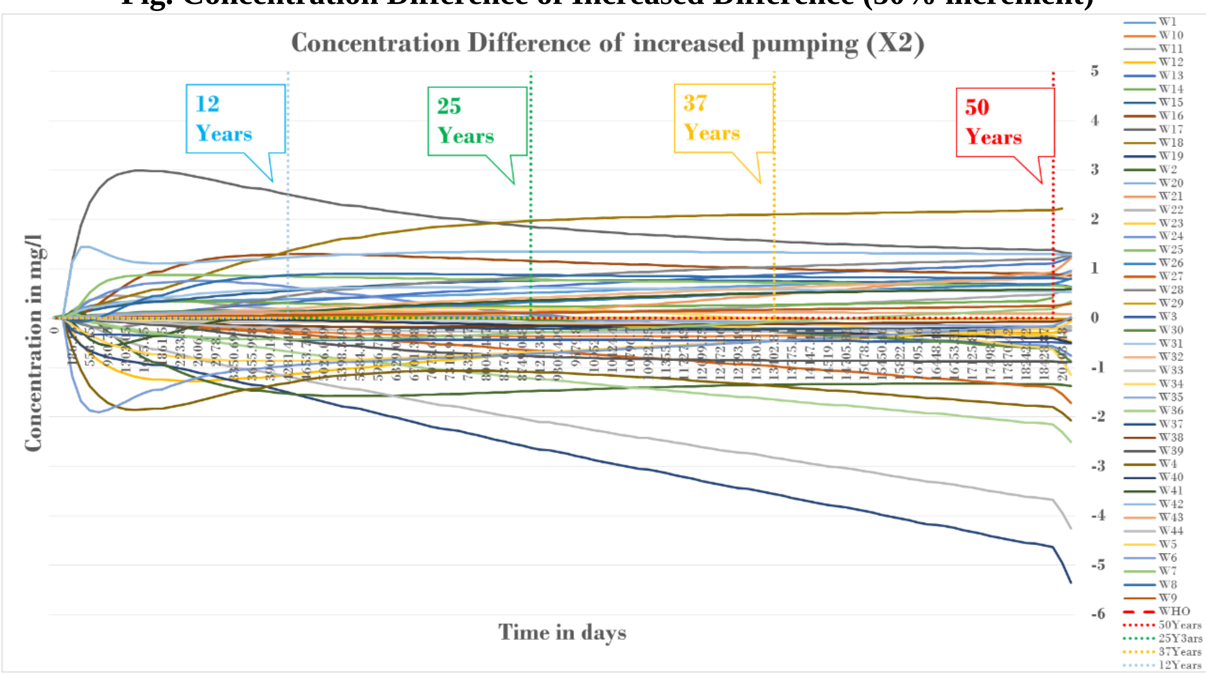

Fig. Concentration Difference of Increased Difference (100% increment)

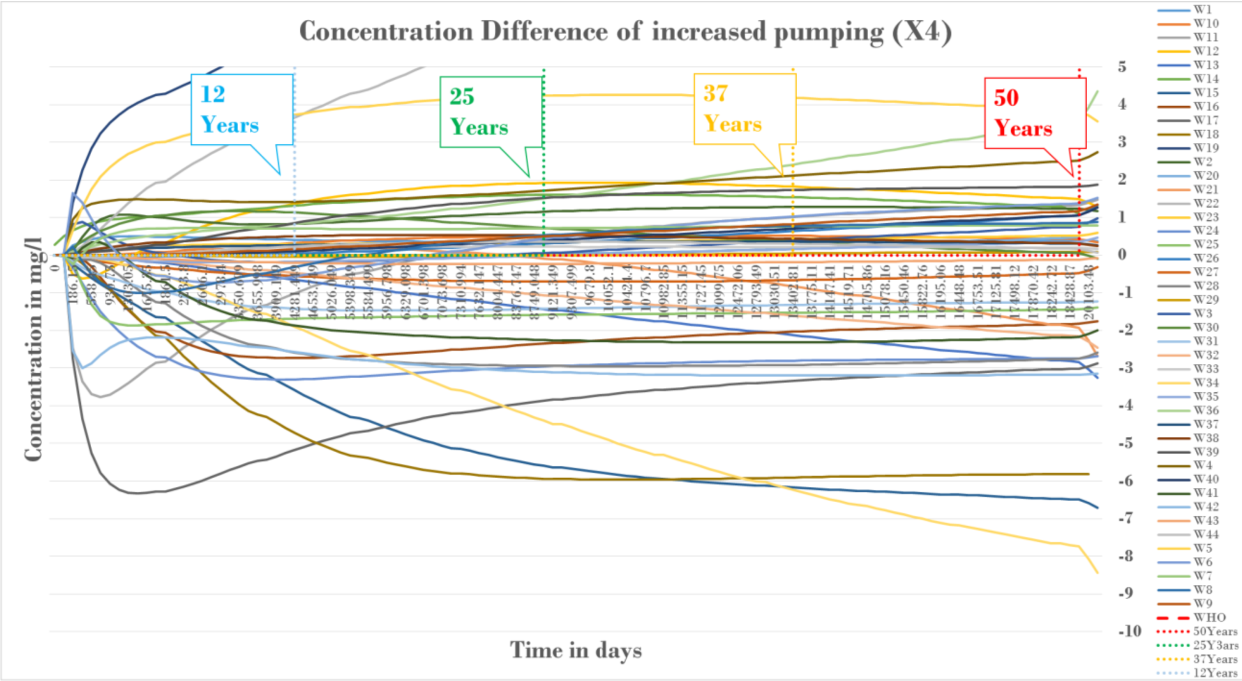

Fig. Concentration Difference of Increased Difference (400% increment)

Appendix-D: List and number of Wells exceeding the WHO drinking water standard in different scenario

Scenario	List of Wells exceeding the WHO drinking water standard				
	Up 25th Year	**Up 37th Year**		**Up 50th Year**	
	List	Old	Added than previous time	Old	Added than previous time
Scenario-1	W17, W18, W19 W22, W24, W25, W28, W41, W42	W17,W18, W19 W22, W24,W 25, W28, W41, W42,	W15, W16, W21, W31, W27, W36, W39	W17, W18, W19 W22, W24, W25, W28, W41, W42, W15, W16, W21, W31, W36, W39,	W13, W40
Scienario-2	W15, W16, W17,W18, W19, W22, W24,W 25, W27, W28, W31,W39, W41, W42	W15, W16, W17,W18, W19, W22, W24,W 25, W27, W28, W31,W39, W41, W42	W13, W21, W36, W40	W15, W16, W17,W18, W19, W22, W24,W 25, W27, W28, W31,W39, W41, W42, W13, W21, W36, W40,	W20, W23, W26, W30, W32, W35, W43, W9
Scenario-3	W15, W17, W18, W19 W22, W24, W25, W28, W41, W42	W15, W17, W18, W19 W22, W24, W25, W28, W41, W42	W16, W21,W27, W31, W36, W39, W40	W15, W17,W18, W19 W22, W24,W 25, W28, W41, W42, , W16, W21,W27, W31, W36, W39, W40,	W13

	Count of Wells exceeding the WHO drinking water standard				
	Up 25th Year	Up 37th Year		Up 50th Year	
		Total	Added than previous	Total	Added than previous
Scenario-1	9	16	7	18	2
Scienario-2	14	18	4	26	8
Scenario-3	10	17	7	18	1

DECLARATION

I, Kassa Aynalem, hereby declare that this thesis entitled "Numerical Groundwater Flow and Nitrate Transport Modeling for the Prediction of Impacts of Land Use Changes on Water Quality in Akaki Catchment" is my original work accompanied under the supervision of Dr. Seifu Kebede, School of Earth sciences, Addis Ababa University during the year 2015 as part of Master of Science Program in Environmental Geology. I further declare that this work has not been submitted to any other university or institution for the award of any degree or diploma and all sources of materials used for the thesis have duly acknowledged.

Kassa Aynalem

Signature