Groundwater Assessment and Vulnerability Mapping of Vindhyan-Ganga Sedimentary formations around Mirzapur district in India

A

Thesis

Submitted in partial fulfillment of the

requirements for the award of the degree of

MASTER OF TECHNOLOGY

in

Hydrology

(With Specialization in Ground Water Hydrology)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this report titled, "**Groundwater Assessment and Vulnerability Mapping of Vindhyan-Ganga Sedimentary formations around Mirzapur district in India**", in partial fulfilment of the requirements for the award of degree of **Master of Technology in Hydrology**, with specialization in Ground Water Hydrology, submitted in the Department of Hydrology, IIT Roorkee, India, is an authentic record of my work carried out during the period from June, 2018 to May, 2019, under the guidance of **Dr. Brijesh Kumar Yadav**, Associate Professor, Department of Hydrology, IIT Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

Date: **MANIK GOEL**

Place: Roorkee. **(17537005)**

Certificate

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGEMENT

I have a great pleasure in expressing my deep gratitude to my guide, **Dr. Brijesh Kumar Yadav**, Associate Professor, department of Hydrology, Indian Institute of Technology Roorkee for his esteemed guidance, invaluable suggestions and generous help throughout the course of this work.

I sincerely thank to **Dr. M.K. Jain, Dr. N.K. Goel, Dr. H. Joshi, Dr. M. Perumal, Dr. D.S. Arya, Dr. S. Sen, Dr. J. Khanna** and other staff for their suggestions and assistance provided during the work. I am also deeply grateful to our then research scholar Dr. Pankaj Kumar Gupta and my colleague Mr. Abhishek who lent me a helping hand from time to time during my stay in Roorkee. Lastly but not the least, my heartiest gratitude to my family for their faith and support, which has been a constant source of inspiration.

The humble thanks are for all those who in any manner lent helping hand in every bit of this research.

Date:

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Abstract

The aim of this study is to assess groundwater resources along the Vindhyan-Ganga sedimentary formation of Mirzapur district in India. Subsurface resistivity data from 12 locations are acquired by performing Vertical Electrical Soundings (VES) in the study area. Quantification of groundwater resources is conducted using groundwater table fluctuation data along with characterization of aquifer system by conducting aquifer tests. Total rechargeable area is calculated by considering slope of the landscape determined by Digital Elevation Model (DEM) prepared using Landsat 8 OLI data. Recharge from surface water sources is determined by considering the capacity of the Upper Khajuri dam, the main irrigation reservoir of the study area. The stage of groundwater development is computed from the annual groundwater use and recharge. On-site measurements for pH, electrical conductivity (EC), total dissolved solids (TDS), and temperature are also performed during the field survey and additional groundwater samples from 10 sites are collected for analyzing other water quality parameters. Heavy metals and other major ions are analyzed using AAS (Atomic Adsorption Spectroscope) and ICP-MS. Principal component analysis (PCA) is performed to establish the correlation amongst the observed groundwater quality parameters. Finding of VES are used to simulate the contaminant movement through vadose zone to the underlying groundwater resources. The classical advection dispersion equation coupled with the Richard equation is numerically simulated at different points using Hydrus simulator for assessing the intrinsic vulnerability of the region. The quantitative estimation of groundwater resources shows that annual total groundwater extraction is 13.89 MCM with the annual groundwater recharge of 51.96 MCM. Majority of the study area showed concentration of Cd, Pb, As, and Fe more than BIS recommended limits. The study area is having patches of high vulnerable zones in the south-eastern and western part. The findings of this study can be used directly in effective management of groundwater resources of the area. This study may also assist in decision making related to planning of industrial locations and groundwater remediation strategies.

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Chapter 1. Introduction

1.1 General

Groundwater resources are globally considered as the reliable and widely distributed source of fresh water. However, intensifying population growth and rapid urbanization have caused the groundwater exploitation which ultimately led to its scarcity and pollution. Out of total water ~ 1386 MKm^3 present on the earth, a large portion (97.5%) is saline and hence unfit for direct use. A large part of freshwater present on earth is stored in glaciers and ice caps and is inaccessible to human beings. Out of remaining freshwater sources, ground water plays a vital role in satisfying the water demand for domestic, industrial and irrigation purposes. India constitutes of 17.75% of world population but has only 4% (432 Km^3) of world fresh water resources. More than 85% of drinking water and about 60% of agriculture are dependent on groundwater in India. Urban residents increasingly rely on groundwater due to unreliable and inadequate municipal water supplies. In irrigation supplies, groundwater acts a critical buffer against the variability (both in space and time) of monsoon rain.

Groundwater aquifers are continuously depleting in the densely populated and economically productive areas of the world. Groundwater resources would be further restrain by climate changes. Groundwater depletion around the northern states of India was found to be 4 cm $\pm$ 1cm yr^{-1} (Rodell et. al., 2009). This will lead to serious implications for the sustainability of agriculture, livelihoods, long-term food security, and economic growth of India (Singh and Singh, 2002). Several inter-state and intra-state ground water crisis occurred in the India in the past few years. Recently, Dagmawi et. al., (2018) highlighted high water scarcity in Gangetic regions, covering target area of this study. As per report of Central Groundwater Board (CGWB, 2017), 2 out of 12 blocks in Mirzapur are in critical state of groundwater development. During the monsoon season, surplus runoff water flows through ephemeral creeks and streams in the area ultimately meeting to river Ganga. The surface runoff in the study area is mostly unchecked which results in less infiltration to the subsurface. Exploratory drilling data of the area show that there are numerous fractures which create secondary porosity in hard rock strata of the area along with porous patches of alluvial formations (Yadav and Singh, 2008). However, the configuration of these fractures and alluvial patches vary significantly within the study area. Hence, micro-region specific assessment of groundwater becomes quite crucial for better management of the groundwater resources.

On the other hand, the qualitative assessment of the groundwater resources around the target area is at very nascent stage (Singh et. al. 2015). Districts along the Gangetic plains of U.P. viz. Ghazipur, Varanasi, and Mirzapur were surveyed for arsenic level in groundwater by Shah (2009). Mostly tube wells have the arsenic concentration above the WHO guideline value of 10 μg/l for arsenic in drinking water and they have a varying iron concentration from 0.1 mg/L to 7 mg/L. Apart from this, subsurface zone of Mirzapur is also polluted by various other heavy metals and carcinogenic compounds (Mohan, 2011). Hence, the area need considerable attention for its proper groundwater assessment and framing of respective policies for its sustainable development.

1.2 Objectives

The main focus of this study is to quantify groundwater resources and to analyze its quality status in Vindhyan Ganga sedimentary formation around Mirzapur district in Uttar Pradesh (U.P), India. Specific objectives of the study are:

1. Estimation of groundwater resources of the area using water table fluctuation pattern and relevant aquifer characteristics.
2. Deciphering the lithology of study area using vertical electrical sounding (VES).
3. To investigate groundwater quality for establishing a correlation between different water quality parameters.
4. Groundwater vulnerability assessment using soil moisture flow and solute transport modelling through vadose zone of the area.

This study provides quantitative and qualitative assessment of groundwater resources of the target area, which may help to frame policy regarding groundwater extraction and its management. Groundwater level estimation along with lithological mapping of the area may help in regulating long term groundwater management policies.

1.3 Organization of Thesis

The Thesis is organized into six chapters and each chapter is further divided into various sub section as per the requirement. Chapter 1 describes the need of this study and the overall objective of this work.

Chapter 2 presents the literature review on Geophysical exploration methods, groundwater resource assessment techniques, groundwater quality measurement methods and numerical modelling of contaminant transport in the vadose zone.

Chapter 3 describe the study area, its location along with the general hydrogeological characteristics of the region.

Chapter 4 presents the working methodology adopted in the study for performing VES, groundwater assessment. It also contains a brief description of AAS used to analyze the groundwater sample for major hydro-chemical parameters. This chapter presents the initial and boundary conditions used to simulate the solute transport in the subsurface.

Chapter 5 depicts the results of this study. It contains the lithologs obtained from VES, concentration contours of critical quality parameters, Aquifer parameters, vulnerability index map, and the assessed stage of development for groundwater resources.

Chapter 6 presents the summary and conclusions for the whole study. The scope for further research and possible application of this work for benefit of society is also presented in the final chapter.

Chapter 2. Literature Review

This chapter presents the literature review on Geophysical exploration methods, groundwater resource assessment techniques, groundwater quality measurement methods and numerical modelling of contaminant transport in the vadose zone.

2.1 Geophysical Exploration Methods

Geophysical exploration techniques delineate the lithology of earth's crust and helps in finding the potential groundwater aquifers. Among numerous geophysical exploration techniques, Vertical Electrical Sounding (VES) has emerged as a powerful technique for exploring the subsurface for groundwater resources (Mishra 2011). VES principle is based on the electrical anomaly in the subsurface. It involves measuring the potential difference developed between the two inner metallic stakes when a specified amount of current is allowed to pass through two outer stakes. All four electrodes are buried into the ground for proper contact with the subsurface. Amount of current flows along the subsurface between the electrodes is inversely proportional to the electric resistivity of a rock formation (following the Ohm's law). If a material of resistance R (ohm) has a cross-sectional area A (m^2) and a length L (m), then its resistivity can be expressed as:

$$\rho = \frac{RA}{L} \tag{1}$$

where ρ is the resistivity of material in ohm-m^2/m, or simply ohm-m. The resistivity offered by the subsurface also depends on water content and existing mineral composition. The resistivity of geological aquifers, mainly composed of unconsolidated materials, decreases with increase in the degree of saturation and salinity of the groundwater. The resistivity of the clay-free rock (ρ_{rock}) is related with resistivity of fluid (ρ_{fluid}) and porosity (Φ) by Archie's law as:

$$\rho_{rock} = \rho_{fluid} A \Phi^{-m} \tag{2}$$

The fitting parameters A and m are constants and depend on the geometry of the pores. For sedimentary rocks the value of these parameters are taken as A = 1 and m = 2 (Nigmatullin et. al. 1992). Rocks having high clay content conduct electric current through their mineral matrix and thus tend to display lower resistivity than the permeable alluvial aquifers. Saturated clay has low resistivity of 5-30 ohm-m range whereas saturated sand and gravel have resistivity 5-10 times higher, and therefore, relatively low resistivity zones are of interest for identifying the productive shallow aquifers. The resistivity of common rocks is shown in figure 1.

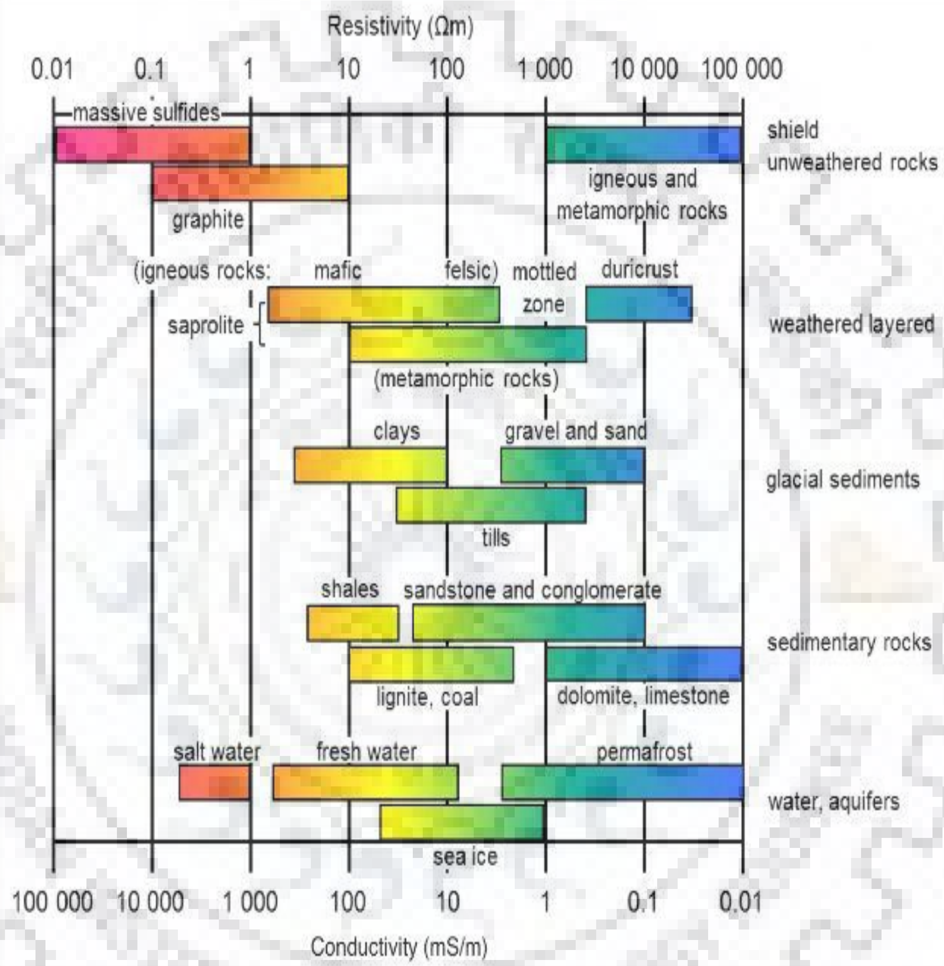


Figure 1: Resistivity (ohm-m) and Conductivity (milli-Siemen per m) for various geological formations (Nigmatullin et. al., 1992).

Owing to its simplicity and accuracy, VES is always encouraged by the researchers for groundwater exploration in the subsurface. Some of the selected work depicting different methods for VES data interpretation is listed in table 1.

Table 1: Selected work that had uses VES for groundwater exploration in the vadose zone.

References	Study Area	Electrode configuration used	No. of sounding done	Highlights
Maiti et. al., 2012	Malvan, and konkan region of Maharashtra, India	Schlumberger configuration	38	Artificial Neural Network (ANN) is used for the interpretation of sounding data.
Sikandar et. al., 2010	Chaj and Rachna Doab, Punjab, Pakistan	Schlumberger configuration	90	Tried to establish a correlation between EC of groundwater samples and electrical resistivity.
Jha et. al., 2008	Salboni block of West Midnapore, West Bengal, India	Schlumberger configuration	48	GA based computer program (coded in C language) is used for the determination of optimal layer parameter.
Hamzah et. al., 2007	Kuala Selangor, Malaysia	Schlumberger configuration	45	RESIX (Interpex Ltd 1990) is used for interpretation of sounding data in terms of 1-D model.

2.2 Groundwater Estimation

Meticulous quantitative assessment methods based on reasonably valid scientific principles are required for sustainable ground water development. Quantification of the rate of ground water recharge is a basic prerequisite for efficient ground water resource management (Sophocleous, 1992). There are number of methods like specific yield method, rainfall infiltration method, water budget method, etc. developed till now that prove to be quite successful in estimation of ground water resources with reasonable accuracy. Every method has its own merits/demerits over another based on the region of study and the data available for the estimation of ground water.

Conventional method involve the use of hydrogeological data collected from bore hole investigations for groundwater recharge zoning (Jang, 2012). With the advancement in the technology in past few years, techniques like aerial photography, spatial analysis tools and satellite monitoring, proved to be beneficial for the estimation of groundwater resources in a region. Although the field-based methods are costly, time-consuming and are to be executed with skilled manpower yet beneficial for accurate estimation of groundwater (Todd, 2005).

Several national and international organizations have recommended some particular methods based on geographic location of the regions. In India, the Ground Water Estimation Committee (GEC) has been the basis of groundwater assessment for about two decades. Various groundwater assessment studies for different geographical region has summarized in table 2.

Table 2: Summary of some latest groundwater estimation studies conducted worldwide.

References	Study Area	Method used	Highlights
Peiyue Li et. al., 2016	Guanzhong Plain, Weinan City of Shaanxi province, China	Use connectivity index, hydrochemistry and isotopic signatures of water samples as well as cluster analysis to characterize the connectivity between river water and groundwater	Connectivity index, various hydro chemical interpretation, stable isotope techniques and cluster analysis were used to compute the connectivity between shallow groundwater and river water. End member mixing models based on the relationships of Cl^- with oxygen and hydrogen isotopes are used to assess the contributions of local precipitation, river leakage and lateral inflow to the total groundwater recharge.
Mare´chal et. al., 2006	Maheshwaram pilot watershed Hyderabad, India	Water table fluctuation method (by determination of specific yield)	Without requirement of any extensive in situ instrumentation network, this technique is well suited to developing countries and semiarid areas, where the presence of many agricultural dug wells and bore wells throughout a basin provides a high-density observation network.
Sharda et. al., 2006	Kheda watershed Gujrat, India	Water table fluctuation (WTF) and chloride mass balance (CMB) methods using water storage structures.	The interaction between potential recharge and the actual groundwater recharge is studied in a situation when a large unsaturated section divides the surface and groundwater body. It is also observed that there exists a definite relationship between the changes in chloride concentration and the rise or fall in the water table.
Arnold et. al., 2000	Upper Mississippi river basin, USA	Water Budget method (using SWAT) and Recursive filter and Hydrograph recession method	Groundwater recharge and discharge (base flow) estimates from both were compare to found that the filter and recession methods have the potential to provide realistic estimates of base flow and recharge for input into regional groundwater models and as a check for surface hydrologic models.

2.3 Groundwater Quality Assessment

Groundwater experiences the purifying effects of vadose zone and soil-moisture column during percolation and hence, its quality is generally considered to be superior to the surface water. Mineralogical composition of the aquifer and residence time of the water controls the final chemical composition of ground water. The processes such as adsorption, hydrolysis, precipitation, dissolution, oxidation, reduction, ion exchange, and bio-chemical reactions affects the quality of groundwater (Matthess, 1982).

Quality of groundwater is getting severely affected by the rapid growth of urbanization and industrialization. Apart from that, various climatic and hydro-geologic phenomenon also creates stress on the groundwater quality. The possible pollutants in ground water are limitless; they may be physical, chemical (organic and inorganic), biological and radiological.

Major water quality parameters tested for assessing the ground water suitability for drinking, irrigation or any other uses includes temperature, total dissolved solids (TDS), carbonate and bicarbonate, pH, hardness, EC (electrical conductivity), and metals like sodium, potassium, magnesium, cadmium, nitrate, and lead. Concentration limits of various pollutants at which they become harmful to the human being had been established first by the U.S. Public Health Service Commission in 1914. As of now there are several water standards available, issued by various National/ Regional/international authorities using a risk-benefit approach. These standards contain guidelines based on environmental and socio-economic condition of the region. Some of the international organizations responsible for issuing water quality guidelines includes:

1. World Health Organization (WHO) Guidelines 2011
2. European Economic Community (EEC) Norm
3. US Environmental Protection Agency (USEPA) Norms

In India, most commonly used water standard is IS: 10500-2012 issued by Bureau of Indian Standards (BIS) (Appendix A).

Method for groundwater quality analysis depends on the parameter interested and material composition of the source aquifer. Some of the recent groundwater quality analysis performed is listed in table 3.

Table 3: Some of the recent work relating to groundwater quality assessment methods.

References	**Study Area**	**Parameters Analyzed**	**Highlights**
Tiwari et. al., 2017	KBNIR (The Khushkhera-Bhiwadi –Neemrana Investment Region) in Rajasthan under the proposed Delhi – Mumbai Industrial Corridor Project (DMIC)	Fluoride (F^-), Nitrate (NO^{3-}), Chloride (Cl^-), TDS, pH and Hardness	A geospatial based water quality index is developed for preparing water quality class suitability maps. Multivariate statistical techniques, such as Correlation Matrix Analysis and Principal Component Analysis (PCA) were carried out. The correlation coefficient showed TDS highly correlated with chloride (r = 0.725), and a negative correlation (r = −0.656) between pH and nitrate.
Rani and Chaudhary, 2015	Hisar district of Haryana, India	Hydrogen ion concentration (pH), TDS, EC, Sodium Adsorption Ratio (SAR) and Residual Sodium Carbonate (RSC)	Spatial distribution maps of pH, EC, TDS, RSC, and SAR were prepared in GIS environment. These maps were integrated using GIS for demarcating different groundwater quality zones for domestic usage. Survey of India Topo Sheet No's.: H43P7, H43P8, H43P10, H43P11, H43P12, H43P14, H43P15, H43P16, H43Q03, H43Q04, H43Q08, H43V09, and H43V13 on 1: 50,000 scales were used for the preparation of digital database of various locations in the District, demarcation of district boundary and other collateral information.
Liu et. al., 2003	Yun-Lin Taiwan, China	EC, TDS, Cl^-, SO_4^{2-}, Na^+, K^+ and Mg^{2+}, Total organic carbon (TOC), alkalis, and arsenic.	Factor analysis was applied to groundwater samples from an area of Blackfoot disease. A two-factor model (Seawater Salinization and Arsenic pollutant) suggested and explains over 77.8% of the total groundwater quality variation in the area. The over extraction of groundwater is the major cause of groundwater salinization and arsenic pollution in the coastal area of Yun-Lin, Taiwan.

2.4 Numerical Modelling

Modeling is an important tool that can be used to understand any hydrological or geo-chemical processes by making predictions in the long run. For the mathematical modelling of solute transport in the variably saturated media, Advection-Dispersion equation is frequently used. Many of the reactive transport models were developed as extensions to the existing flow and transport models for example HYDRUS, MODFLOW etc. Initially these models were developed as a simple one dimensional finite element model to simulate soil-moisture flow and solute transport, later they were added with the interaction reactions and other complexities to developed as commercial software for analyzing three dimensional field problems. Since this research work focuses on contaminant transport modelling in equilibrium condition for vulnerability assessment of the area, HYDRUS 1-D is used in this study.

HYDRU 1-D is a subsurface flow and simulation model which is used to solve the Richard's equation for the unsaturated flow and the Fickian-based advection dispersion equation for solute transport. Some selected studies using this software for soil-moisture flow and contamination modelling is listed in table 4.

Table 4: Some selected work on soil-moisture flow and contamination modelling.

References	**Study Area**	**Model Used**	**Highlights**
Kanzari et. al., 2018	Semi-arid region of Tunisia	HYDRUS 1-D and Thermal Dispersion model	In this study a comparison of classical soil physics model (HYDRUS 1-D) and thermal dispersion model is made by taking the temperature factor into account while simulating the soil-moisture flow in semi-arid region of Tunisia.
Li et. al., 2015	Tahiu lake basin of East China	HYDRUS 1-D	The two most important source of Nitrogen i.e., fertilization and mineralization are considered for evaluating nitrogen balance in field. Simulated N concentration and fluxes are verified with observed well data.
Yadav and Junaid, 2014	Doon Valley watershed in Northern India	HYDRUS 1-D	The classical advection-dispersion equation is coupled with Richard's equation for assessing the intrinsic vulnerability of the valley. The simulated travel time required by the solute peak to reach the water table is used for computing the vulnerability index.

Chapter 3. Study Area

This chapter describe the study area, its location along with the general hydrogeological characteristics of the region.

The study area falls in the Mirzapur district which is one of the southernmost district of U.P. having a population of 2,494,533 distributed over an area of 4522 km^2 (ENVIS U.P., 2017). The district is administratively divided into 4 tehsils namely *Chunar*, *Marihan*, *Lalganj*, and *Mirzapur Sadar* that are further categorized into 12 development blocks. The study area is located near Dadri Khurd village of district Mirzapur having latitude 24º 52'12"- 25º 12'43.2" North and 82º 33'18" - 82º 53'45.6" East coordinates as shown in figure 2.

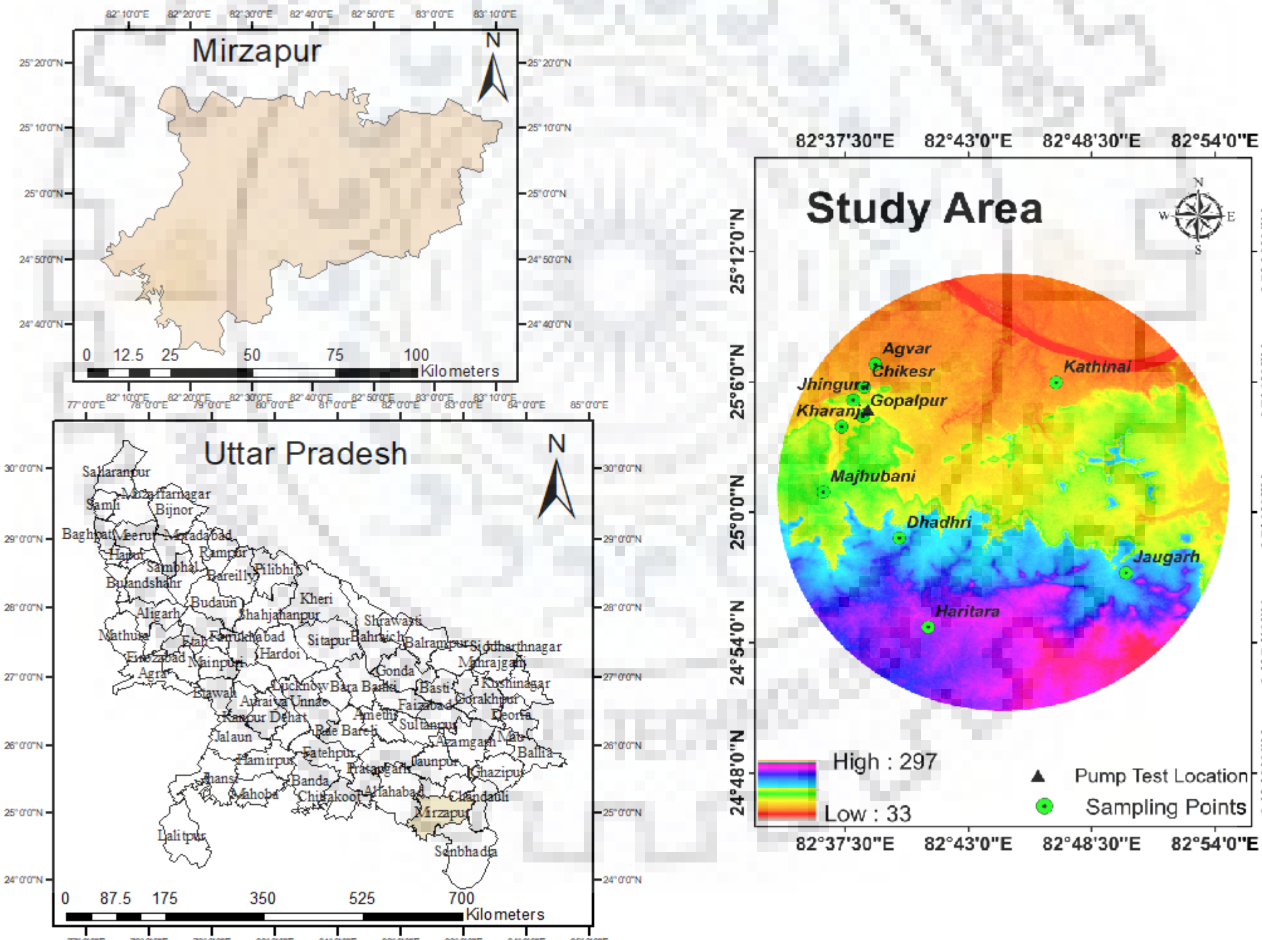


Figure 2: Study area map indicating sampling points and pumping test location in Vindhyan-Ganga sedimentary formation.

The center of target area is located about 17 km toward NE of river Ganges and 5 km west from Upper Khajuri dam. The study area occupies part of Survey of India topographic sheet 63K/12, 63K/16, and 63L9/13 on 1: 50,000 scale. Geologically the area is characterized by the Vindhyan sedimentary system overlain by Quaternary alluvium (Singh et. al., 2015).

The climate of the study area is characterized by hot summer and pleasant monsoon with short cold seasons. As per Indian Meteorological Department (IMD), the average annual rainfall in the area is 1085 mm and about 90% of which takes place between June to September. The average temperature of the area ranges from 14.15 ^{0}C to 39.80 ^{0}C having average relative humidity of 85%. Winds are generally strong in the area with some increase in force during summer and southwest monsoon season. The mean wind velocity is 2 knots and average potential evapotranspiration rate is 1456.7 mm as reported in Central Ground Water Board (CGWB) report (2017).

The groundwater condition in the area is greatly influenced by the occurrence of two distinct lithological formations. The entire area is mainly comprised of: 1) Unconsolidated sediments in the Northern part (marginal alluvium), 2) Hard rock formation comprising Upper Vindhyan sandstone and shale in the Southern part. The average water levels are generally 10-20m bgl around the area.

Chapter 4. Methodology

This chapter presents the working methodology adopted in the study for performing VES, groundwater *assessment. It contains a brief description of AAS used to analyze the groundwater sample for major hydro-chemical parameters. The initial and boundary conditions used to simulate the solute transport in the subsurface are also listed in this section of the thesis.*

4.1 Vertical Electrical Sounding (VES)

A total of 12 Vertical Electrical Sounding (VES) randomly distributed around the study area has been conducted to explore the subsurface for potential water bearing stratum. Location of these sounding sites are shown in table 5.

Table 5: Location of VES sites in the study area along with their respective UGS coordinates.

S.No.	Northing	Easting	Location
VES I	24^0 58.80’	82^0 39.91’	Dan Khurd
VES II	24^0 54.71’	82^0 41.20’	Haritara Village(Marihan)
VES III	24^0 59.96’	82^0 36.94’	Upper Khajuri Dam (Kotarwa Village)
VES IV	25^0 05.16’	82^0 37.85’	Gopalpur
VES V	25^0 6.41’	82^0 46.69’	Bharpura Village
VES VI	24^0 91.84’	82^0 58.92’	Patehara (Kalvari-Lalganj Raod)
VES VII	24^0 87.58’	82^0 72.05’	SemaraVillage (Mirzapur-Ghorawal Road)
VES VIII	25^0 2.44’	82^0 51.08’	Chhitampur
VES IX	24^0 57.21’	82^0 50.03’	Jaugarh Village
VES X	24^0 52.93’	82^0 49.00’	Lusa and Atari Village
VES XI	24^0 2.39’	82^0 35.18’	Ballhara mor (near BHU campus)
VES XII	24^0 59.24’	82^0 40.18’	Dadhri Khurd Village

The basic principles of VES involves finding the electrical anomaly in the subsurface by measuring the potential between one pair of electrodes while transmitting a direct current between another pair of electrodes. Depth of current penetration is proportional to the spacing between the two electrodes in the homogeneous ground. Equipment required for performing VES sounding is an ABEM SAS 300 C terrameter for measuring the earth resistance, one-meter length of 1.5 cm diameter cylindrical steel stakes as electrodes, and wire to connect the electrodes to the Terrameter. The wire is coiled around reels for ease in winding and unwinding as electrode separation changes. The length of wire on reels connecting the resistivity meter to the current electrodes is 500+ m while the length of wire for connecting the potential electrodes is 40+ m. The ABEM SAS 300 C model terrameter is light and powerful for deep current penetration (Koefoed, 1979). The electrode configuration used for performing VES in this study is schlumberger array configuration.

In the schlumberger method, all four electrodes are placed in a straight line in such a way that the distance between the outer current electrodes (*l*) is always larger than the two inner potential electrodes (*b*). The distance between the current electrodes should preferably be more than five times of the distance between potential electrodes, at any stage during the operation of the probing. Centre of the electrode array is used for the calculation of apparent resistivity of the layers underneath. Arrangement of electrode in Schlumberger configuration is shown in figure 3.

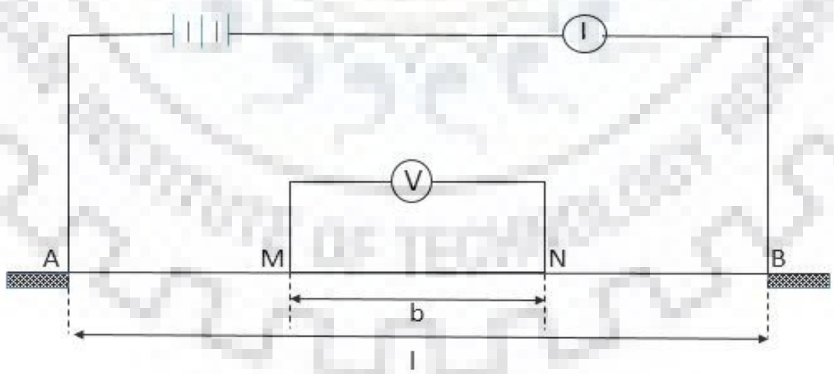


Figure 3: Schematic diagram of arrangement of electrode in Schlumberger configuration used in this study.

The VES are carried out with current electrode spacing (AB) ranging from 2 to 1000 m (AB/2 = 1 m to 500 m). The distance used for potential electrode spacing (MN) ranged from 1 to 80 m (MN/2 = 0.5 m to 40 m). The field data acquisition is generally carried out by moving two or four of the electrodes used, between each measurement. Variation in apparent resistivity values forms a pattern with each electrode separation that forms the basis for quantitative interpretation of the VES data. Qualitative interpretation of resistivity distribution in earth's crust can be performed by analyzing the shape of the field curve. Field curves are obtained by plotting the apparent resistivity data against the electrode spacing and they are matched with the master curve (Orellana and Mooney, 1966) of two, three and four layer cases for various ratios of absolute resistivity. Due to the presence of very high heterogeneity in the subsurface, it has not been possible to use the software for direct interpretation of field resistivity data as the electrical anisotropy may be quite high, leading to inaccuracy in the interpretation. So, in this study, field curve obtained are matched with the three layered master curves categorized into H, K, A, and Q type curves. The distribution of resistivity for different category of subsurface layers is as below: H-type: $\rho1>\rho2<\rho3$, A-type: $\rho1<\rho2<\rho3$, K-type: $\rho1<\rho2>\rho3$, Q-type: $\rho1>\rho2>\rho3$. The results of VES are coupled with the aquifer test results leading to the characterization of the aquifer system.

4.2 Aquifer Tests

Aquifer test (pump test) is a field experiment performed in controlled condition for estimation of hydraulic properties of the aquifer system such as storativity and transmissivity. It is often followed by recovery test for the validation of parameters obtained. In this study, a pump test followed by a recovery test is performed in the Khatinai village of the study area (figure 1) for determining aquifer parameters, Storativity (S) and Transmissivity (T). Two existing boreholes of diameter 7.32 cm each are selected as control- and observation well for the test. Both the wells are drilled in a confined aquifer of thickness 50 ft., extending from 100 to 150 ft. bgl (below ground level). Pump test with a constant discharge of 60.02 m^3/day are performed for a period of 35 minutes.

The Cooper-Jacob method is used for finding S and T values. Drawdown (s) after time (t) from start of pumping is related with well function W(u) as,

$$s = \frac{Q}{4\Pi T} W(u) \tag{3}$$

The well function is represented in form of auxiliary parameter (u) as,

$$W(u) = -0.5772 - \ln u + u - \frac{u^2}{2.2!} + \frac{u^3}{3.3!} \dots \dots \quad (4)$$

The auxiliary parameter is defined as $u = \frac{r^2 S}{4Tt}$, where r is the radial distance from control well. Plot of drawdown (s) versus time since pumping starts (t), known as Data curve is matched with the Theis type curve for obtaining the s and $r^2/4t$ values for a corresponding well function value. Then the value of S and T can be calculated from the well function.

After pumping has stopped, value of residual drawdown (s′) is also measured in the observation well. A plot of residual drawdown s' versus the logarithm of t/t ' is then plotted to obtain a best fit line. The slope of the line ($\Delta s'$ per log cycle of $\frac{t}{t'}$) given by Cooper and Jacob as,

$$\Delta s' = \frac{2.303Q}{4\Pi T} \quad (5)$$

The results of recovery test are used to validate the pumping test results. After aquifer characterization, next step is to estimate the groundwater resources.

4.3 Water Table Fluctuation Method

WTF method along with specific yield method is used in this study for quantification of groundwater resources in the study area. Assessment of total groundwater resources includes quantification of dynamic and static groundwater resources as follows:

- *Monsoon Recharge from rainfall* (R_{rf}): It is calculated by WTF method and rainfall infiltration method both and maximum of the two is taken for groundwater assessment.
- *Recharge from canals and surface water irrigation (*R_{SW}*):* The Upper Khajuri dam is the main irrigation reservoir falling the study area and its total estimated water capacity of this dam is reported about 37.8 million m^3 by U.P. Irrigation and water resource department. Other sources of surface water resources are ponds which are seasonal and very small in capacity and hence are not considered for the recharge calculations.
- *Total groundwater use*, D_G = Population × per capita demand + Area× irrigation use per unit area. D_G is calculated by combining use for domestic and irrigation requirements (as there is no major industry in the area). It is considered that the requirement of water for domestic use is 60 Lpd per head and use for irrigation is taken as 65 cm/ha based on the local cropping pattern of the study area.

Stage of Groundwater Development is calculated as:

$$\text{Stage of groundwater development} = \frac{Annual\ GW\ use}{Annual\ GW\ recharge} \times 100 \quad (6)$$

For estimation of monsoon recharge, GEC (2015) recommended that there should be at least three wells spatially distributed in the area of interest, and groundwater level data should be available for a minimum period of 5 years and preferably for 10 years, along with corresponding rainfall amount. In this study, a total of five wells distributed fairly throughout the study area are considered. Location of these wells are show in figure 5. A data set of rainfall (figure 4) for a period of nine years (2009-2017) is taken in this study for estimation purposes (Kaur and Purohit, 2012).

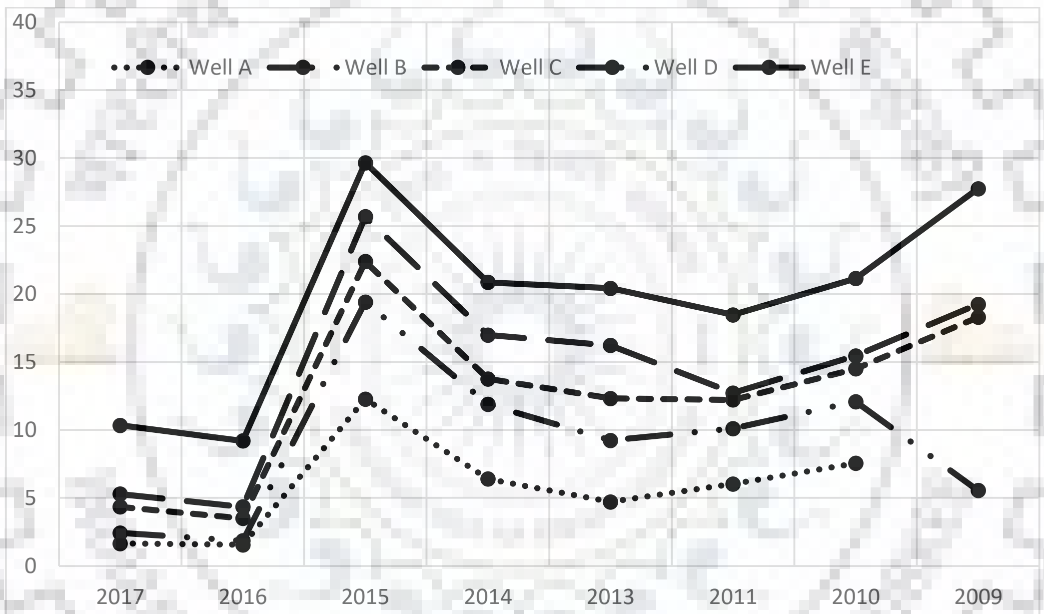


Figure 4: Water Table dynamics of five wells (A to E) plotted against the time chronologically.

4.3.1 Parameters Estimation

Various parameters like net rechargeable area, land use/cover pattern are computed for groundwater estimation. GEC (2015) recommended that for estimating the total net rechargeable area, high slope (>20%) areas should be identified and subtracted from the total geographical area of a target site as these areas have more runoff than infiltration amount. The Landsat 8 OLI (Operational Land Imager) data, taken from USGS Earth Explorer (www.earthexplorer.com), used for obtaining the Digital Elevation Model (DEM) of the area as shown in figure 5.

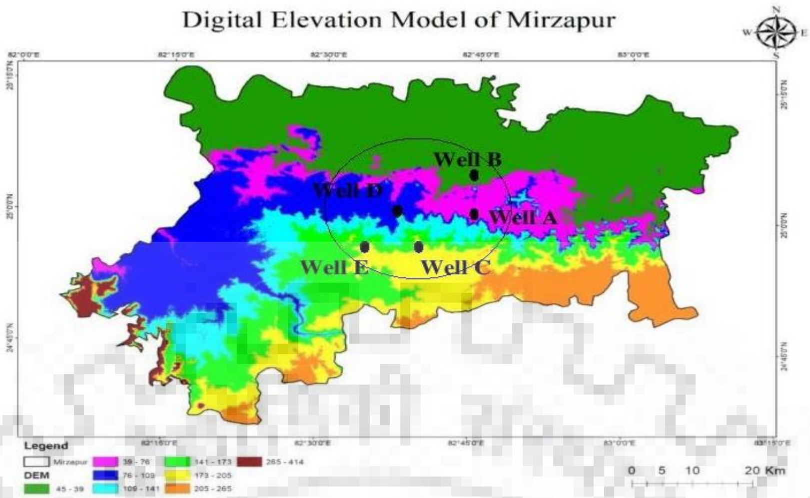


Figure 5: DEM of Mirzapur with a mark for the study area and location of wells used for estimation of average rainfall.

DEM is then analyzed to demarcate the areas having slope greater than 20%. From DEM,

Total suitable recharge area (area with less than 20% slope), A = 192.8 km^2 (7)

Land use and Land cover map of an area helps in quantifying the amount of runoff generated over the surface. Land use classification is done using supervised classification in Erdas Imagine by classifying the total area in eight types of land cover viz. Forest land, cultivable waste land, present fallow land, non-cultivable land, pasture land, grooves and gardens, net sown area, and other fallow land. Land use classification obtained is shown in figure 6.

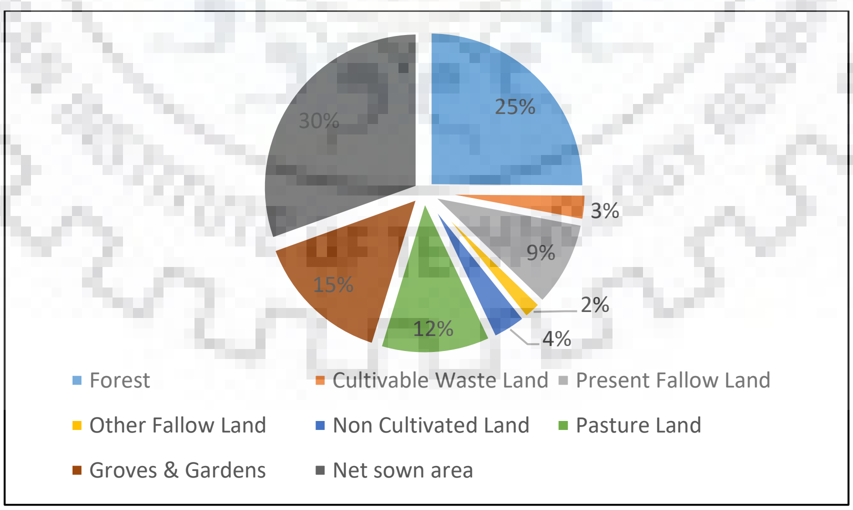


Figure 6: Land Cover calculated from Landsat 8 OLI data for the target area.

4.4 Water Quality Analysis

This study attempts to analyze all major groundwater quality parameter of the target area and results are compared with standard BIS and WHO limits for drinking water.

4.4.1 Samples Collection

For estimation of heavy metals and other ions in groundwater, a total of 10 sampling points scattered in the entire area are selected (Figure 1). Sampling bottle are sterilized in laboratory for the sample collections. Three sets of groundwater samples from each location are then collected in theses bottles for ex-situ analysis. One of the three sampling bottle for each site is acidified with 2% (v/v) HNO_3 solution 2ml per 100 ml of sample for keeping the dissolved metal in ionic form. These samples are stored in a cool and dry place for prevention of alteration of chemical constitution of samples.

In-situ analysis of groundwater for pH, EC (electrical conductivity), temperature and dissolved oxygen are performed using multi-meter sensor (Model: Hach-HQ40d).

4.4.2 Samples Analysis

The collected samples are first diluted to suitable concentration and then analyzed with the help of AAS (atomic absorption spectroscopy) which outperforms the other methods in estimating the trace quantities of elements in groundwater. AAS is capable of analyzing both liquid and solid samples. It first atomizes the sample and then assess the concentration of elements using atomic absorption spectrum using Beer-Lambert law. AAS comes with three type of atomizers:

1) Flame atomization system
2) Graphite tube atomizer
3) Vapor Generation Accessory (VGA)

Each set of sample is analyzed using graphite tube atomizer for finding the concentration of major hydro-chemical ions like Na, Pb, Mg, Al, Li, Cd, V, Cr, As, Se, Ba, Ni, Zn, Be, K, Ca, Mn, Fe, Co, Cu, Sr, and Ag. Principal component analysis (PCA) is also performed for observed groundwater quality parameters to establish the correlation among them.

4.5 HYDRUS-1D

Vulnerability assessment to contamination transport for the study area is performed using soil-moisture flow and contamination modelling using HYDRUS-1D. It is a public domain software developed by Simunek et.al having window-based modelling environment used to analysis groundwater flow and contamination transport in the variably saturated subsurface. It is used to solve the Richard's equation for the unsaturated flow and the Fickian-based advection dispersion equation for solute transport. In dissolved and gaseous phase, advective-dispersive solute transport is used. The flow equation may also consider dual porosity and dual permeability methods, in which matrix is consider as immobile and fracture as mobile in Dual porosity and both matrix and macro-pores as mobile in Dual permeability method.

4.5.1 Governing Equations

The lithological results from VES is used for contamination transport modelling up to the groundwater level at different location of the study area. Equation of soil-moisture flow in vadose zone is Richard equation that comes by combining the Darcy's law and mass balance equation. By neglecting the water flow due to thermal gradient and neglecting the effect of air phase in liquid flow, we get the modified Richard's equation used for moisture flow in unsaturated media is as follow:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} + 1\right)\right] \pm S \tag{8}$$

where, h = pressure head [L]; θ = volumetric moisture content [L^3L^{-3}]; t = time [T]; z = the spatial coordinate [L] (positive upward); S = Source/Sink term; k(h) = unsaturated hydraulic conductivity function (L/T).

Unsaturated hydraulic properties θ(h) and k(h) are highly nonlinear and HYDRUS permit the use of five different analytic model for solving the nonlinear parabolic equation. Van Genuchten (1980) model combine with statistical pore-size distribution model of Mualem (1976) is used in this study due to the heterogeneous condition in the study area. The expression is given as:

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m}; h < 0 \\ \\ \theta_s \qquad ; h > 0 \end{cases} \tag{9}$$

$$k(h) = k_s S_e^l \left[1 - \left(1 - S_e^{\frac{1}{m}}\right)^m\right]^2 \tag{10}$$

$$m = 1 - \frac{1}{n} \tag{11}$$

where, θ_r= residual soil moisture content; θ_s= soil moisture content in saturated condition; k_s = saturated hydraulic conductivity, α and n = curve fitting parameters, S_e= effective saturation, and l = pore connectivity function estimated by Mualem (1976) to be about 0.5 for an average of many soils.

Contaminant transport in the study area is modelled using modified form of advective-dispersive equation (Mathur and Yadav, 2009) obtained after combining Fick's law with continuity equation. The expression for nonreactive conservative solute is given as:

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left(D\theta\frac{\partial C}{\partial z} - qC\right) + S_c \tag{12}$$

where, C = contaminant/solute concentration (M/L^3); D = hydrodynamic dispersion coefficient (L^2/T); q = soil-water flux; S_c =Solute uptake term expressed as mg of solute per unit volume of solute per unit time.

4.5.2 Initial and Boundary Conditions

The solution of above mentioned modelling equations requires the upper and lower boundary conditions along with initial distribution of pressure head (h) within the soil domain. Pressure head at top of the soil for all lithologs are taken as h (z=0) = -100 m i.e, completely dry soil and for bottom of soil it is taken as h (x=L) = 0 m representing the water table. For solute transport modelling, it is assumed that soil is devoid of any solute concentration at time t=0. HYDRUS allows the user to choose from six upper boundary conditions and eight lower boundary conditions for the model simulation depending upon the site condition. Boundary condition used in this study are as:

Upper Boundary Condition: A constant flux of q = -2 cm/day (downward) is assumed from above for the whole simulation periods i.e., 500 days. Only one contaminant pulse of t = 100 days is considered for simulations.

Lower Boundary Condition: As water table is to be expected at lower bottom of soil profile, free drainage condition is taken at lower boundary in this study.

4.5.3 Numerical Solutions

The solute and soil-moisture transport modelling equations are solved numerically by Galerkin-type finite-element scheme used in HYDRUS. Each governing equations are solved in an iterative process for each time steps to obtain the solution. The iterative process terminates when the obtained values of soil-moisture head or solute concentration are similar at all defined nodes for two successive iterations in a variably saturated region. The van-Genuchten (1980) parameters used for different soil texture classes are listed in table 6.

Table 6: Parameters used for Soil Moisture flow and Solute Transport Simulation.

S. No.	Soil Type	Bulk density (g/cm^3)	Dispersivity (cm)	n	θ_r	θ_s	α (1/cm)	k_s (cm/ day)
1.	Loamy Sand	1.5	20	2.28	0.057	0.41	0.124	350.2
2.	Sandy Clay loam	1.26	30	1.48	0.1	0.39	0.059	45
3.	Clay Loam	1.39	40	1.31	0.095	0.41	0.019	40
4.	Sand	1.6	20	2.68	0.045	0.43	0.145	712.8

The time taken by solute to reach its maximum concentration at the groundwater level is used for quantifying the vulnerability index.

Chapter 5. Result and Discussions

This section depicts the results of this study. It contains the lithologs obtained from VES, concentration contours of critical quality parameters, aquifer parameters, vulnerability index map, and the assessed stage of development for groundwater resources.

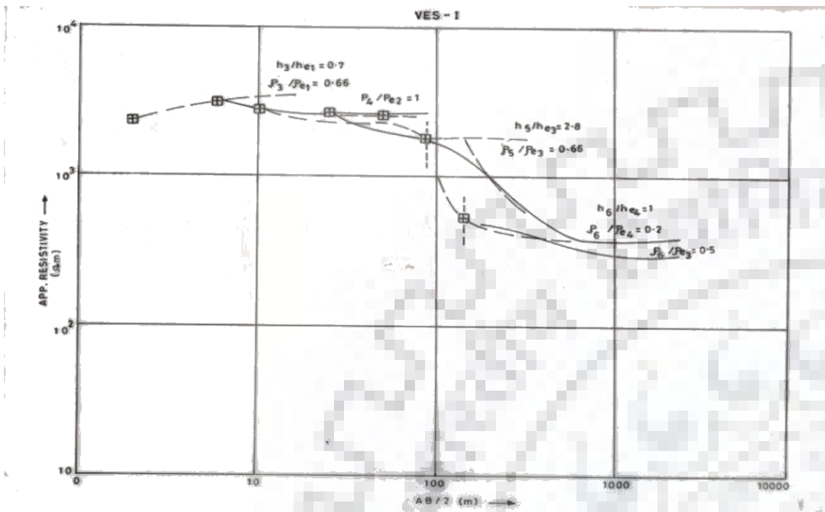
5.1 Vertical Electrical Sounding (VES)

Study area is found to have diversified lithology ranging from hard rocks to clay. The topsoil layer in the study area is composed by a sedimentary, clay and sandy clay layers, of few meter thickness. The obtained apparent resistivity value and half current electrode separation (AB/2) are plotted on the log-log graph of modulus 62.5 mm to obtain the field curves a shown in figure 7 (a-i). These data curves indicate that our study area is comprised of 3-6 different lithological layers for different locations. Field curves are further interpreted for categorization of various lithological formations around the area. Resistivity ranges for the existing geological formations in the target area are determined by comparison of the available background geological data and are shown in table 7.

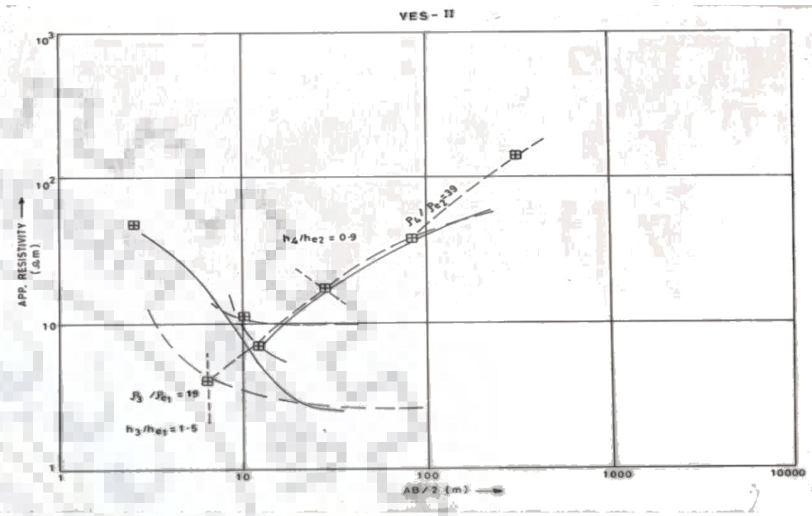
Table 7: Resistivity ranges of existing geological formations in area. (Kumar and Yadav, 2014)

Geological Formation	Resistivity (ohm-m)
Clay Bed	<18
Sand layer	20-50
Weathered Sandstone	70-150
Fractured Sandstone	150-250
Compact Sandstone	250-500
Topsoil layer (Near surface)	25-250
Quartzite	500-100 0
Hard rocks	>1000

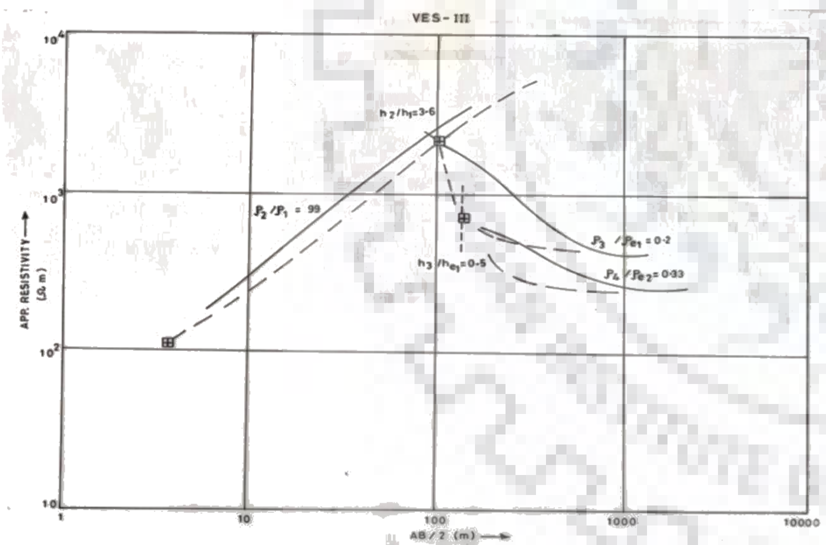
The lithologs for each VES location are shown in figure 8 (a-b). Lithological information obtained indicate the absence of the sedimentary horizon for VES sites I, III, IV, IX, X, X1, and XII. Whereas, sites of VES II, V, VIII are expected to contain water-bearing stratum often at a depth varying between 4 to 8m bgl.


VES - I
APP. RESISTIVITY (Ω.m)
AB / 2 (m)
h3/he1 = 0·7
ρ3 /ρe1 = 0·66
ρ4 /ρe2 = 1
h5/he3 = 2·8
ρ5 /ρe3 = 0·66
h6 /he4 = 1
ρ6 /ρe4 = 0·2
ρ6 /ρe3 = 0·5

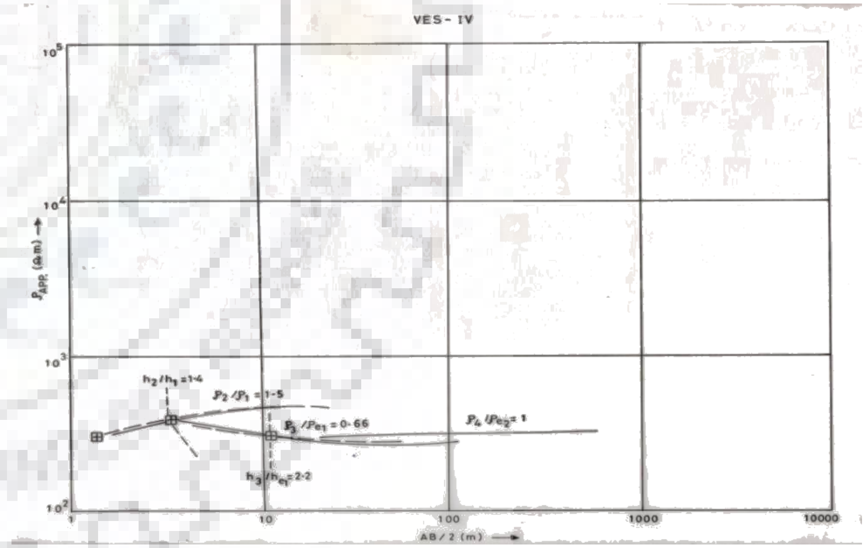
(a)


VES - II
APP. RESISTIVITY (Ω.m)
AB / 2 (m)
h4/he2 = 0·9
ρ4 /ρe2 = 39
ρ3 /ρe1 = 19
h3/he1 = 1·5

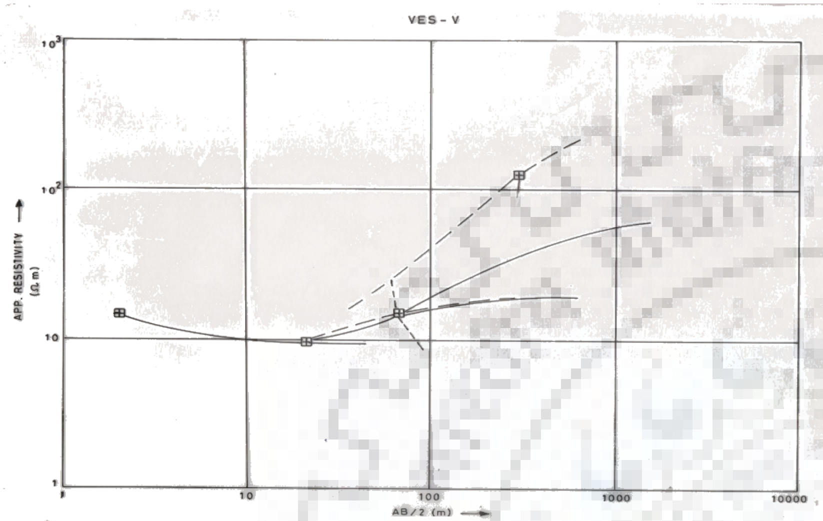
(b)


VES - III
APP. RESISTIVITY (Ω.m)
AB / 2 (m)
h2/h1 = 3·6
ρ2 /ρ1 = 99
h3 /he1 = 0·5
ρ3 /ρe1 = 0·2
ρ4 /ρe2 = 0·33

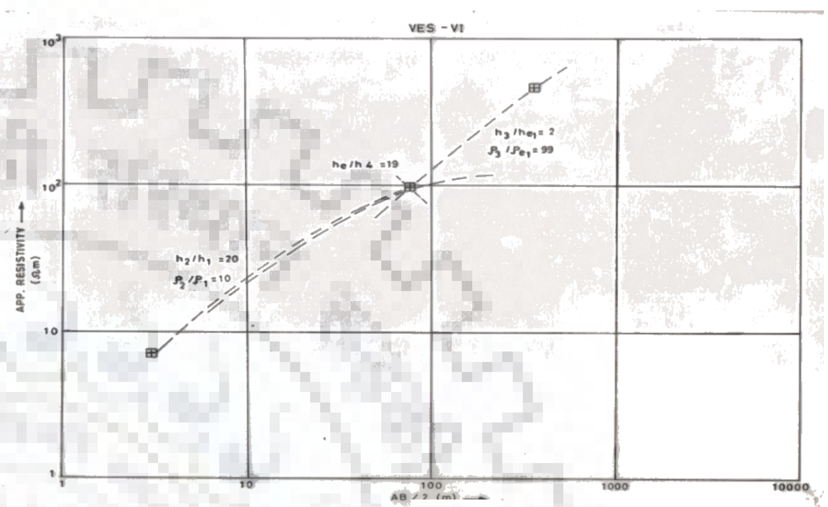
(c)


VES - IV
ρAPP (Ω.m)
AB / 2 (m)
h2/h1 = 1·4
ρ2 /ρ1 = 1·5
ρ3 /ρe1 = 0·66
ρ4 /ρe2 = 1
h3 /he1 = 2·2

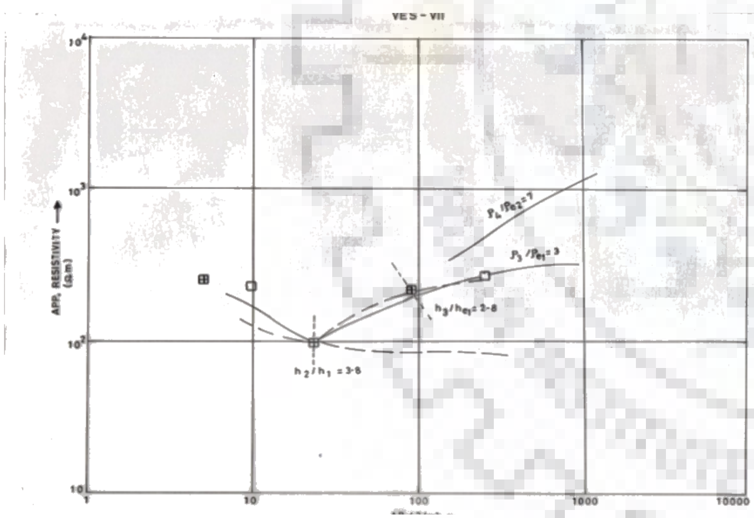
(d)


VES - V
APP. RESISTIVITY (Ω.m)
AB / 2 (m)

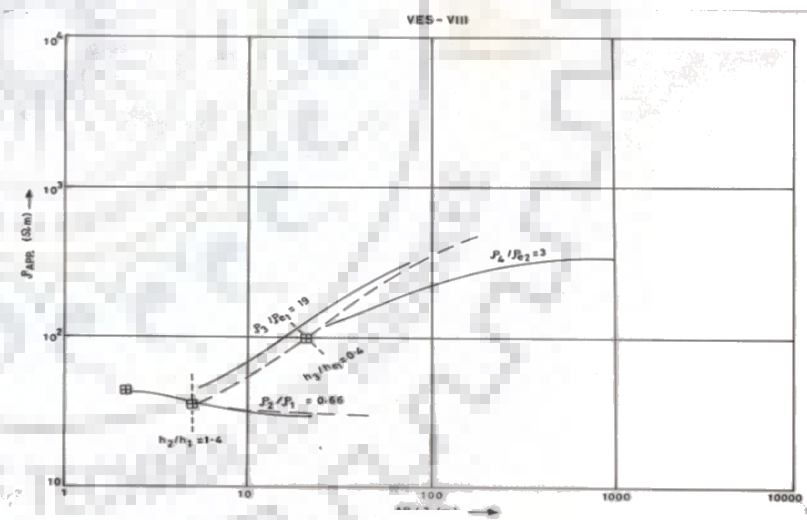
(e)


VES - VI
APP. RESISTIVITY (Ω.m)
h2 / h1 = 20
h3 / he1 = 2

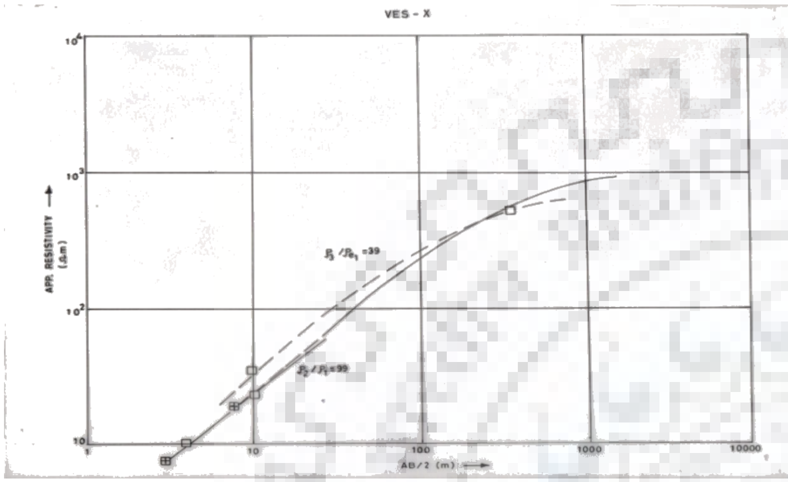
(f)


VES - VII
APP. RESISTIVITY (Ω.m)
h2 / h1 = 3·8

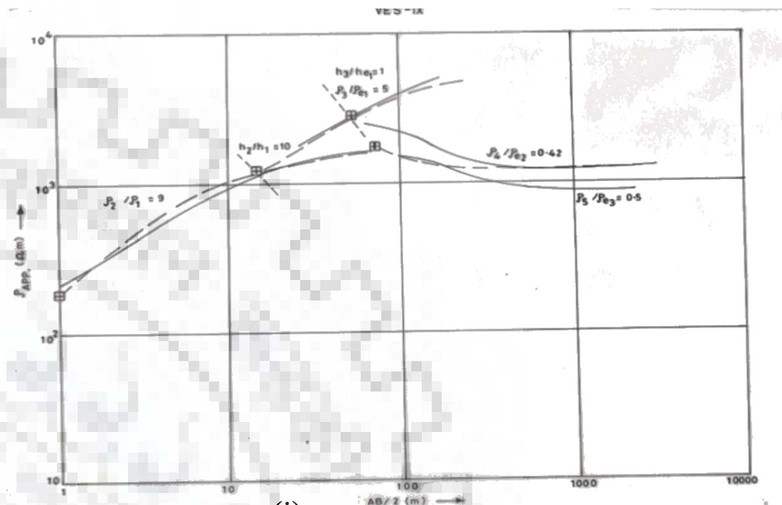
(g)


VES - VIII
h2 / h1 = 1·4

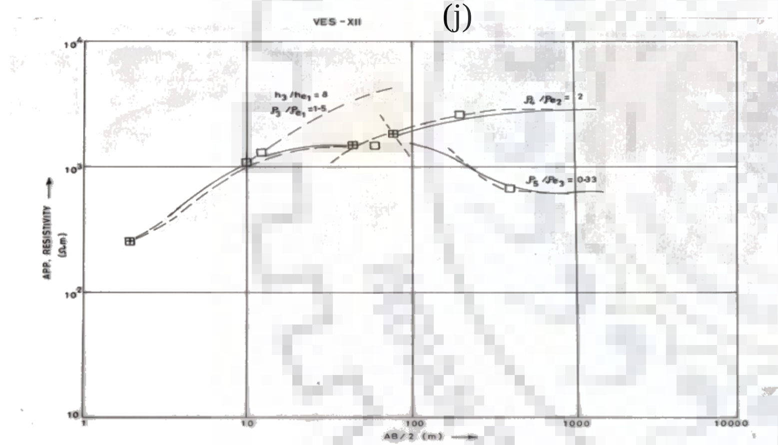
(h)



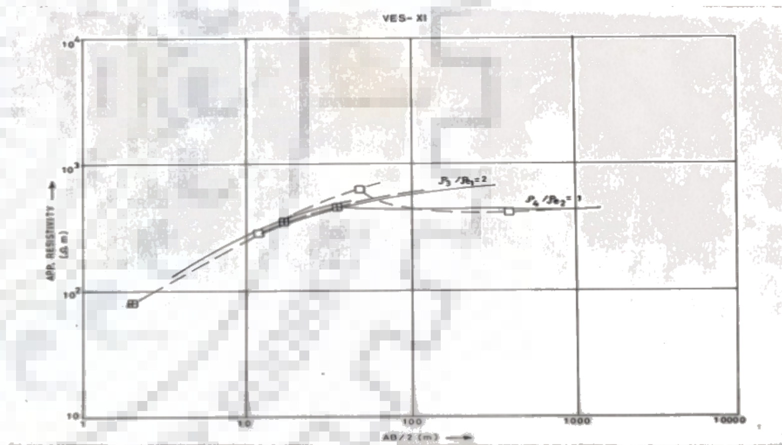
(j)



(j)

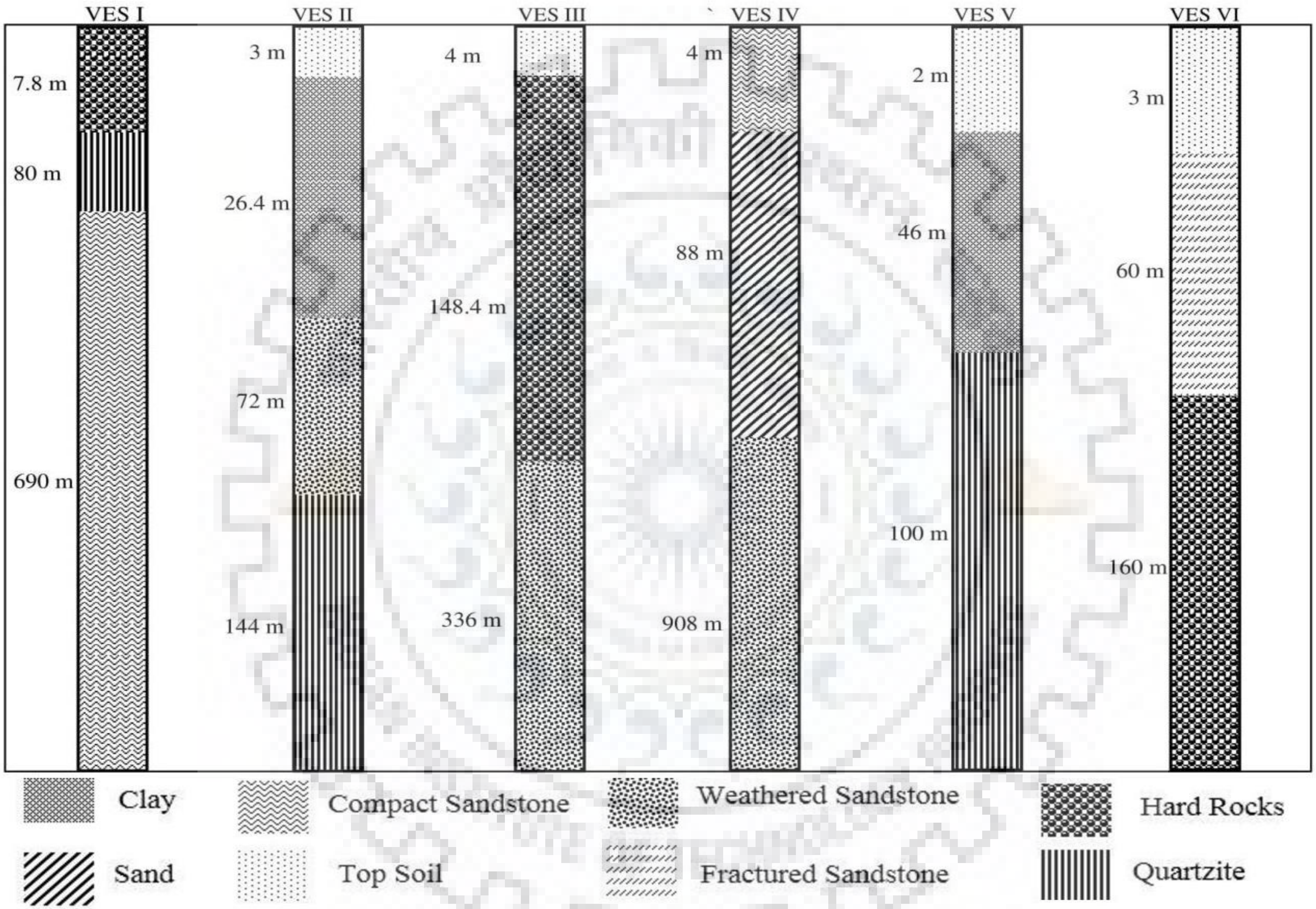


(k)



(l)

Figure 7: Interpreted field curves of VES for (a) Dan Khurd South, (b) Haritara, (c) Upper Khajuri, (d) Jhingura, (e) Bharpura, (f) Patehara, (g) Semara, (h) Chhitampur, (i) Jaugarh, (j) Lusa, (k) Ballhara mor, and (l) Dan Khurd North locations.


VES I
VES II
VES III
VES IV
VES V
VES VI
7.8 m
80 m
690 m
3 m
26.4 m
72 m
144 m
4 m
148.4 m
336 m
4 m
88 m
908 m
2 m
46 m
100 m
3 m
60 m
160 m
Clay
Compact Sandstone
Weathered Sandstone
Hard Rocks
Sand
Top Soil
Fractured Sandstone
Quartzite

(a)

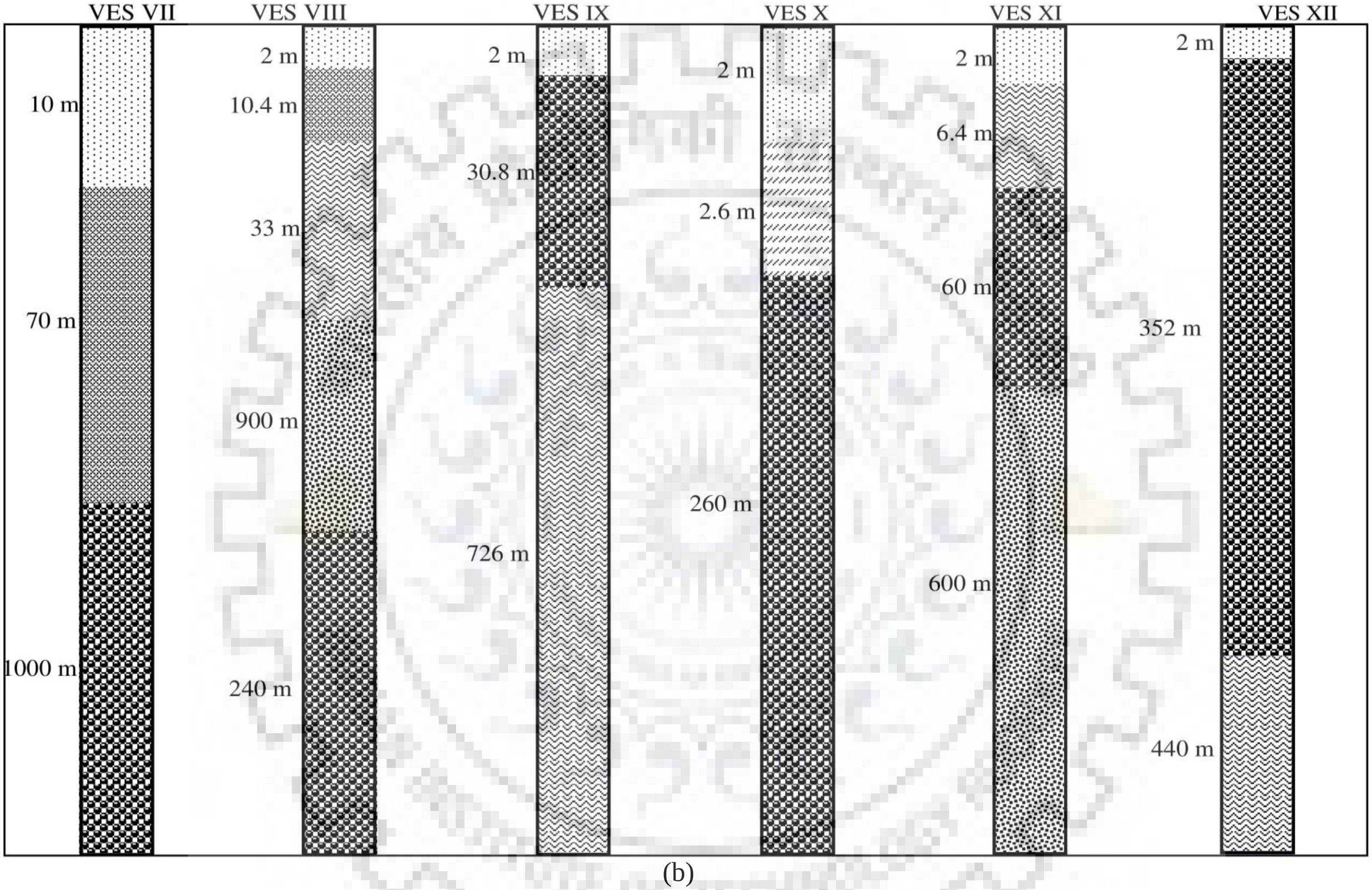


Figure 8: Lithologs for each VES location (VES I- VES XII) with the thickness of each layer is shown on the left hand side of their respective figure.

The interpreted results of the resistivity sounding (VES 1) do not indicate presence of any potential water bearing zone as all the upper layers pertain to hard sandstone except the last (deepest) one occurring at a depth of approx. 180 m bgl. While, at VES II, where a 5.85 m thick layer of weathered sandstone is indicated to be present at a depth of approx. 7-8 m bgl. This layer has a resistivity of 83.6 ohm-m and seems to pertain to weathered sandstone which may be productive aquifer.

5.2 Aquifer Parameters

The plot of time vs. drawdown data of monitoring well obtained from the pumping test is shown in figure 9.

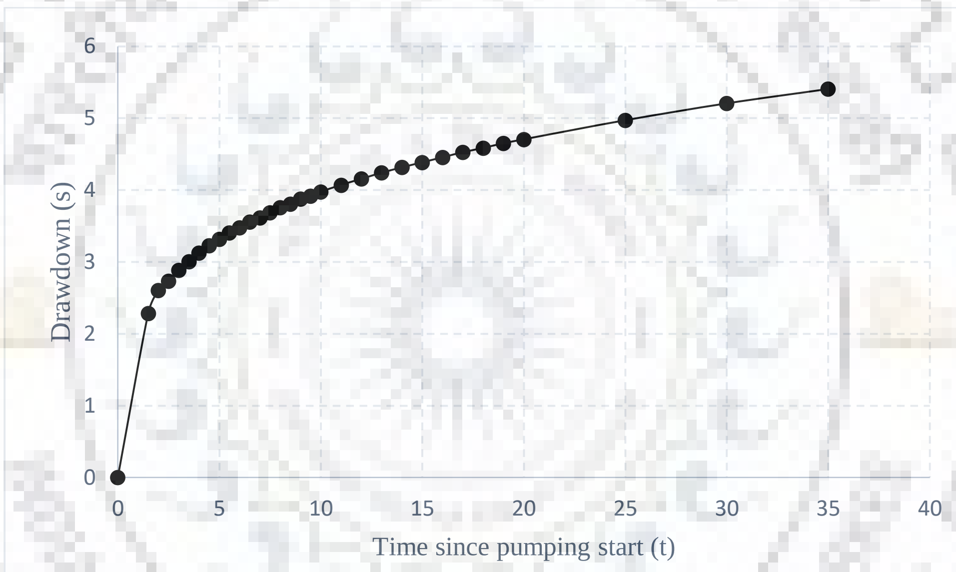


Figure 9: Data curve obtained after plotting the drawdown recorded in the observation well against time since pumping start.

This Data Curve is then matched with the Theis type curve for obtaining the values as:

- Well function W (u) =1,
- Auxiliary parameter u=10^{-2},
- Drawdown s=0.9 m and,
- $\frac{r^2}{t}$ = 47 m^2/min or 67,680 m^2/day.

Transmissivity (T) and Storativity (S) of the aquifer system is calculated using Cooper Jacob equation and were found as *5.307* m^2/day and 3.13×10^{-6}, respectively. Hydraulic conductivity (K) of the aquifer is found as:

$$K = \frac{T}{B} = \frac{5.307}{15.24} = 0.34882 \text{ m/day.} \quad (13)$$

A plot of residual drawdown s′ vs. log (t/t′) is plotted and slope of best fit straight line is obtained (figure 10) as, Δs = 2.08 from which,

$$T = \frac{2.303Q}{4\Pi\Delta s} = 5.28 \text{ m}^2\text{/day.} \quad (14)$$

These values are in good agreement with the study carried out by Yadav and Singh (2008).

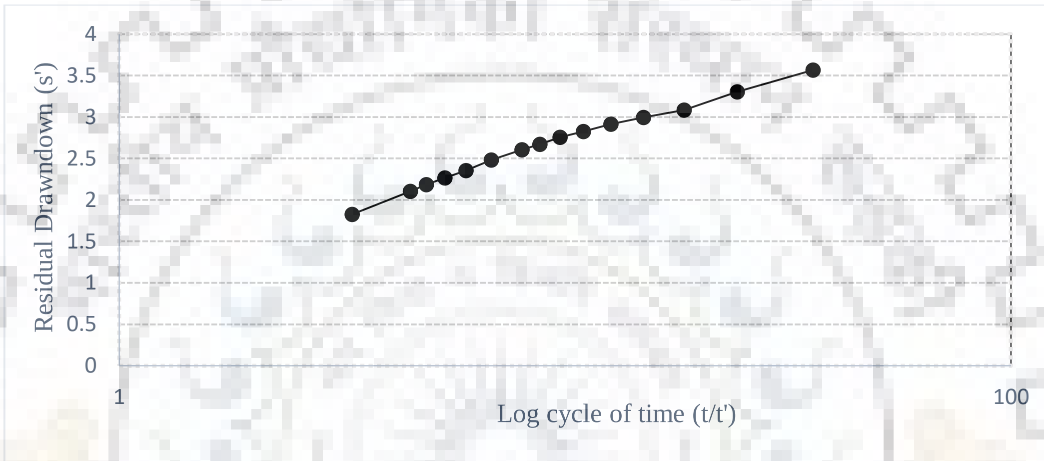


Figure 10: Recovery test plot of the observation well obtained after plotting the residual drawdown per log cycle of time.

5.3 Groundwater Quantification

Groundwater resources in the area is estimated by water table fluctuation method coupled with rainfall infiltration method. Assessment of total groundwater resources includes quantification of dynamic and static groundwater resources as follows:

- *Monsoon Recharge from rainfall by WTF* (R_{rf}) = (h_{wtf} × S × A), h_{wtf} = 4.261 m (from well fluctuation data), S = 3 %, recharge from water table fluctuation method (WTF): R_{rf} (WTF) = 192.8 km^2 x 10^6 m^2/km^2 x 3/100 x 4.261m = 24645624/10^4 ha-m = 2464.5624 ha-m **= 24.65 MCM**
- *Monsoon Recharge from rainfall* by *rainfall infiltration method (*R_{rf}*)*: Average monsoon rainfall (h) = 912.6 mm and Rainfall infiltration index for SST terrain (from GEC, 2015) = 10%. The monsoon GW recharge (R_{rf}) = 192.8 km^2 × 912.6 mm /1000 × 10/100 × 10^6 m^2/km^2 = 1759.4928 ha-m = **17.60 MCM**

- *Recharge from canals and surface water irrigation:* Total irrigated area = 9511.76 ha, area irrigated through surface water = 9107.79 ha, and applied irrigation = 0.75 m/ha. Then, R_{SW} = 2732.32 ha-m = **27.32 MCM**
- *Total groundwater use,* D_G = Population × per capita demand + Area× irrigation use per unit area = (514944 × 60 lpcd/ 1000 L/m^3 × 365 days/year) +(403. 97 ha*0.65m/ha) = 11.27 + 2.62 MCM= **13.89 MCM**

As groundwater recharge calculated from WTF method is higher (24.64 MCM) than that calculated from rainfall infiltration method, the former is accepted. Recharge through rainfall (in WTF method) = 24.65 MCM and recharge from surface water irrigation = 27.32 MCM. So, total annual groundwater recharge = (24.64 + 27.32) MCM **= 51.96 MCM.**

$$\text{Stage of groundwater development} = \frac{13.89}{51.96} \times 100 = 26.73\ \%. \quad (15)$$

Category (As per GEC) = **Safe**. Summary of groundwater assessment is shown on table 8.

Table 8: Summary of water quantification for the study area.

Sr. No.	Observations	Values
1	Surface water	37.8 MCM
2	Recharge from water table fluctuation method	24.65 MCM
3	Return flow from surface irrigation at the rate of applied water (R_{SW})	27.32 MCM
4	Rainfall recharge from Infiltration Method (R_{rf})	17.60 MCM
5	Annual Groundwater Recharge	51.96 MCM
6	Stage of Groundwater Development	26.73 %
7	Category (as per GEC-15)	Safe

5.4 Groundwater Quality Parameters

The collected samples are analyzed for all major groundwater quality parameters all over the study area to assess the general trend of water quality status in the subsurface. The observed values of different water quality parameters are also compared with respect to the Bureau of Indian Standards (BIS) of water quality as per IS 10500:2012 for drinking purposes. The values exceeding the required standards are highlighted as bold in the Table 9 and 10.

5.4.1 Physical Parameters

The in-situ observed values of pH, EC, temperature, TDS along with carbonate, bicarbonate, and hardness of groundwater samples for their respective sites are shown in Table 9. Extreme observed values of pH; maximum of 7.8 for Haritara and minimum of 6.18 for Jaugarh, both are well within acceptable BIS standard of drinking water. Electrical Conductivity values for all samples (except at Haritara which shows EC = 750 µS/cm) are exceeding the BIS standard (IS 10500:2012) i.e. 800 µS/cm. Generally observed values of TDS (Total Dissolved solids) are found within limits, except at three sites named Jhingura, Gopalpur, and Agvar showing high values of TDS as 611, 689, and 877 mg/L respectively. The results show the satisfactory status of nitrate concentration for all sampling sites, except at Jaugar (66.76 ppm) and Chikesr (169.82 ppm) sites indicating contamination from some nearby source.

Groundwater is generally found to be hard everywhere exceeding the lower limit of IS 10500:2012 but all values are found to be lower than the maximum permissible limit for drinking water i.e. 600 ppm. The maximum value of hardness obtain are 600 ppm at Jaugar and minimum is 200 ppm at Majhubani.

5.4.2 Heavy metals and other ions

The concentration of heavy metals and other ions analyzed with the help of AAS are listed in Table 10. Magnesium (Mg), Calcium (Ca), Chromium (Cr), Manganese (Mn), Nickel (Ni) and Barium (Ba) concentrations are also found to be in limits except at some location, possibly by practice of sewage farming in those areas (Chakarvorty, 2015).

Table 9: Values of pH, EC, temperature, TDS, carbonate, bicarbonate, total hardness, and Nitrate for the groundwater with their respective sampling location in the study area.

Site Number	Jaugarh	Haritara	Jhingura	Kathinai	Dhadhri	Majhubani	Kharanja	Gopalpur	Chikesr	Agvar	BIS Limits (IS 10500:2012)
pH	7.5	7.8	7.3	7	6.8	6.2	7.1	7.2	7.2	6.9	6.5-9.2
EC	**1087**	750	**1077**	**1076**	**1092**	**1083**	**1080**	**1082**	**1082**	**1084**	<800
Temp(^{0}C)	**17**	12	13	15	13	10	11.2	10.2	28.7	15.5	10-15.6
TDS(mg/L)	266	150	**611**	392	39.3	76.6	118.1	**689**	213	**877**	<500
Carbonate (ppm)	0.57	0.83	0.4	0.17	0.08	0.01	0.18	0.26	0.05	0.18	-----
Bicarbonate (ppm)	169.42	139.14	209.59	179.83	129.91	39.99	139.81	159.73	29.94	199.82	-----
Hardness (ppm)	**600**	**220**	**280**	**310**	**250**	**410**	200	**360**	**320**	**480**	<200
NO^{3-} (ppm)	**66.76**	0.39	0	4.56	1.82	7.55	2.37	1.82	**169.82**	18.24	45

Table 10: Mean value of Na, Pb, Mg, Al, Li, Cd, V, Cr, As, Se, Ba, Ni, Zn, Be, K, Ca, Mn, Fe, Co, Cu, Sr, and Ag concentration for the groundwater with their respective sampling location in the study area.

Site No.	Jaugarh	Haritara	Jhingura	Kathinai	Dhadhri	Majhubani	Kharanja	Gopalpur	Chikesr	Agvar	BIS Limits (IS 10500: 2012)
Li (ppm)	0.03	0.03	1.32	0.05	0.04	0.04	0.04	0.52	0.05	0.11	____
Be (ppb)	0.6	0.5	01	0.7	1.8	3.05	2.75	1.3	2	1.4	____
Na (ppm)	0.51	8.05	244.24	82.32	5.32	5.31	11.71	159.92	11.98	**821.91**	<300
Mg (ppm)	0.07	6.28	14.99	18.74	27.46	5.52	9.52	21.83	13.77	**184.25**	<100
Al (ppb)	6.95	98.8	216.7	22.4	1274	96.85	834.75	272.95	285.55	2997.55	____
K (ppm)	2.86	3.64	9.59	3.65	5.93	3.76	8.11	4.16	3.44	9.15	____
Ca (ppm)	5.02	35.78	45.29	32.43	**586.80**	17.74	40.98	59.35	52.69	114.45	<200
V (ppb)	3.4	3.3	3.7	11.2	8.95	5.1	12.55	7.15	8.25	30.3	____
Cr (ppb)	23.55	24.15	21.65	36.05	**53.05**	21.7	24.2	23.85	24.2	40.7	<50
Mn (ppm)	0.008	0.021	0.086	0.05	**1.22**	0.022	**0.313**	0.042	0.037	0.149	<0.3
Fe (ppm)	**1.66**	**1.97**	**4.10**	**1.88**	**6.42**	**2.46**	**3.12**	**2.54**	**3.22**	**13.15**	<0.3
Co (ppb)	0.45	0.7	0.85	0.95	4	1.15	3.05	1.45	1.15	2.85	____
Cu (ppm)	0.008	0.028	0.035	0.055	0.043	0.027	0.392	0.275	0.389	0.150	1.5
As (ppm)	**0.133**	**0.127**	**0.143**	**0.130**	**0.137**	**0.133**	**0.151**	**0.135**	**0.135**	**0.289**	<0.05
Se (ppm)	0.062	0.039	0.068	0.049	0.068	0.083	0.078	0.071	0.060	0.066	____
Rb (ppb)	0.65	2.05	14.7	2.4	7.75	3.3	7.95	3.1	2.05	12.95	____
Sr (ppm)	0.001	0.116	0.491	0.23	0.57	0.046	0.2	0.217	0.155	1.63	____
Ag (ppb)	0.15	0.8	1.55	0.25	0.5	3.2	1.95	2.25	1.15	1.45	<100
Cd (ppm)	0.0004	**0.009**	0.0025	**0.0151**	**0.0102**	**0.0858**	**0.0787**	**0.0798**	**1.4439**	**0.0045**	<0.003
Ba (ppm)	0.009	0.071	**0.817**	0.081	0.656	0.069	0.247	0.156	0.122	0.248	<0.7
Pb (ppb)	0.45	3.7	**17.55**	5.75	2.35	6.3	**481**	**99.3**	**260.65**	**39.65**	<10
Ni (ppm)	0.002	0.015	0.009	0.008	**0.055**	0.015	**0.046**	**0.022**	0.012	0.11	<0.02
Zn (ppm)	0.05	2.16	1.09	0.37	8.99	0.5	3.92	2.13	2.55	2.20	<15

Most of the sites are generally exceeding the concentration of Cadmium (Cd) and Lead (Pb) with their respective peak values at Chickesr (1.44 ppm) and Kharanja (481 ppb). Groundwater around the area is found to have high concentration of Arsenic (As) and Iron (Fe) with peak values of 0.29 ppm and 13.15 ppm, respectively, both at Agvar.

5.4.3 Principal Component Analysis (PCA)

Principal component analysis is done for the hydro-chemical parameters listed in table 6 and PCA plot among maximum correlating component is shown in figure 11.

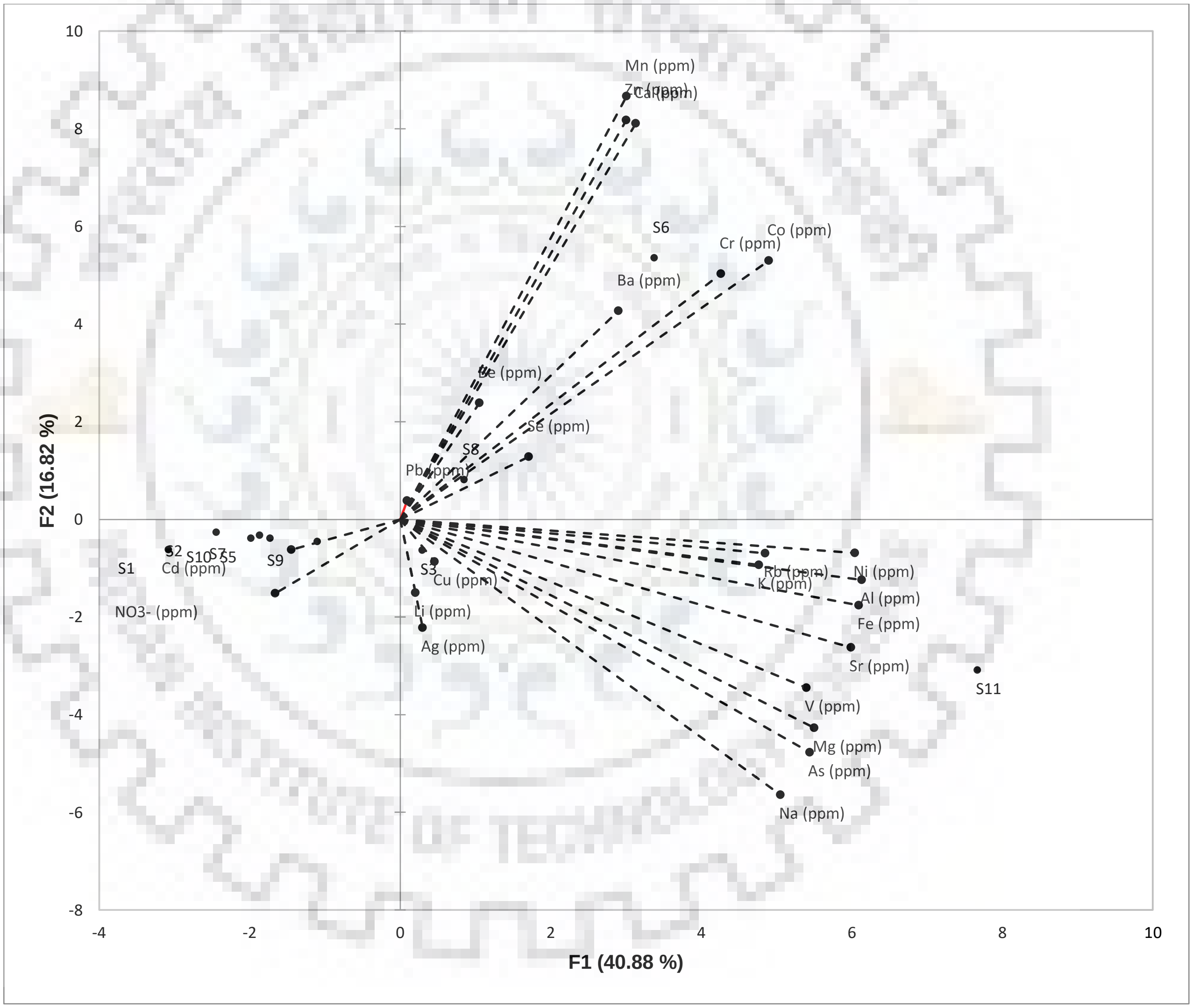


Figure 11: PCA plot among the principal component that are having maximum correlation of 40.88% and 16.82% for various parameters analyzed.

Plot shows that ions like Mn, Ca, and Zn are positively correlated while ion like As, Al, Mg, Na are negatively correlated. An increase in first principal component is associated with increase in cadmium and nitrate while an increase in second component is linked to the increase in Ni, Fe, Sr, Al, Mg, Na, and As. All Sampling locations tend to be clustered into the third quadrant of the Cartesian plane except Jhingura, Kharanja, Majhubani, and Agvar. This suggests an increase of contamination while moving along this bisecting line away from the origin of the Cartesian plane. The maximum correlation possible between the analyzed elements along the two principal axis is only 40.88% and 16.82%. The groundwater from all the locations barely exhibit a general trend because of the parameters of both first and second component.

5.4.4 Critical Parameters Mapping

Concentration of the critical groundwater quality parameters i.e., Iron, Arsenic, Lead, and Cadmium are interpolated over the area of interest using GIS techniques. Map showing the spatial distribution of these parameters are shown in figure 12 (a-d).

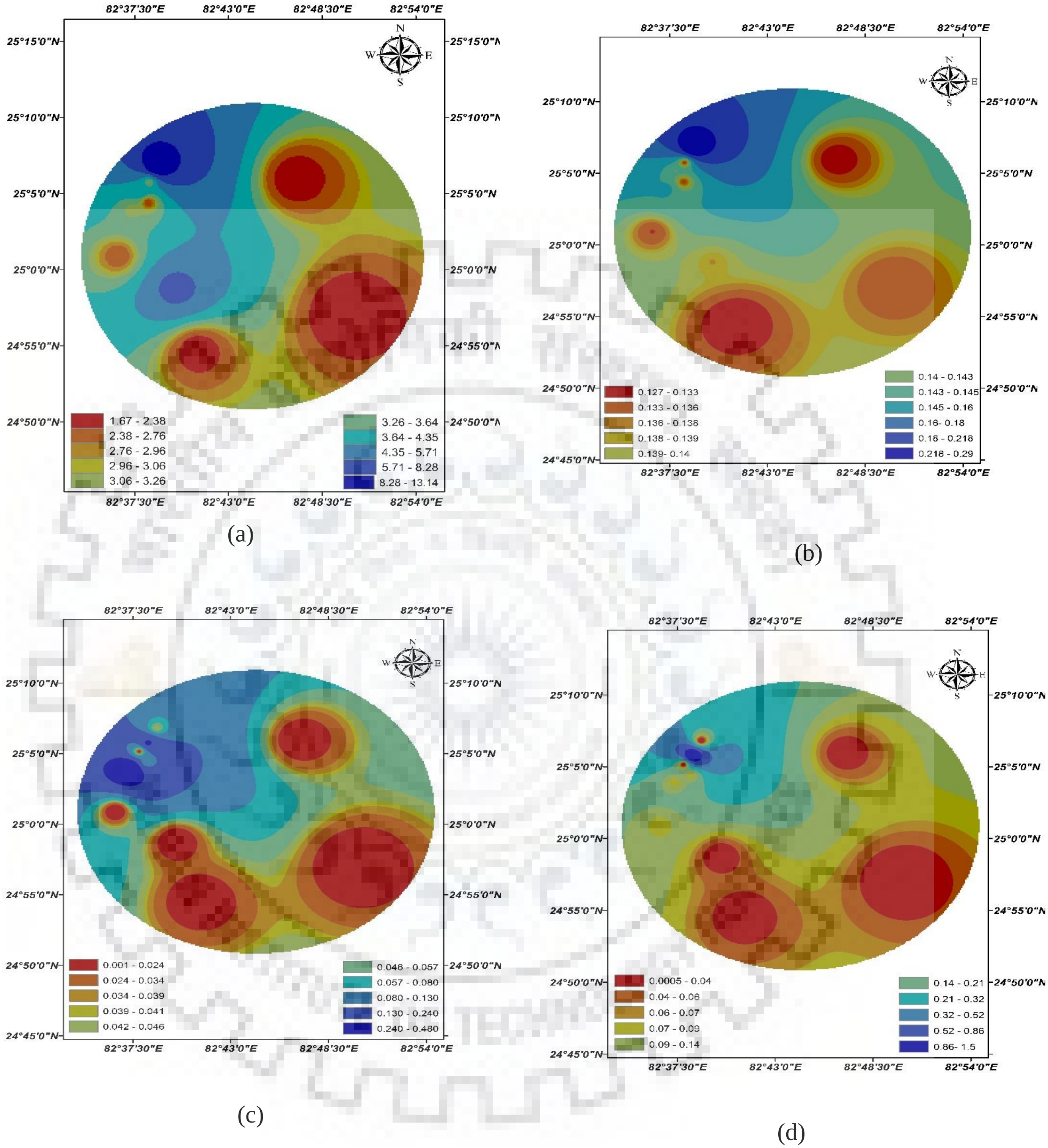


Figure 12: Concentration contours of critical parameters: (a) Iron, (b) Arsenic, (c) Lead, and (d) Cadmium over the study area.

5.5 Contaminant Transport modelling

The modified form of classical advective-dispersive equation (equation 12) is used for contaminant transport modelling in partially saturated vadose zone. Results obtained from HYDRUS 1-D are listed below.

5.5.1 Solute Concentration Profiles

The variation of solute concentration along the depth is plotted after every 100^{th} day represented by lines T0 as the initial solute concentration at t = 0 days and T1, T2, T3, T4, and T5 for solute concentration after 100, 200, 300, 400, and 500 days respectively. The computed solute concentration profiles at different time for different locations in the study area are shown in figure 13. The figure shows that variation of solute concentration profiles at different location due to the varying lithology of the area.

5.5.2 Node Concentration Curves

For each of the hydrogeological locations three different nodes at top, middle and bottom of soil strata is selected for computing the varying solute concentration with time. The Computed solute transport profiles at selected nodes of varying hydrogeological conditions associated with different locations in the study area are shown in figure 14. The solute concentration at some of the location reach the groundwater table after 40-50 days while at some places it reaches after 450-500 days of simulation. This again highlight the existing heterogeneity in the area.

5.5.3 Mass Balance of In-Out Fluxes

The cumulative solute flux applied at the surface and collected at bottom most node (representing groundwater table) is plotted against time and is represented by figure 16 and figure 15 respectively. For the same cumulative surface flux at all locations, output bottom flux is varying with hydrogeological conditions associated with different locations. Difference between the two fluxes after 500^{th} days of simulation gives the amount of solute remains trapped in the soil matric at the end of simulation period and thus representing the contaminant storage potential of the soil strata. Maximum Solute retention is observed for the haritara, Semara and Chhitampur locations.

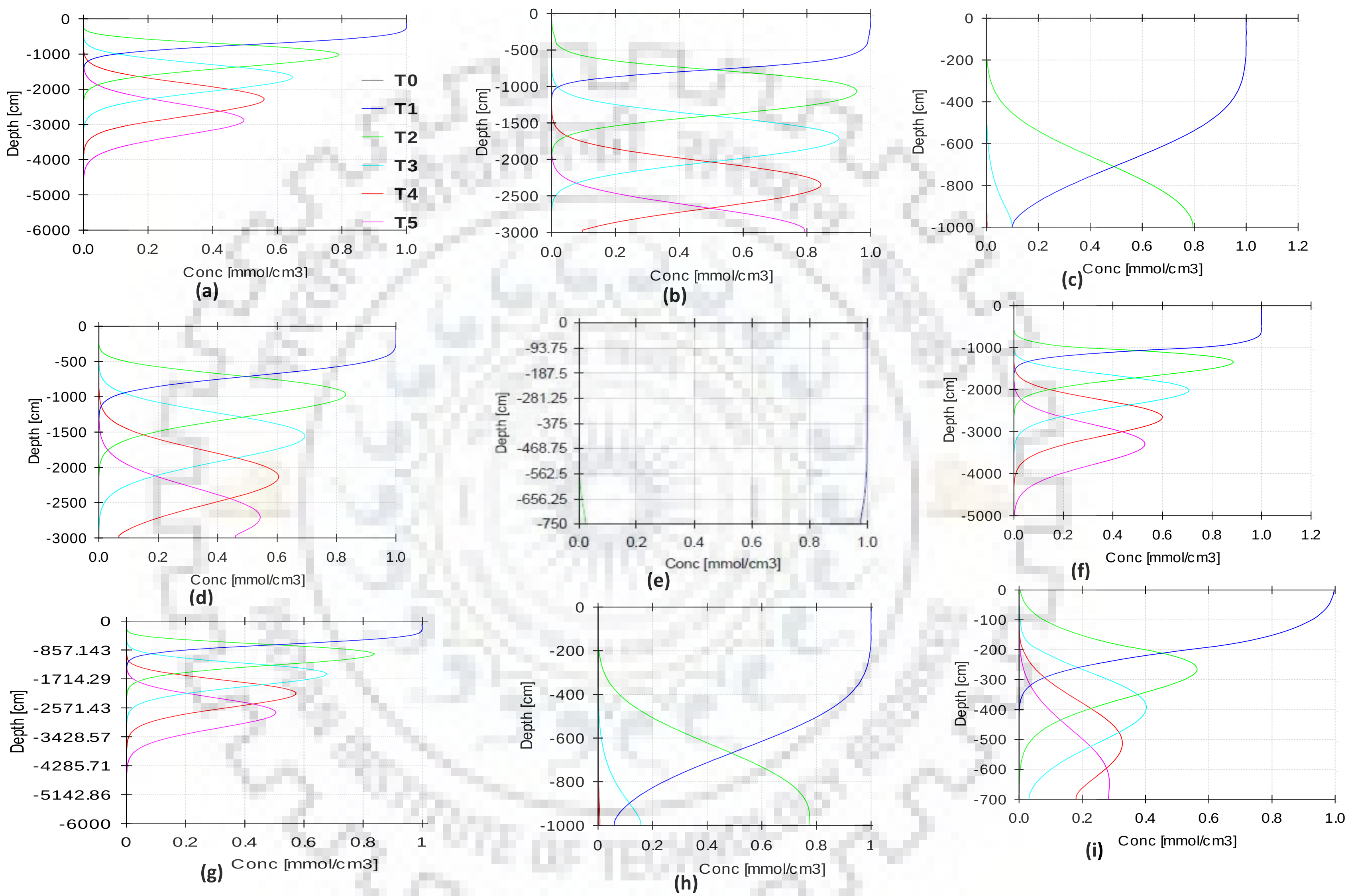


Figure 13: Solute concentration profiles at different locations under constant flux of q = -2cm/day: (a) Haritara, (b) Gopalpur, (c) Bharapura, (d) Patchara, (e) Upper Khajuri Dam, (f) Semara, (g) Chhitampur, (h) Ballhara Mor, and (i) Lusa-Atari Village; T0 represent initial solute concentration and T5 represent concentration after 500 days.

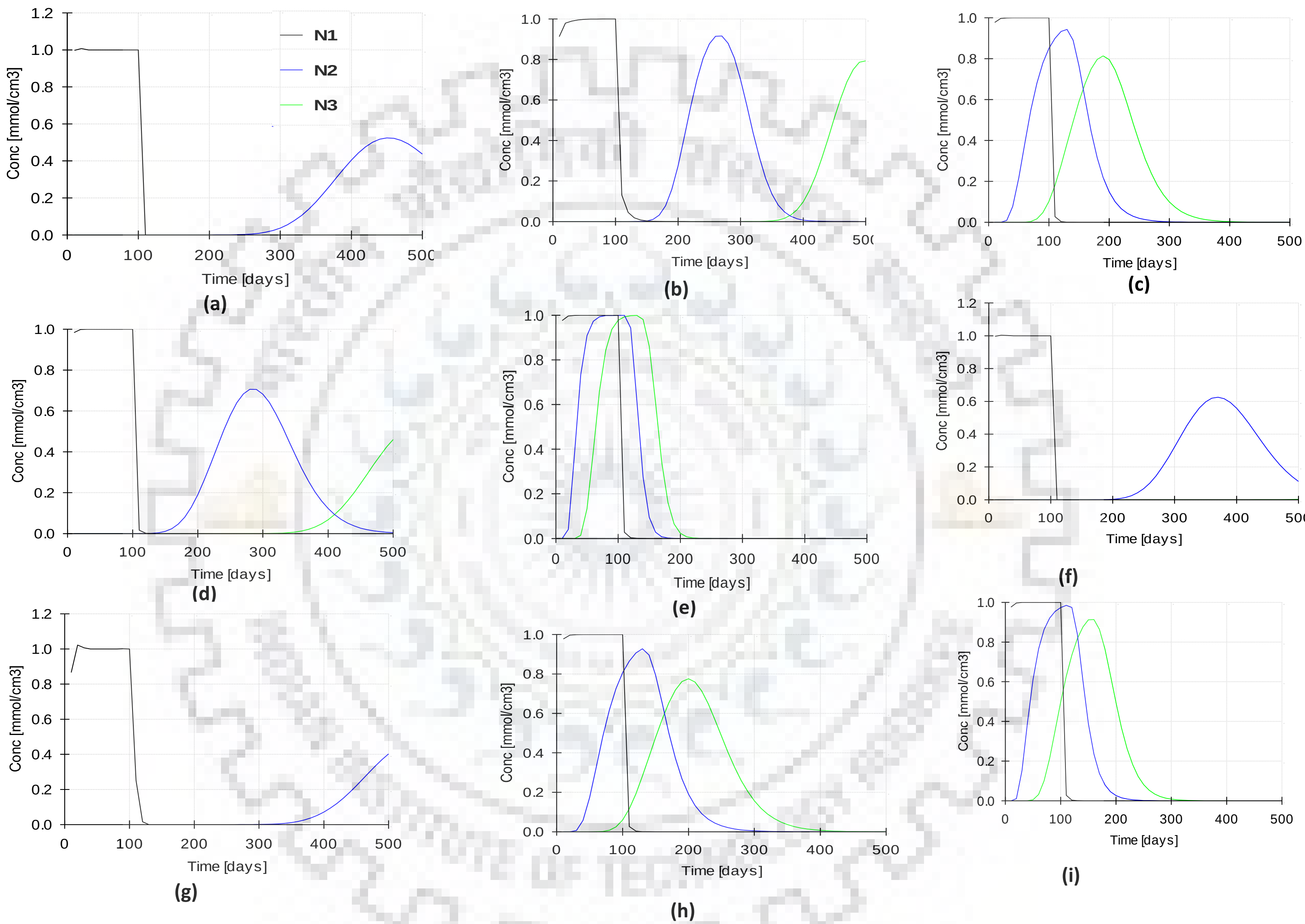


Figure 14: Progression in solute concentration constant flux of q = -2cm/day (a) Haritara, (b) Gopalpur, (c) Bharapura, (d) Patchara, (e) Upper Khajuri Dam, (f) Semara, (g) Chhitampur, (h) Ballhara Mor, and (i) Lusa-Atari Village; N1, N2, and N3 represent solute concentration at top, middle and bottom of respective soil profiles.

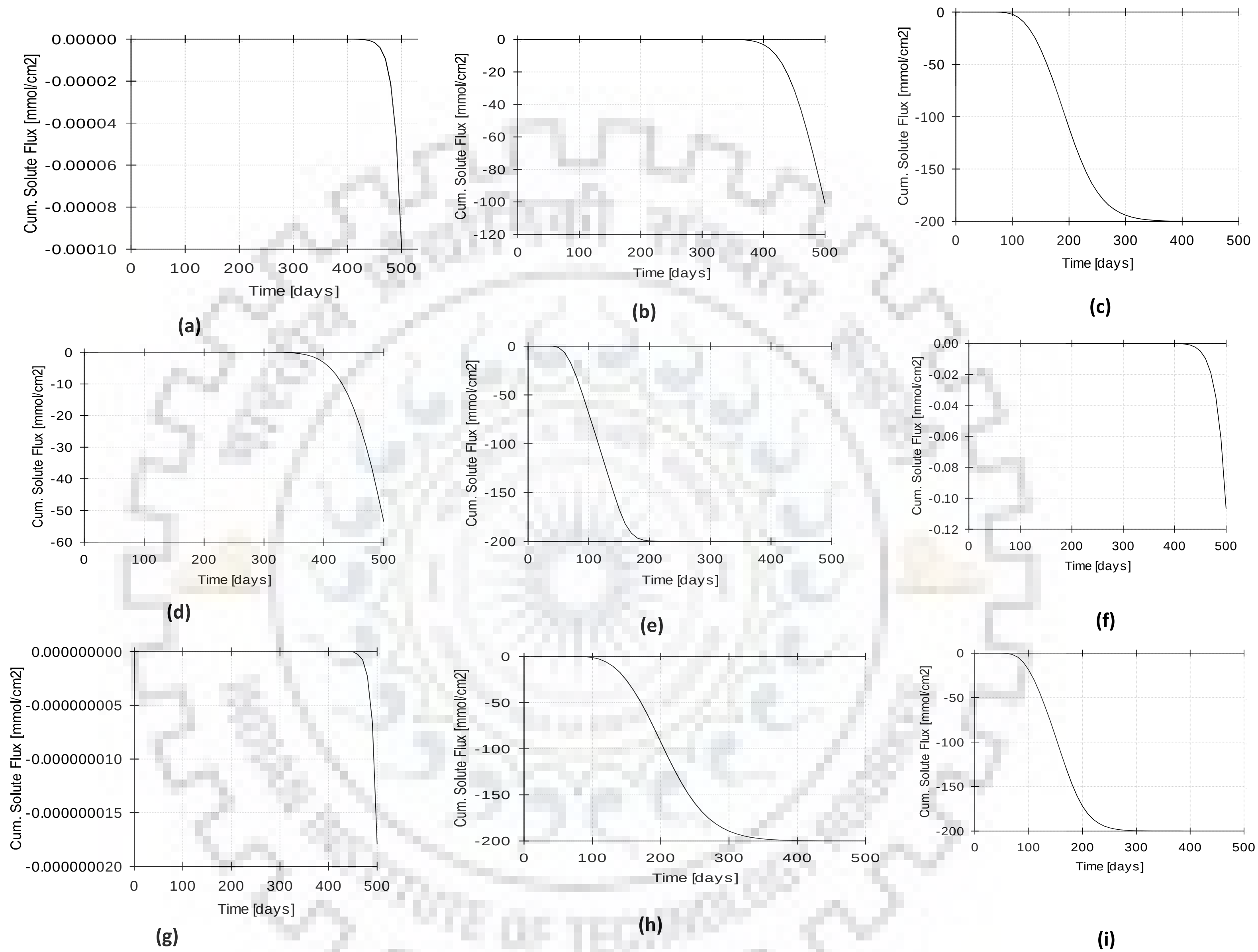


Figure 15: Cumulative out flux from the bottom of the soil strata for (a) Haritara, (b) Gopalpur, (c) Bharapura, (d) Patchara, (e) Upper Khajuri Dam, (f) Semara, (g) Chhitampur, (h) Ballhara Mor, and (i) Lusa-Atari Village locations.

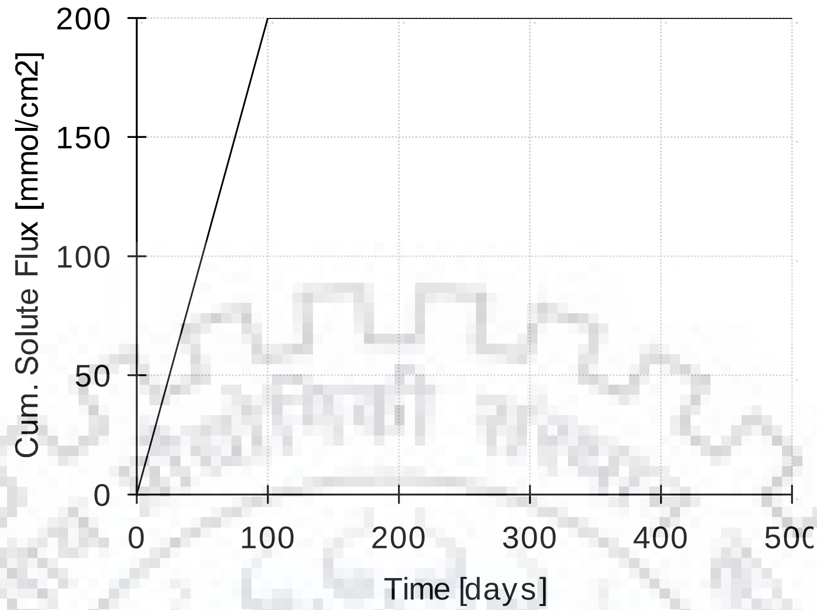


Figure 16: Cumulative solute inflow flux applied at all locations.

5.5.4 Vulnerability Index

An area is said to be more vulnerable to contaminant pollution if time taken by the contaminant plume to reach the groundwater table is less for that area compare to others. The reciprocal of time taken by the surface solute plume to reach the groundwater resources is used for quantifying the vulnerability index. Vulnerability to groundwater pollution for the study area is shown in figure 17.

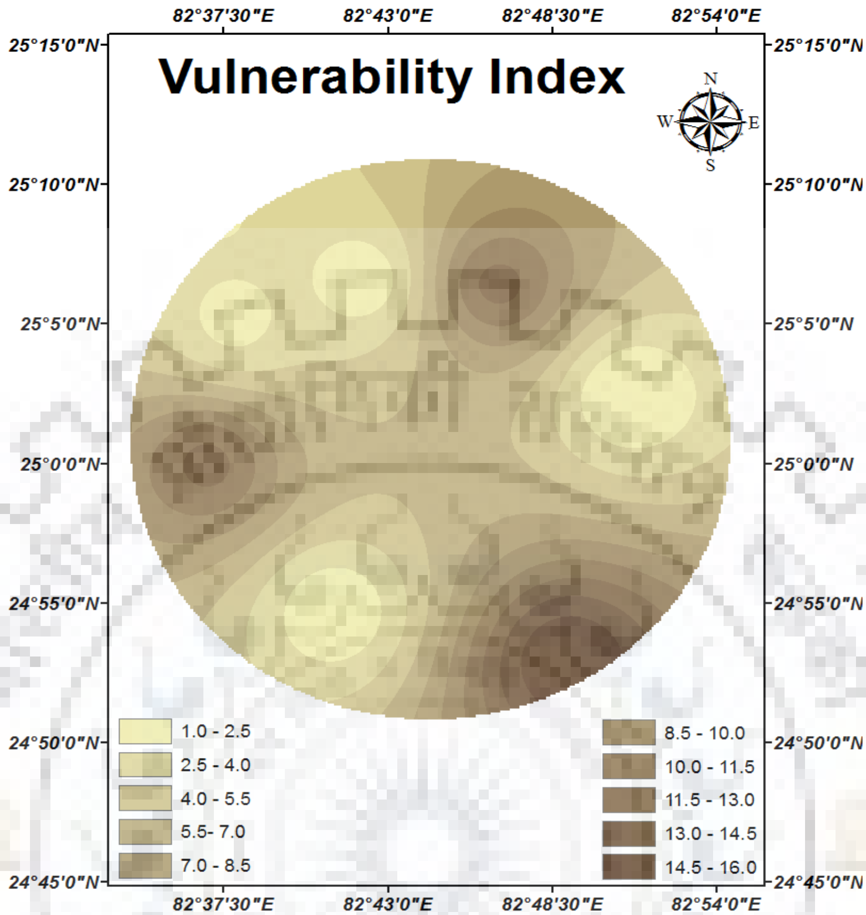


Figure 17: Map showing the comparative vulnerability at different regions in the study area using the constant flux boundary conditions.

The time required for surface solute to reach the underground resources is found to be highest for Chhitampur; therefore, this location is assigned a lowest vulnerability index value of 1. Comparative values of vulnerability index for remaining locations is obtained by normalizing their respective transit time. For the study area, groundwater near the Lusa-Atari is more vulnerable to pollution as the time taken by contaminant plume to reach the water table is minimum for this location.

Chapter 6. Conclusion

In this study, stress on the existing groundwater resources for meeting the groundwater demand is assessed along with its quality and vulnerability assessment over the Indo-Gangetic plain around Mirzapur, India. For quantification of groundwater resources, the water table fluctuation data is used along with findings of geophysical investigations coupled with the aquifer tests. Groundwater samples from ten sites are collected for hydro-geochemical analysis. Lithologs prepared from VES findings are used to compute the vulnerability of the area toward groundwater pollution.

The results from VES shows that the lithology of the area is heterogeneous due to which spatial distribution of groundwater resources is high. The northern, central and eastern parts of study area having sandstone occurred directly beneath the topsoil indicating the absence of the potential sedimentary horizon. The clay horizon beneath the topsoil in south-eastern part of the study area is expected to be water-bearing often at a depth varying between 4 to 8 m bgl. Average stage of groundwater development is 26.73 %. AAS analysis indicated that most of the sites are polluted with Cd and Pb. Concentration of these elements is maximum at Chikesr and Kharanja with values 1.44 mg/L and 0.48 mg/L, respectively. Due to geology of the area and topographical location, As and Fe is also observed more than permissible limits of BIS at all sites with a maximum concentration of 0.29 mg/L and 13.15 mg/L, respectively, both at Agvar. One of the sampling location, Agvar is found to be extremely polluted, possibly by sewage mismanagement. PCA reveals little correlation between the sampling sites that validates the heterogeneity of the area. The study fortifies that study area is not very well connected hydro-geologically and also contaminated with various anthropogenic elements. Groundwater contamination modelling reveals that the Lusa-Atari location is the most vulnerable and Chhitampur is the least vulnerable to groundwater contamination.

This study will help in developing safe groundwater extraction strategies, aquifer management plans and techniques like managed aquifer recharges and to establish a technological approach for implementation of remediation plans.

The outcomes of this study may help to:

- Development of safe groundwater strategies.
- Implement aquifer management techniques like managed aquifer recharge.

- Establish a technical approach for implementation of remediation plans.

The results of this study may further be improved by considering post-monsoon in-situ observation of various groundwater quality parameters (Rai 2011). Use of 3-D modelling software for interpretation of VES data can gives the more accurate representation of subsurface lithology. Modelling results of solute transport through vadose zone of the study area can be improved by considering actual atmospheric boundary conditions.

Appendix A

Table 11: Limits comparison by IS 10500-2012 and WHO 2011 for drinking water.

Constituent	**Drinking water standards recommended by BIS and WHO (in mg/l)**			**Effect on the body if present excess than the specified limit**
	BIS (2012)		***WHO (2011)***	
	Acceptable Limit	*Permissible limit in the absence of alternate source*	*Guideline Values*	
Arsenic	0.01	0.05	0.01	It is poisonous and Carcinogenic.
Total Chromium	.05	No relaxation	0.05	Toxic in nature and causes Ulcers and Dermatitis.
Manganese	0.1	0.3	---	Taste and aesthetic values of water are adversely affected.
Silica	---	---	---	Harmful in boiler scale and steam of high-pressure boilers to form deposits on turbine blades. Silicon compounds cause silicosis leading to tuberculosis, bronchitis, and chronic obstructive pulmonary disease.
Total dissolved Solids	500	2000	1000	May causes Gastrointestinal irritation.
Strontium .	---	---	---	Radioactive strontium is more harmful, it may cause anemia and oxygen shortages, affects the growth of bone and at extremely high concentrations it is even known to cause cancer.
Fluoride	1.0	1.5	1.5	Requires in the body to prevent dental caries but if present greater than 1.5 mg/L causes Fluorosis.

Iron	0.3	No Relaxation	---	Aesthetic taste, essential for human health [Hemoglobin Synthesis] Excess stored in Spleen, Liver, Bone marrow. Total concentration of Manganese (as Mn) and Iron (as Fe) shall not exceed 0.3 mg/l
Selenium	0.01	No relaxation	0.01	Traces of selenium status in humans have been associated with multifocal myocarditis called Keshan disease, juvenile, and chondrodystrophy called Kaschin-Beck disease. Symptoms in people with high urinary selenium levels include Gastrointestinal disturbances, discoloration of the skin and decay of teeth.
Radon	---	---	---	It is a primary cause of Lung cancer.
Uranium	---	---	0.015	Carcinogenic, liver damage. Long term chronic intakes of uranium isotopes in food, water, or air can lead to internal Irradiation.
Nitrates	45	No relaxation	50	Generally harmless but cause methaemoglobinamia in children popularly called as “Blue baby syndrome”.

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