

# Assessment of LNAPL in Subsurface under Fluctuating Groundwater Table using 2D Sand Tank Experiments

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## Abstract

The focus of this study was to investigate fate and transport of toluene, a light non-aqueous phase liquids (LNAPL), in subsurface under dynamic groundwater table conditions. A series of experiments were conducted using two-dimensional (2-D) sand tank setup having the dimension of 125cm L×90cm H×10cm W and integrated with an auxiliary column of inner diameter 14 cm and height 120 cm. In the beginning a steady state flow and LNAPL transport experiment was conducted under stable groundwater table condition. Thereafter, three groundwater table fluctuation experiments were conducted by rising and falling groundwater table in 2, 4 and 8 hours to maintain a rapid, general, and slow fluctuation conditions respectively. Pure phase of toluene was injected at the rate of 1mL/minute for a total duration of 5 minutes. The soil-water and soil vapor samples were periodically collected and analyzed for toluene concentrations. Later, the representation of 2-D sand tank setup was numerically simulated to get the response of flow and the LNAPL transport under varying groundwater table conditions. The analysis of the results show that a large LNAPL pool area (250 cm<sup>2</sup>) gets developed under rapid fluctuating groundwater condition which significantly enhances the dissolution rate and contributes for a high concentration of

dissolved LNAPL to the receiving receptors. The mass transfer coefficient value of  $9.50\text{E-}02$ ;  $5.80\text{E-}03$ ;  $3.50\text{E-}03$ ;  $1.20\text{E-}04$  m/s was estimated for rapid, general, slow and stable groundwater table conditions, respectively. Furthermore, the estimated Sherwood numbers ( $Sh$ ) were found 0.95, 16.20, 16.95 and 19.30 while Peclet numbers ( $Pe$ ) were 1.80, 75.47, 80.14, and 95.06 for rapid, general, slow and stable cases respectively. This shows that the dissolution is highly affected by groundwater table which may cause loss of pollutant mass as a dissolved phase. However, the transport of dissolved LNAPL plume is comparatively fast in case of rapid fluctuating groundwater, resulting in closely space concentration isolines of toluene containing plume. A high biodegradation rate is observed in plume regions having concentration ranges from 140-160 ppm, while it decreases in the plume regions having high concentrations ( $>160$  ppm) and low concentrations ( $<140$  ppm) in these cases. In sand tank, the microbial growth was found to be increasing as plume moves away from the LNAPL pool towards low-gradient, which fortifies detrimental impact of toluene on survival of indigenous microorganisms near the LNAPL pool. The results of this study may help in implementing effective remediation technique to decontaminate LNAPL polluted sites under fluctuating groundwater table conditions, especially in (semi)-arid coastal aquifers.

**Keywords:** LNAPL, Groundwater fluctuation, Dissolution, Biodegradation, 2D tank experiments, Numerical modeling

## 1. Introduction

The subsurface contamination by LNAPL is widespread and challenging environmental problem, especially in coastal regions having dynamic groundwater table condition due to tidal effects. Most of the petroleum industries and refineries are located in coastal regions. The leakage of LNAPL from subsurface storage tanks and disposal sites of effluents (Nema and Gupta, 1999; Kumar et al. 2016) on surface are major source of hydrocarbons pollution of the receiving environment, especially under varying subsurface conditions. When LNAPL is released into (sub)-surface, it starts moving downward through the partially saturated zone, in response to gravitational force, until it reaches to the capillary fringe (Das and Mirzaei, 2012; Power et al. 1992a, b; 1994a, b; Illangasekare et al. 1995). A fraction of LNAPL mass is being retained in partially saturated zone and LNAPL-air mass partition (i.e. volatilization process) contributes as vapor phase contamination (Nambi and Powers, 2000; Brusseau et al. 2002, Nambi and Powers, 2003, Patterson and Davis, 2009). The remaining pool of LNAPL provides

sufficient dissolving area to the underlying groundwater in smear zone which starts dissolving with flowing groundwater and create a dissolved phase plume (Lee and Chrysikopoulos, 1998; Kim and Chrysikopoulos, 1999; Nema and Gupta, 2003; Oostrom et al. 2006; 2007). Molecular diffusion and mechanical dispersion along with advective flux cause spreading of dissolved plume to downgradient receiving locations (Das, 2002; Yadav and Hassanizadeh, 2011; Picone et al. 2013). On the other hand, native potential microbes play significant role to degrade the dissolved LNAPL from polluted zone (Yadav et al. 2013; Basu et al. 2015, Mustapha et al. 2018).

Groundwater flow regimes play a significant role in the dissolution of pure phase LNAPL pool and its movement to the surrounding locations (Das and Nassehi, 2003; Dobson et al. 2007; Sulaymon and Gzar, 2011, Kamaruddin et al. 2011; Yadav et al. 2012). Dynamic nature of groundwater table causes significant spreading of pooled LNAPL in smear zone, which considerably increases the LNAPL-water interphase area and resulted in accelerated dissolution (Mobile et al. 2012; Vasudevan et al. 2014). Variations in groundwater table not only causes changes in the soil-water system, but also impacts the LNAPL pool behavior, if it is present on the water table and in the underlying saturated zone. The LNAPL lying on the top of the groundwater table moves down with it when the water table lowers and leave a trail of LNAPL in the unsaturated zone in the form of isolated ganglia. Subsequently when the groundwater table rises, the LNAPL pool also moves upward leaving behind a trapped amount of LNAPL in the form of disconnected blobs in the saturated zone (Lenhard et al. 2004; Kechavarzi et al. 2005). A part of the residual LNAPL in unsaturated zone gets mobilized again when the groundwater table rises. Thus, a dynamic groundwater table accelerates the dissolution of pure phase LNAPL resulting in high concentration of LNAPL plume (Legout et al. 2009). The dissolved LNAPL plume then moves along with groundwater and forms a polluted zone which features with varying concentration levels (Neale et al. 2000; Rolle et al. 2009; Zhang et al. 2014; Zhou et al. 2015; Sarikurt et al. 2017).

There is a paucity of knowledge on the impact of dynamic groundwater table conditions on LNAPL behaviors in subsurface. Groundwater fluctuation is significantly affected by heavy pumping rates to irrigate agricultural land and concurrent recharge due to return flow. Typically for shallow aquifers, a high pumping rates and return flow/recharge may cause rapid fluctuation of groundwater table. While, a slow pumping and less return flow/recharge may lead to general/slow groundwater table fluctuation. Different nature of rainfall events is also responsible for such a rapid and slow fluctuation of groundwater table. Fluctuations in the groundwater table due to various reasons including tidal effects have a profound influence on

the spatial distribution, dissolution and biodegradation of LNAPL in the subsurface environment. This phenomenon is predominantly observed in shallow aquifer regions where most of the petrochemical industries and refineries are located and potentially at high risk of LNAPL release from the subsurface storage tanks. Thus, an extensive study was conducted to investigate LNAPL fate and transport under fluctuating groundwater table conditions using a series of 2-D sand tank experiments. A better understanding of fate and transport of LNAPL under varying subsurface water table condition is required which in turn can help in designing effectively remediation technologies and to accurately predict their clean-up times and the associated cost.

## **2. Materials and Methods**

In this study, the behavior of pooled pure phase LNAPL and its dissolved plume in subsurface under stable and fluctuating groundwater table conditions is investigated using a series of two-dimensional laboratory experiments and numerical modelling. The preliminary experiments were conducted to characterize the flow and transport parameters of the developed subsurface soil-water system. Mechanical sieve analysis was performed to find the particle size distribution of the sand which is listed in Table 1 along with other physical parameters. The porosity of sand packing was determined using oven dry and volumetric methods. Further, the hydraulic conductivity of the system was estimated using a constant head permeameter. To see the behavior of the pooled LNAPL and dissolved phase plume, a series of two dimensional sand tank experiments were performed by considering varying groundwater table conditions. A two dimensional sand tank setup filled with homogenous sand was used to conduct the laboratory experiment under (1) steady-state groundwater condition and (2) three different dynamic groundwater table fluctuation conditions, separately. Lastly, the soil-water system was numerically simulated using HYDRUS 2D model considering the laboratory investigated soil-water and solute transport parameters.

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Table 1. Properties of the sand used in the laboratory experiments.

| Characteristic          | Values                     |
|-------------------------|----------------------------|
| Type                    | Medium Sand                |
| Grain Size              | 0.5-1 mm                   |
| Particle Size > 1 mm    | 1.71±0.5%                  |
| Particle Size 0.5mm-1mm | 98.27±0.5%                 |
| Particle Size < 0.5 mm  | 0.02±0.01%                 |
| Effective Porosity      | 0.33±0.02%                 |
| Bulk Density            | 1.52 ±0.1g/cm <sup>3</sup> |
| Grain Density           | 2.31±0.1 g/cm <sup>3</sup> |

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## 137 2.1 Two Dimensional Sand Tank Setup

138 Two dimensional sand tank setup used in the study was specially designed using 2.5 mm thick  
139 stainless steel formed box with inner dimensions of 150 cm-long × 120 cm-high ×10 cm-deep  
140 (Figure 1). Two wells were installed at each side of tank and front cover of the tank was made-  
141 up of a thick glass sheet for enabling observations. Indian standard clean sand (650 grade-II)  
142 of particle size 0.5-1mm free from organic matter was packed in the central chamber between  
143 both the wells up to a height of 90 cm. The top 30 cm thick sand pack was kept as head-space  
144 to maintain aerobic condition. The porous media was oversaturated before pouring it into the  
145 column setup to create a homogenous packing. During this filling, a comb-like metallic tool  
146 was used to smooth the sand surface for avoiding a layered structure of the porous media. The  
147 extra water was then gravitationally drained out from the bottom of tank setup. The system was  
148 then flushed at maximum velocity until the effluent water was free of suspended fine material.  
149 After each of the experiments, the used sand was replaced with fresh sand pack the new set of  
150 the experiments following the packing procedure as describes earlier. The wells were used as  
151 upstream (high pressure) and downstream (low pressure) reservoir to maintain the water table.  
152 An auxiliary column containing the collected groundwater was connected to the inlet port of  
153 upstream well with viton tubes of a peristaltic pump. This peristaltic pump refers as “upstream  
154 pump” was used to supply the groundwater to the sand tank through the upstream well. The  
155 objective of this auxiliary column was to provide sufficient groundwater storage required to  
156 maintain the dynamic groundwater table conditions (Figure 1a). Similarly, the outlet of the

downstream well was connected to another peristaltic pump (refer herein as downstream pump) to extract the groundwater and recirculate to the auxiliary column. The flow rate of the pumps was adjustable so that the desired pressure difference in the two reservoirs can be maintained and thereby controlling the groundwater flow within the tank setup. A LNAPL release port was installed just below the top surface of sand packing about 20 cm from the upstream well. The sampling ports having equal horizontal spacing of 15.5 cm are situated at 30 and 60 cm height from the bottom of the tank setup in two horizontal layers (figure 1b). Piezometers were attached to the tank to measure the positions of the groundwater table during experiments. Filtration screens were fixed around the inlet and outlet valves to prevent the entrance of the sand particles in the connecting viton tubes.

A series of tracer transport experiments were performed to determine the longitudinal and vertical dispersivity of sand under fast, base and slow groundwater velocities. A solution of tap water and sodium chloride with an initial concentration of 1000 mg/l was continuously injected to the tank for the selected groundwater fluctuation cases. The water samples were routinely collected from the sampling port located at 50 cm away (at X:45; Y:50 cm) in the lower-gradient side from the injection port of the top sampling layer and the tracer concentrations were measured using portable conductivity meter. The longitudinal dispersivity ( $D_L$ ) resulted from the dispersivity flux were estimated using the breakthrough curves (BTCs) obtained from the tracer experiments. Time values corresponding to relative concentration ratios of 84%, 50%, and 16% were used in calculating the dispersion coefficient ( $D_L$ ) and longitudinal dispersivity ( $\alpha_L$ ) as proposed by Sulaymon and Gzar (2011). In the equation,  $D_{ij} = \tau D_* + D_x$ , the first term resulted from diffusive flux was estimated by multiplying the diffusion coefficient of toluene i.e.  $6.3 \times 10^{-6}$  [cm<sup>2</sup>/sec] and tortuosity of sand i.e. 1.43 (Sulaymon and Gzar, 2011). The vertical dispersivity ( $D_v$ ) were considered 0.1 times of the obtained longitudinal dispersivity (Dobson et al. 2007).

A series of LNAPL transport experiments were performed using 2D sand tank setup for stable/steady and three different groundwater table level conditions. Under steady-state condition, a constant groundwater flux was applied as inflow (using the upstream pump) and the same was extracted as outflow (using the down-stream pump) to maintain a constant flow velocity in the horizontal direction and, hence, keeping the water table location at a constant height. However, in rapid, general and slow groundwater level fluctuation experiments the inflow/outflow flux were controlled by peristaltic pump to maintain a raising of the water

table by 5cm in 1, 2, and 4 hours respectively. The groundwater table was then lowered in the same manner; a drop of 5 cm was achieved in subsequent 1, 2 and 4 hours for rapid, general and slow fluctuation conditions, respectively. It may be noted herein that “one fluctuation cycle” refers to a complete high-low-high cycle of groundwater table levels.

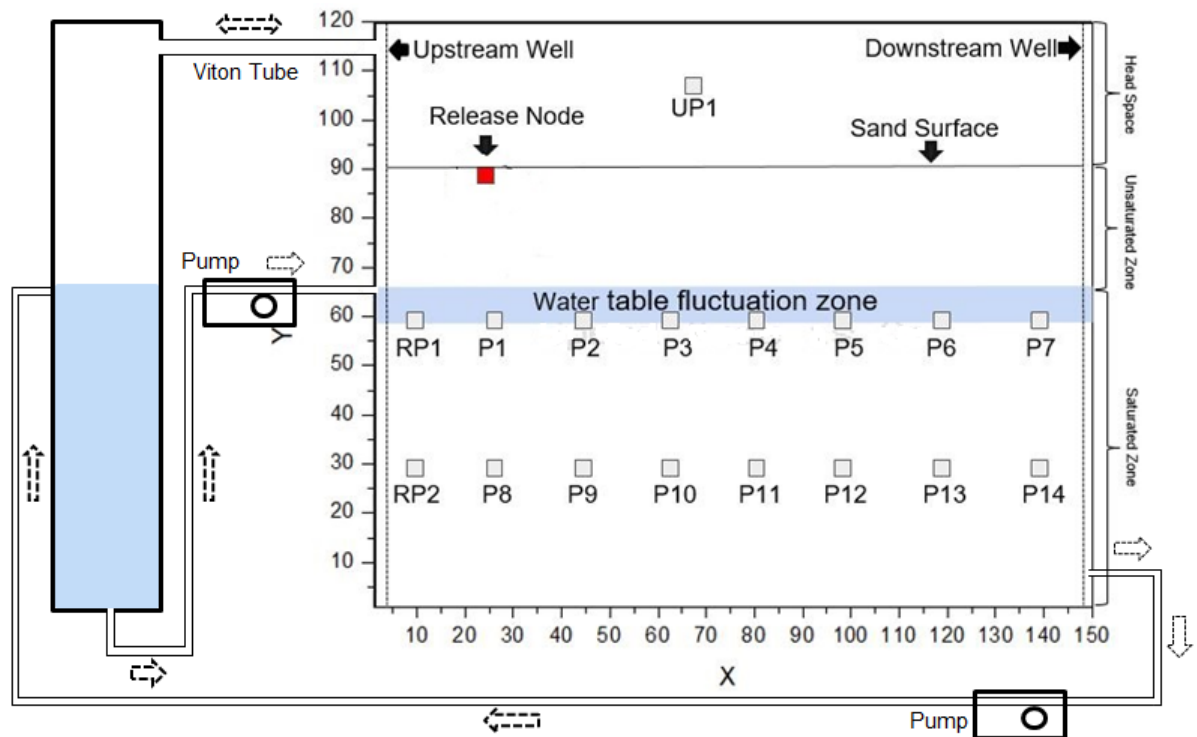


Figure 1. Schematic diagram of 2D sand tank setup integrated with an auxiliary column used to investigate fate and transport of LNAPL in subsurface under dynamic groundwater table conditions.

Rising of groundwater table was maintained by pumping the water from the auxiliary column to the upstream well and closing the outflow from the downstream well for a target duration of respective fluctuation conditions. Likewise, groundwater falling was maintained by extracting water from the downstream well and closing the inflow to the sand tank from the auxiliary column for the same duration. Such switching of the peristaltic pump was adjustable and calibrated for a target duration of respective fluctuation conditions. A brief pumping details of different considered cases are listed in Table 2. To maintain a rise and fall of 5 cm, (150 cm-long  $\times$  05 cm-magnitude of fluctuation  $\times$  10 cm-deep  $\times$  33% porosity)  $0.002475 \text{ m}^3$  or 2.475 liters of groundwater was required as inflow and outflow. Pure phase toluene was released from the top surface of the tank set up

to create a pool of the LNAPL above the groundwater table which was varied in the range of 55-60 cm level from the tank bottom. The toluene (Merck with 99.9 % purity) was injected at a constant rate of 02 ml/min for a duration of 5 minutes using an air-tight syringe. Periodically, a small amount of soil water samples from both the layers and the soil vapor samples from head-space were collected carefully for the analysis.

Table 2. Inflow and outflow pumping strategies of groundwater table fluctuation cases.

| Conditions          | Inflow  |      | Outflow |         | Total<br>Duration | Pumping Rate |
|---------------------|---------|------|---------|---------|-------------------|--------------|
|                     | Pumping |      | pumping |         |                   |              |
|                     | Rise    | Fall | Rise    | Fall    |                   |              |
| Rapid fluctuation   | 1 hour  | ×    | ×       | 1 hour  | 2 hours           | 2475.0 mL/hr |
| General fluctuation | 2 hours | ×    | ×       | 2 hours | 4 hours           | 1237.5 mL/hr |
| Slow fluctuation    | 4 hours | ×    | ×       | 4 hours | 8 hours           | 618.7 mL/hr  |

## 2.2 Sample Analysis

Soil water samples were collected periodically using needles attached with syringes (Hamilton gold) from the sampling ports embedded in the sampling layers in saturated zone (Figure 1). The samples were transferred into vials (Agilent vials: Agilent Product No. 5190/1599) having air tight red septa caps without any air contacts. Similarly, soil vapor samples were collected from sampling ports installed in the headspace. The collected samples were analyzed using Gas chromatography-mass spectrometry (GC-MS) (Agilent 7890B) in triplicates. A chrompack capillary column (30m×0.25mm, Silicone coating of 0.25µm) was used for toluene analysis. Helium was employed as the carrier gas at a flow rate of 25 mL/min. Similarly, air and nitrogen were used with a flow rate of 20 mL/min during GC-MS analysis. During the measurements, temperature of injection port, oven, and detector port was kept at 150°C, 120°C, and 150°C, respectively. One set of collected samples were also analyzed using gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) technique to capture pure phase LNAPL (Dempster et al. 1997).

### 2.3 Microbiological Analysis

The microbial population in the soil water zone was counted using heterotrophic or standard plate count methods (No. 9215C). In this method, colony forming units (CFU) for live heterotrophic bacteria was estimated from the collected soil-water samples during laboratory experiments. The soil water samples for microbial population count were collected from M1 and M7 ports of top layer and M8 and M14 ports of bottom layer (Fig 2). After the sample collection, all the collected samples were diluted with a factor of  $10^1$  to  $10^{-5}$  and mechanically shaken for 15 seconds. Growth media was prepared using a combination of 20g protease peptone; 1.5g of  $K_2HPO_4$ ; 1.5 g of  $MgSO_4 \cdot 7H_2O$ ; and 20g of Agar. Final pH of media was adjusted to 7.2 by adding 1N NaOH, before autoclaving at  $121^\circ C$  for 15 minutes. The laminar air flow setup was wiped with the 70% ethanol and UV light for the 15 minutes to avoid any background microbial contaminations. Well marked (sample number, dilution, and date) plates were poured with 30mL prepared growth media and kept still for few minutes to solidify agar surface. Thereafter, diluted samples were inoculated with the help of spreader on agar surface of respective plates. Successively, all the plates were incubated for 48 hours at  $36 \pm 1^\circ C$  for. After the incubation, colony was counted manually using the quadrate method. Plates having an un-countable number (or too numerous) was considered as overgrowth. In this study, microbial populations were counted with the 12 hours' interval to see the impact of LNAPL transport on microbial growth under fluctuating groundwater table conditions. Thus, above mentioned microbial counting procedures were performed for each experiments separately. A comparative account of such bacterial count during groundwater table fluctuation experiments gives a clear idea on how groundwater fluctuating conditions affects the LNAPL fate and transport in the subsurface.

### 3. Numerical Modeling

To solve the dissolved phase LNAPL transport in saturated zone 2D form of mass balance equation used as:

$$\frac{\partial}{\partial t}(nS_f C_{if}) = -\nabla \cdot (q_f C_{if}) + \nabla \cdot (nS_f D_{if} \cdot \nabla C_{if}) + K_{if} - S \quad (1)$$

Where  $C_{if}$  is NAPL compound in  $f$  phase [ $ML^{-3}$ ],  $q_f$  is discharge through soil profile [ $LT^{-1}$ ],  $n$  is porosity of soil [ $L^3L^{-3}$ ],  $t$  is time [ $T$ ],  $K_{if}$  is the dissolution rate of LNAPL [ $ML^{-3}T^{-1}$ ] was observed using characteristic length of LNAPL pool and equilibrium concentration in dissolved

phase. Likewise,  $S$  is biodegradation rate [ $\text{ML}^{-3}\text{T}^{-1}$ ] (as sink term) was obtained using (control and live) microcosms experiments.  $D_{if}$  is hydrodynamic dispersion [ $\text{L}^2\text{T}^{-1}$ ] which was obtained using breakthrough curves (BTCs) of tracer transport experiment. The HYDRUS 2D model was used to solve governing equation for water flow and solute transport (Simunek et al. 1996). A two dimensional numerical domain having similar dimension of sand tank was created to simulate soil water flow and LNAPL transport through saturated zones. Thus, in this case  $S_f$  i.e. fluid saturation in pore space [ $\text{L}^3\text{L}^{-3}$ ] was taken as 1 as the media fully saturated. The simulation domain was discretised in small grids of size 1 mm in a hexahedral geometry for solving the governing equation numerically. The Galerkin finite elements method integrated with Crank-Nicholson iterative scheme was used for the solution. The soil water flow and solute transport parameters listed in table 1 were used as model input parameters. The hydraulic behavior or parameters were obtained by inverse solution in HYDRUS 2D (Simunek et al., 2012).

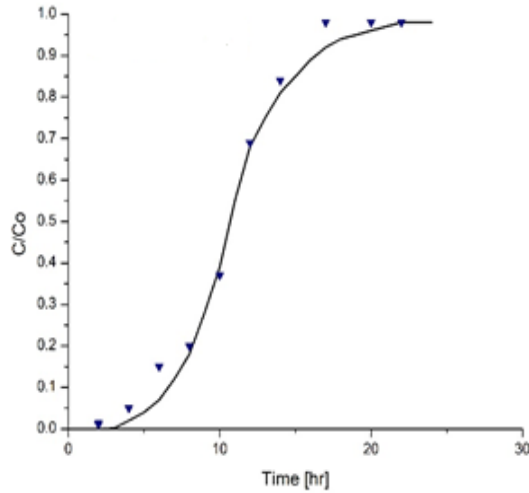
### 3.1 Initial and boundary conditions

The simulation domain was assigned no background concentration (zero) as initial solute condition. The saturated moisture content was taken as the initial moisture level of the domain and the top boundary was considered as the water table. Right side boundary (was taken as continuous flux by incorporating respective pulse of influx for 1, 2, and 4 hours to maintain groundwater table fluctuation along with base groundwater velocity. Similarly, left side boundary was taken as a pulse out-flux for the respective cases. In case of stable groundwater table condition, constant influx and out-flux was taken without pulse condition. No flux condition was considered as the lower boundary condition. A LNAPL releasing point was incorporated at same location as of two dimensional laboratory sand tank setup.

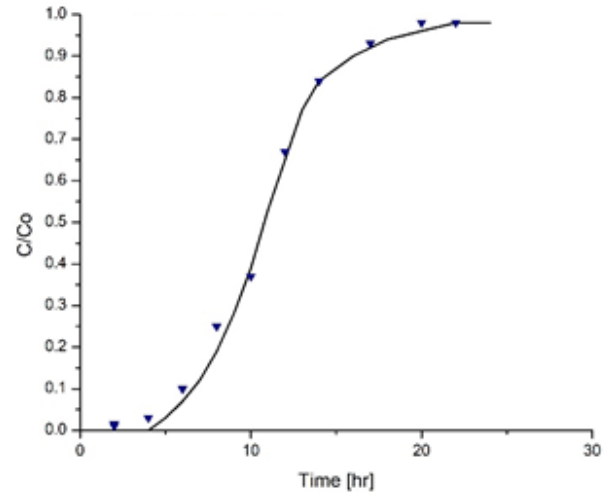
## 4. Results and Discussion

The breakthrough curves (BTCs) of tracer experiments under stable and different groundwater fluctuation cases are presented in Figure 2 for rapid, general and slow groundwater table fluctuation conditions represented as GWTF-C1, GWTF-C2, GWTF-C3, respectively. The slope of the BTCs shown in Figure 2 are of similar trend, suggesting that the sand was packed uniformly in each set of experiments without any significant preferential flow paths. The best fit values of dispersion coefficient values are 0.000246, 0.0000171, 0.0000108, 0.0000073

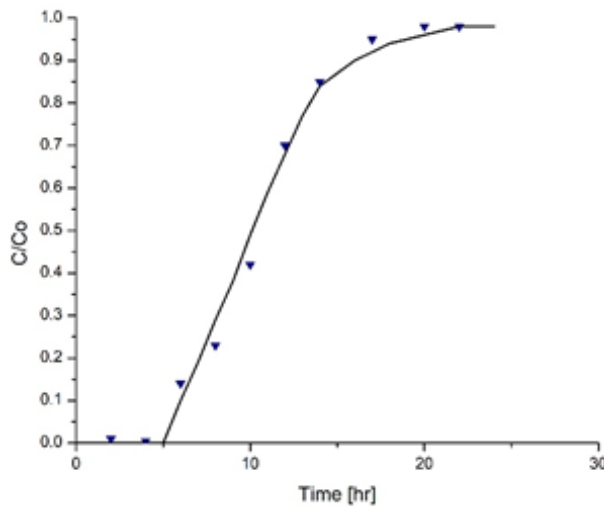
m<sup>2</sup>/s for rapid, general, slow, and stable groundwater table fluctuation conditions respectively. Similarly, estimated longitudinal dispersivity values are 1.23, 0.72, 0.28, 0.12m for rapid, general, slow, and stable groundwater table fluctuation conditions respectively. The observed values of dispersivity was used to simulate dissolved LNAPL plume in identified domain under corresponding groundwater table case.



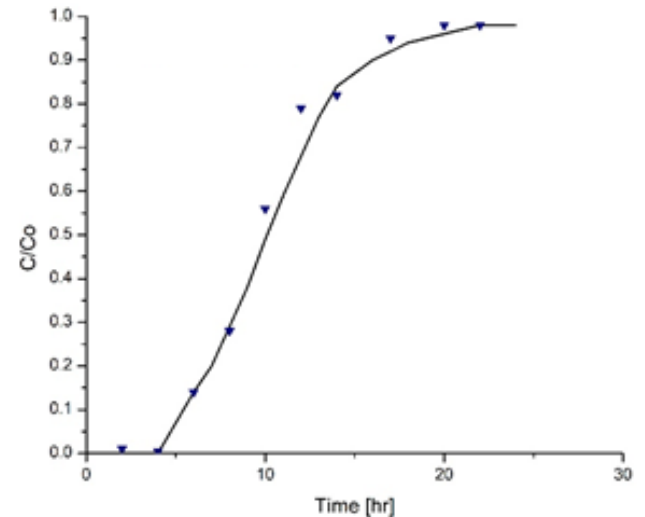
(a) GWTF-C1



(b) GWTF-C2



(c) GWTF-C3



(d) GWTF-C4

Figure 2: BTCs obtained from tracer test analysis for (a) rapid, (b) general, (c) slow and (d) stable groundwater fluctuation conditions.

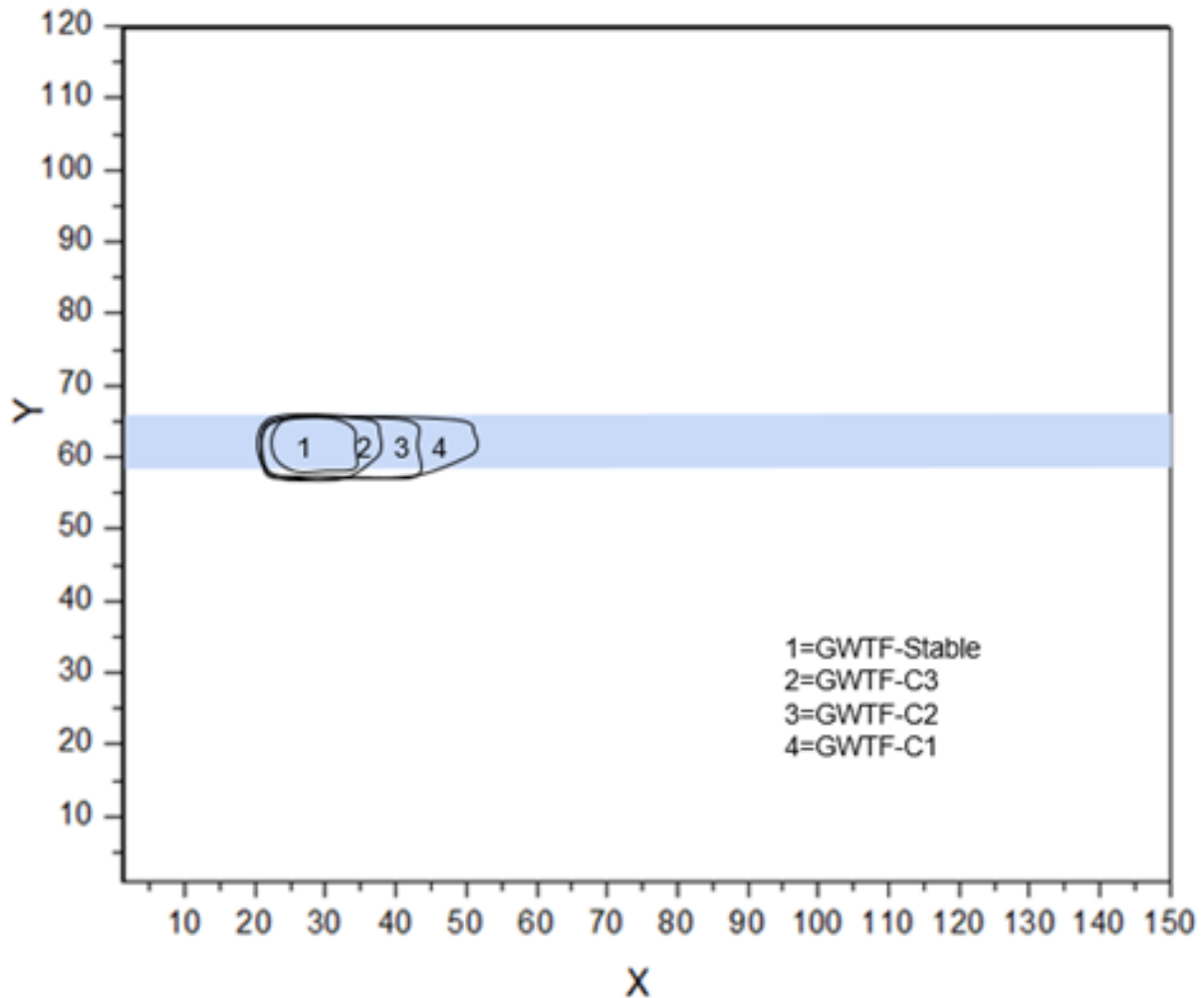


Figure 3: Coverage of the LNAPL pool in smear zone subjected to different groundwater fluctuation conditions.

#### 4.1 Pure phase LNAPL coverage and dissolution

An effort has been made to capture LNAPL pool area in two dimensional sand tank experiments under stable and fluctuating groundwater cases. For this purpose, periodically soil-water samples were analyzed by GC-MS/IRMS technique (Dempster et al. 1997). The interpreted boundary of pure phase LNAPL pool is presented in Figure 3 which shows a total area of 250, 200, 160 and 70 cm<sup>2</sup> covered under rapid, general, slow and stable groundwater fluctuation cases, respectively.

Experimentally observed area of pure phase LNAPL pool was used to determine the characteristic length of the pool and for the estimation of dissolution rate. It can be observed from the results that the rapid groundwater fluctuation causes the pure phase LNAPL pool to spread over more area than the stable groundwater case. A high groundwater velocity

due to rapid fluctuation in groundwater governs the excess spreading of LNAPL in flow directions. Spreading of pure phase LNAPL over a large area provides more dissolving surface as LNAPL-water interphase to underlying flowing groundwater resulting into more dissolution rates. Similarly, the large LNAPL pool contributes more LNAPL vapour to the overlying unsaturated zone. Further, the volume of water contacting the LNAPL pool surface increases as it spread in large area which also leads to high dissolution rates. This in turn significantly increases dissolved phase concentration load to receiving groundwater and vapor contamination to unsaturated pore air (Dobson et al. 2007; Vasudevan et al. 2014). On the other hand, large coverage of pool contributes more LNAPL mass to capillary ganglia as smaller blobs/fingering, which also play significant role in dissolution under rapid groundwater table conditions. As noted by Sarikurt et al. (2017), the contact time and area of LNAPL-water interphase is significant for dissolution rate and subsequent transport of dissolved LNAPL in subsurface. Similarly, Sulaymon and Gzar (2011) highlighted that length of LNAPL-water interphase plays important role to control the equilibrium concentration of dissolved LNAPL plume. Results of this study confirm that the groundwater table fluctuation causes more spreading of pure phase LNAPL pool itself which ultimately provide more LNAPL-water dissolving area in smear zone. High dissolution rate from large LNAPL pool contributes high concentration of dissolved LNAPL to the downgradient ports. The estimated LNAPL pool coverage area under different cases can be used to forecast dissolved LNAPL plume under dynamic groundwater flow conditions.

#### **4.2 Vapor phase concentrations**

The vapor phase LNAPL concentrations are plotted as BTC in Figure 4. The BTC shows a high LNAPL concentration in case of rapid fluctuating groundwater table followed by general, slow and stable groundwater table case. The vapor equilibrium concentration was observed as 210-230 ppm in fluctuating condition while 180-185 ppm was observed in stable groundwater case. This means a raising groundwater table carries pure phase LNAPL mass upward and a falling groundwater allows LNAPL to move downward. During dynamics of groundwater level, the trapped LNAPL remain behind in smear zone which creates a large interphase area of air-LNAPL/water (Powers et al. 1992). Therefore, more vapor phase concentration was observed from the residual LNAPL. These results are in line with the findings of study conducted by Oostrom et al. (2006) with 2D experiments under water table dynamic conditions. The study found a considerable residual LNAPL saturation in smear zone. The high vapor concentration can also be attributed to the partition of LNAPL from large dissolved phase plume having high

concentration. Further, lowering of groundwater table increases air-filled porosity in smear zone, which eventually affects vapor phase LNAPL partition. The BTC of different groundwater table fluctuation experiments confirms that the vapor intrusion is highly dependent on the nature of groundwater table conditions (Patterson and Davis, 2009). High vapor LNAPL in unsaturated pores may become toxic for the indigenous microorganisms.

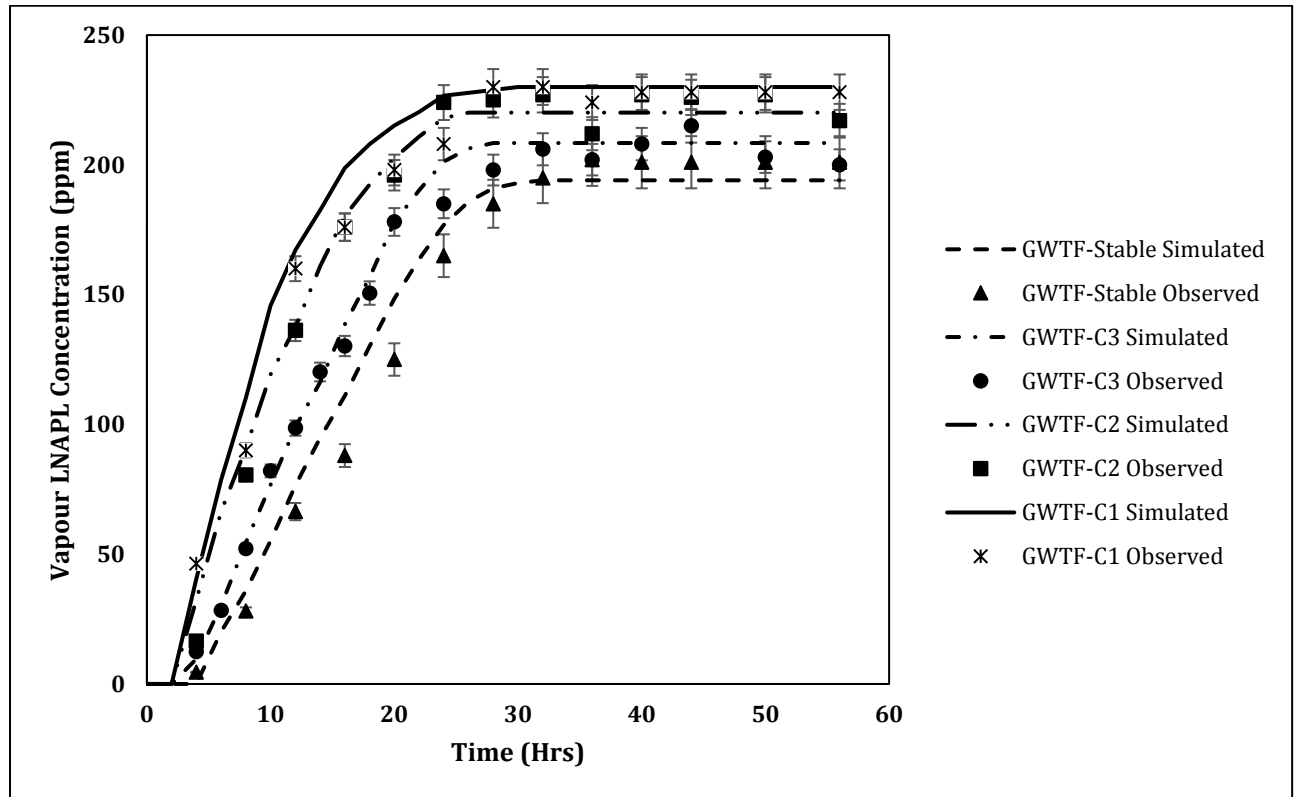


Figure 4: BTC representing LNAPL concentration in soil air in 2D sand tank under stable and fluctuation groundwater table conditions.

The measured pure phase LNAPL pool area was used to estimate its characteristic length of LNAPL pool ( $l_{(c)}$ ) under stable and fluctuating groundwater conditions. The observed values of  $l_{(c)}$  was found 15.81, 14.15, 12.64, and 8.36 cm under rapid, general, slow and stable groundwater fluctuation conditions, respectively. The estimated value of mass transfer coefficient ( $k^*$ ) are listed in Table 3. The estimated Sherwood numbers ( $Sh$ ) were found 0.95, 16.20, 16.95 and 19.30 while Peclet numbers ( $P_e$ ) were 1.80, 75.47, 80.14, and 95.06 for rapid, general, slow and stable cases respectively. A high value of  $Sh$  indicates that dissolution was a dominating process under fluctuating groundwater conditions. The reason for high  $Sh$  can be

attributed to the large pool spreading, which provides more LNAPL-water interphase under  
 fluctuating groundwater condition. Further, more contact time of underlying groundwater with  
 the large dissolving LNAPL pool also accelerate the dissolution rate. Likewise, high  $P_e$   
 indicates that the advective flow was dominant than the diffusive flow under fluctuating  
 groundwater conditions. However, one cannot ignore the importance of diffusive flux under  
 stable groundwater flow regimes. The correlation  $Sh$  with  $P_e$  is presented in Figure 5 with the  
 coefficient of determination ( $R^2$ ) value of 0.998. This kind of high correlation between  $Sh$  and  
 $P_e$  was also reported in a recent study by Sarikurt et al. (2017).

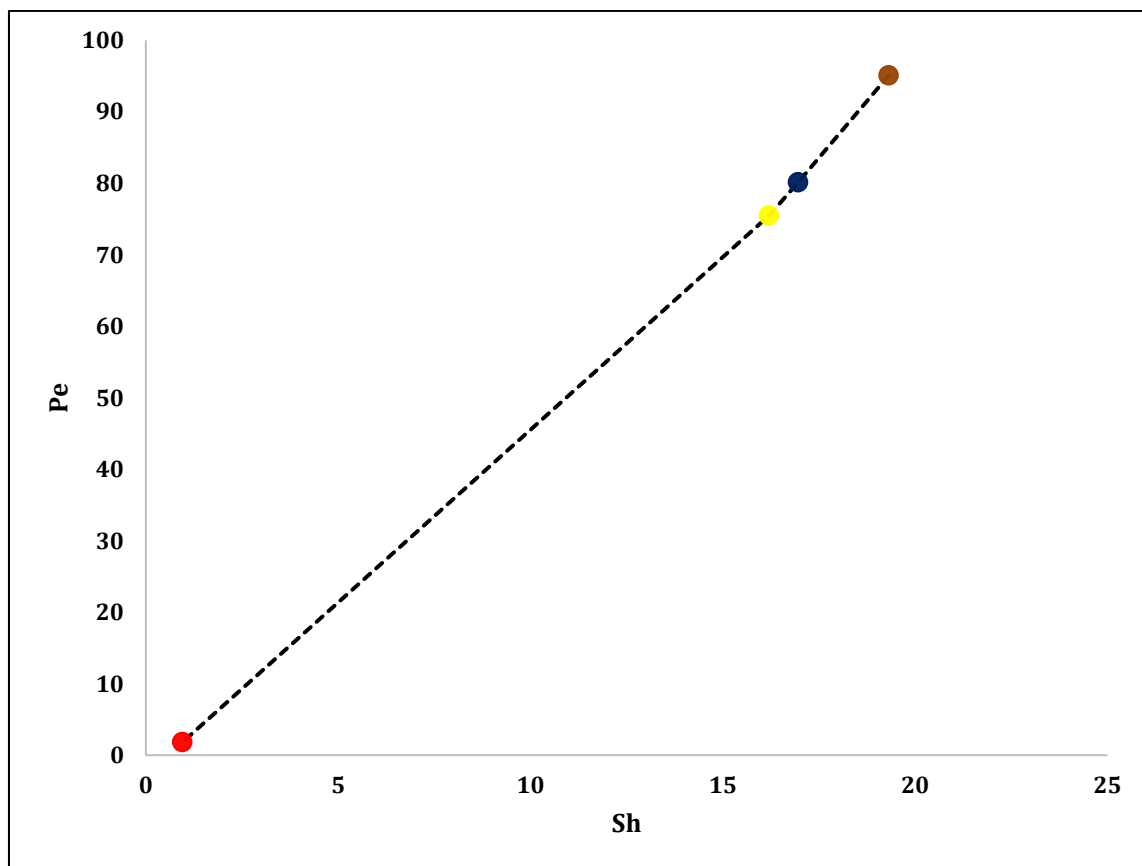


Figure 5: Correlation between  $Sh$  and  $P_e$ . Red, yellow, blue and green circle represent  
 stable, slow, general and rapid groundwater fluctuation conditions respectively.

Table 3: Estimated values of  $k^*$  and corresponding values of  $Sh$  and  $P_e$  under dynamic groundwater table conditions

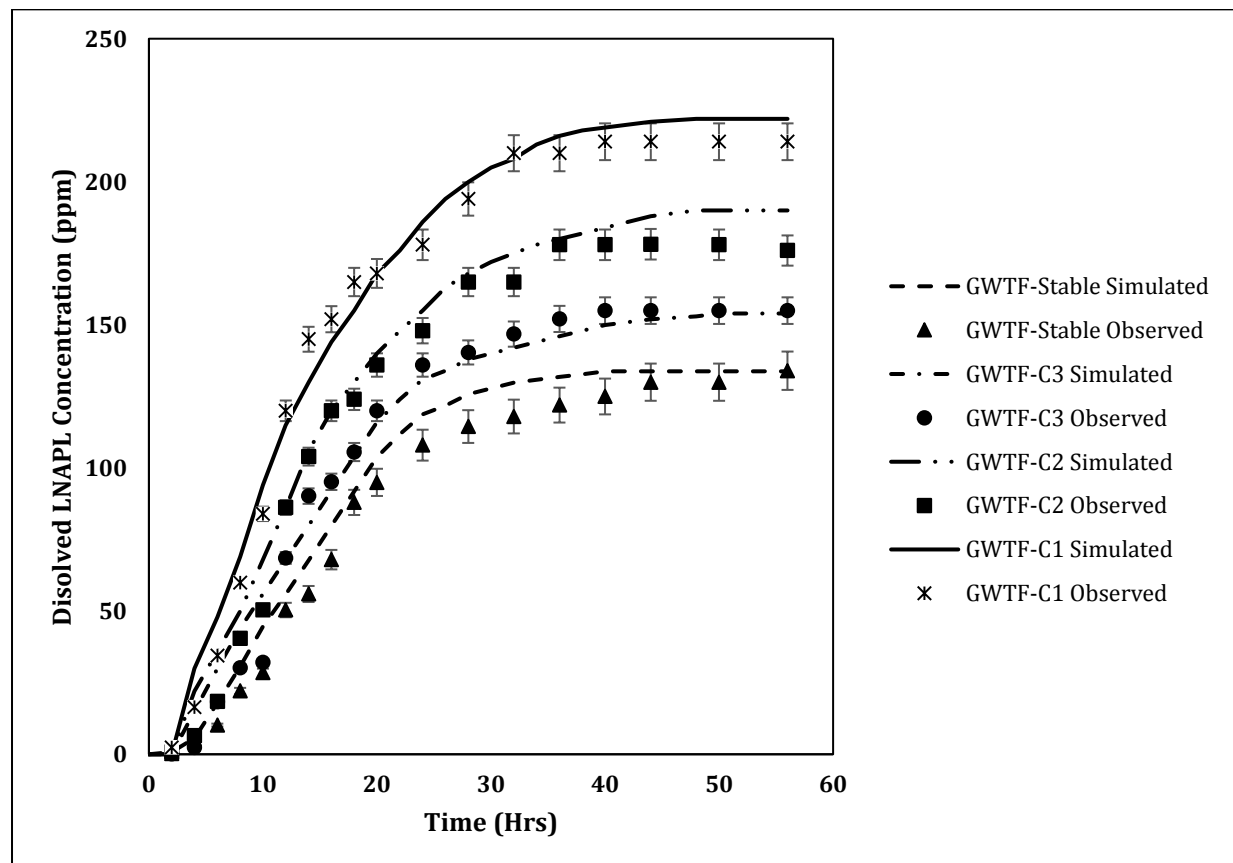
| Conditions  | Mass transfer coefficient<br>$k^*$<br>(m/s) | Sherwood Number<br>$Sh$<br>(-) | Peclet Number<br>$P_e$<br>(-) |
|-------------|---------------------------------------------|--------------------------------|-------------------------------|
| GWTF-C1     | 9.50E-02                                    | 19.30                          | 95.06                         |
| GWTF-C2     | 5.80E-03                                    | 16.95                          | 80.14                         |
| GWTF-C3     | 3.50E-03                                    | 16.20                          | 75.47                         |
| GWTF-Stable | 1.20E-04                                    | 0.95                           | 1.80                          |

### 4.3 Dissolved phase concentrations

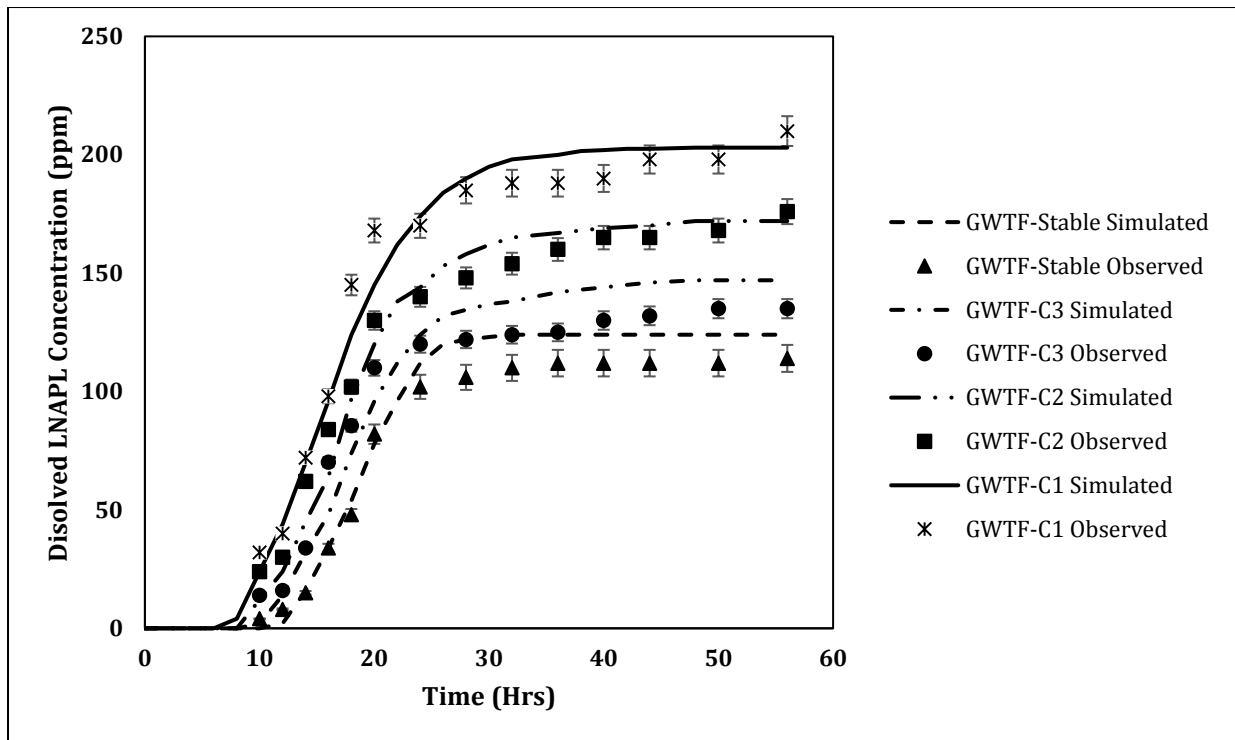
Dissolved LNAPL concentrations as a function of time for all four cases are presented in figures 6-7. In figure 6a, BTC is presented for port 1 (top sampling layer: X:25cm; Y:60 cm) which was situated just below the water table and nearby LNAPL pool. It shows that toluene concentration starts rising after few hours and increases rapidly and then starts attenuating before reaching to a concentration of 200-230 ppm for rapid fluctuating groundwater case. Similar trends were observed for the remaining fluctuating groundwater cases. The higher concentration in the rapid fluctuation case was due to more dissolving LNAPL pool area than general, followed by slow and stable fluctuation conditions. Likewise, BTCs of port 4 and port 7 of upper layer are presented in figure 6b and 6c respectively. LNAPL concentration takes 10-12 hours and 20-26 hours to reach port 4 and port 7, which was 55 cm and 115 cm away from pool respectively. However, a significant difference in the final equilibrium concentration (plateau) was observed amongst different groundwater table fluctuation cases. At this stage the supply from the source and the out flux at the observed down-gradient port (port 7) was reaching to an equilibrium condition. A decreasing trend in the equilibrium concentration was observed as plume moves from up gradient location (port 1) to down-gradient locations (Port 4/7) which represents the dependency of biodegradation rate on dissolved LNAPL concentration. In general, the equilibrium concentration of toluene in earlier studies was found quite nearby to its dissolution limit. In this study, the observed concentration of toluene was not able to reach the maximum solubility value of toluene because of (a) limited contact (water-toluene) time of opportunity, (b) the concurrent biodegradation of the dissolved LNAPL in sand tank setup. The study shows that more than 150 ppm dissolved LNAPL concentration was found to start inhibiting metabolic actions of microbes causing lower degradation rates then its

potential rate. Similarly, a concentration less than 100 ppm provides insufficient carbon sources to microbes resulting in comparatively low biodegradation rate of toluene. The optimal biodegradation rate was found in plume area having concentrations ranges from 120-150 ppm, especially under general groundwater condition. While biodegradation rate become quite slow at port 1 due to high dissolved LNAPL concentration ( $>150$  ppm) and causes toxicity to potential microbes. The biodegradation rate in upper layer was accelerated by high diffusion of oxygen from head space by fluctuating groundwater table.

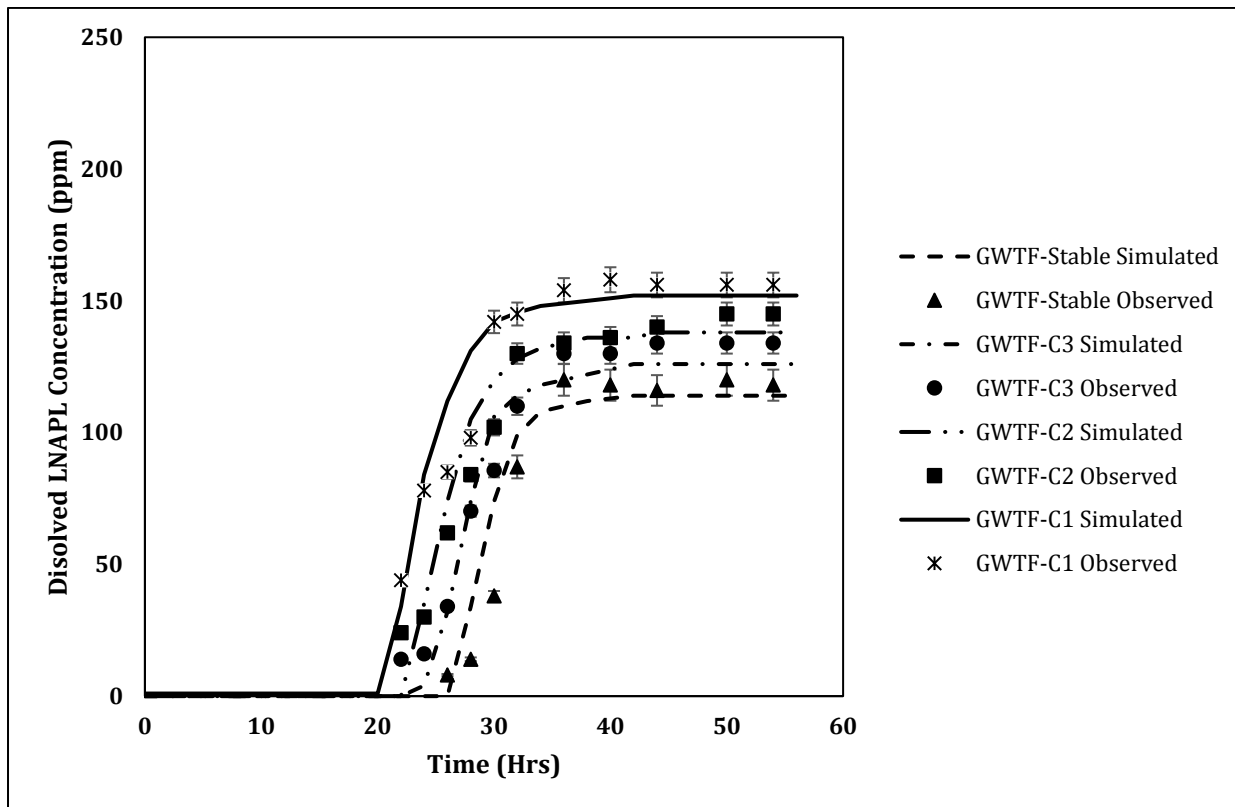
Likewise, the dissolved LNAPL concentrations are presented in figures 7a-c for ports 8, 11 and 14 situated in bottom layer. Figure 7a shows that the dissolved LNAPL plume takes 10-12 hours to reach at port 8, which is at 30 cm downward from the pool. At port 8, there is very less difference in equilibrium concentrations as compared to port 1. Whereas, a large difference was found in equilibrium concentration of port 11 (Figure 7b) and port 14 (Figure 7c) in comparison to port 8 (Figure 7a). This seems due to high biodegradation rates at port 11 as compared to port 8, even the port 11 is situated in bottom layers where background oxygen level is low.



(a) Port 1: X:25; Y60

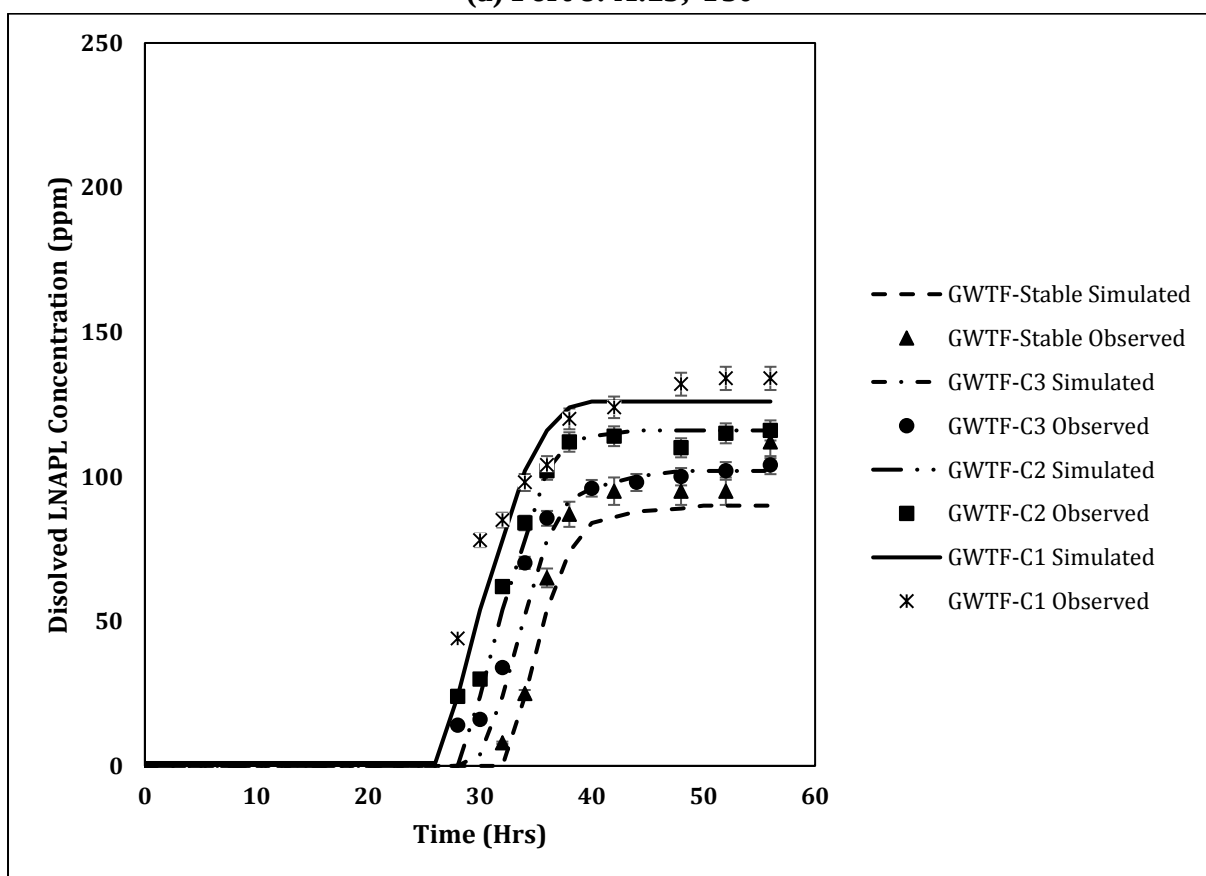
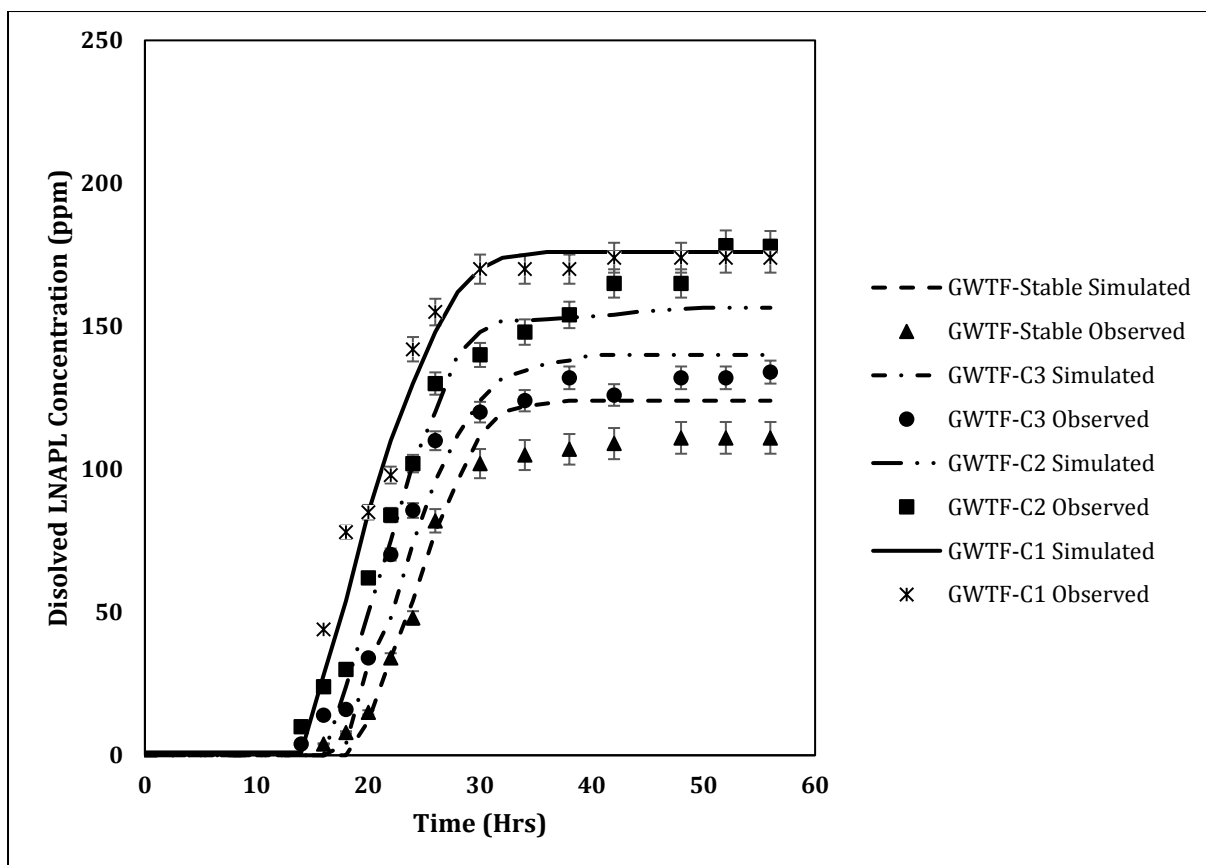


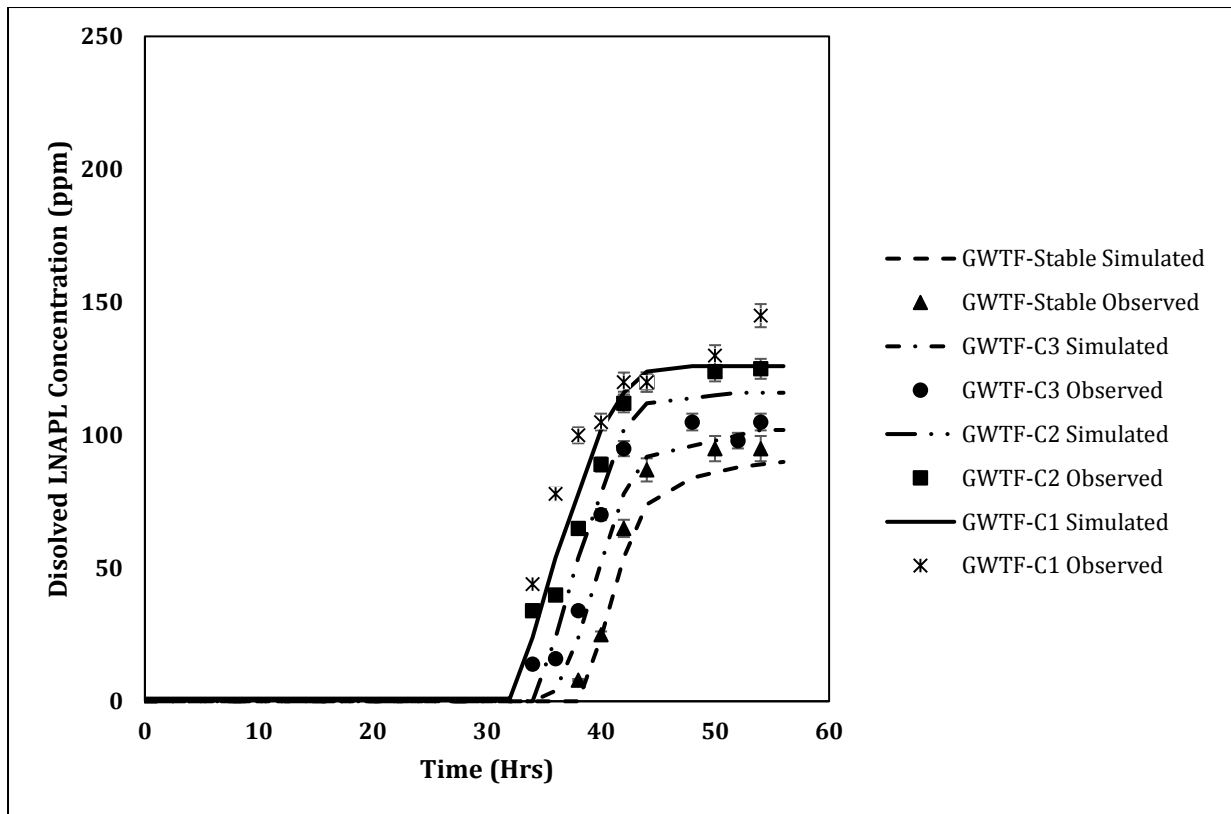
(b) Port 4: X:80; Y60



(c) Port 7: X:140; Y60

Figure 6: BTCs of (a) port 1, (b) port 4 and (c) port 7 under stable and fluctuating groundwater table conditions.





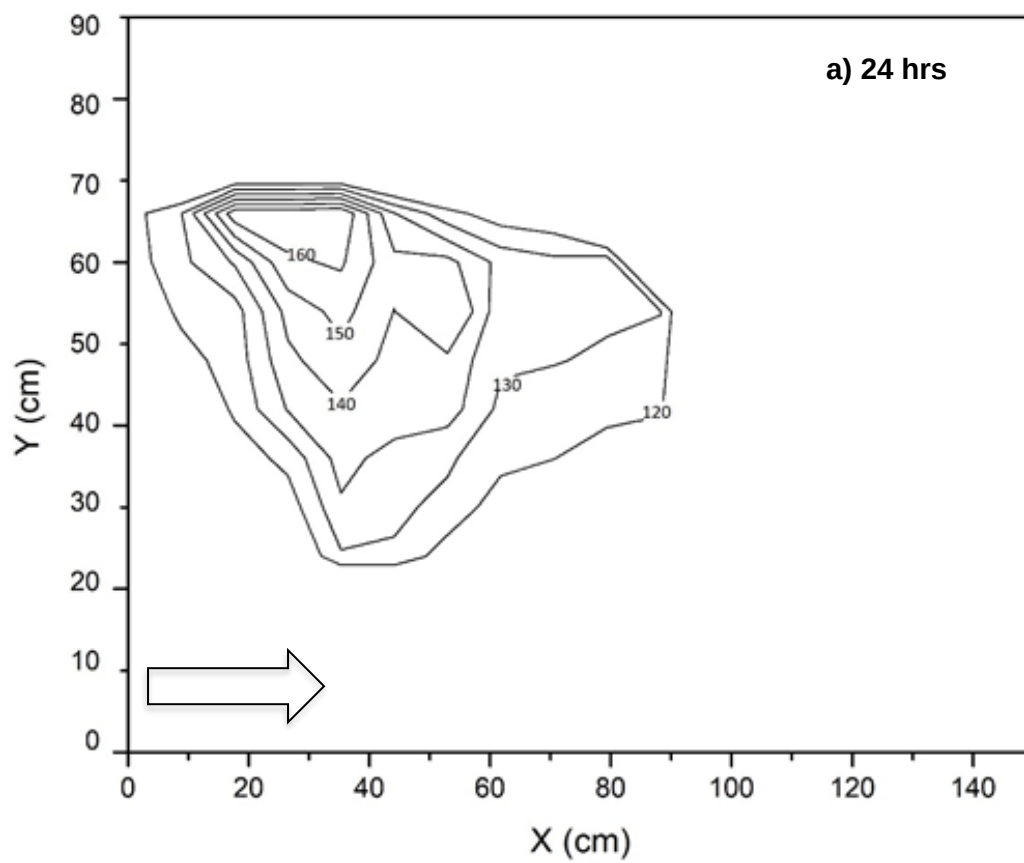
(c) Port 14: X:140; Y:30

Figure 7: BTCs of (a) port 8, (b) port 11 and (c) port 14 under stable and fluctuating groundwater table conditions.

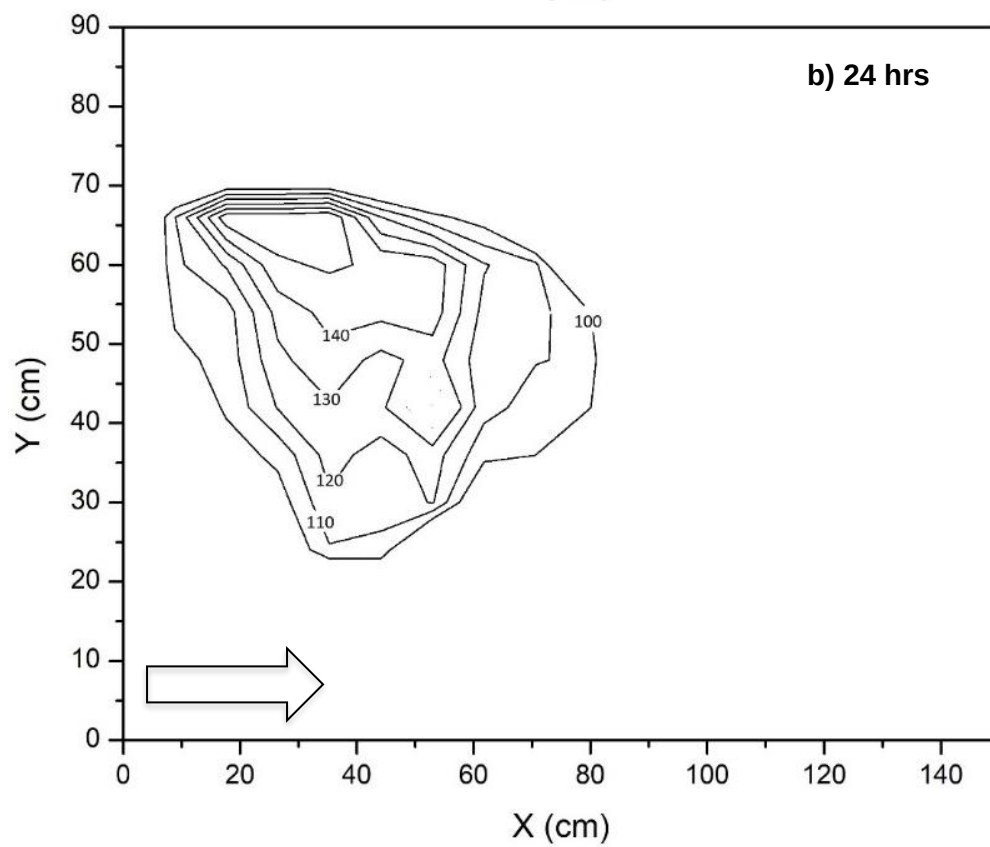
The experimentally observed dissolved LNAPL concentrations isolines are plotted as a function of space in figures 8a-d. These concentration isolines were plotted using experimentally measured data from all sampling ports (port1-14) including ports situated opposite to flow directions (port RP1-RP2). The objective of these isolines plot is to present different concentration zone originated from LNAPL pool under different selected groundwater table conditions. Figure 8a represents concentration isolines originated from large LNAPL pool having 15.81 cm under rapid groundwater table fluctuation condition. Thus, large dissolved plume was created with a concentration ranges from 120-160 ppm in initial 12 hours and later reaches up to 200 ppm nearby the pool location. A large area covered by high concentration i.e. greater than 150 ppm causes toxicity to potential microbes and thus low biodegradation rate was observed in this case. Thus, a closely spaced isolines were observed in rapid fluctuating groundwater conditions. Whereas, figure 8b represented isolines of dissolved plume originated from a pure phase LNAPL pool of characteristic length of 14.15 cm under general groundwater table fluctuation condition. In this case, the dissolved plume

concentration ranges 110 ppm-140 ppm in initial 12 hours and continuously increases upto 160 ppm. Less concentration (20ppm) of dissolved plume under general groundwater table fluctuation condition was due to smaller LNAPL pool length then the rapid case. Thus, in general groundwater table fluctuation case, a large area covered by 130-150ppm concentration LNAPL plume become carbon source to potential microbes and causes enhanced biodegradation rates. Similar trends were observed in case of slow groundwater table fluctuation condition as presented in figure 8c. While, comparatively small dissolved LNAPL plume (figure 8d) having less concentration (i.e. range of 70 ppm-100 ppm in initial 12 hours and 80-120 ppm in 56 hours) was observed in case of stable groundwater case.

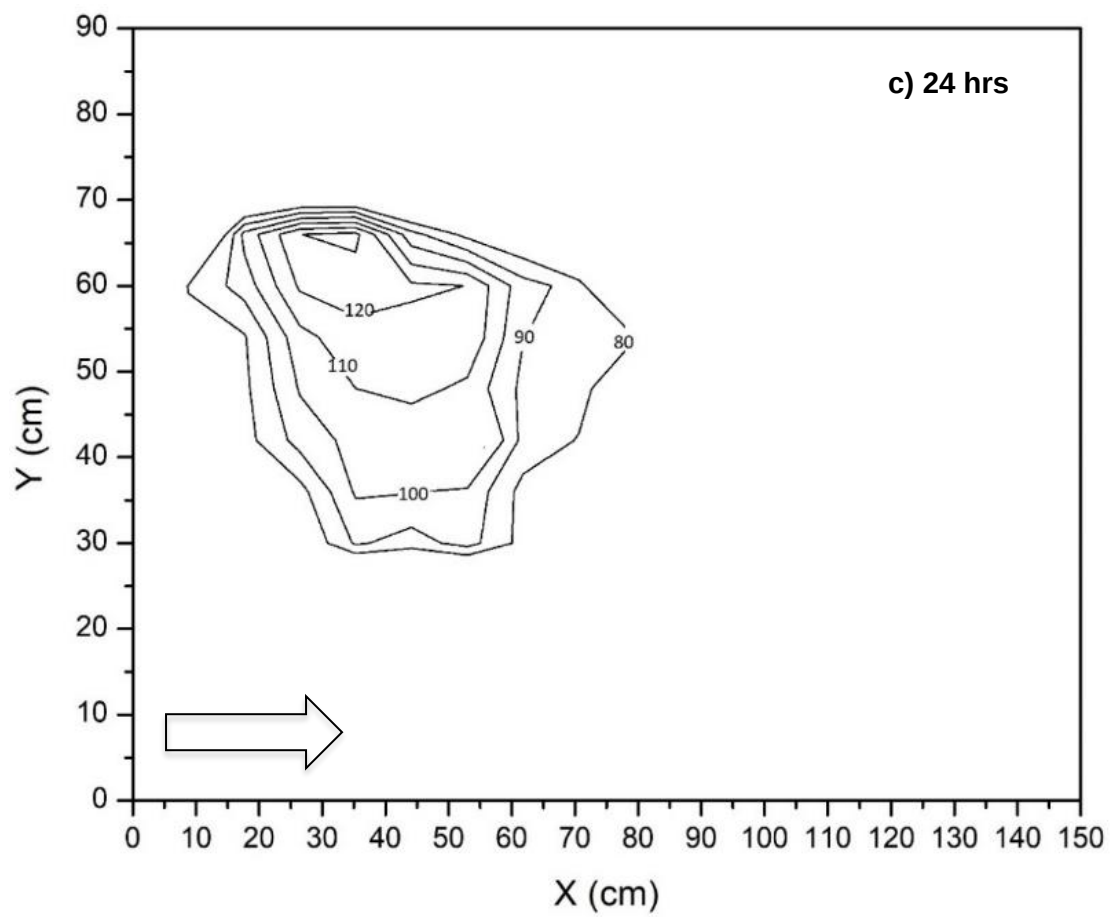
In this study, the concentration isolines clearly show the fast transport of dissolved plume in horizontal direction than its transverse movement under stable and fluctuating groundwater conditions. The horizontal spreading of plume was due to advection dominated flow of the dissolved toluene originating from large contact area between LNAPL pool and water. Dissolved LNAPL plume movement in opposite direction of groundwater flow driven by diffusive flux is comparative very slow. Whereas, the expansion of dissolved LNAPL plume in the vertical direction under fluctuating groundwater shows the crucial role of dispersive flux. The diffusive flux of the dissolved LNAPL can play a crucial role in LNAPL movement under stable groundwater regimes.



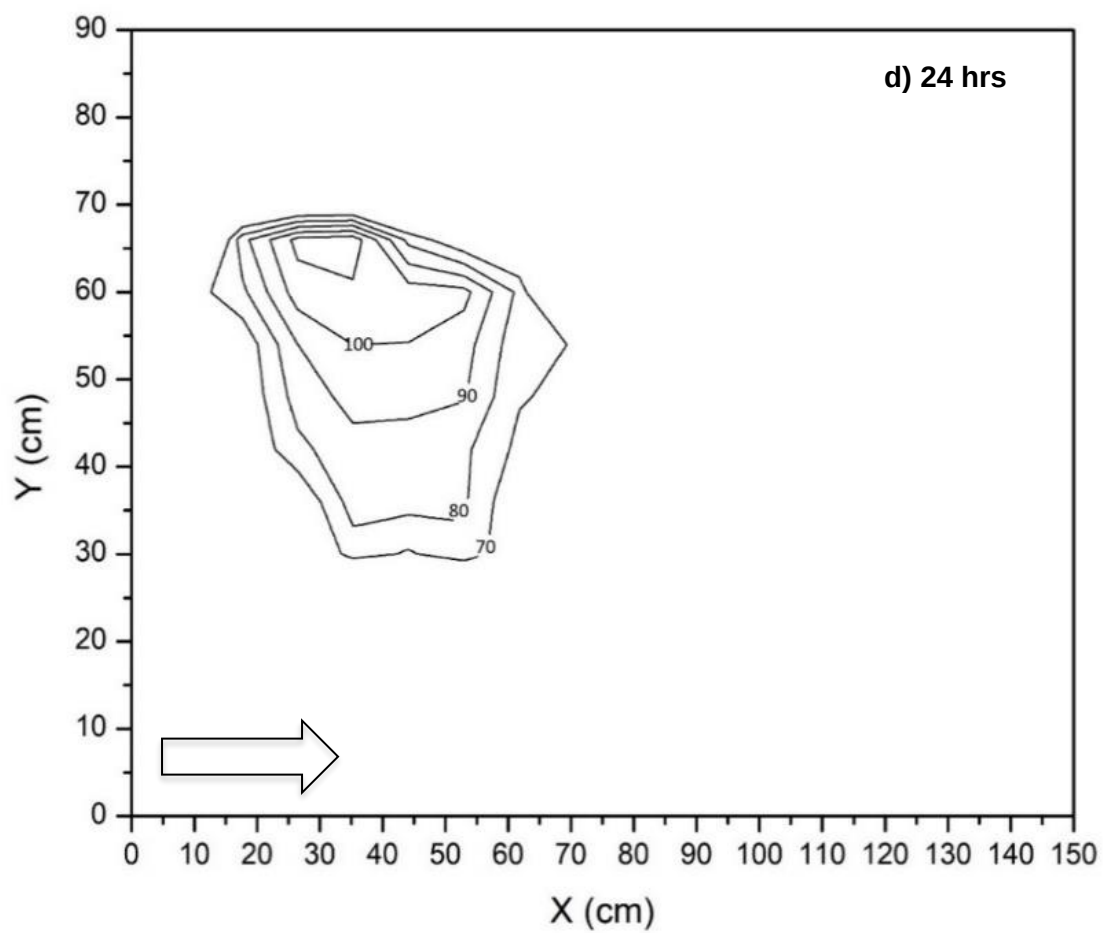
493



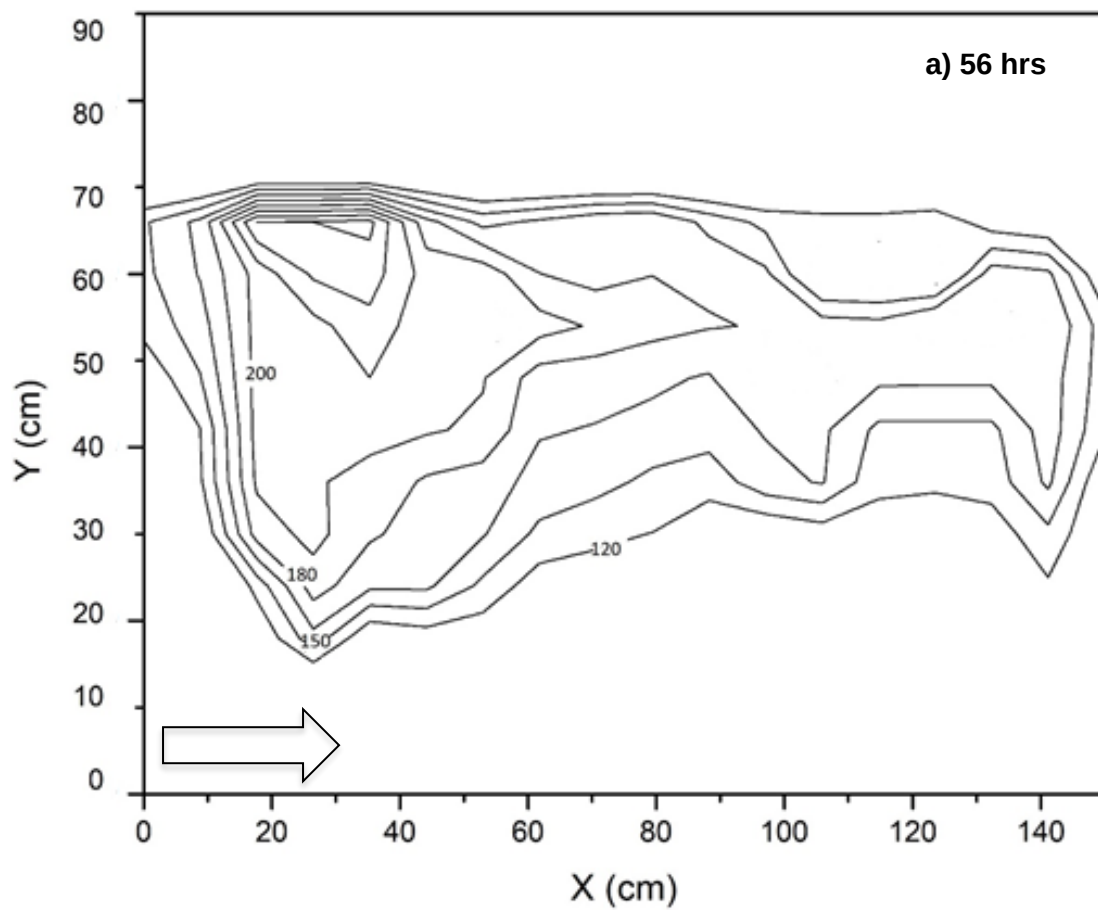
494



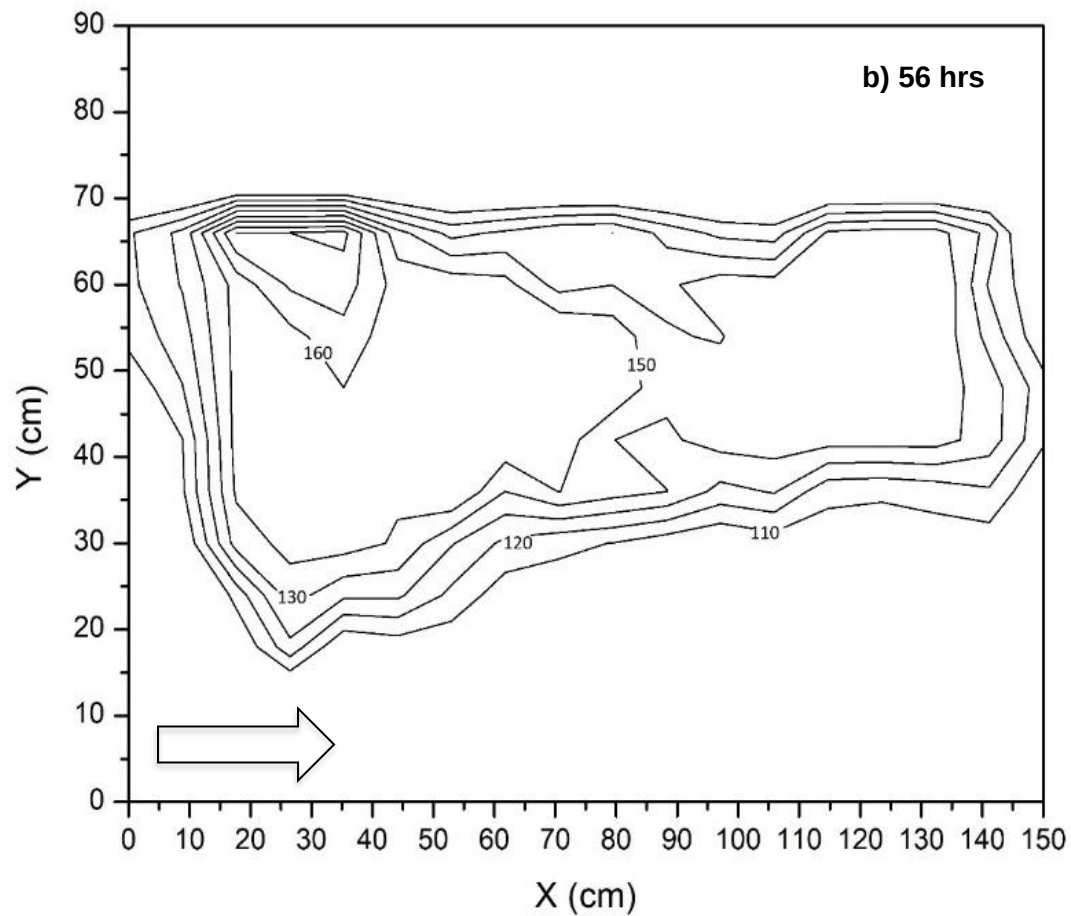
495



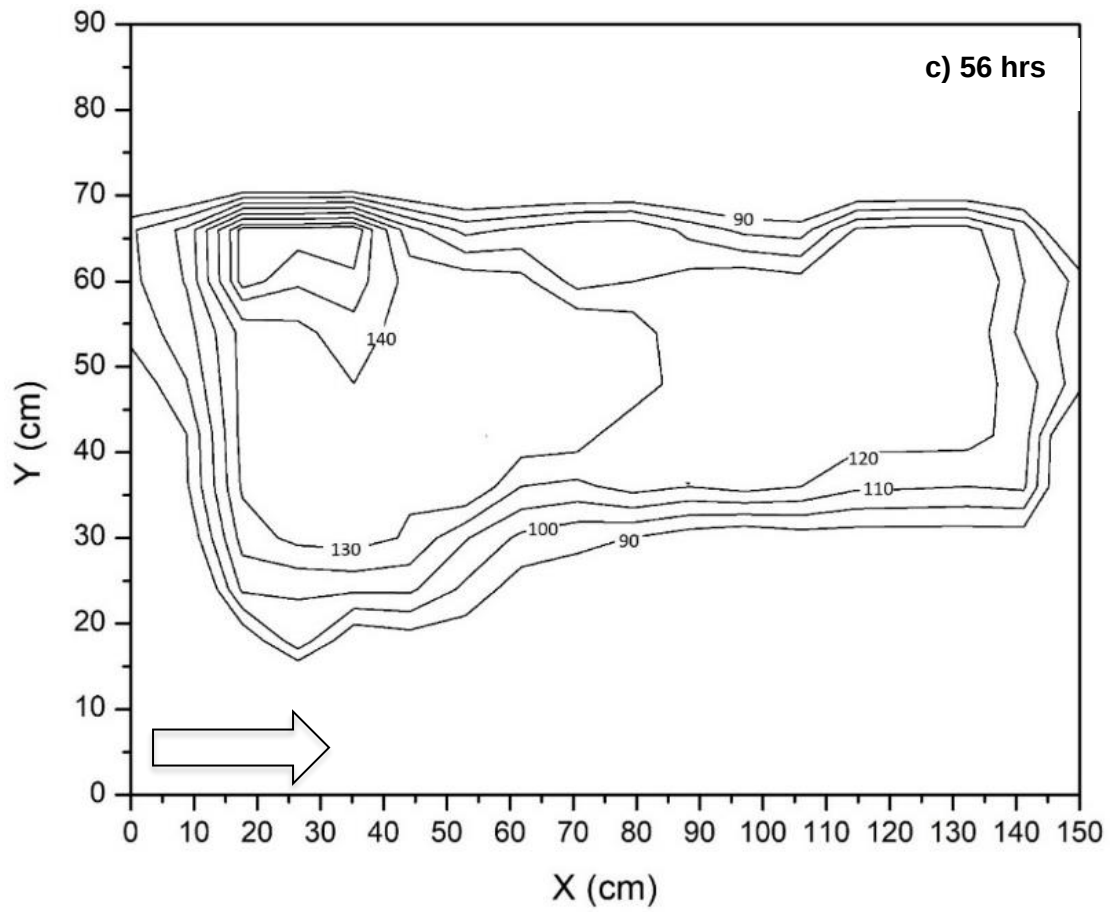
496



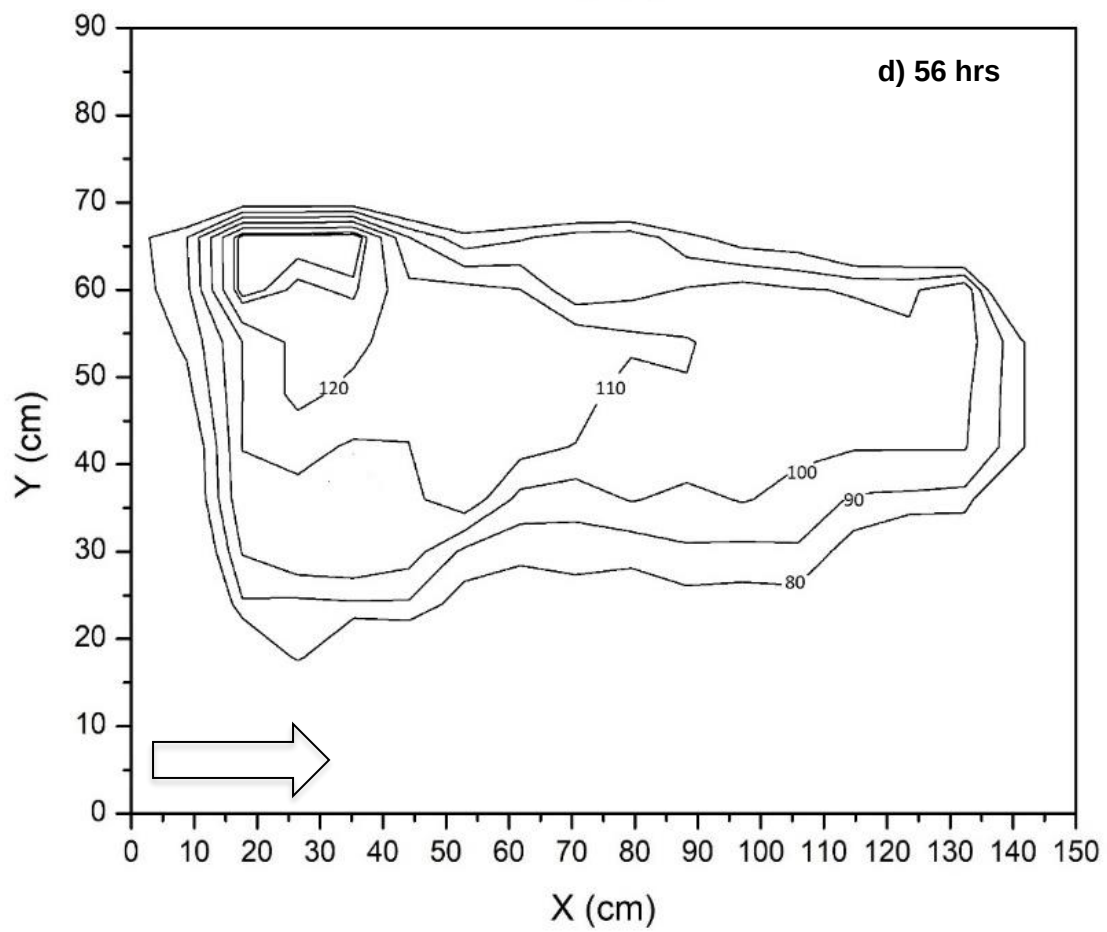
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Figure 8: Concentration isolines presenting the extension of dissolved LNAPL plume originated from pure phase source under a) rapid, b) general, c) slow and d) stable groundwater table fluctuation cases.

#### 4.4 Biodegradation under different groundwater table fluctuation conditions

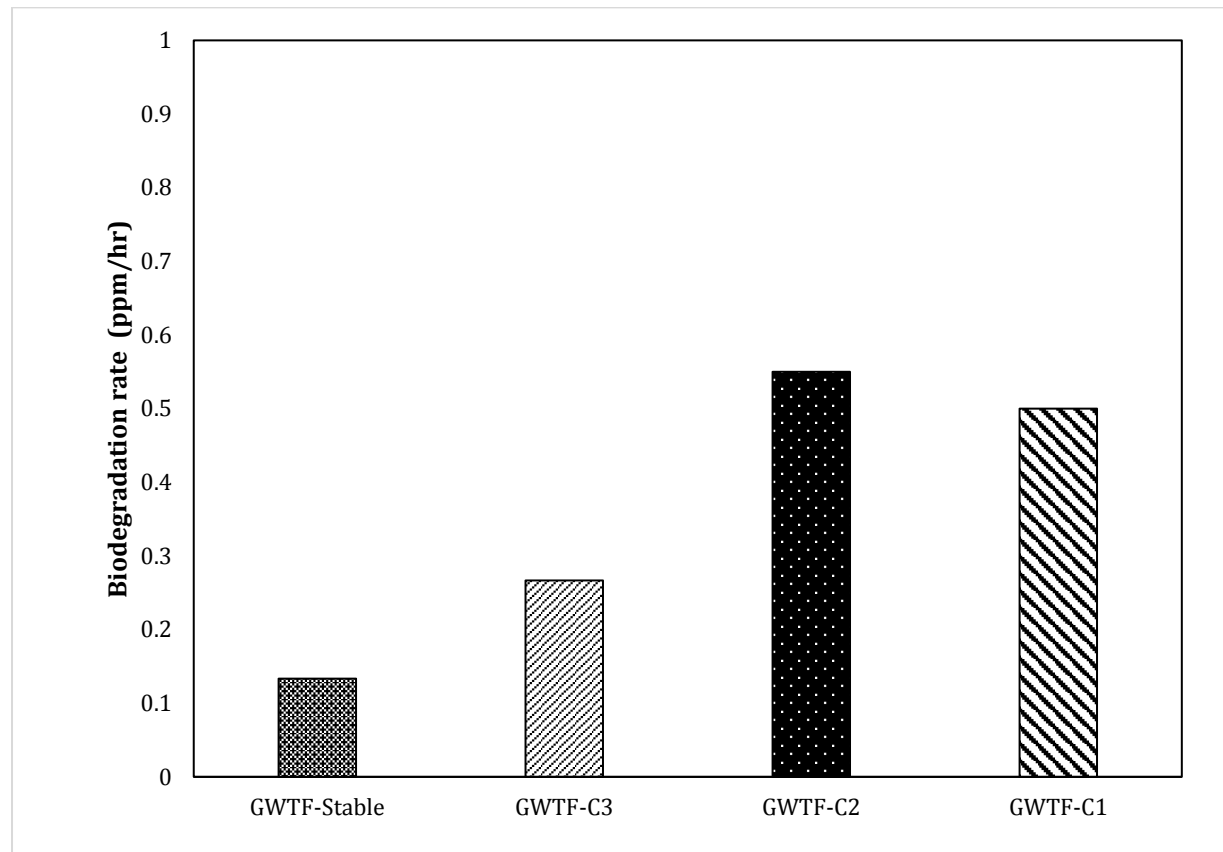
Biodegradation rate of dissolved LNAPL plume originated from pooled LNAPL under stable and fluctuating groundwater conditions was also investigated. For this purpose, spatial biodegradation rates were estimated for port 1 and port 4 of upper sampling layer and port 8 and 14 of lower sampling layer. In Figure 9, the biodegradation rates were estimated using corresponding values of equilibrium concentration of upward port and subsequent downward port. Figure 9a presents biodegradation rate of port 4 situated 55 cm away from LNAPL pool. At this location, biodegradation rates of 0.5 ppm/hour, 0.55 ppm/hour, 0.26 ppm/hour, and 0.13 ppm/hour were observed for dissolved LNAPL zone with the concentration of 180 ppm, 150 ppm, 120 ppm, and 100 ppm under rapid, general, slow and stable groundwater table condition, respectively.

The biodegradation rate was found comparatively low in case of rapid fluctuation than general fluctuation because of large high concentration (>150 ppm) region which causes toxic effects on potential microbes lies in this region. While, the high biodegradation rate in case of general than slow and stable groundwater fluctuation conditions proves the dependency of microbes on dissolved LNAPL concentrations. Figure 9b represents biodegradation rates for port 7 of upper layer having dissolved LNAPL concentration in the range of 100 ppm-150 ppm. Similarly, Figure 9c and 9d shows the biodegradation rates for port 8 and port 14 of lower layer respectively. Comparatively low biodegradation rates were observed in lower layer ports under stable groundwater conditions, even if the dissolved LNAPL concentration was in the optimum range of 100 ppm-150 ppm. These low biodegradation rate at lower ports was due to comparatively less populated potential microbes due to low oxygen level. While, the biodegradation rates were also increases at lower port in case of fluctuating groundwater conditions. These accelerated biodegradation rate can attribute to the fact that the additional oxygen to background level was added due to fluctuation in water table, which enhance the microbial growth.

Microbial population was also counted using standard plate count method for periodically collected soil-water samples from port 1 and port 7 of upper layer and port 8 and port 14 of lower layer. The estimated CFU of collected soil-water samples were listed in table 4. Initially, microbial count of  $216.2\text{--}258 \times 10^4$  CFU/mL and  $142.5\text{--}147.2 \times 10^4$  CFU/mL was

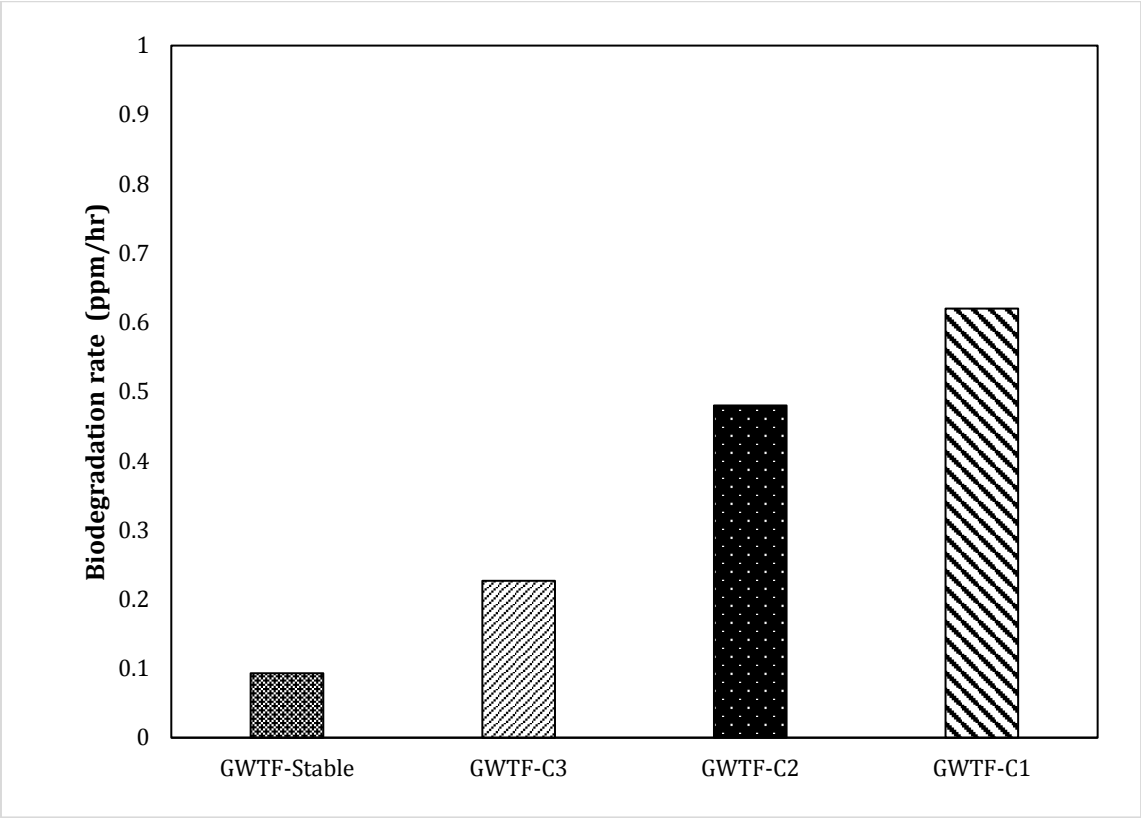
observed at upper and lower layer respectively. In GWTF-C1 case, the microbial count at port 1 increases upto  $305 \times 10^4$  CFU/mL in 24 hours and then decreases to  $78 \times 10^4$  CFU/mL in 56 hours. Similarly, at port 7, overgrowth was recorded after 24 hours thereafter decreases to  $224 \times 10^4$  CFU/mL in 56 hours.

The enhanced microbial growth was observed as dissolved LNAPL concentration reached around 140-150 ppm at this location which provides sufficient carbon source to microbes. However, when the dissolved LNAPL concentration reaches higher than 150 ppm, it become toxic to microbial community. Increasing microbial count was recorded at both port of top layer due to optimum dissolved LNAPL concentration and sufficient oxygen level in general and slow groundwater fluctuation. Microbial count was recorded very low at port 14 of lower layer due to low concentration of dissolved LNAPL and insufficient oxygen level under all groundwater table conditions. Growing population of the microbial community at petroleum hydrocarbon-contaminated groundwater observed due to seasonal groundwater level fluctuations by Zhou et al. (2015). Such microbial analysis may help to implement nutrient and or electron acceptor plan to enhance petrochemical degrading microbes.



(a)

554

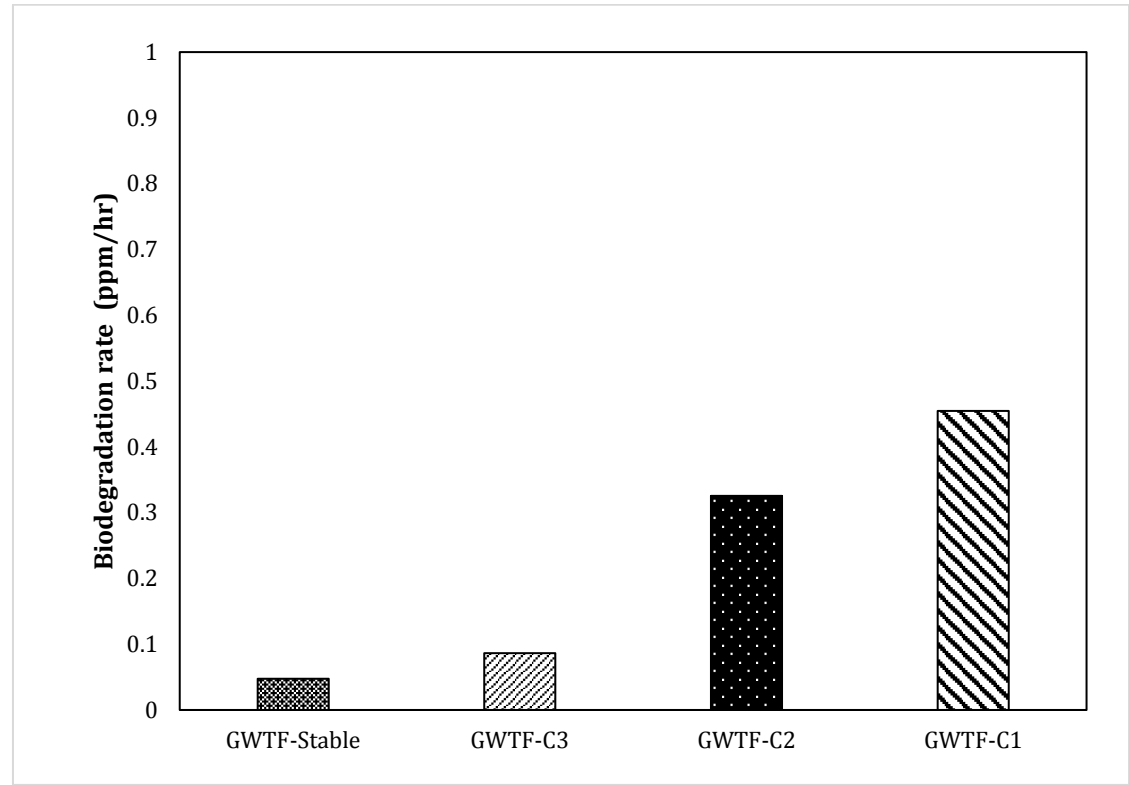


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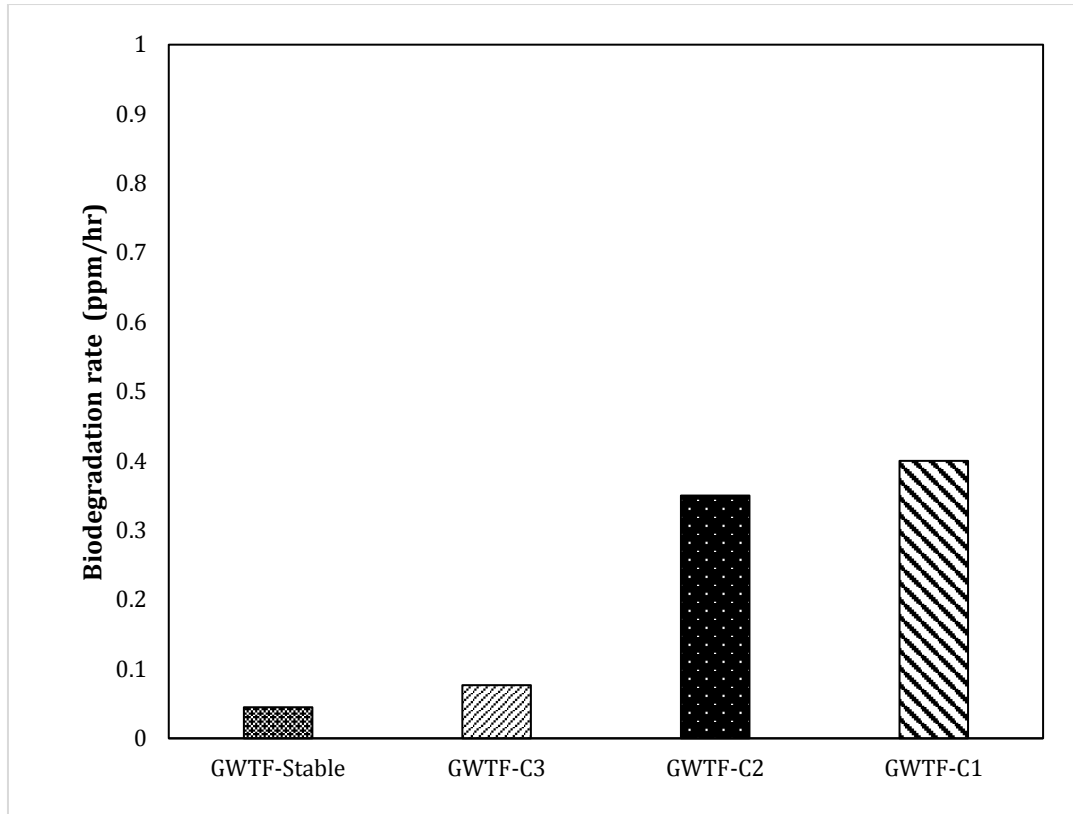
(b)



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(c)



(d)

Figure 9: Biodegradation rates under stable and fluctuating groundwater conditions observed at (a) port 1 and (b) port 7 of upper sampling layer and (c) port 8 and (d) port 14 of bottom sampling layer of 2D sand tank setup.

Table 4. Microbial population count of samples collected from the experimental setup under different groundwater table conditions.

| Condition | Port 1                 |       |       | Port 7                 |       |       | Port 8                 |       |       | Port 14                |       |       |
|-----------|------------------------|-------|-------|------------------------|-------|-------|------------------------|-------|-------|------------------------|-------|-------|
|           | 10 <sup>4</sup> CFU/mL |       |       | 10 <sup>4</sup> CFU/mL |       |       | 10 <sup>4</sup> CFU/mL |       |       | 10 <sup>4</sup> CFU/mL |       |       |
|           | 0hr                    | 24hr  | 48hr  | 0hr                    | 24hr  | 48hr  | 0hr                    | 24hr  | 48hr  | 0hr                    | 24hr  | 48hr  |
| GWTF-C1   | 254.5                  | 305   | 78    | 258.0                  | O     | 224.5 | 147.2                  | 165   | 135.4 | 142.5                  | 145.8 | 165   |
| GWTF-C2   | 232.1                  | 294.8 | 304.6 | -                      | 285.0 | O     | 145                    | 174.2 | 235.0 | -                      | 164.5 | 218   |
| GWTF-C3   | 216.2                  | 285.4 | 277.5 | 224.5                  | 288.0 | O     | 144.5                  | 210.5 | 270.6 | -                      | 164.2 | 235.6 |

O= Overgrowth

## 5. Conclusion

In this study, a series of laboratory experiments and numerical modelling was performed to investigate fate and transport of LNAPL originated from pure phase LNAPL pool under stable and fluctuating groundwater conditions. Three different groundwater fluctuating experiments representing rapid, general and slow groundwater table fluctuation scenarios were conducted by raising/falling water table by 5cm of magnitude in 1, 2, and 4 hours respectively. Estimated pool area shows a large pure phase LNAPL pool in smear zone under fluctuating groundwater conditions, resulting in accelerating dissolution rate from large LNAPL-water interphase area. Simulated and observed BTCs show high dissolved LNAPL concentration and large plume originated from large LNAPL-water interphase area under rapid groundwater fluctuation condition. The time of arrival of plume shows that transport of dissolved LNAPL was comparatively more in case of rapid fluctuating groundwater condition. A high biodegradation rate was observed in regions having concentration ranges from 140-160 ppm of dissolved LNAPL. While, low biodegradation rates were observed for low dissolved LNAPL concentrations (<140 ppm) and also high concentrations (>160ppm) which fortifies the dependency on initial dissolved LNAPL concentrations. Further, microbial growth was found to be increasing as plume moves away from the LNAPL pool, which shows detrimental impact of high concentration of toluene on survival of indigenous microorganisms. Overall, this study suggest that groundwater table fluctuations significantly affects the distribution, transport, and biodegradation of the LNAPL contaminants in subsurface. The results of this study may be improved by considering subsurface heterogeneity and fractures. This study may help in design, establishment and implementation of bioremediation techniques to decontaminate LNAPL polluted sites, especially under varying subsurface conditions.

## Acknowledgment

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## **Assessment of LNAPL in subsurface under fluctuating groundwater table using 2D sand tank experiments**

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