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Assessment and Prediction of Groundwater Quality using Hydrochemical, Flow and Transport Modeling in the Kolhar Industrial Area, Bidar District, Karnataka, India

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Abstract
Groundwater samples for pre and post-monsoon seasons were collected from the watershed covering Kolhar Industrial Area (KIA), Bidar District, Karnataka for assessment of groundwater quality and its possible contaminant migration from the industrial area. Major ions and heavy metal chemistry was analyses for collected samples. Groundwater samples from industrial area shows elevated Total Dissolved Solids (TDS) concentration than groundwater samples from the other part of the watershed. Based on groundwater quality analyses results, four high TDS concentrations zones of 2000 to 8000 mg/l were identified in an industrial area wells. Groundwater flow and transport modeling was carried out to decipher the possible migration pathways and direction of contaminant migration. Groundwater flow and transport modeling suggests that the high TDS concentration were follows general topographic level trend of contaminant migration. The groundwater transport model was calibrated for fifty years. The modeling study also suggests that the different high TDS concentration plumes were joins together after fifty years.
Keywords: Kolhar Industrial Area (KIA), Total Dissolved Solids (TDS), Flow and Contaminant transport modelling.

1. INTRODUCTION

Long term and sustained industrial activity in any given area can often lead to soil and groundwater contamination (Ramesh et al. 2012; Machender et al. 2014). Improper waste disposal practices might contaminate the soils and gradually the contaminants enter into the groundwater regime in the area, impairing groundwater quality for many applications including drinking. The study of underground contamination will be of immense help to researchers and environmental regulators working in the area to understand and evolve by initiating remedial measures. The detrimental alteration of the naturally occurring physical, chemical, thermal or biological quality of groundwater is called groundwater contamination. Groundwater pollution works differently from surface water pollution. Unlike surface water, groundwater does not typically flow toward a single outlet at the topographic bottom of the watershed, whereas the cumulative effect of watershed pollution and improvements in watershed management can be directly measured. Groundwater discharge depends on topography and hydrogeology (confined or unconfined aquifers, fractured rock or sediments and aquifer geometry).

The composition of groundwater in a region can be changed through the operation of the processes such as evaporation and transpiration, wet and dry depositions of atmospheric salts, selective uptake by vegetation, oxidation/reduction reactions, cation exchange, dissociation of minerals (soil-rock-water interactions), precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure, pollution due to improper discharge of effluents from industrial areas, and biological process (Appelo & Postma 1993). Quality of surface water, weathered mantle, underlying soil characteristics, and atmosphere are responsible for contribution of dissolved solids to water and in deter-mining the composition and quality of the groundwater in a region. The type and extent of chemical contamination of the groundwater is largely dependent on the geochemistry of the soil through which the water flows prior to reaching the aquifers (Zuane 1990). Since it is impossible to control the dissolution of undesirable constituents in the waters after they enter the ground and joins the aquifer regime (Johnson 1979; Sastri 1994; Kaushik and Kaushik 2006).

Groundwater quality data gives important clues to the geologic history of rocks of the area and indications of groundwater pollution, recharge, movement, storage and the residence time of water in contact with rock material (Walton 1970). It was observed that the criteria used in the classification of waters for a particular purpose considering the individual concentration don't find its suitability for other purposes, and better results can be obtained only by considering the combined chemistry of all the ions rather than individual or paired ionic characters (Sadashivaiah et al. 2008; Lalitha et al. 2012; Inayathulla & Paul 2013). Hence, in order to assess the fate and the impact of the chemical discharge into the soil, it is important to understand the hydro-geochemistry of the chemical, soil and groundwater interactions (Miller 1985) and to determine the origin of chemical composition of groundwater (Zaporozec 1972).

A number of studies on groundwater quality with respect to drinking and irrigation purposes have been carried out in the different parts of India (Durvey et al. 1997; Niranjan Babu et al. 1997; Kaplay 1998; Pawar et al. 1998; Ballukraya et al. 1999; Subba Rao et al. 1999; Majumdar & Gupta 2000; Dasgupta & Purohit 2001; Khurshid et al. 2002; Sujatha & Reddy 2003; Sreedevi 2004; Pulle et al. 2005; Hussain et al. 2005; Sunitha et al. 2005; Subba Rao 2006; Machender et al. 2014). The industrial areas have frequently groundwater and surface water contamination problems due to lack of improper effluent treatment facility. In most of the industrial areas within India have these problems. It is, therefore become necessary to study the groundwater/surface water chemistry within and around the industrial areas to ascertain the level of groundwater pollution due to operation of industries and suggest suitable remedial measures to protect the groundwater from pollution.

In the present article, Kolhar Industrial Area (KIA), situated near Bidar town, Karnataka, India was chosen for ascertaining the groundwater quality in and around the industrial belt. Groundwater samples for pre-monsoon and post-monsoon were collected and analyses for major ion and heavy metals chemistry. Groundwater quality results suggest that few well in industrial area have elevated TDS concentration and high level of few heavy metal pollution and acts as source for contaminating the groundwater regime in the industrial watershed. Groundwater flow and transport modeling was carried out to ascertain the possible contamination zones and its migration in the groundwater regime. The results of these indicators are discussed in the article.

2. STUDY AREA

The study area is situated about 10km from the Bidar town, Karnataka and lies in Survey of India Toposheet No. 56 G/5 and covers Latitude 17^0 50' to 17^0 55' North and Longitude 77^0 20' to 77^0 30' East. The drainage pattern is sub-dentric and flows in the direction East to West and Northeast to Southwest and joins to a major stream Malar Halla. Kolhar Industrial Area lies in an elevated plateau. The elevation of the area ranges from 632 to 662 m (amsl). The general slope of the area is towards South-West direction. The key map of the study showing drainage pattern and Kolhar Industrial Area was shown in Fig.1.

3. GEOLOGY OF THE AREA

The entire study area consists of Deccan Basalts covered with lateritic capping with various thicknesses. Deccan Basalts are grouped under hard rocks, as they have limited inter-granular porosity. The thickness of Laterite capping in the area varies from 20-30 m. These laterites are the products of intensive and long lasting tropical rock weathering which is intensified by high rainfall and elevated temperatures. Laterite forms potential aquifers along valleys. The occurrence and movement of groundwater in the laterites are mainly controlled by the topography. The porosity and permeability of Basalts rock varies within an individual flow and also from different lava flows to lava flows. The weathered zone, jointed and fractured in massive and vesicular Basalts forms the water bearing horizons. Abundance of vesicles with interconnecting nature coupled with joints and horizontal partings in the vesicular Basalt make it a good aquifer. The geological map of the study area covering KIA was shown in Fig.2 (GSI 2004).

4. HYDROLOGY OF THE AREA

Groundwater occurs under water table conditions in shallow aquifers up to a depth of 20m (bgl) and semi-confined to confined aquifers in deeper aquifer. The inter-trappean red bole acts as an aquiclude to form as a confined aquifer. The weathered zone occurs to a depth of 25m bgl and semi-confined conditions occur below 25-40m. The jointed and fractured Basalts formations carry the groundwater to greater depths. Laterite is highly porous rock formation, which can form potential aquifers along topographic lows. However, due to this porous nature, groundwater is drained from elevated places and slopes at shortest duration after monsoon due to which scarcity is experienced in the elevated places and slopes. The depth of the open wells in the area varies from 20-25m. The depth of the bore wells varies from 90-120m. The yield of the open wells ranges from 50-75 cum/day, whereas bore wells yield ranges from 5000-6000 lt/hr (Sankaran et al. 2013).

The groundwater levels were monitored in the watershed covering KIA by establishing 57 observation wells including dug wells and bore wells during pre-monsoon and 66 observation wells during post-monsoon seasons. The location of these observation wells are shown in Fig.3a and location of observation well in an industrial area are shown in Fig.3b. All these wells have been connected mean sea level (Fig. 4). Depth to the groundwater level is varying from 6.19 m - 28.29 m bgl (614.21 - 654.6 amsl) during pre-monsoon 4.27 m to 51.29 m bgl (610.46 - 656.05 amsl) and post-monsoon respectively. The depth to groundwater level (amsl) for these periods are shown in Fig. 4. The groundwater level contours of pre-monsoon indicates that groundwater in general flows from central part of the Industrial Area towards West and also from Northeast to Southwest in the Southern part of industrial area. The highest groundwater elevation reported was 656 m (amsl) from Central part of the industrial area whereas, lowest groundwater elevation was found as 614 m (amsl) near Zamistapur village in the Southern part. Groundwater flows from central part of industrial area passes through Nizampur village and later flows towards the Baghchaudi village. The groundwater level contours of post-monsoon period indicate that

similar flow directions as indicated during pre-monsoon season. In general the groundwater flow follows the topographic elevations. Transmissivity values observed were ranges from 1.99 m^2/day to 111 m^2/day and hydraulic conductivity values ranges from 0. 28 m/day to 13.8 m/day in the watershed.

5. MATERIAL AND METHODS

Fifty seven and sixty six groundwater samples were collected each during pre-monsoon and post-monsoon seasons (Fig.3a&b) and analyzed for various Physico-chemical parameters like pH, EC, TDS & TH, major ions and trace element chemistry. The methods of collection of samples play an important role for maintaining the high degree of accuracy of analytical data and its application to hydrochemical studies. The water samples were analyzed as per the standard **(**APHA 2005) procedures.

The pH measured using the digital pH meter of Elico make, and EC was estimated by the EC analyzer CM 183 model of ELICO make, temperature by simple thermometer, the classical methods of analysis were applied for the estimation of calcium, magnesium, carbonate, bi-carbonate, and chloride, Sodium and potassium were analyzed by flame photometry using CL-345 flame photometer of ELICO make.

Sulfate was estimated by the turbidity method using the Digital Nephelo-Turbidity meter 132 model of Systronics make. Nitrate was analyzed applying the UV-Vis screen method using UV-visible spectrophotometer UV-1201 model of Shimadzu make. Fluoride was analyzed by the ion selective electrode method using Orion 290A+ model of Thermo-electron Corporation. The TDS were estimated by the summation of cations and anions (epm) method after (Hem 1991). Perkin Elmer–Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), Inductively Coupled Plasma Mass Spectrometer (ICP-MS) instruments used for major and trace elements in water samples.

The results obtained were tested for accuracy by calculating the normalized inorganic charge balance (Mandel & Shiftan 1981; Huh et al. 1998) and analytical precision was within ±5% for all the samples. Standard titration method of (BIS 1991) was used for carbonates and bicarbonates. The statistical summary for the major ions and trace elements of the collected sample for pre and post-monsoon seasons was given in Table 1.

6. GROUNDWATER QUALITY

6.1Hydrogen ion concentration (pH)

The pH is the most frequently used for water quality test. The pH value is based on the product of the H^+ and the OH^- concentration. The desirable range of pH in drinking water is 6.5 to 8.5 (BIS 1991; CPHEEO 1991, 2005) standards of the pH value suitable for drinking water. In the KIA watershed, the groundwater samples of pre-monsoon period have pH values ranges from 4.22 to 8.57 and those in post-monsoon the pH value ranges from 2.0 to 8.4. The average pH value in the KIA watershed is 8.01 and 7.24 from pre and post-monsoons respectively (Table 1). The pH is generally an alkaline/basic in nature in the watershed except few samples from industrial area shows acidic in nature.

6.2 Total Dissolved Solids (TDS)

TDS of groundwater contain all ionized materials. It is directly proportional to specific conductivity. Different limits of TDS content are fixed for different purposes by various organizations and individuals (Davis & Dewiest 1967). The groundwater of pre-monsoon has low to high TDS values ranging from 45 mg/l to 10560 mg/l in pre-monsoon period and 28 mg/l to 8620 mg/l in post-monsoon. The average TDS of pre-monsoon samples is 681.40 mg/l, while 766.83 mg/l for post-monsoon samples (Table 1). The spatial distribution of TDS of groundwater samples display in concentration maps (Fig. 5a & 5b) for pre and post-monsoon periods. It has been observed that the TDS concentration is high in industrial area compared to other area of the watershed. Four prominent high TDS zone was observed in KIA (Fig. 5a & 5b).

6.3 Major Anions (Ca, K, Mg & Na)

6.3.1 Calcium (Ca^{2+})

Calcium (Ca^{2+}) shows considerable variation in groundwater samples from the pre to post-monsoon periods. The permissible limit of Calcium is 200 mg/l (BIS 1991). Calcium in groundwater ranges from 8 mg/l to 960 mg/l during pre-monsoon and 15 mg/l to 1536 mg/l during post-monsoon period (Table 1). The average amount of calcium present in water samples of the pre-monsoon season is 84.35 mg/l and in post-monsoon season is 122.79 mg/l. It seems that the average values of Calcium are within the permissible limits as per standard value of 200 mg/l (WHO 1984; BIS 19991).

6.3.2 Potassium (K^+)

Potassium (K^+) is found in low concentration in natural waters since rocks which contain potassium are relatively resistant to weathering. However, potassium salts are widely used in industry and in fertilizers for agriculture and enter freshwaters with industrial discharges and runoff from agricultural land. Potassium concentrations found in natural waters are usually < 10 mg/l. Potassium concentration in groundwater has been

found to be varies from 0.1 mg/l to 145 mg/l with average of 6.14 mg/l in the pre monsoon period. During post-monsoon period it varies from 0.5-154.6 mg/l with average concentration of 5.97 mg/l (Table 1).

6.3.3 Magnesium (Mg^{2+})

Magnesium content in the groundwater samples collected during pre-monsoon ranges from 1 mg/l to 292 mg/l and during post-monsoon it is ranges from 1 mg/l to 120 mg/l. The average concentration of Magnesium was 22.78 mg/l and 10.70 mg/l during pre and post-monsoon period (Table 1). However there are few deviations from normal range of Mg^{2+} (20-50 mg/l) were observed in KIA area. The source of magnesium in the groundwater is due to the ionic exchange between water and rocks (or soils) interaction and due to discharge of effluents from the industrial area. Mg^{2+} less than permissible limits is a good nutrient for plants and animals but it exceeds from normal value may create human hazards like fever, chills, nausea, hypotension, vomiting & muscle pain and bradycardia.

6.3.4 Sodium (Na^{2+})

Sodium (Na^{2+}) was found in all natural waters, since the salts are highly soluble in water and it is one of the most abundant elements on earth's crust. WHO (1984) guide limit for Sodium in drinking water is 200 mg/l. Many surface waters, including those receiving wastewaters, have levels well below 50 mg/l. However, groundwater concentrations frequently exceed 50 mg/l. Sodium concentration varies from 2-2174 mg/l with average values 104.40 mg/l for pre-monsoon period, while it is varies from 3-2017mg/l with an average of 161.32 mg/l during post-monsoon period (Table 1). Sodium concentration exceeds the permissible limit < 200 mg/l (WHO 1984) in few samples collected from industrial area than in groundwater sample in the watershed. Sodium is one of the most important elements for classification of water for irrigation uses.

6.4 Major Cations (Cl, SO_4, NO_3-N & HCO_3)

6.4.1 Chloride (Cl^-)

Most chlorine occurs as chloride (Cl^-) in water. Higher concentrations can occur near sewage and other waste outlets, irrigation drains, saltwater intrusions, in arid areas and in wet coastal areas. Chloride is frequently associated with sewage discharge water; it is often used as indicator in the assessments of possible fiscal contamination or as a measure of the extent of the dispersion of sewage discharge in surface water bodies. In the study area Cl^- concentration varies from 5-5570 mg/l in the pre-monsoon period with average value of 284.39 mg/l, while during post-monsoon period it is varies from 3-3890 mg/l with average value of 282.47 mg/l. High chloride concentrations during post-monsoon period were found in 17 samples collected from industrial area.

6.4.2 Sulphate (SO_4)

Sulphate is naturally present in surface waters as SO_4^{2-}. It arises from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as pyrite, from sedimentary rocks. It is easily oxidized and is readily soluble in water. Industrial discharges and atmospheric precipitation can also add significant amount of sulphate to surface water. Sulphate can be used as an oxygen source by bacteria which convert it to hydrogen sulphide (H_2S, HS-) under anaerobic conditions. Sulphate concentrations in natural waters are usually between 2 and 80 mg/l, although levels may exceed 1000 mg/l near industrial discharges or in arid regions where sulphate minerals are present. High levels of sulphate (>400 mg/l) may make water unpleasant to drink. In the study area SO_4^{2-} concentration varies from 0.20-300 mg/l with average values of 27.61 mg/l during pre-monsoon period. During post-monsoon period it is varies from 0.4-1743 mg/l with average value of 81.11 mg/l. High concentration of sulphate was found only in 4 samples during this period in the industrial area sample.

6.4.3 Nitrate as N (NO_3-N)

Natural sources of nitrate to surface water include igneous rocks, land drainage and plant and animal debris. Natural levels which seldom exceed 0.1 mg/l NO_3-N may be enhanced by municipal and industrial wastewaters, including leachates from waste disposal sites and sanitary landfills. In rural and suburban areas the use of inorganic nitrate fertilizers can be a significant source. When influenced by human activities, surface waters normally contain nitrate concentrations up to 5 mg/l NO_3-N but often less than 1 mg/l NO_3-N. Levels in excess of 5 mg/l NO_3-N usually indicate pollution by human and animal waste or fertilizer runoff. In cases of extreme pollution, concentrations may reach 200 mg/l NO_3-N. WHO (1984) recommended maximum limit for drinking water as 10 mg/l NO_3-N, waters with higher concentrations represent a significant health risk. In lakes, levels of nitrate in excess of 0.2 mg/l NO_3-N tend to stimulate algal growth and indicate possible eutrophication conditions. The nitrate as nitrate concentration of groundwater sample during pre-monsoon was found to be ranging from 0.01-27.5 mg/l with average value of 3.93 mg/l. Similarly, during post-monsoon sample it is ranges from 0.3-398 mg/l with average concentration of 23.13 mg/l. High concentrations of Nitrate were found more than permissible limit in 5 samples in the industrial area.

6.4.4 Bicarbonates (HCO_3)

The presence of bicarbonates (HCO_3^-) influences the hardness and alkalinity of water. The inorganic carbon component (CO_2) arises from the atmosphere and biological respiration. The weathering of rocks contributes

carbonate and bicarbonate salts. The relative amounts of carbonates, bicarbonates and carbonic acid in pure water are related to the pH. Bicarbonate is the dominant anion in most surface waters. Carbonate is uncommon in natural surface waters because they rarely exceed pH 9, whereas groundwater can be more alkaline and may have concentrations of carbonate up to 10 mg/l. The concentration of bicarbonates in pre-monsoon period varies from 4-276 mg/l with average value of 75.07 mg/l. Similarly, bicarbonates in groundwater have been found varying from 18-531 mg/l with average values of 116.32 mg/l during post-monsoon period.

6.5 Heavy metals

Besides major chemistry, heavy metal analyses like B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb were analyzed for pre-monsoon samples and Al, Ag. As, Ba, Be, Cd, Co, Cr, Cu, Fe and Mn were analyses for post-monsoon period respectively in the watershed covering 5 km radius of Kolhar Industrial Area. The statistical results of some of the heavy metals like Be, Cd, Cr, Cu, Fe, Ni, Pb and zinc were given in Table 1. It is observed that few heavy metals were found to be more than permissible limits in the industrial area water samples and cause further contamination to the groundwater regime.

7. GROUNDWATER FLOW AND TRANSPORT MODELLING

7.1 IMPACT OF INDUSTRIAL EFFLUENT ON GROUNDWATER QUALITY

In order to understand the movement of pollutant and seepages from the industrial area in to groundwater regime in the watershed an attempt has been made to construct a mathematical model using software Visual MODFLOW for Windows version 2.61 (Guiger & Franz 1996). Essentially, mathematical modeling of a system implies obtaining solutions to one or more partial differential equations describing groundwater regime. In the present case, it was assumed that the groundwater system is a two-dimensional one wherein the Dupuit-Forchheimer condition is valid. The partial differential equation describing two-dimensional groundwater flows may be written in a homogeneous aquifer as

$$\frac{\partial}{\partial y}\left(T_x \frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial y}\left(T_y \frac{\partial h}{\partial y}\right)=S\frac{\partial h}{\partial t}\pm W \quad (1)$$

Where T_x, T_y = the transmissivity values along x and y directions respectively,
h = the hydraulic head, S = storativity,
W = the groundwater volume flux per unit area (+ve for outflow and -ve for inflow),
x and y = the Cartesian co-ordinates.

Usually, it is difficult to find exact solution of Eq. (1) and one has to resort to numerical techniques for obtaining their approximate solutions. In the present case, finite difference method was used to solve the above equation. The partial differential equation is then replaced by a set of simultaneous algebraic equations valid at different node points. Thereafter, using standard methods of matrix inversion these equations are solved for the water level.

7.2 Physical framework for groundwater modeling

The groundwater flow model in the watershed covering Kolhar Industrial Area (KIA), Bidar, Karnataka was conceptualized as a two layered weathered and fractured aquifer system in basaltic rocks (Fig. 6). The size of each grid is considered as 200m×200m. The total thickness of the two layer aquifer was considered 40m with first layer is 20m and second layer is 20m thick. The groundwater flow model has 100 rows and 80 columns of variable cell sizes of 110m x 110m and 55m x 55m. The vertical cross section of layer for row 22 and column 33 is shown (Fig.7a&b). The permeability of the saturated basaltic rocks was estimated from pumping tests was assigned in the model as 1.5 m/day in the northern part of the area whereas due to greater weathering in the south and presence of lake the permeability has been slightly higher as 2.0 m/day and along the stream channels slightly higher permeability of 3 m/day was assigned in the eastern part. The variation of permeability in the study area is shown in Fig.8. The elevated permeability values along the stream channel were based on the lineament/fracture zone inferred from groundwater prospects maps prepared by National Remote Sensing Service Centre. The permeability distribution has been assigned following the preferential groundwater flow paths having higher permeability. The permeability has been assumed to be one tenth of the horizontal permeability in the vertical direction.

Constant head boundary condition has been simulated at the outlet on the west side with a groundwater head varying from 548-550 m (amsl) from southwest to northeast. Some lateral inflow enters the watershed along southern boundary close to the industrial area and same was simulated with a constant head of 598 m (amsl) in the flow model. The four major stream courses are leaving the industrial area and were simulated with appropriate river boundary. Intervening hydraulic conductance between stream and aquifer has been varying from 10 to 25 m/day. The lake in the campus was also simulated with river head boundary condition with water column of 5 m and the hydraulic conductance assumed was 100 m/day.

The natural groundwater recharge from rainfall infiltration was assumed as 90 mm/yr in the flat terrain of south eastern parts and a lower recharge of 65 mm/yr in the steep slope areas in the western part has been assumed and same was assigned in the groundwater flow model (Fig.9). There are few pumping wells inside the industrial area serving the horticulture needs and few outside the industrial area particularly in the eastern part. The pumping rates are varying from 100-200 m^3/day. The pumping wells inside the industrial area are heavy duty wells and are simulated with a pumping rate 200 m^3/day and out side wells were assumed to be pumping rate 100 m^3/day. The computed groundwater level contours in the groundwater flow model has been showing groundwater flow direction towards the Marar Halla stream and following closely the trend of observed water level contours during pre-monsoon period. The computed vs. observed hydraulic heads at 35 observation wells in the watershed have been found matching closely. The groundwater velocity field has been computed from the flow model by assuming an effective porosity of 0.1. The computed groundwater velocity field represents maximum groundwater velocity > 40 m/year.

7.3 Mass Transport Modeling

An equation describing the transport and dispersion of a dissolved chemical in flowing groundwater may be derived from the principle of conservation of mass by considering all fluxes into and out of a Representative Elementary Volume (REV). A generalized form of the solute transport equation, in which terms are incorporated to represent chemical reactions and solute concentration both in the pore fluid and on the solid surface, as:

$$\frac{\partial(\varepsilon C)}{\partial t} = \frac{\partial}{\partial x_i}\left(\varepsilon D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(\varepsilon C V_i) - C'W^* + CHEM \quad \text{-------} \quad (2)$$

Where CHEM equals one or more of the following:

$-\rho_b \frac{\partial \bar{C}}{\partial t}$ for linear equilibrium controlled sorption or ion-exchange reactions

$\sum_{k=1}^{s} R_k$ for chemical rate-controlled reactions, and (or)

$-\lambda\left(\varepsilon C + \rho_b \bar{C}\right)$ For decay

and where D_{ij} is coefficient of hydrodynamic dispersion (a second order tensor), L^2T^{-1}, C' is the concentration of the solute in the source or sink fluid, C is the concentration of the species adsorbed on the solid (mass of solute/mass of solid), ρ_b is the bulk density of the sediment ML^{-3}, R_k is the rate of production of the solute in reaction k, $ML^{-3}T^{-1}$, and λ is the decay constant T^{-1}.

The first term on the right hand side of equation (2) represents the change in concentration due to hydrodynamic dispersion. This expression is analogous to Fick's law describing diffusive flux. This Fickian model assumes that the driving force is the concentration gradient and that the dispersive flux occurs in a direction from higher to lower concentrations. The coefficient of hydrodynamic dispersion is defined as the sum of mechanical dispersion and molecular diffusion (Bear 1979). The mechanical dispersion is a function of both the intrinsic properties of the porous medium (such as heterogeneities in hydraulic conductivity and porosity) and of the fluid flow. Molecular diffusion in a porous medium will differ from that in free water because of the effects of tortuous paths of fluid connectivity in porous media. These relations are commonly expressed as

$$D_{ij} = \alpha_{ijmn}\frac{V_m V_n}{|V|} + D_m \qquad i, j, m, n=1,2,3 \quad (3)$$

Where α_{ijmn} is the dispersivity of the porous medium (a fourth order tensor), L; V_m and V_n are the components of the flow velocity of the fluid in the m and n directions respectively, LT^{-1}, D_m is the effective coefficient of molecular diffusion, L^2T^{-1}; and |V| = sq root $V_x^2 + V_y^2 + V_z^2$ (Bear 1979; Domenico & Schwartz 1990).

The dispersivity of an isotropic porous medium can be defined by two constants. These are the longitudinal dispersivity of the medium α_L and the transverse dispersivity of the medium α_T. These are related to the longitudinal and transverse dispersion coefficients by $D_L = \alpha_L|V|$ and $D_T = \alpha_T|V|$. Most of the reported transport models of groundwater problems relate to the conventional formulation, even for cases in which the hydraulic conductivity is assumed to be anisotropic.

Although conventional theory holds that α_L is generally an intrinsic property of the aquifer, it is found in practice to be dependent and proportional to the scale of the measurement. Most reported values of α_L fall in a range from 0.01 to 1.0 times the scale of the measurement, although the ratio of α_L to scale of measurement tends

to decrease at larger scales (Anderson & Woessner 1992, Gelhar et al. 1992). Field dispersion (macro dispersion) results from large scale spatial variations in hydraulic properties. Representing a transient flow field by a mean steady state flow field, as is commonly done, inherently ignores some of the variability in velocity and must be compensated for by using increased values of dispersivity (primarily transverse dispersivity). Overall, the more accurately a model can simulate the true velocity distribution in space and time, the less of a problem will be the uncertainty concerning representation of dispersion processes.

The mathematical solute transport model requires at least two partial differential equations. One is the equation of flow, from which groundwater flow velocities are obtained, and the second is the solute transport equation, whose solution gives chemical concentration in groundwater. If the properties of water are affected significantly by changes in solute concentration, as in a seawater intrusion problem, then the flow and transport equations should be solved simultaneously. If the properties of the water remain constant, then the flow and transport equations can be decomposed and solved sequentially.

The numerical approaches for solving mass transport equations are based on computer based particle tracking methods. They are approximate forms of the advection-dispersion equation (3) as a system of algebraic equations or alternately simulating transport through the spread of a large number of moving reference particles. Second step is to provide boundary condition at a large number of node points and assign values of concentration or loading rates defining various boundary conditions for all nodes located along boundary of the domain. Continuity consideration of numerical solutions of solute transport requires a smooth and accurate representation of velocity field, which was obtained by simulation of groundwater flow model. Velocity values are computed from calculated hydraulic heads and porosity values by applying Darcy's equation. The transport model was coupled to the flow model by velocity terms. The water level configuration of particular time period will be considered for solving groundwater flow equation under steady state and thereby a single velocity field determined for the mass transport simulation for all times. With a small time step, this particle motion traces a path line through the system (Konikow & Grove 1977). Dispersion was accounted for in the particle motion by adding to the deterministic motion a random component, which is a function of the dispersivities. The mean concentration for each grid block was calculated as the sum of the mass carried by all the particles located in a given block divided by the total volume of water in the block. The head solution is obtained using Visual MODFLOW (McDonald & Harbough 1988).

8. RESULTS AND DISCUSSION

Using the computed velocity field from the groundwater flow model, a mass transport model was simulated using the MT3D software. The source concentration was assigned at 4 locations in the Kolhar Industrial Area based on the reported maximum concentration during groundwater quality monitoring for pre and post-monsoon (Fig. 10). The initial concentration of groundwater was assumed as 600 mg/l and the source concentrations varied from 2000-8000 mg/l during last 20 years (Fig. 10). The computed TDS plumes indicate the migration of contaminant in groundwater originating from the sources. The predicted TDS concentration in groundwater for different years presents that the TDS plume migration is limited to four clusters within the Kolhar Industrial Area and is towards the south western part from Eastern boundary (Fig. 11). The computed TDS concentration plume for the year 2012 was used for calibration of the mass transport model during last 20 years. The mass transport model was later used for making prediction during next 50 years. The mass transport model for next year of predictions indicate that significantly TDS concentration plumes are extending towards Western boundary of the Kolhar Industrial Area, but not crossing the boundary of industrial area (Fig.12). Major contaminant TDS plume could be seen emanating from Observation well No. 15 on the Eastern boundary. There is no migration of contaminant TDS plume towards the Air Force Base Station as there is no heavy pumping taking place outside along eastern boundary of the Kolhar Industrial Area. Further as the industrial area is situated on high ground sloping towards west, the contaminant migration if any, through storm water disposal would be towards the western boundary of industrial area. The mass transport model for next 50 years indicates the plumes were joins the flow towards the western part of the watershed (Fig. 13).

The migration of TDS concentration plume along vertical direction was predicted along Row 22 and Column 33 for steady state condition understands the dispersion pattern of contaminant within the Kolhar Industrial Area during next 50 years (Fig. 14a&b). The vertical migration of TDS concentration from other two sources in the industrial area with depth along Row 22 & column 33 for next 20 year indicate very low concentrations (Fig. 15a & b). Similarly, the vertical migration of TDS concentration from other two sources in the industrial area with depth along Row 22 & column 33 for next 50 year shown in (Fig. 16a & b). The groundwater flow and mass transport modeling has only demonstrated extent of likely migration of TDS contaminant plume from Eastern boundary towards the Western boundary in the northern part of the Kolhar Industrial Area. Further it is confirmed that contaminant plumes movement will be towards the western boundary. The plume can move fast as ground surface possess good infiltration characteristic. It is suggested to monitor the groundwater quality rigorously in all the observation wells for reporting elevated TDS in

groundwater in the industrial area. The liquid waste disposal should be made by sending the treated effluent to a Common Effluent Treatment Plant.

9. CONCLUSIONS AND SUGGESTIONS

Groundwater monitoring was carried out on 57 and 66 observation wells during pre and post-monsoon season for ascertaining the groundwater flow direction from the kolhar industrial area, bidar. the groundwater flow direction is from kolhar industrial area towards the marar halla stream on the west. four tds contaminant plumes were identified through water quality monitoring within the kolhar industrial area reporting concentrations varying from 2000-8000 mg/l. the open wells monitored in the basaltic terrain suggest that once the recharge enters the groundwater regime through the top laterite it migrates along groundwater flow path with groundwater velocity. the aquifer characteristics as well as the infiltration rates determined in the industrial area indicated that the area is a favorable region for groundwater recharge. hence any pollution from top surface enters the groundwater regime it migrates with groundwater velocity and dispersion properties of the medium. the hydraulic gradient in the watershed is controlled by pumping within the industrial area as well as neighboring irrigation well pumping.

The observed groundwater quality database also suggests that the contaminant plumes with regard to tds are moving towards the west of the industrial area from eastern boundary. the ground is also sloping towards the west. major contaminants include, tds, chloride and nitrate with little elevated heavy metal presence in the groundwater was noticed during the water quality monitoring. but their concentrations are only slightly elevated along groundwater flow path. similarly, the trace element concentration like barium, cobalt, chromium and manganese shows elevated concentration in the wells inside the industrial area only. there is no threat to the public water supply wells or irrigation wells outside the industrial area. significantly there is no problem encountered with regard to elevated concentrations towards the air force base station, bidar.

The industrial area should have a common effluent treatment plant to process their liquid effluent from different industries. most of the unused open wells in the industrial area need to be protected from surface water contamination during rainy season through storm water runoff. the unused wells may be thoroughly cleaned through groundwater pumping to arrest migration of contaminant to the downstream area. stagnation of storm water should be avoided in industrial area otherwise it may drive the nascent elevated concentrations to the downstream areas.

10. Acknowledgement

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Table 1: Statistical summary of pH, TDS, major ions and trace element for the groundwater samples for pre and post-monsoon season in KIA watershed

Chemical Parameters	Pre-Monsoon (57 Samples)					Post-Monsoon (66 Samples)				
	Min	Max	Ave	SD	Med	Min	Max	Ave	SD	Med
pH	4.22	8.57	8.01	0.63	8.19	2.0	8.4	7.24	1.12	7.6
TDS (mg/l)	45	10560	681.40	1567.87	173	28	8620	766.82	1591.33	163
Ca (mg/l)	8	960	84.35	164.57	40	15	1536	122.79	269.67	50
Mg (mg/l)	1	292	22.78	47.37	5	1	120	10.70	19.93	4
Na (mg/l)	2	2174	104.40	308.44	12	3	2017	161.32	392.94	19.5
K (mg/l)	0.1	145	6.14	20.44	1	0.5	154.6	5.97	21.31	1.05
Cl (mg/l)	5	5570	282.38	819.61	20	3	3497	297.90	649.50	23
SO_4 (mg/l)	0.2	300	27.67	62.44	5	0.3	1743	81.11	281.71	4
NO_3-N (mg/l)	0.01	27.5	3.93	5.85	2.3	0.3	398	23.13	51.75	11.5
HCO_3 (mg/l)	4	276	75.07	64.10	57	18	531	116.32	86.86	98
Be (ppb)	0	6.19	0.8	0.82	7	0	2.21	0.04	0.28	0.01
Cd (ppb)	0	29.6	1	4.2	0	0	0.14	0.03	0.02	0.02
Cr (ppb)	0	27.7	6.4	6.8	4.1	0	1.51	0.38	0.36	0.39
Cu (ppb)	0	266	13	37	8	0	27.04	1.04	3.61	4.88
Fe (ppb)	0	869	60	122	34	13	13660	670	2293	57
Ni (ppb)	0	230	6.11	32.56	0	0	76.55	3.21	9.99	1.26
Pb (ppb)	0	34.1	9.12	8.68	6.75	0	5.7	0.52	0.84	0.27
Zn (ppb)	5.92	5103	154	717	37	0.74	83.81	8.5	14.48	3.91

NOTE: Min = Minimum, Max = Maximum, Ave = Average, SD = Standard Deviation, Med = Median

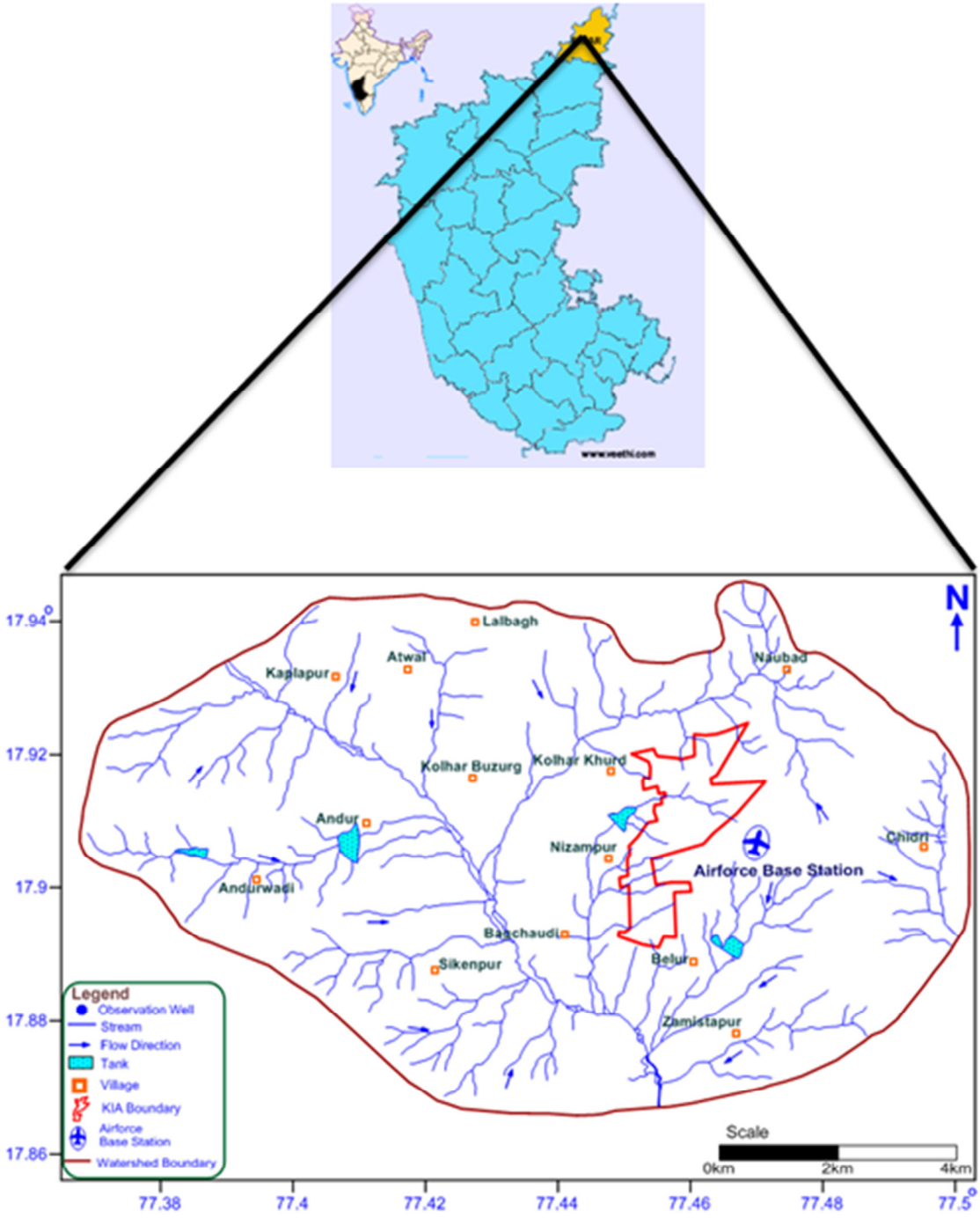


Fig. 1: Key map of the study area showing Kolhar Industrial Area (KIA)

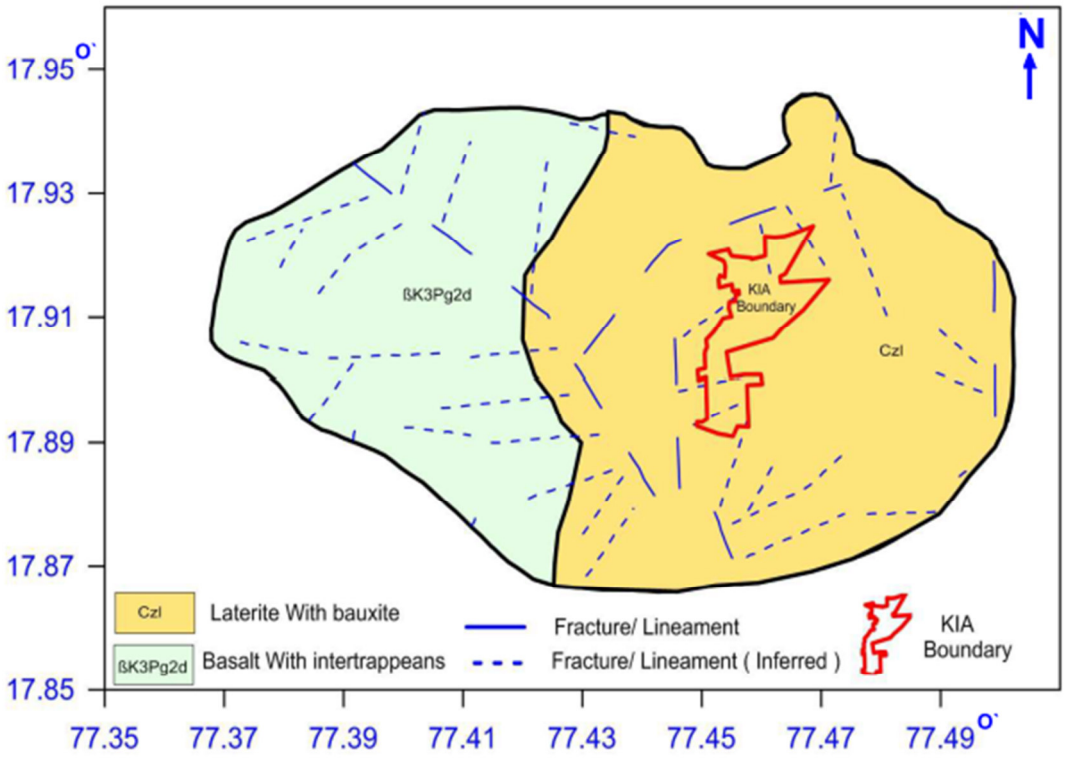


Fig. 2: Geological Map of the watershed covering Kolhar Industrial Area

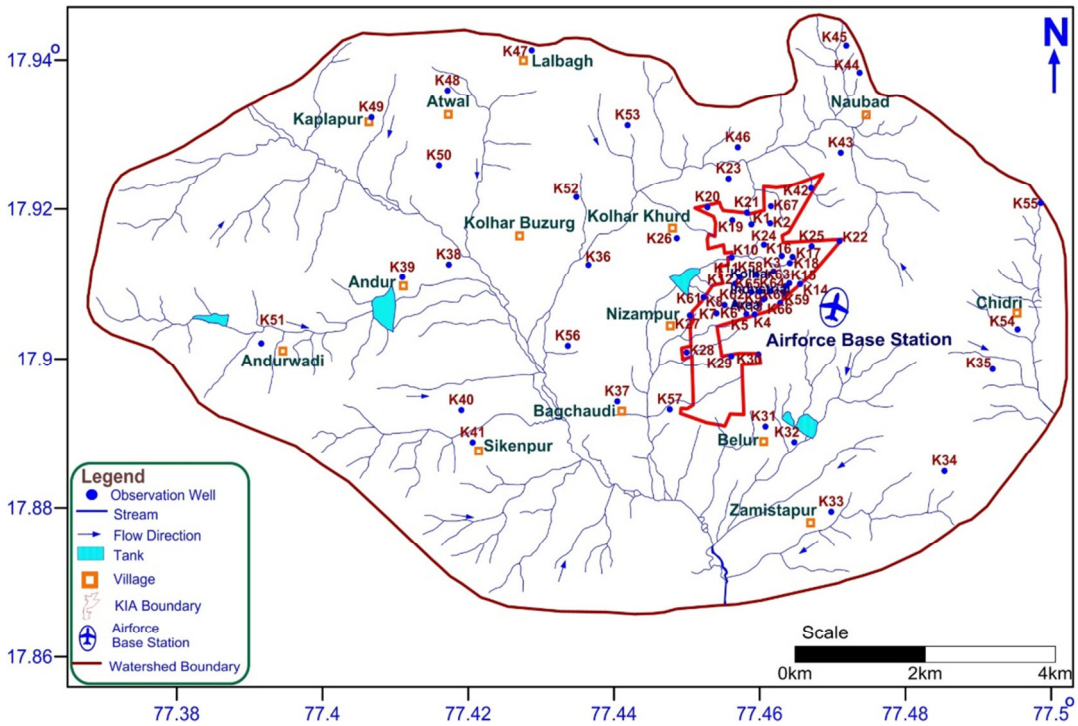


Fig.3a: Observation Wells Location in watershed covering Kolhar Industrial Area, Bidar, Karnataka

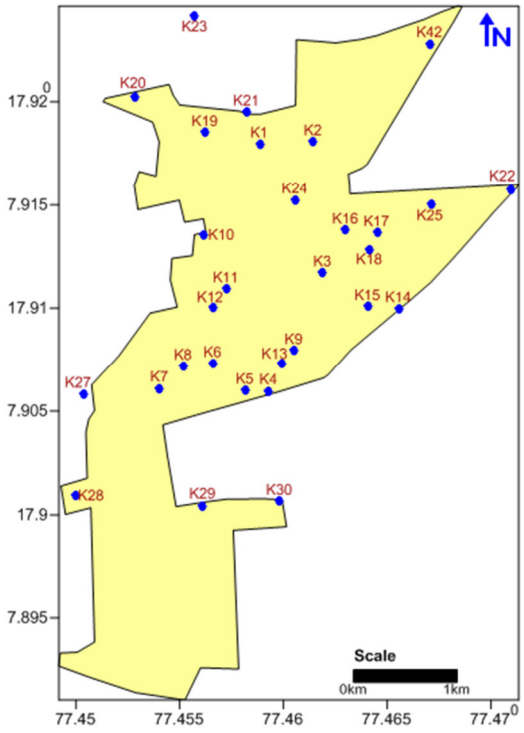


Fig.3b: Observation Wells Location in Kolhar Industrial Area, Bidar, Karnataka

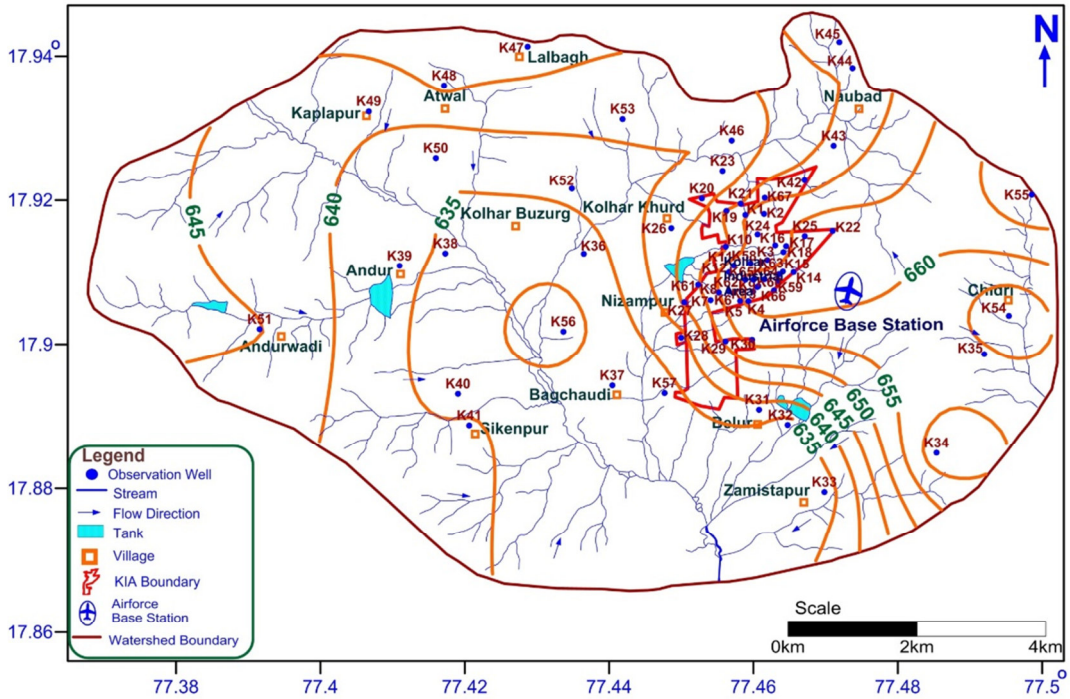
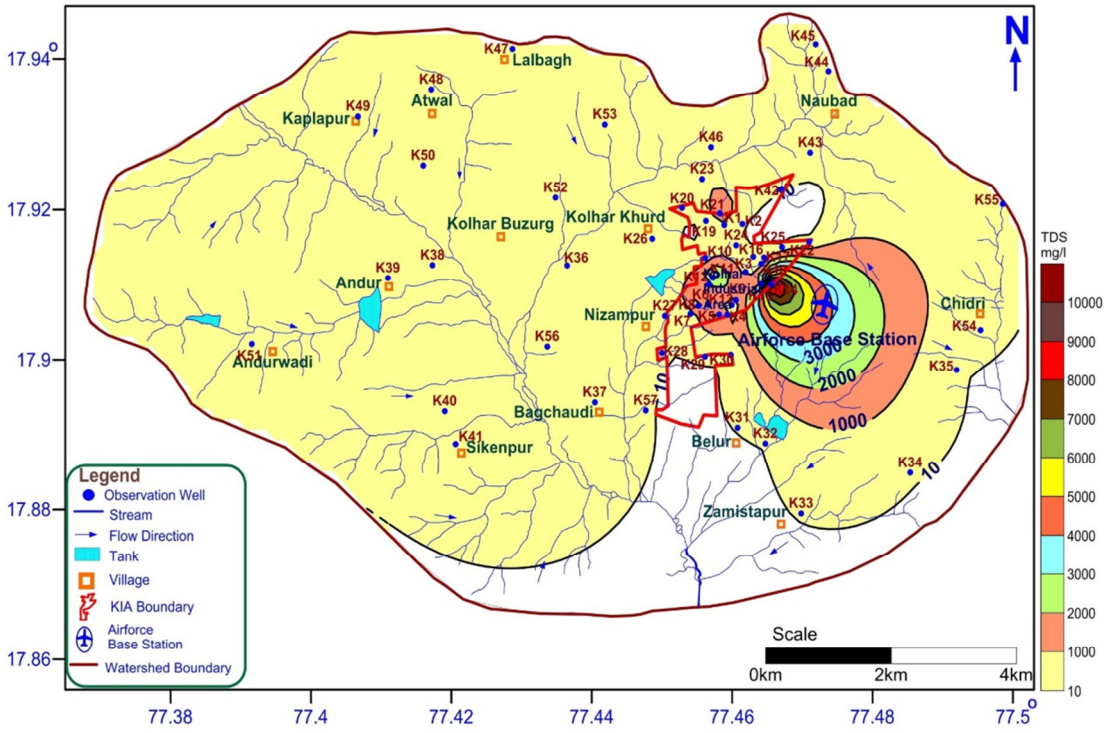
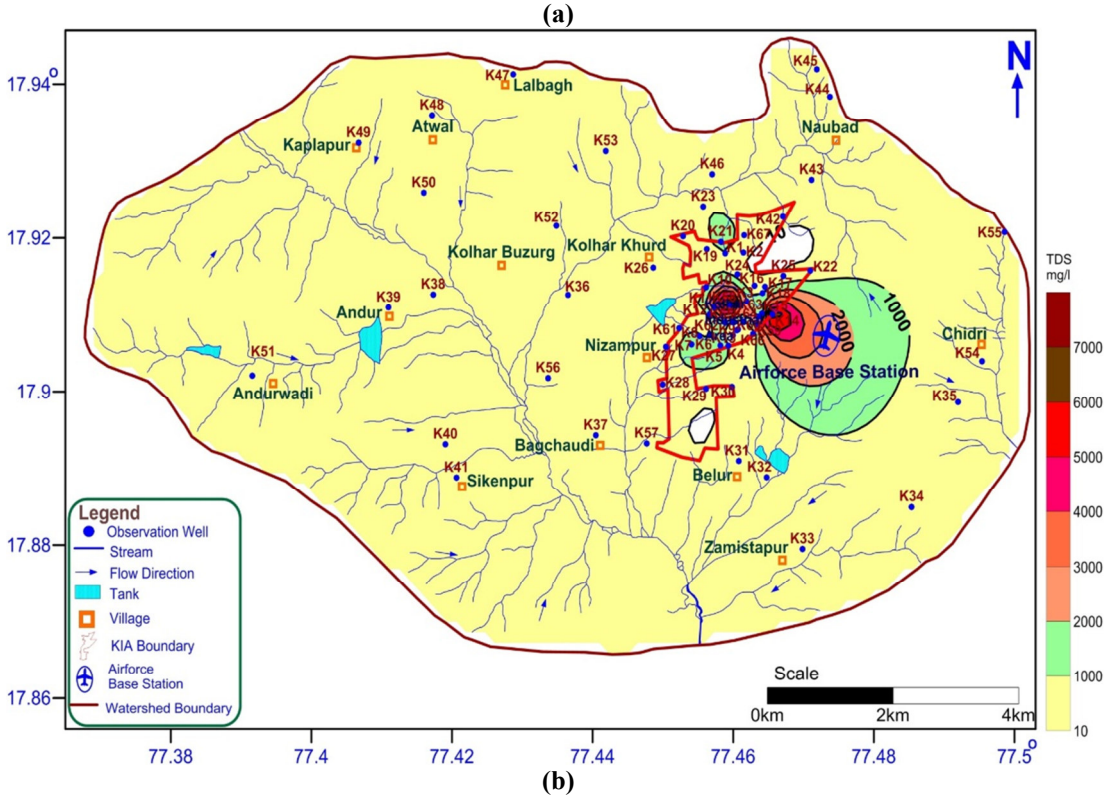


Fig. 4: Topography contours in m (amsl) in the watershed covering Kolhar Industrial Area, Bidar, Karnataka



(a)



(b)

Fig. 5(a & b): TDS concentration (mg/l) in Observation wells of watershed covering Kolhar Industrial Area, Bidar, Karnataka (a) Pre-monsoon and (b) Post-monsoon

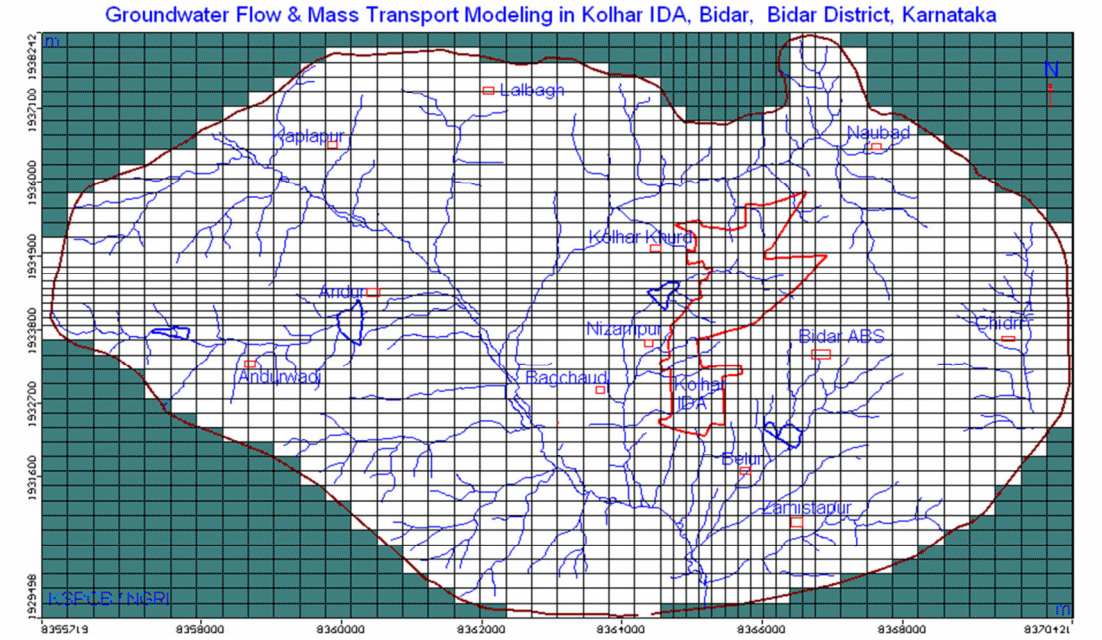
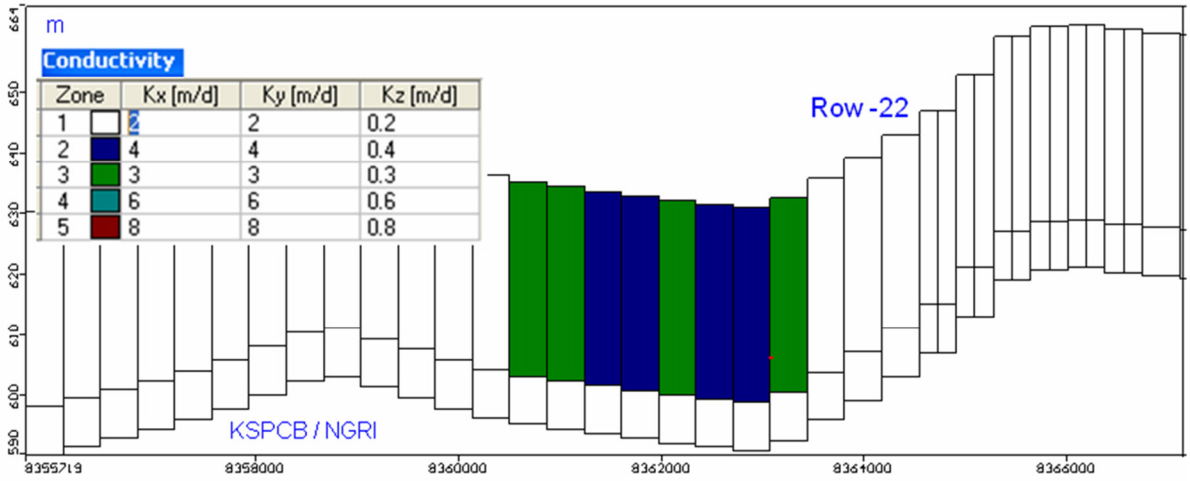
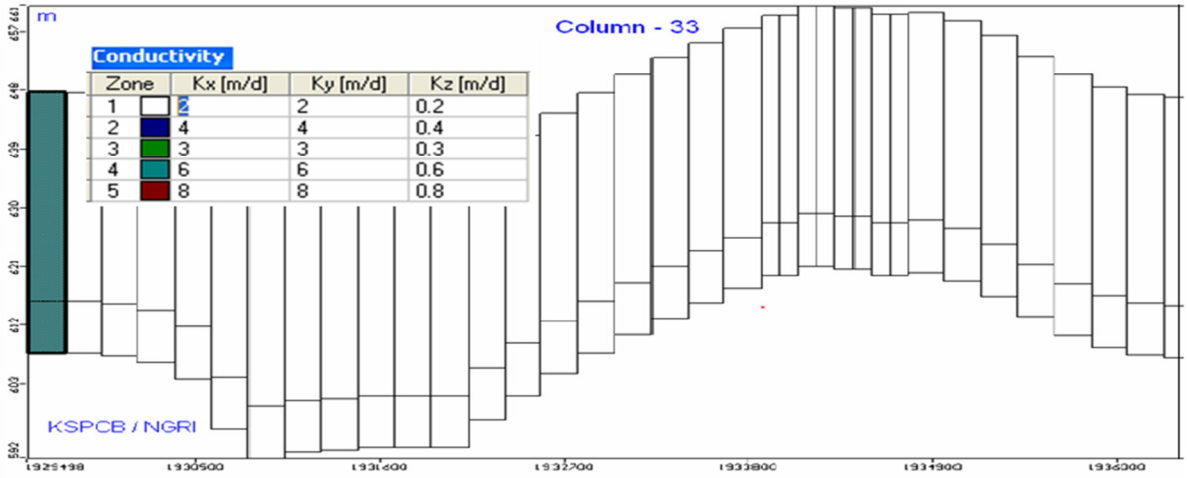


Fig. 6: Groundwater Flow Model Domain of Watershed covering Kolhar Industrial Area, Bidar, Karnataka



(a)



(b)

Fig. 7(a & b): Vertical Cross Section along Row-22 and along Column-33 in the Groundwater Flow Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka

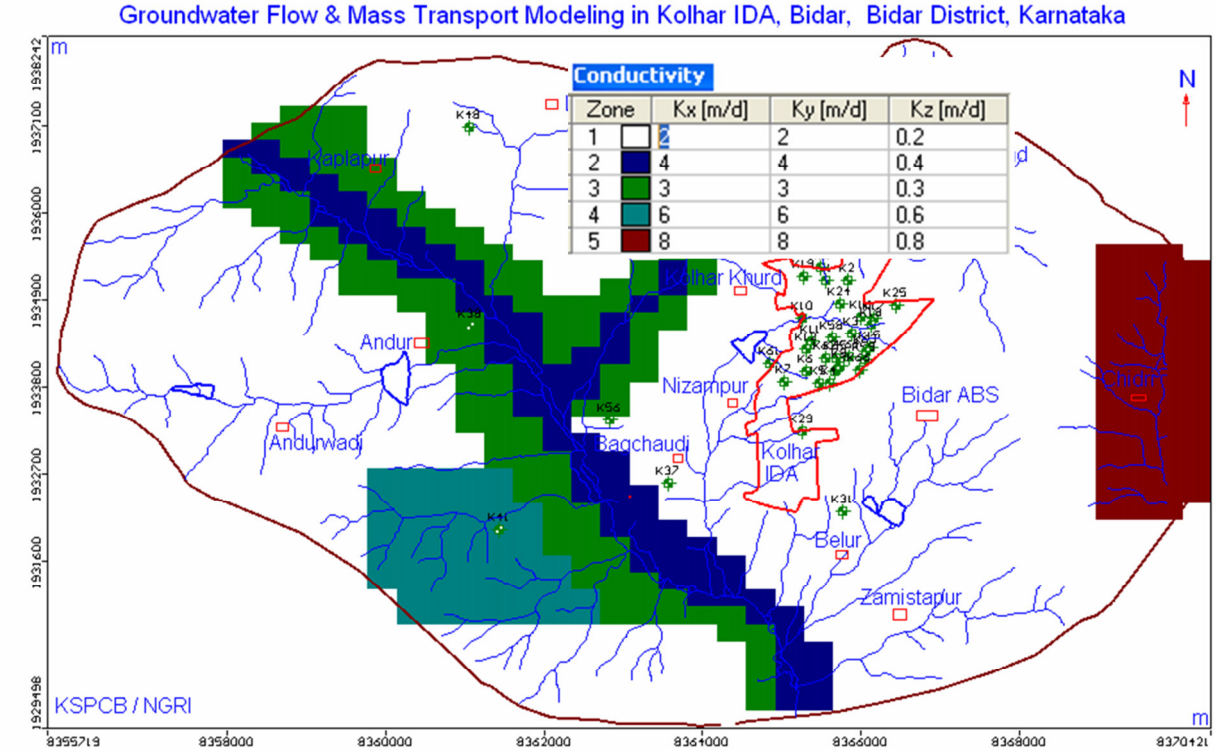


Fig. 8: Block wise Permeability (m/day) in Groundwater Flow Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka

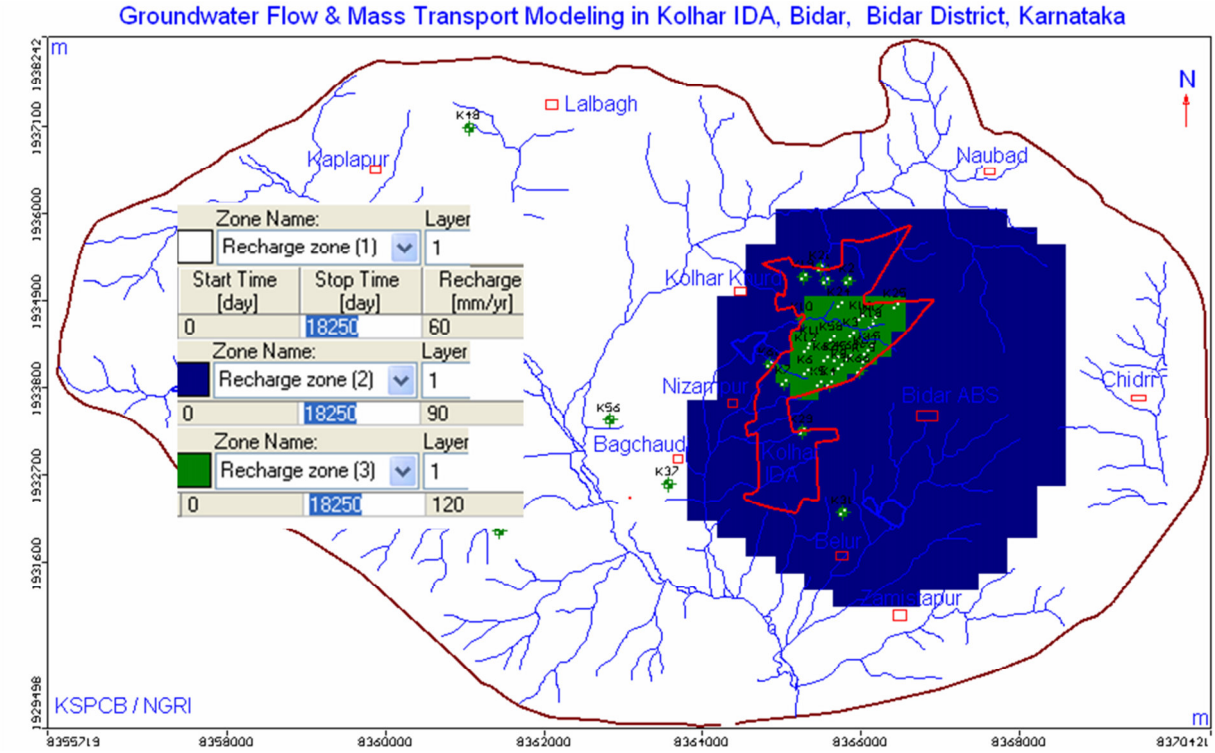


Fig. 9: Groundwater Recharge (mm/yr) in Groundwater Flow Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka

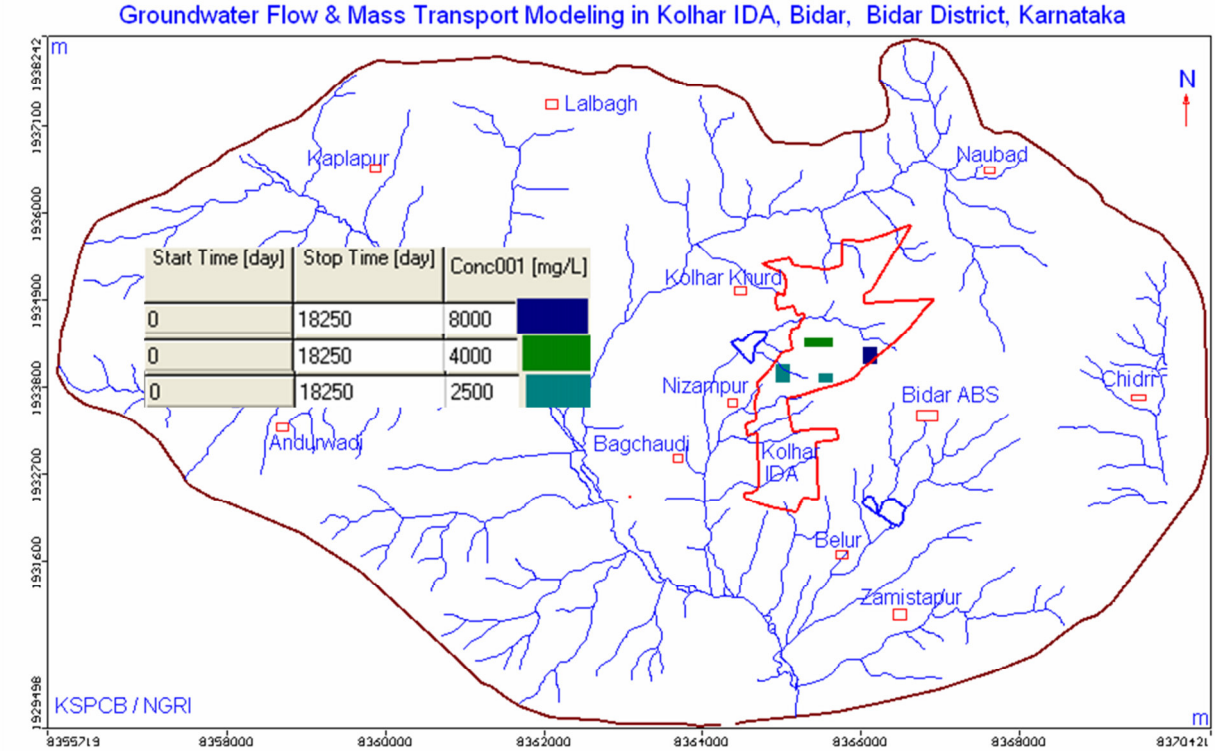


Fig. 10: Source TDS Concentration (mg/l) in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka

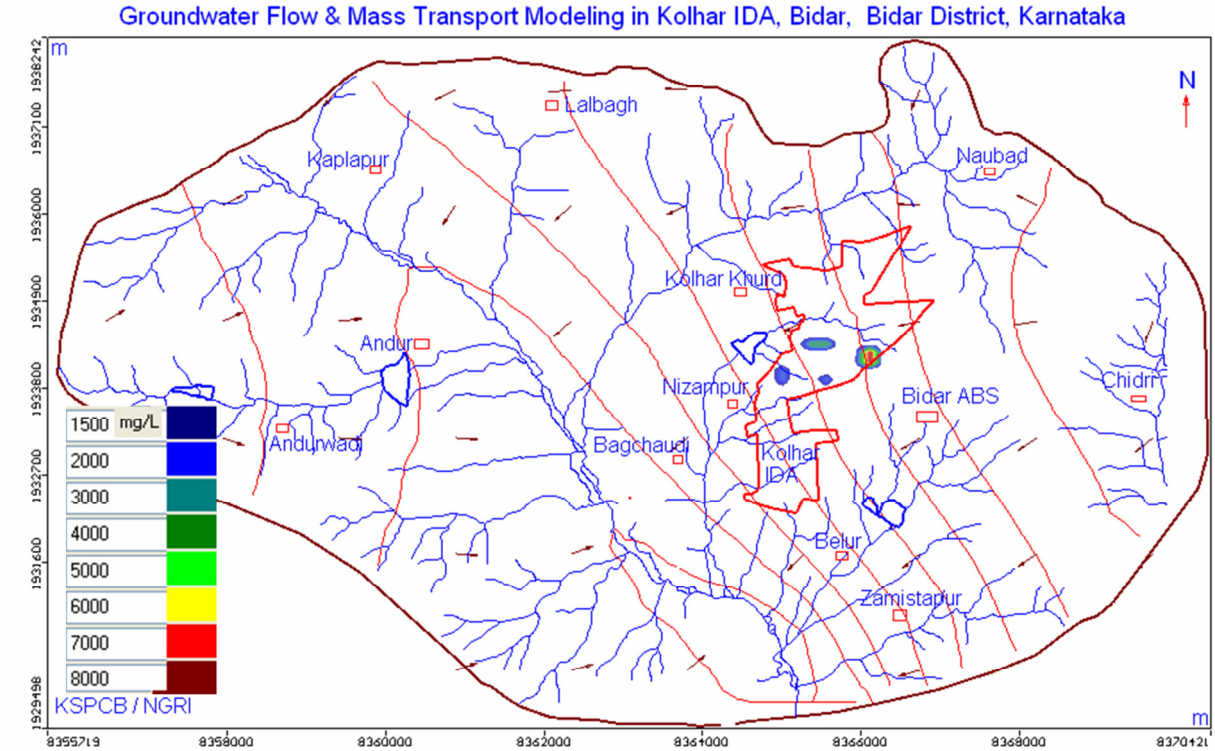


Fig. 11: Computed TDS Concentration plumes (mg/l) in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka after First Year

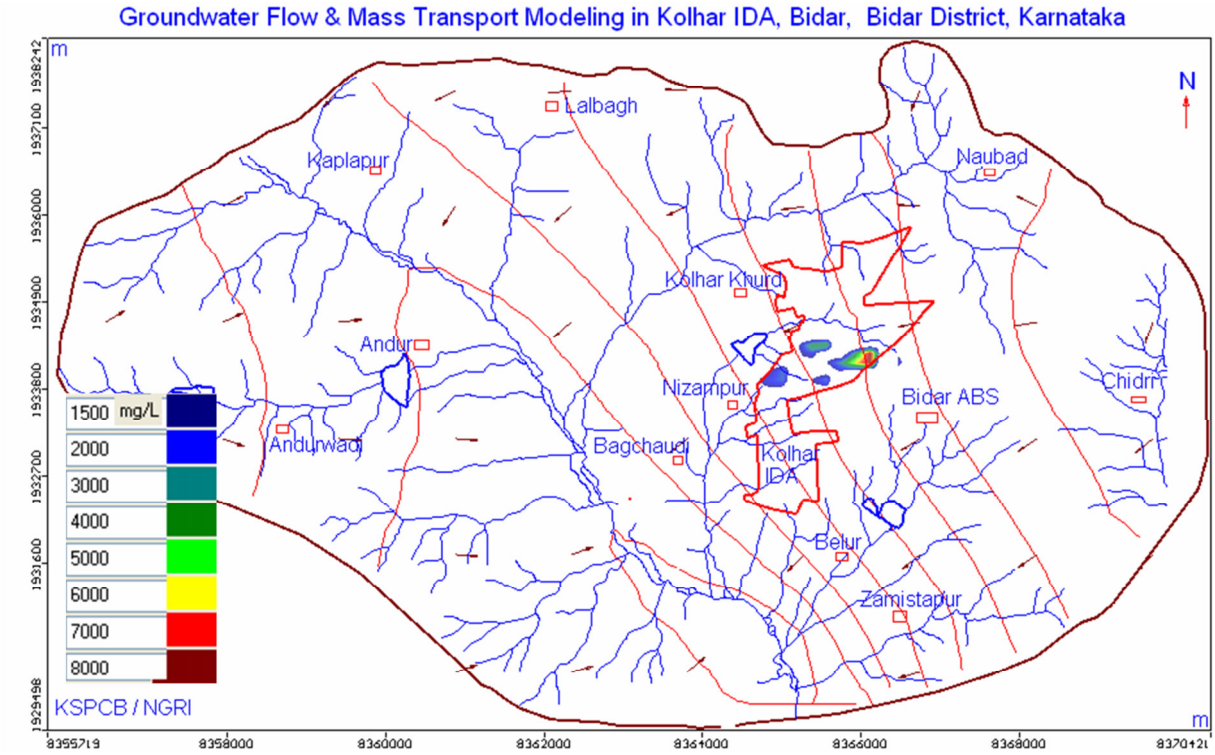


Fig. 12: Computed TDS Concentration plumes (mg/l) in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka after 20 Years

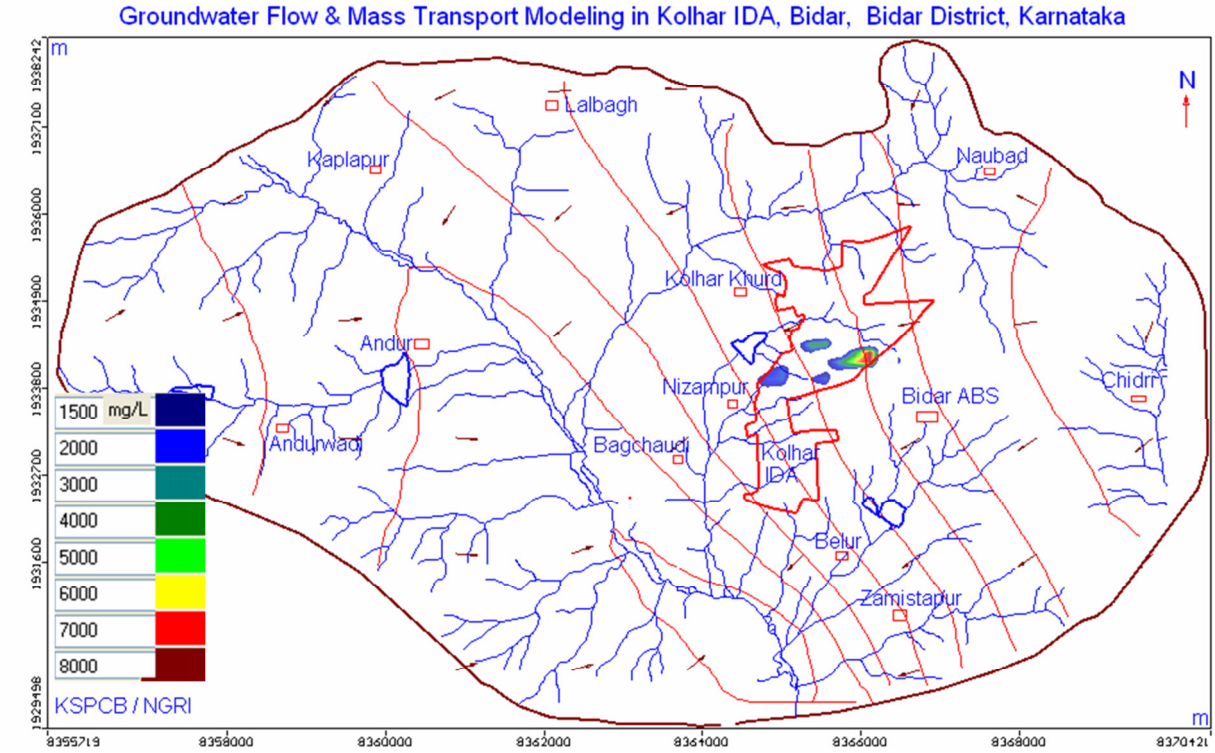
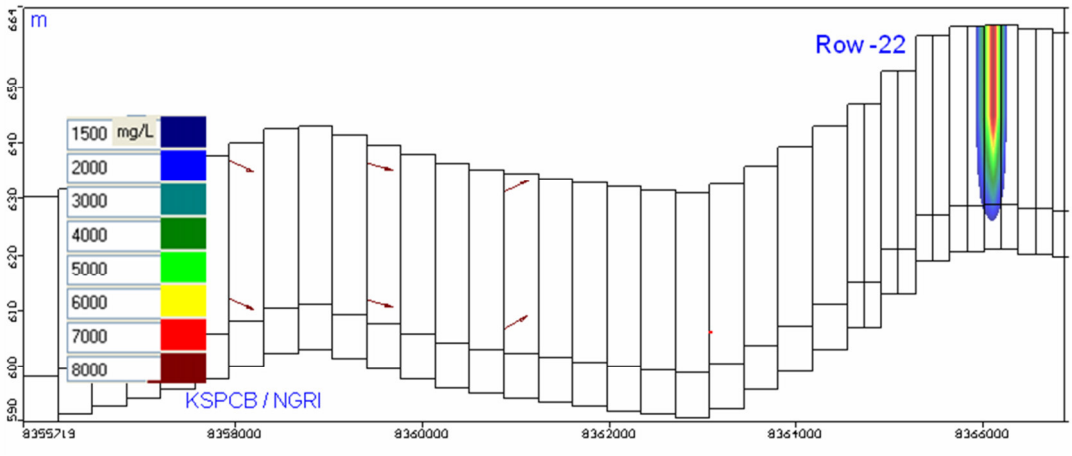
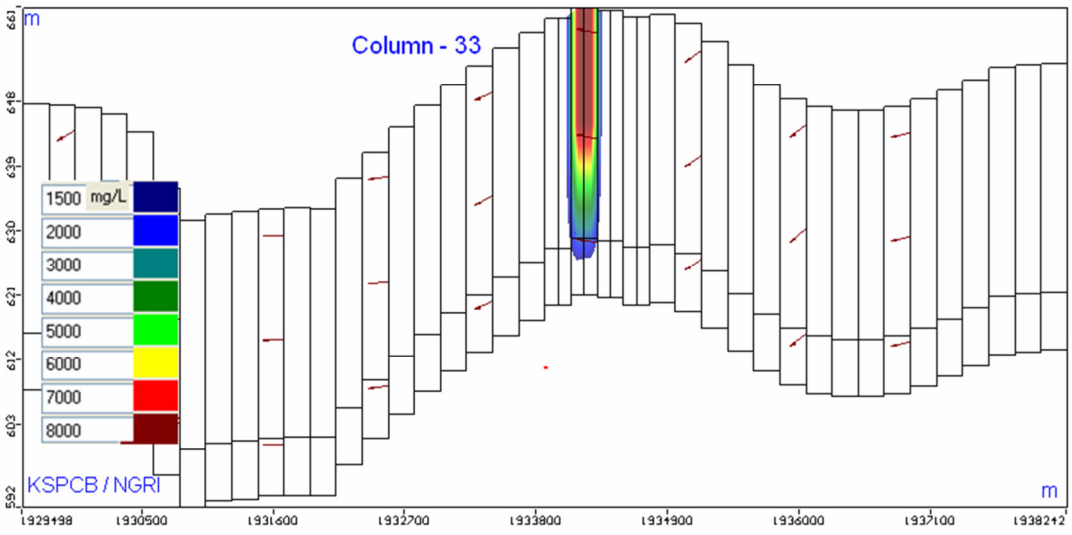


Fig. 13: Computed TDS Concentration plumes (mg/l) in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka after 50 Years

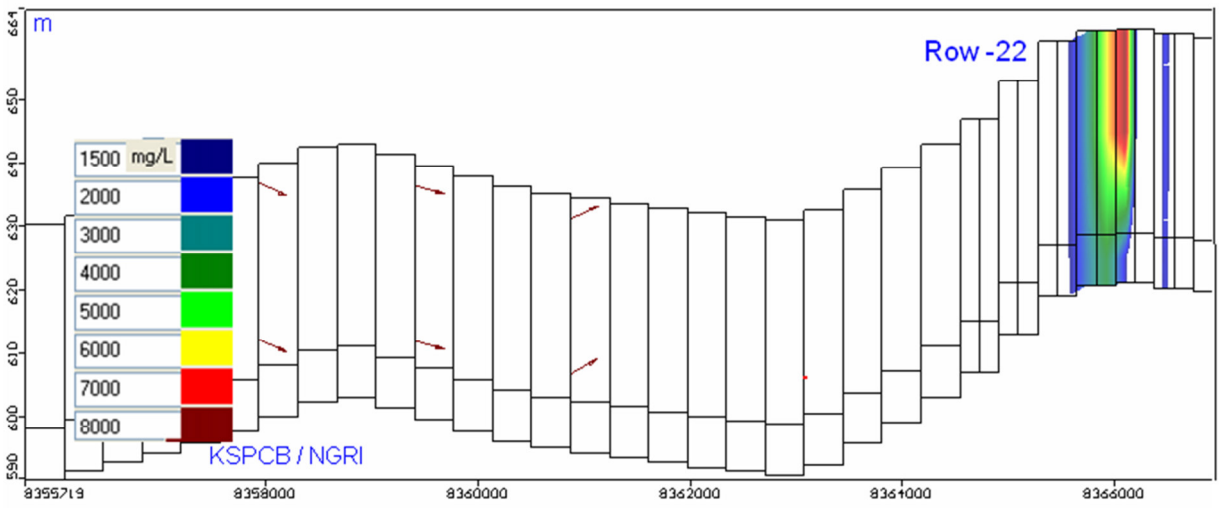


(a)

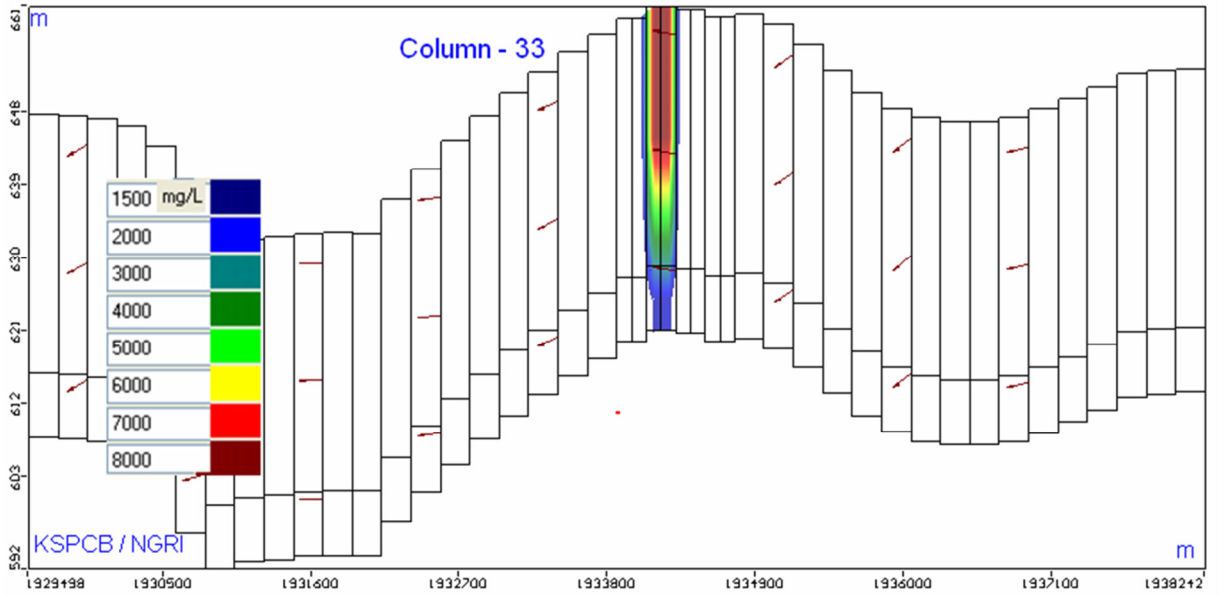


(b)

Fig. 14 (a & b): Computed Vertical TDS Concentration plume (mg/l) along Row-22 and along Column-33 in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka after One Year

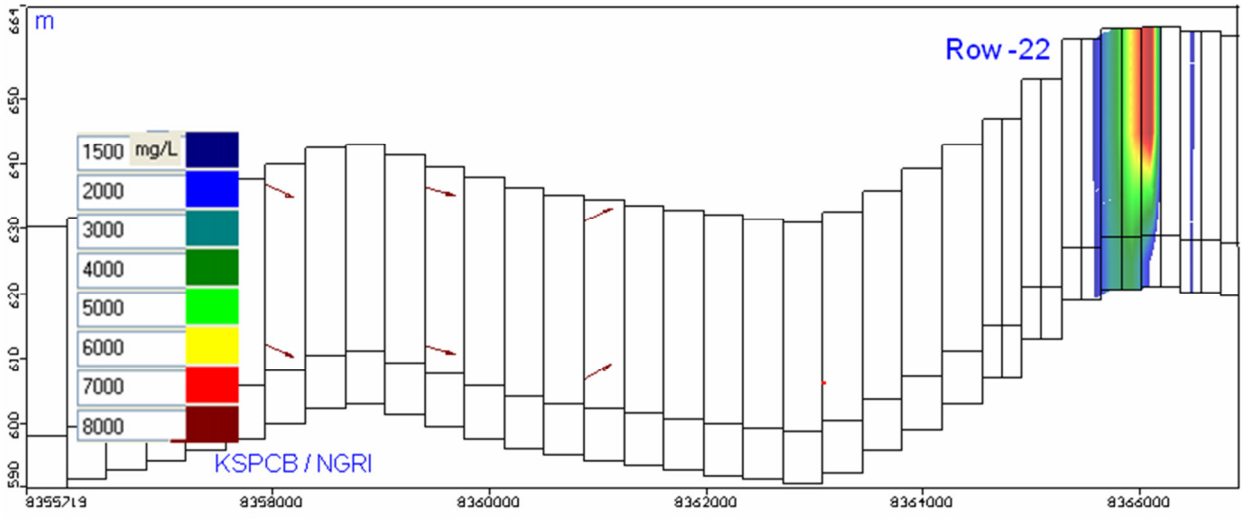


(a)

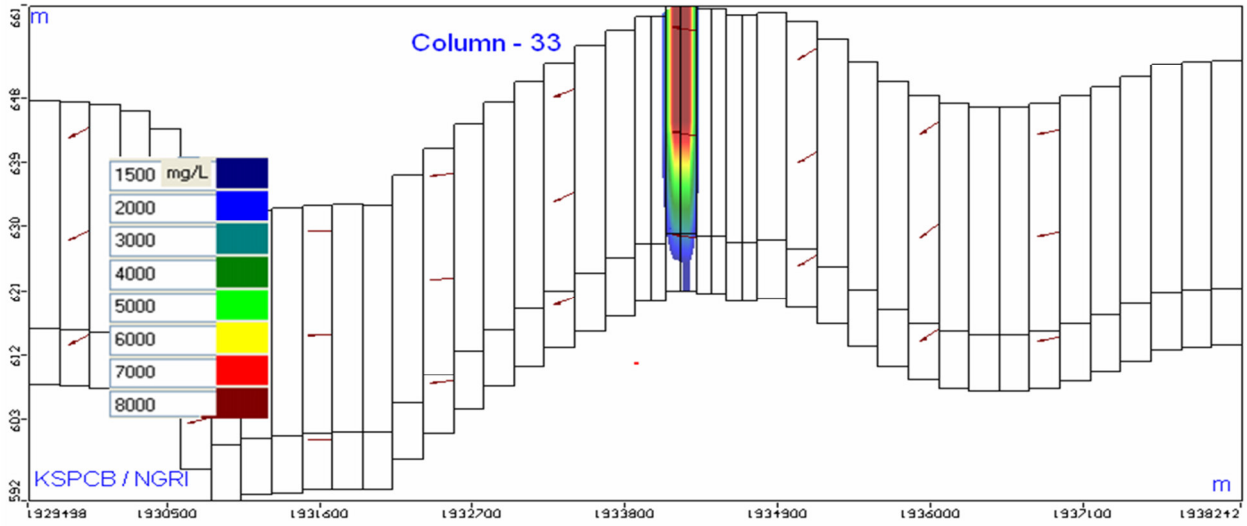


(b)

Fig. 15 (a & b): Computed Vertical TDS Concentration plume (mg/l) along Row-22 and along Column-33 in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka after 20 Year



(a)



(b)

Fig. 16 (a & b): Computed Vertical TDS Concentration plume (mg/l) along Row-22 and along Column-33 in the Mass Transport Model of Watershed covering Kolhar Industrial Area, Bidar, Karnataka after 50 Year