

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

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## 16 17 **Abstract**

18  
19 The focus of this study was to investigate fate and transport of toluene, a light non-aqueous  
20 phase liquids (LNAPL), in subsurface under dynamic groundwater table conditions. A series  
21 of experiments were conducted using two-dimensional (2-D) sand tank setup having the  
22 dimension of 125cm L×90cm H×10cm W and integrated with an auxiliary column of inner  
23 diameter 14 cm and height 120 cm. In the beginning a steady state flow and LNAPL transport  
24 experiment was conducted under stable groundwater table condition. Thereafter, three  
25 groundwater table fluctuation experiments were conducted by rising and falling  
26 groundwater table in 2, 4 and 8 hours to maintain a rapid, general, and slow fluctuation  
27 conditions respectively. Pure phase of toluene was injected at the rate of 1mL/minute for  
28 a total duration of 5 minutes. The soil-water and soil vapor samples were periodically  
29 collected and analyzed for toluene concentrations. Later, the representation of 2-D sand  
30 tank setup was numerically simulated to get the response of flow and the LNAPL transport  
31 under varying groundwater table conditions. The analysis of the results show that a large  
32 LNAPL pool area (250 cm<sup>2</sup>) gets developed under rapid fluctuating groundwater condition  
33 which significantly enhances the dissolution rate and contributes for a high concentration of

34 dissolved LNAPL to the receiving receptors. The mass transfer coefficient value of  $9.50E-02$ ;  
35  $5.80E-03$ ;  $3.50E-03$ ;  $1.20E-04$  m/s was estimated for rapid, general, slow and stable  
36 groundwater table conditions, respectively. Furthermore, the estimated Sherwood numbers ( $Sh$ )  
37 were found 0.95, 16.20, 16.95 and 19.30 while Peclet numbers ( $Pe$ ) were 1.80, 75.47,  
38 80.14, and 95.06 for rapid, general, slow and stable cases respectively. This shows that the  
39 dissolution is highly affected by groundwater table which may cause loss of pollutant mass as  
40 a dissolved phase. However, the transport of dissolved LNAPL plume is comparatively fast in  
41 case of rapid fluctuating groundwater, resulting in closely space concentration isolines of  
42 toluene containing plume. A high biodegradation rate is observed in plume regions having  
43 concentration ranges from 140-160 ppm, while it decreases in the plume regions having high  
44 concentrations ( $>160$  ppm) and low concentrations ( $<140$ ppm) in these cases. In sand tank,  
45 the microbial growth was found to be increasing as plume moves away from the LNAPL pool  
46 towards low-gradient, which fortifies detrimental impact of toluene on survival of indigenous  
47 microorganisms near the LNAPL pool. The results of this study may help in implementing  
48 effective remediation technique to decontaminate LNAPL polluted sites under fluctuating  
49 groundwater table conditions, especially in (semi)-arid coastal aquifers.

50

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

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## 54 **1. Introduction**

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

67 sufficient dissolving area to the underlying groundwater in smear zone which starts dissolving  
68 with flowing groundwater and create a dissolved phase plume (Lee and Chrysikopoulos, 1998;  
69 Kim and Chrysikopoulos, 1999; Nema and Gupta, 2003; Oostrom et al. 2006; 2007). Molecular  
70 diffusion and mechanical dispersion along with advective flux cause spreading of dissolved  
71 plume to downgradient receiving locations (Das, 2002; Yadav and Hassanizadeh, 2011; Picone  
72 et al. 2013). On the other hand, native potential microbes play significant role to degrade the  
73 dissolved LNAPL from polluted zone (Yadav et al. 2013; Basu et al. 2015, Mustapha et al.  
74 2018).

75 Groundwater flow regimes play a significant role in the dissolution of pure phase  
76 LNAPL pool and its movement to the surrounding locations (Das and Nassehi, 2003; Dobson  
77 et al. 2007; Sulaymon and Gzar, 2011, Kamaruddin et al. 2011; Yadav et al. 2012). Dynamic  
78 nature of groundwater table causes significant spreading of pooled LNAPL in smear zone,  
79 which considerably increases the LNAPL-water interphase area and resulted in accelerated  
80 dissolution (Mobile et al. 2012; Vasudevan et al. 2014). Variations in groundwater table not  
81 only causes changes in the soil-water system, but also impacts the LNAPL pool behavior, if it  
82 is present on the water table and in the underlying saturated zone. The LNAPL lying on the top  
83 of the groundwater table moves down with it when the water table lowers and leave a trail of  
84 LNAPL in the unsaturated zone in the form of isolated ganglia. Subsequently when the  
85 groundwater table rises, the LNAPL pool also moves upward leaving behind a trapped amount  
86 of LNAPL in the form of disconnected blobs in the saturated zone (Lenhard et al. 2004;  
87 Kechavarzi et al. 2005). A part of the residual LNAPL in unsaturated zone gets mobilized again  
88 when the groundwater table rises. Thus, a dynamic groundwater table accelerates the  
89 dissolution of pure phase LNAPL resulting in high concentration of LNAPL plume (Legout et  
90 al. 2009). The dissolved LNAPL plume then moves along with groundwater and forms a  
91 polluted zone which features with varying concentration levels (Neale et al. 2000; Rolle et al.  
92 2009; Zhang et al. 2014; Zhou et al. 2015; Sarikurt et al. 2017).

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

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

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## 111 **2. Materials and Methods**

112 In this study, the behavior of pooled pure phase LNAPL and its dissolved plume in subsurface  
113 under stable and fluctuating groundwater table conditions is investigated using a series of two-  
114 dimensional laboratory experiments and numerical modelling. The preliminary experiments  
115 were conducted to characterize the flow and transport parameters of the developed  
116 subsurface soil-water system. Mechanical sieve analysis was performed to find the  
117 particle size distribution of the sand which is listed in Table 1 along with other physical  
118 parameters. The porosity of sand packing was determined using oven dry and volumetric  
119 methods. Further, the hydraulic conductivity of the system was estimated using a constant  
120 head permeameter. To see the behavior of the pooled LNAPL and dissolved phase plume, a  
121 series of two dimensional sand tank experiments were performed by considering varying  
122 groundwater table conditions. A two dimensional sand tank setup filled with homogenous sand  
123 was used to conduct the laboratory experiment under (1) steady-state groundwater condition  
124 and (2) three different dynamic groundwater table fluctuation conditions, separately. Lastly,  
125 the soil-water system was numerically simulated using HYDRUS 2D model considering the  
126 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**

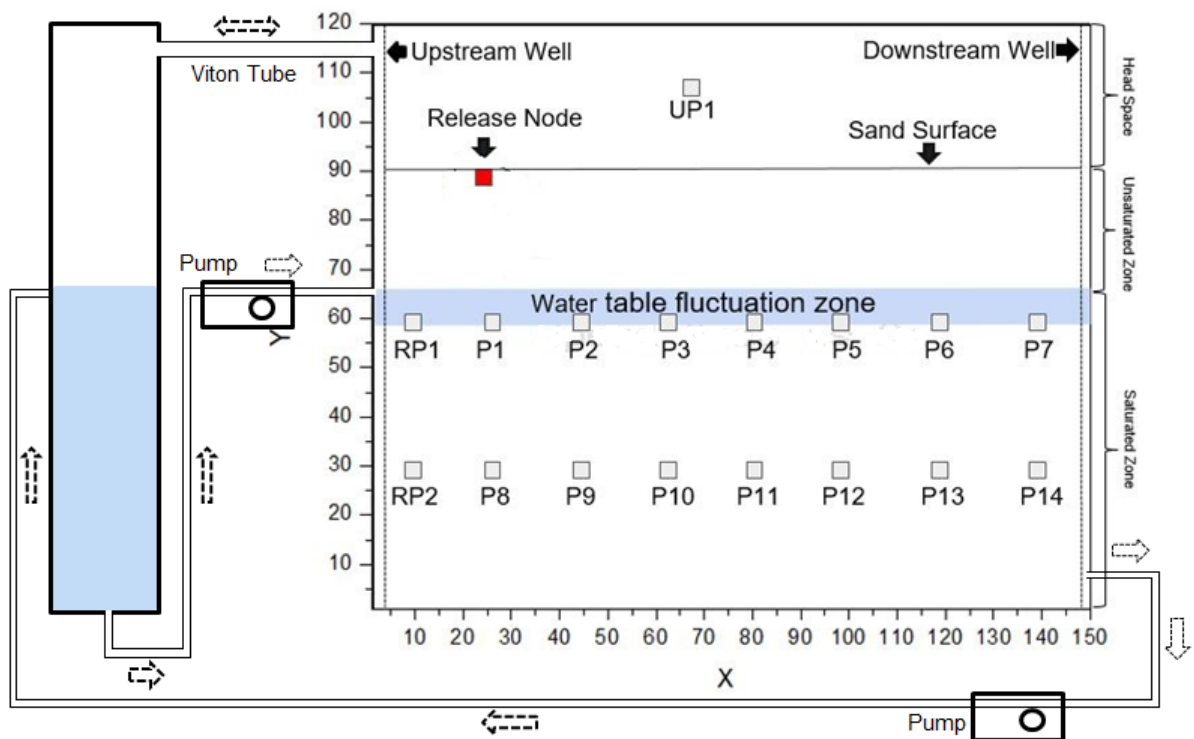
138 Two dimensional sand tank setup used in the study was specially designed using 2.5 mm thick  
 139 stainless steel formed box with inner dimensions of 150 cm-long × 120 cm-high ×10 cm-deep  
 140 (Figure 1). Two wells were installed at each side of tank and front cover of the tank was made-  
 141 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

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

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

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

189 table by 5cm in 1, 2, and 4 hours respectively. The groundwater table was then lowered  
 190 in the same manner; a drop of 5 cm was achieved in subsequent 1, 2 and 4 hours for rapid,  
 191 general and slow fluctuation conditions, respectively. It may be noted herein that “one  
 192 fluctuation cycle” refers to a complete high-low-high cycle of groundwater table levels.  
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195  
 196 Figure 1. Schematic diagram of 2D sand tank setup integrated with an auxiliary column  
 197 used to investigate fate and transport of LNAPL in subsurface under dynamic  
 198 groundwater table conditions.  
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200 Rising of groundwater table was maintained by pumping the water from the  
 201 auxiliary column to the upstream well and closing the outflow from the downstream well  
 202 for a target duration of respective fluctuation conditions. Likewise, groundwater falling  
 203 was maintained by extracting water from the downstream well and closing the inflow to  
 204 the sand tank from the auxiliary column for the same duration. Such switching of the  
 205 peristaltic pump was adjustable and calibrated for a target duration of respective  
 206 fluctuation conditions. A brief pumping details of different considered cases are listed in  
 207 Table 2. To maintain a rise and fall of 5 cm, (150 cm-long  $\times$  05 cm-magnitude of fluctuation  
 208  $\times$  10 cm-deep  $\times$  33% porosity) 0.002475 m<sup>3</sup> or 2.475 liters of groundwater was required as  
 209 inflow and outflow. Pure phase toluene was released from the top surface of the tank set up

210 to create a pool of the LNAPL above the groundwater table which was varied in the range of  
 211 55-60 cm level from the tank bottom. The toluene (Merck with 99.9 % purity) was injected  
 212 at a constant rate of 02 ml/min for a duration of 5 minutes using an air-tight syringe.  
 213 Periodically, a small amount of soil water samples from both the layers and the soil vapor  
 214 samples from head-space were collected carefully for the analysis.

215

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

Conditions	Inflow		Outflow		Total 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

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## 219 2.2 Sample Analysis

220 Soil water samples were collected periodically using needles attached with syringes  
 221 (Hamilton gold) from the sampling ports embedded in the sampling layers in saturated zone  
 222 (Figure 1). The samples were transferred into vials (Agilent vials: Agilent Product No.  
 223 5190/1599) having air tight red septa caps without any air contacts. Similarly, soil vapor  
 224 samples were collected from sampling ports installed in the headspace. The collected  
 225 samples were analyzed using Gas chromatography-mass spectrometry (GC-MS) (Agilent  
 226 7890B) in triplicates. A chrompack capillary column (30m×0.25mm, Silicone coating of  
 227 0.25µm) was used for toluene analysis. Helium was employed as the carrier gas at a flow rate  
 228 of 25 mL/min. Similarly, air and nitrogen were used with a flow rate of 20 mL/min during GC-  
 229 MS analysis. During the measurements, temperature of injection port, oven, and detector port  
 230 was kept at 150°C, 120°C, and 150°C, respectively. One set of collected samples were also  
 231 analyzed using gas chromatography/combustion/isotope ratio mass spectrometry  
 232 (GC/C/IRMS) technique to capture pure phase LNAPL (Dempster et al. 1997).

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### 235 2.3 Microbiological Analysis

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

259

### 260 3. Numerical Modeling

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

$$263 \quad \frac{\partial}{\partial t}(nS_f C_{if}) = -\nabla \cdot (q_f C_{if}) + \nabla \cdot (nS_f D_{if} \cdot \nabla C_{if}) + K_{if} - S \quad (1)$$

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

267 phase. Likewise,  $S$  is biodegradation rate [ $\text{ML}^{-3}\text{T}^{-1}$ ] (as sink term) was obtained using (control  
268 and live) microcosms experiments.  $D_{if}$  is hydrodynamic dispersion [ $\text{L}^2\text{T}^{-1}$ ] which was obtained  
269 using breakthrough curves (BTCs) of tracer transport experiment. The HYDRUS 2D model  
270 was used to solve governing equation for water flow and solute transport (Simunek et al. 1996).  
271 A two dimensional numerical domain having similar dimension of sand tank was created to  
272 simulate soil water flow and LNAPL transport through saturated zones. Thus, in this case  $S_f$   
273 i.e. fluid saturation in pore space [ $\text{L}^3\text{L}^{-3}$ ] was taken as 1 as the media fully saturated. The  
274 simulation domain was discretised in small grids of size 1 mm in a hexahedral geometry for  
275 solving the governing equation numerically. The Galerkin finite elements method integrated  
276 with Crank-Nicholson iterative scheme was used for the solution. The soil water flow and  
277 solute transport parameters listed in table 1 were used as model input parameters. The hydraulic  
278 behavior or parameters were obtained by inverse solution in HYDRUS 2D (Simunek et al.,  
279 2012).

280

### 281 **3.1 Initial and boundary conditions**

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

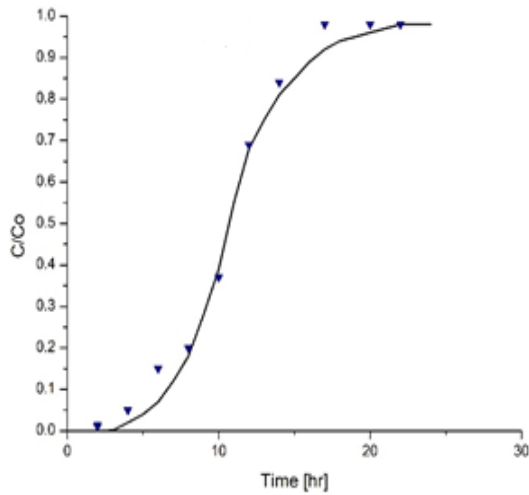
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## 292 **4. Results and Discussion**

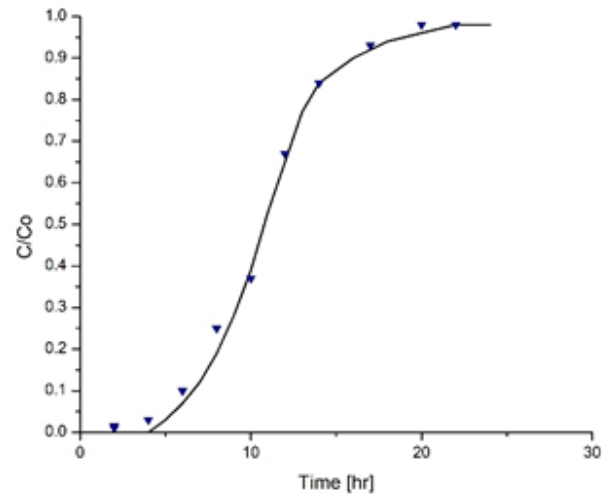
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294 The breakthrough curves (BTCs) of tracer experiments under stable and different groundwater  
295 fluctuation cases are presented in Figure 2 for rapid, general and slow groundwater table  
296 fluctuation conditions represented as GWTF-C1, GWTF-C2,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

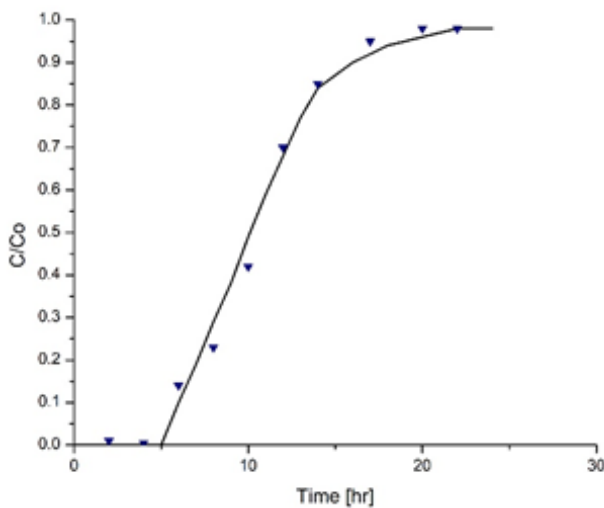
300  $m^2/s$  for rapid, general, slow, and stable groundwater table fluctuation conditions respectively.  
301 Similarly, estimated longitudinal dispersivity values are 1.23, 0.72, 0.28, 0.12m for rapid,  
302 general, slow, and stable groundwater table fluctuation conditions respectively. The observed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



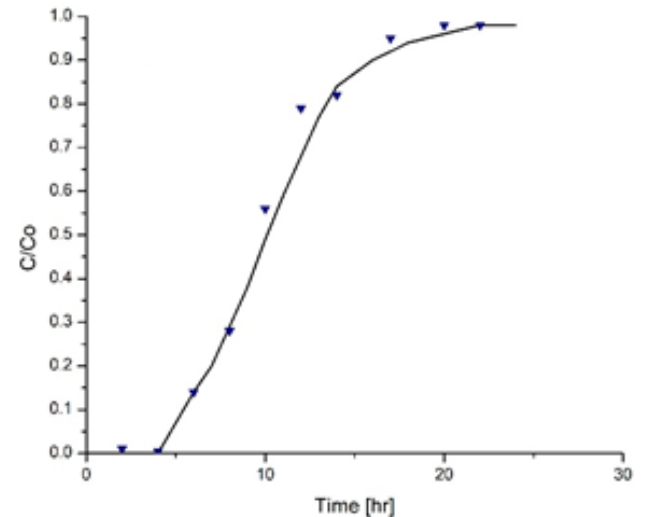
(a) GWTF-C1



(b) GWTF-C2



(c) GWTF-C3

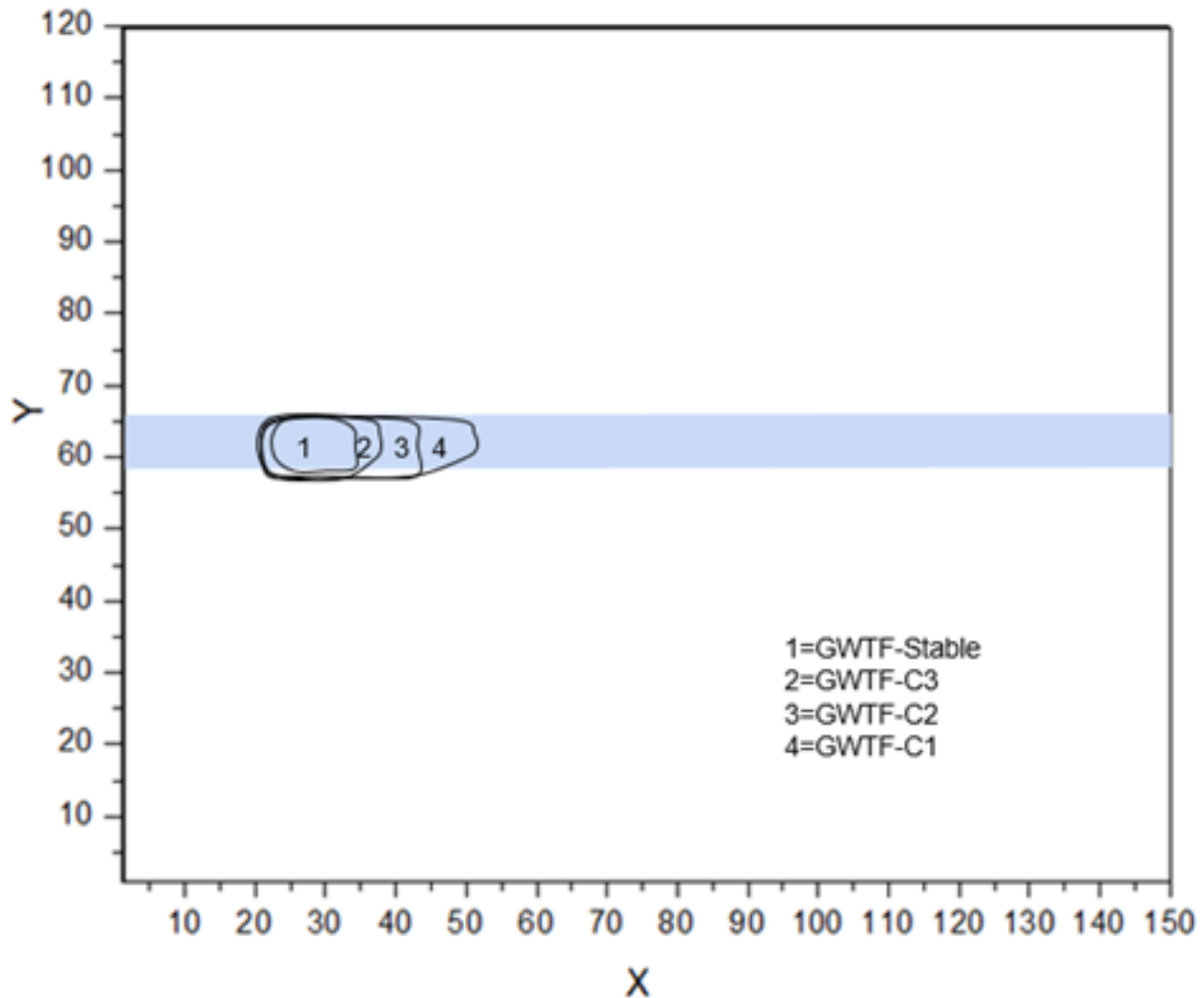


(d) GWTF-C4

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

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

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316 **4.1 Pure phase LNAPL coverage and dissolution**

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

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

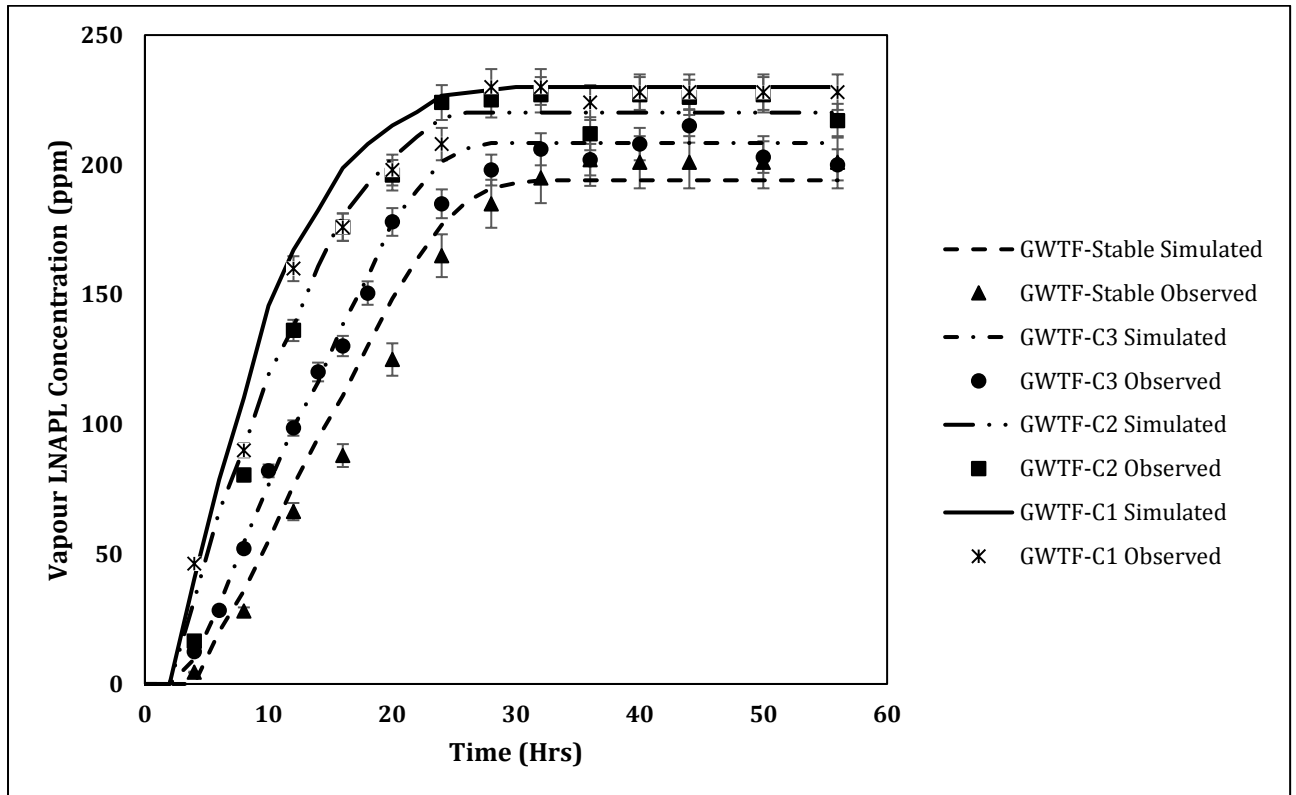
327 due to rapid fluctuation in groundwater governs the excess spreading of LNAPL in flow  
328 directions. Spreading of pure phase LNAPL over a large area provides more dissolving surface  
329 as LNAPL-water interphase to underlying flowing groundwater resulting into more dissolution  
330 rates. Similarly,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

347

#### 348 **4.2 Vapor phase concentrations**

349 The vapor phase LNAPL concentrations are plotted as BTC in Figure 4. The BTC shows a high  
350 LNAPL concentration in case of rapid fluctuating groundwater table followed by general, slow  
351 and stable groundwater table case. The vapor equilibrium concentration was observed as 210-  
352 230 ppm in fluctuating condition while 180-185 ppm was observed in stable groundwater case.  
353 This means a raising groundwater table carries pure phase LNAPL mass upward and a falling  
354 groundwater allows LNAPL to move downward. During dynamics of groundwater level, the  
355 trapped LNAPL remain behind in smear zone which creates a large interphase area of air-  
356 LNAPL/water (Powers et al. 1992). Therefore, more vapor phase concentration was observed  
357 from the residual LNAPL. These results are in line with the findings of study conducted by  
358 Oostrom et al. (2006) with 2D experiments under water table dynamic conditions. The study  
359 found a considerable residual LNAPL saturation in smear zone. The high vapor concentration  
360 can also be attributed to the partition of LNAPL from large dissolved phase plume having high

361 concentration. Further, lowering of groundwater table increases air-filled porosity in smear  
 362 zone, which eventually affects vapor phase LNAPL partition. The BTC of different  
 363 groundwater table fluctuation experiments confirms that the vapor intrusion is highly  
 364 dependent on the nature of groundwater table conditions (Patterson and Davis, 2009). High  
 365 vapor LNAPL in unsaturated pores may become toxic for the indigenous microorganisms.  
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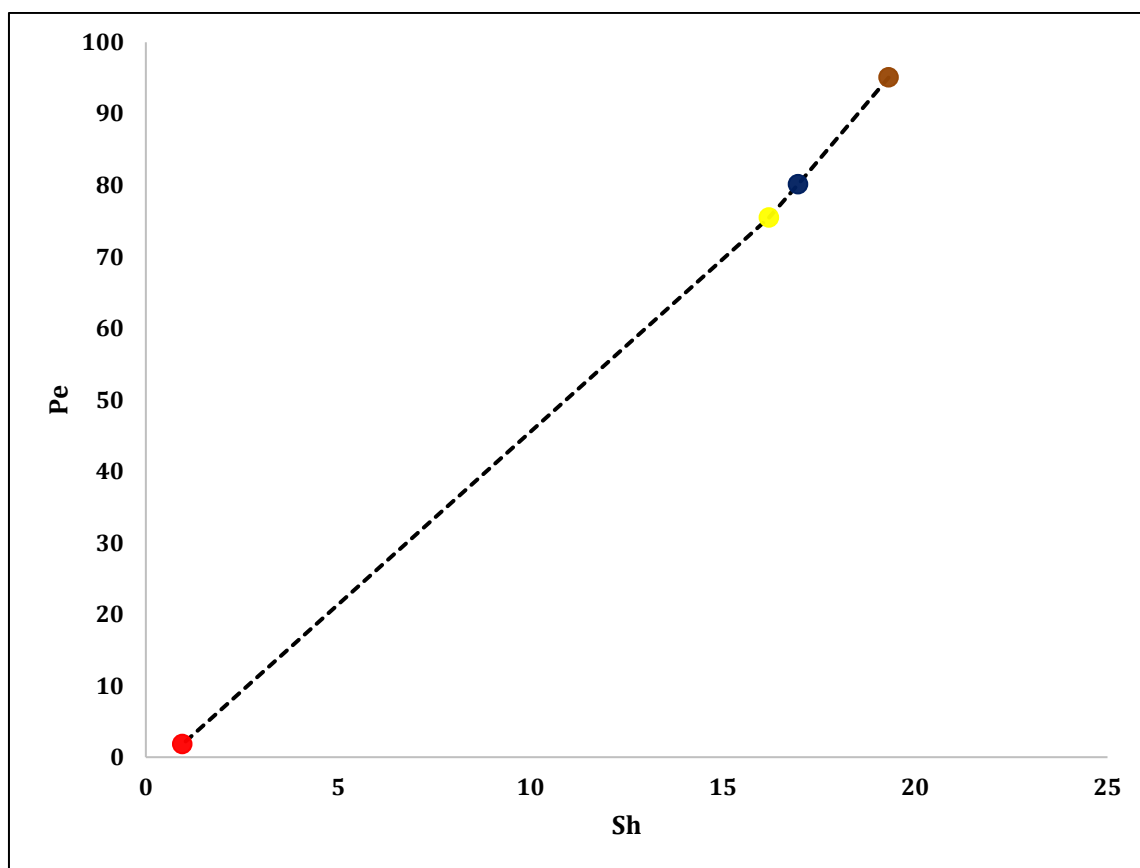
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 370 Figure 4: BTC representing LNAPL concentration in soil air in 2D sand tank under stable and  
 371 fluctuation groundwater table conditions.

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 373 The measured pure phase LNAPL pool area was used to estimate its characteristic length of  
 374 LNAPL pool ( $l_{(c)}$ ) under stable and fluctuating groundwater conditions. The observed values  
 375 of  $l_{(c)}$  was found 15.81, 14.15, 12.64, and 8.36 cm under rapid, general, slow and stable  
 376 groundwater fluctuation conditions, respectively. The estimated value of mass transfer  
 377 coefficient ( $k^*$ ) are listed in Table 3. The estimated Sherwood numbers ( $Sh$ ) were found 0.95,  
 378 16.20, 16.95 and 19.30 while Peclet numbers ( $P_e$ ) were 1.80, 75.47, 80.14, and 95.06 for rapid,  
 379 general, slow and stable cases respectively. A high value of  $Sh$  indicates that dissolution was  
 380 a dominating process under fluctuating groundwater conditions. The reason for high  $Sh$  can be

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

389

390



391

392 Figure 5: Correlation between  $Sh$  and  $P_e$ . Red, yellow, blue and green circle represent

393 stable, slow, general and rapid groundwater fluctuation conditions respectively.

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

Conditions	Mass transfer coefficient $k^*$ (m/s)	Sherwood Number $Sh$ (-)	Peclet Number $P_e$ (-)
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

400

### 401 4.3 Dissolved phase concentrations

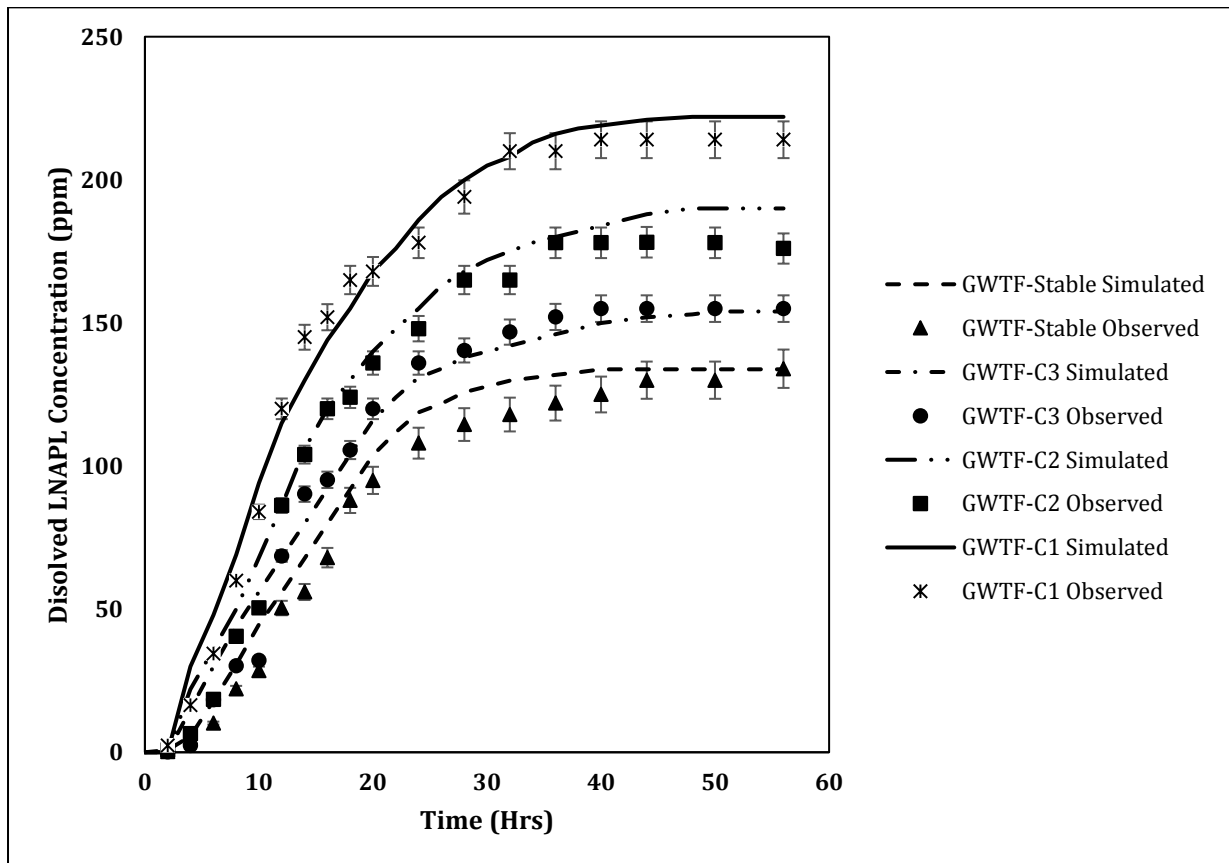
402 Dissolved LNAPL concentrations as a function of time for all four cases are presented in  
 403 figures 6-7. In figure 6a, BTC is presented for port 1 (top sampling layer: X:25cm; Y:60 cm)  
 404 which was situated just below the water table and nearby LNAPL pool. It shows that toluene  
 405 concentration starts rising after few hours and increases rapidly and then starts attenuating  
 406 before reaching to a concentration of 200-230 ppm for rapid fluctuating groundwater case.  
 407 Similar trends were observed for the remaining fluctuating groundwater cases. The higher  
 408 concentration in the rapid fluctuation case was due to more dissolving LNAPL pool area than  
 409 general, followed by slow and stable fluctuation conditions. Likewise, BTCs of port 4 and port  
 410 7 of upper layer are presented in figure 6b and 6c respectively. LNAPL concentration takes 10-  
 411 12 hours and 20-26 hours to reach port 4 and port 7, which was 55 cm and 115 cm away from  
 412 pool respectively. However, a significant difference in the final equilibrium concentration  
 413 (plateau) was observed amongst different groundwater table fluctuation cases. At this stage the  
 414 supply from the source and the out flux at the observed down-gradient port (port 7) was  
 415 reaching to an equilibrium condition. A decreasing trend in the equilibrium concentration was  
 416 observed as plume moves from up gradient location (port 1) to down-gradient locations (Port  
 417 4/7) which represents the dependency of biodegradation rate on dissolved LNAPL  
 418 concentration. In general, the equilibrium concentration of toluene in earlier studies was found  
 419 quite nearby to its dissolution limit. In this study, the observed concentration of toluene was  
 420 not able to reach the maximum solubility value of toluene because of (a) limited contact (water-  
 421 toluene) time of opportunity, (b) the concurrent biodegradation of the dissolved LNAPL in  
 422 sand tank setup. The study shows that more than 150 ppm dissolved LNAPL concentration was  
 423 found to start inhibiting metabolic actions of microbes causing lower degradation rates then its



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

431 Likewise, the dissolved LNAPL concentrations are presented in figures 7a-c for ports  
 432 8, 11 and 14 situated in bottom layer. Figure 7a shows that the dissolved LNAPL plume takes  
 433 10-12 hours to reach at port 8, which is at 30 cm downward from the pool. At port 8, there is  
 434 very less difference in equilibrium concentrations as compared to port 1. Whereas, a large  
 435 difference was found in equilibrium concentration of port 11 (Figure 7b) and port 14 (Figure  
 436 7c) in comparison to port 8 (Figure 7a). This seems due to high biodegradation rates at port 11  
 437 as compared to port 8, even the port 11 is situated in bottom layers where background oxygen  
 438 level is low.

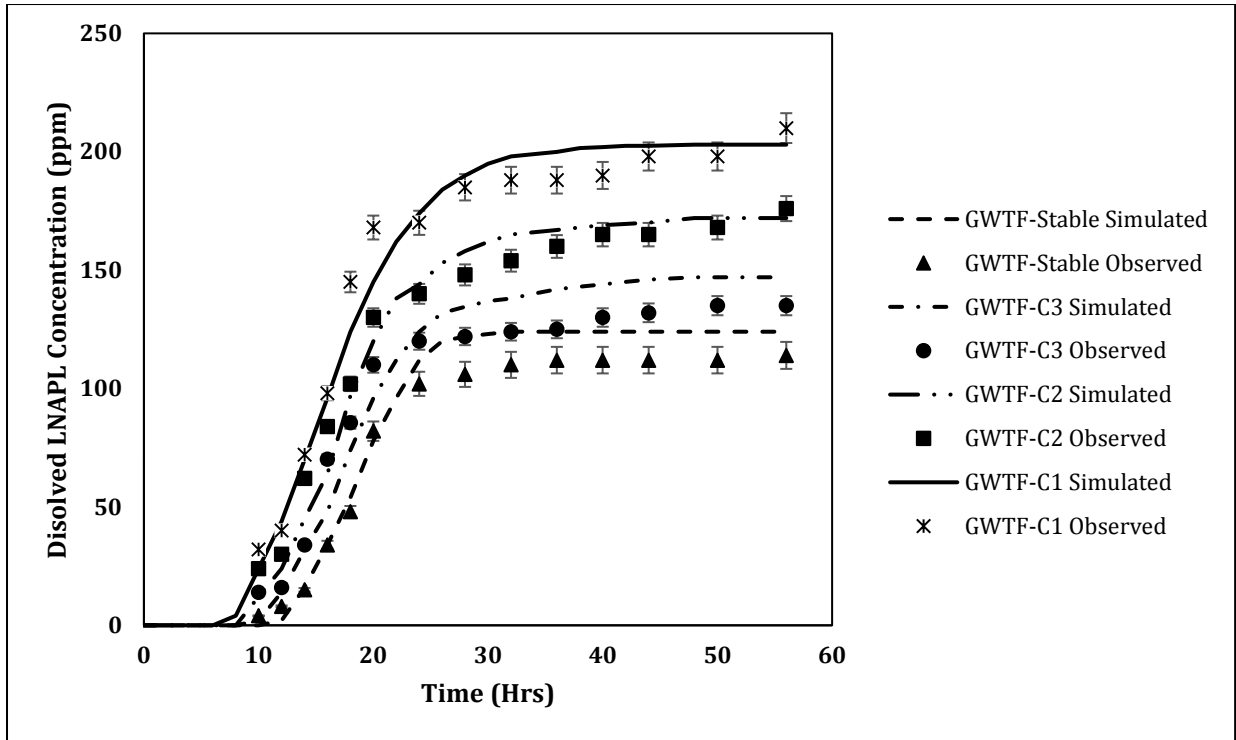
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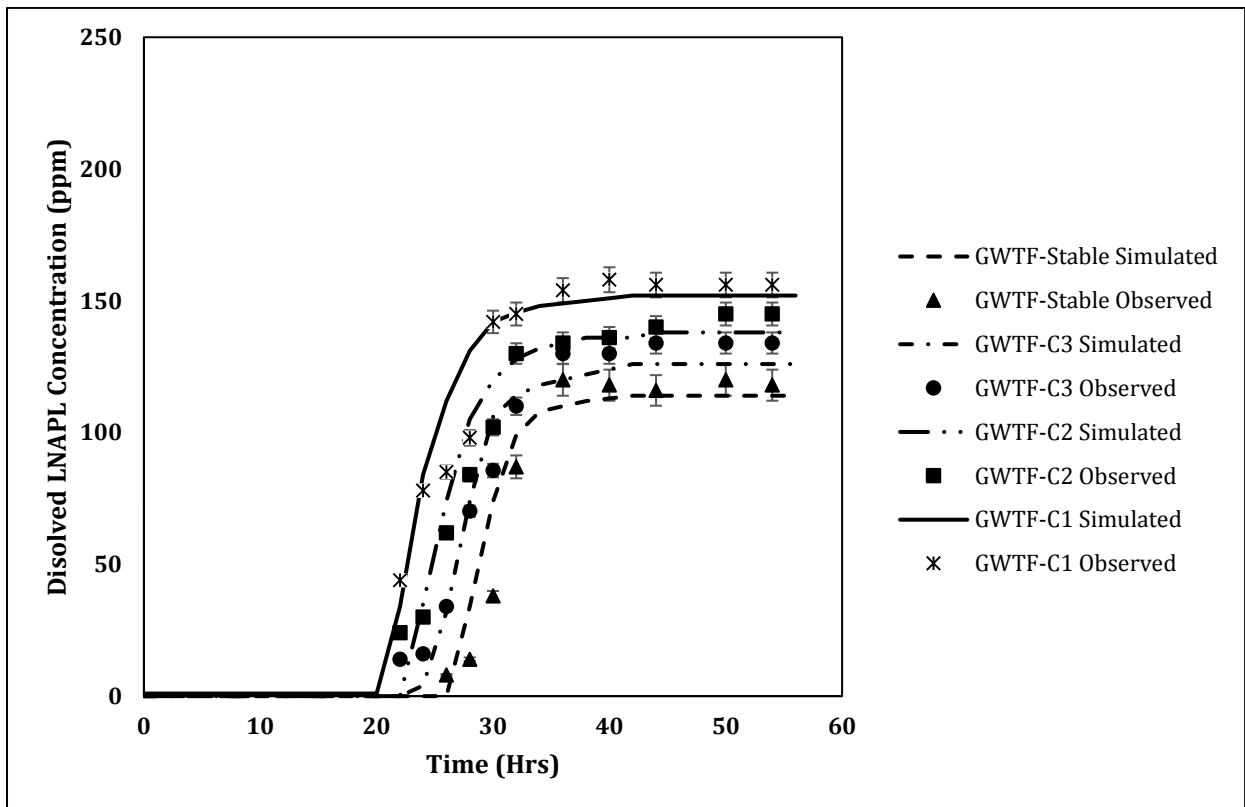
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(a) Port 1: X:25; Y60

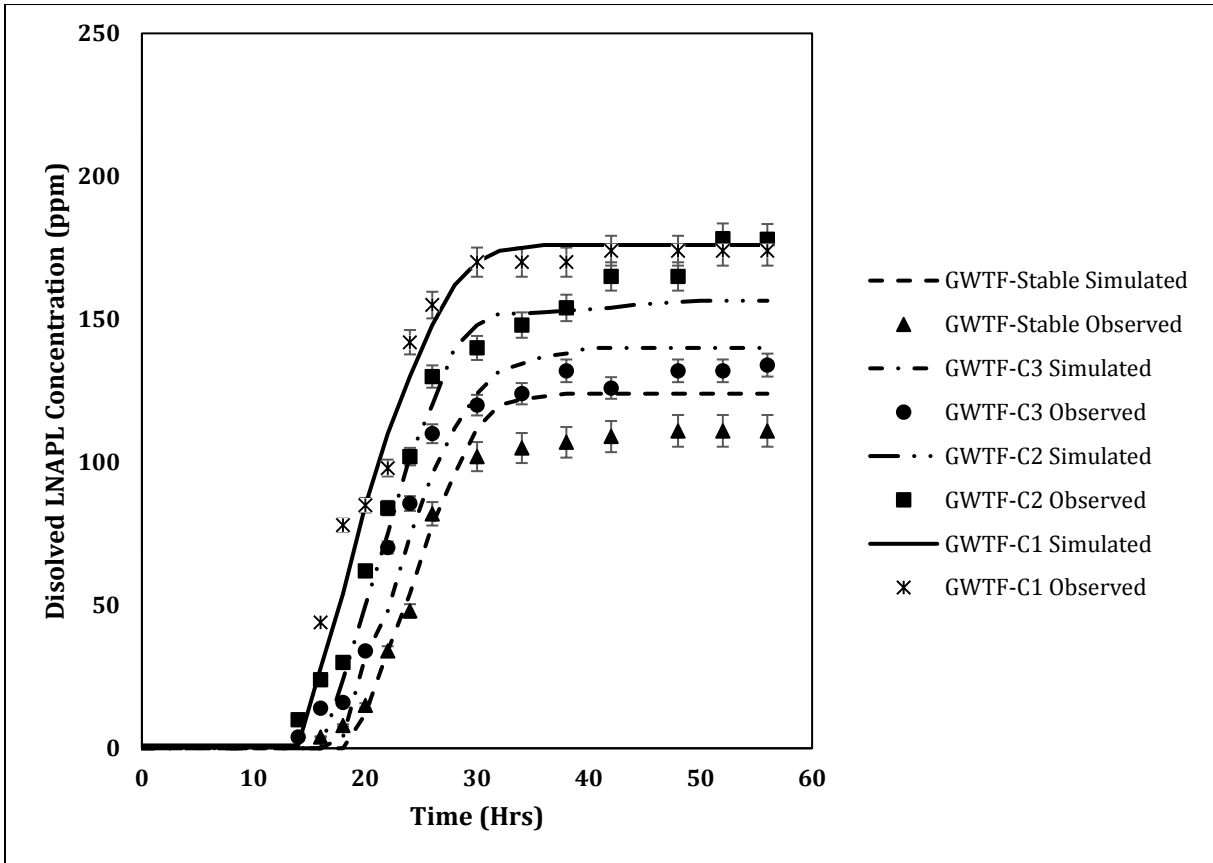


(b) Port 4: X:80; Y60



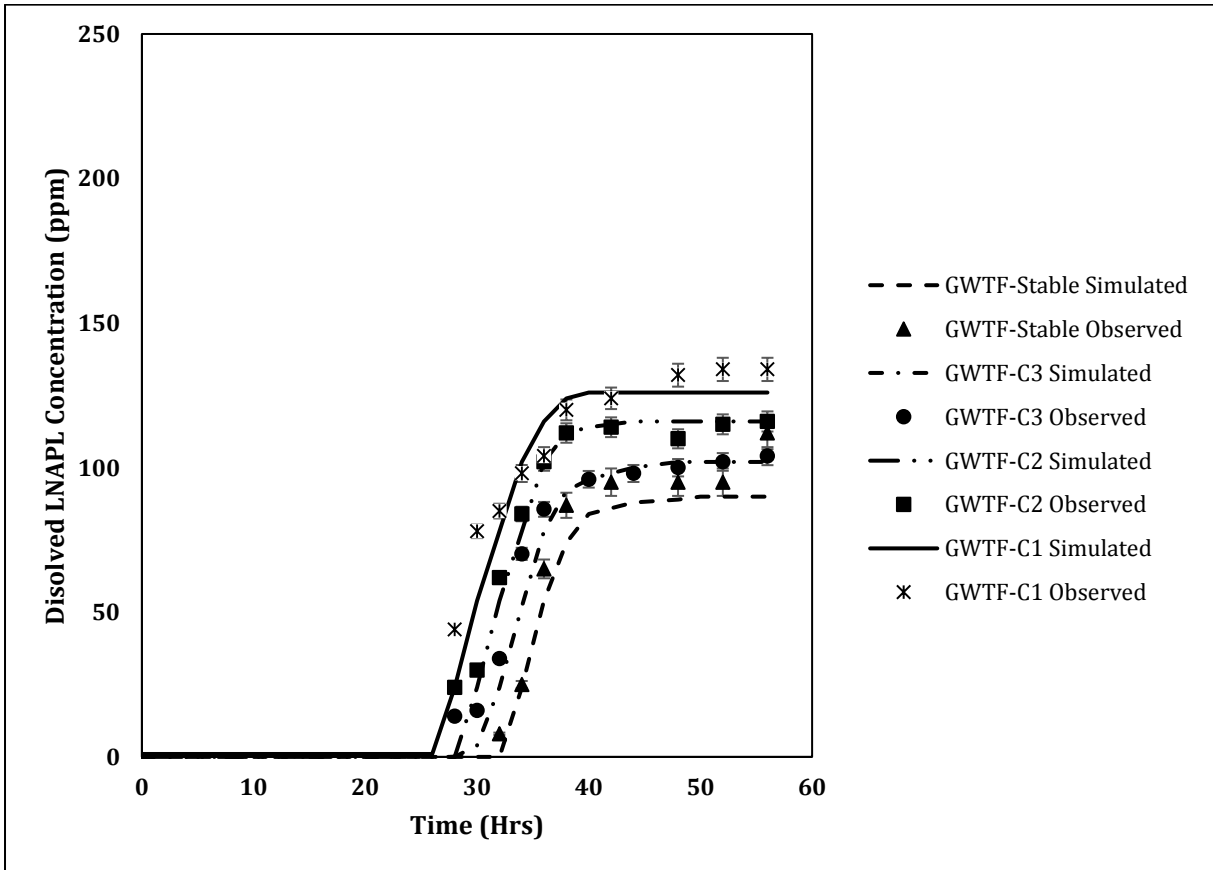
(c) Port 7: X:140; Y60

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



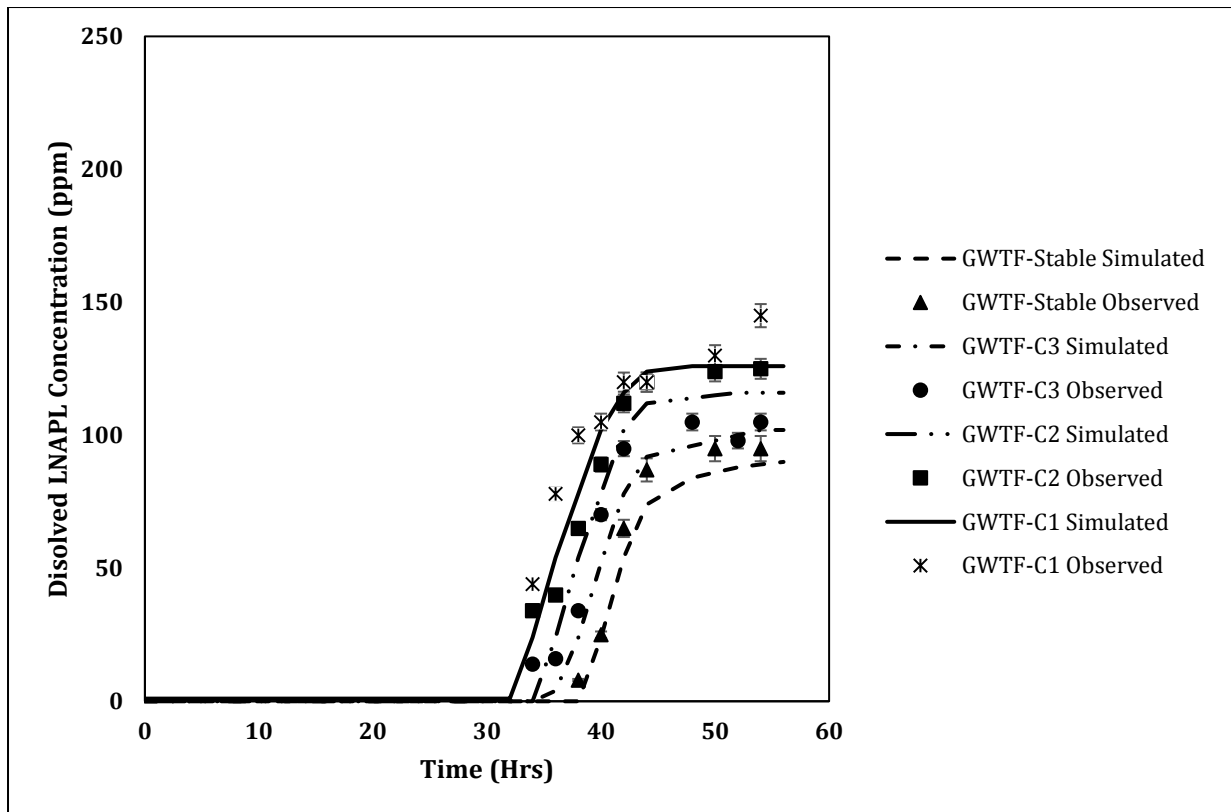
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(a) Port 8: X:25; Y30



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(b) Port 11: X:80; Y30



(c) Port 14: X:140; Y30

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

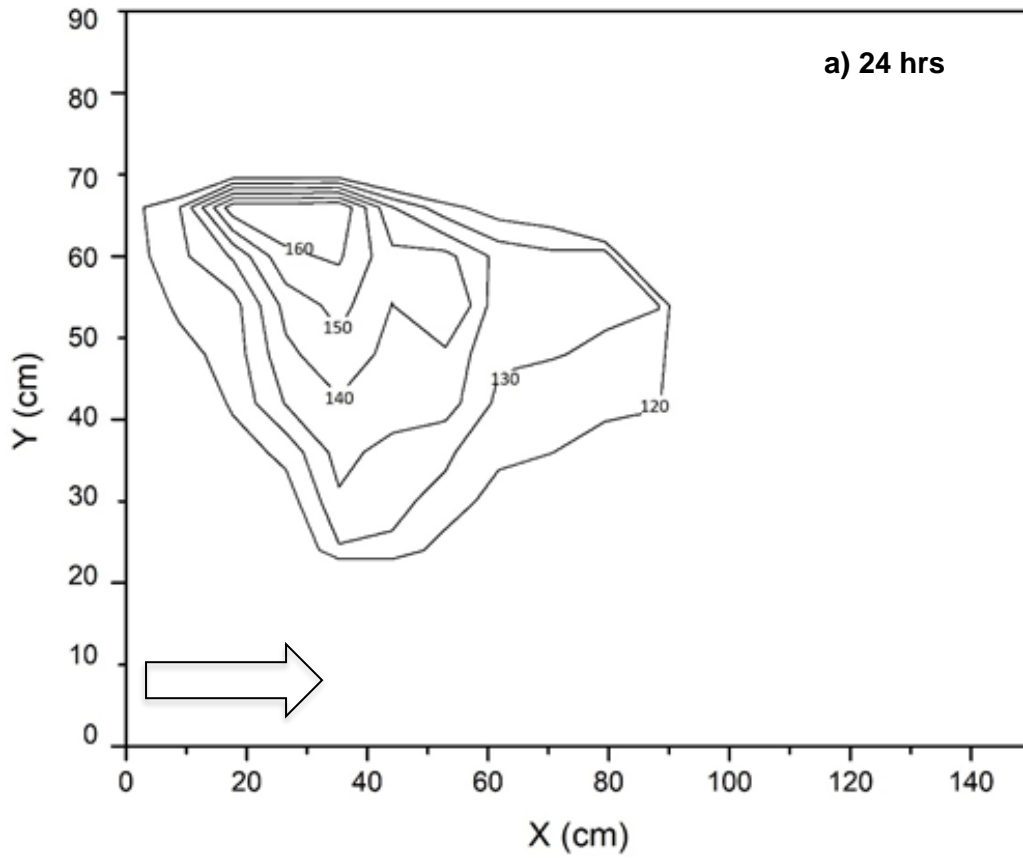
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The experimentally observed dissolved LNAPL concentrations isolines are plotted as a function of space in figures 8a-d. These concentration isolines were plotted using experimentally measured data from all sampling ports (port1-14) including ports 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

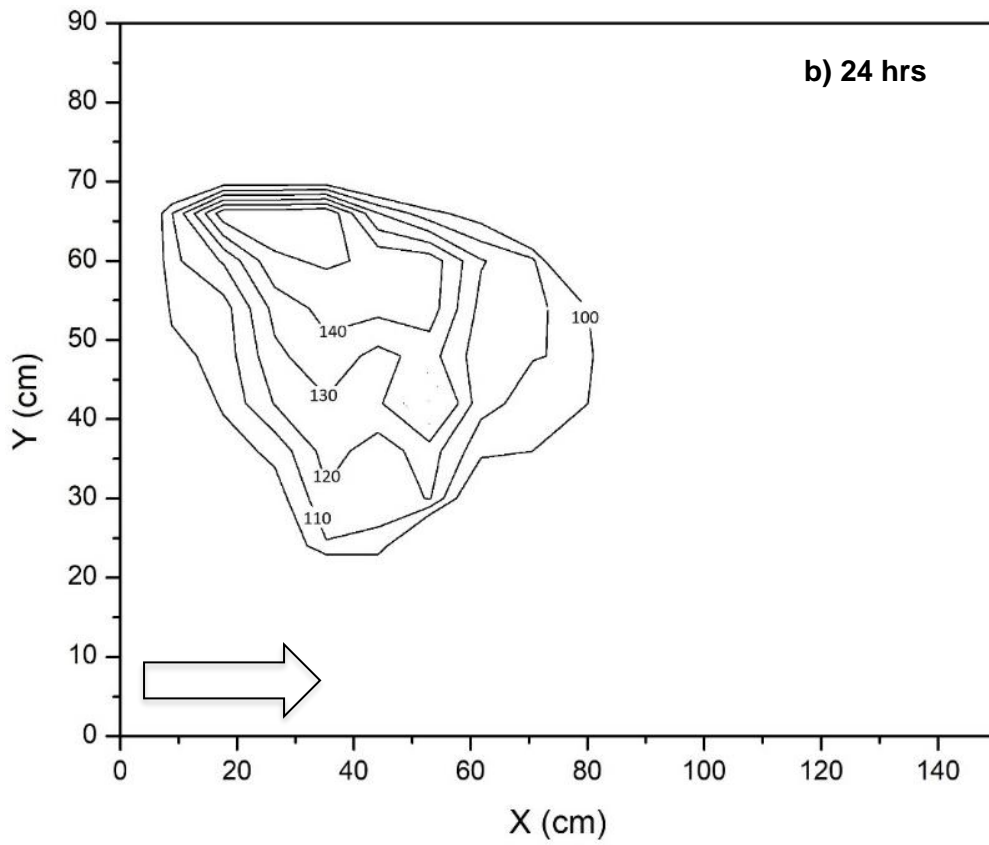
474 concentration ranges 110 ppm-140 ppm in initial 12 hours and continuously increases upto 160  
475 ppm. Less concentration (20ppm) of dissolved plume under general groundwater table  
476 fluctuation condition was due to smaller LNAPL pool length then the rapid case. Thus, in  
477 general groundwater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

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

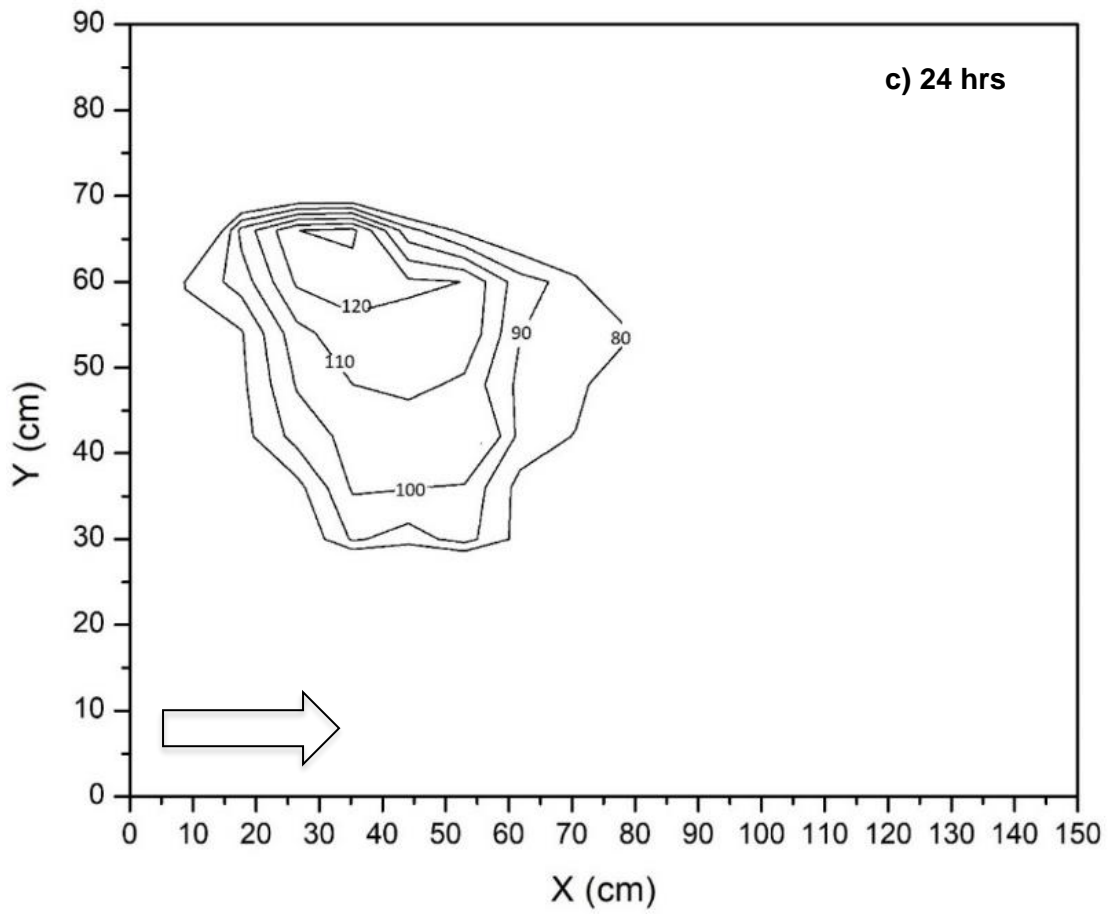
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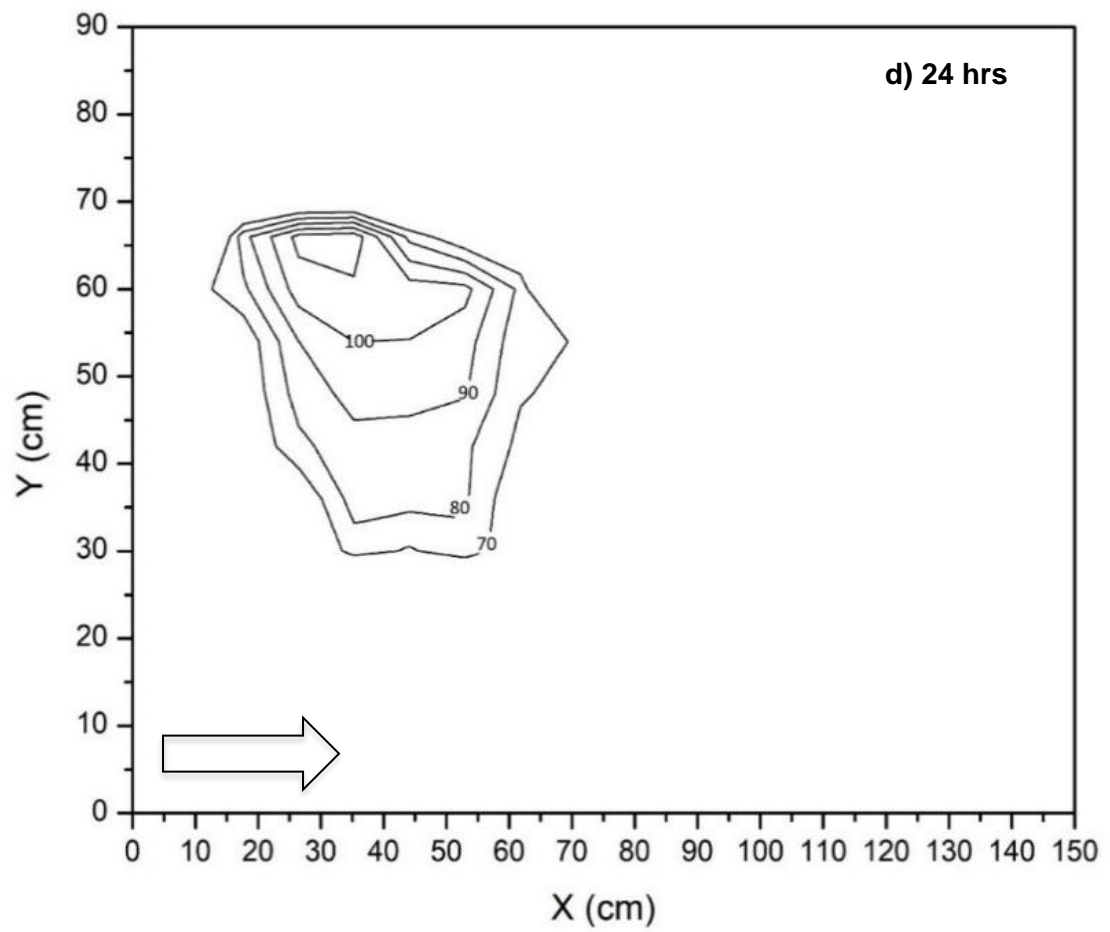
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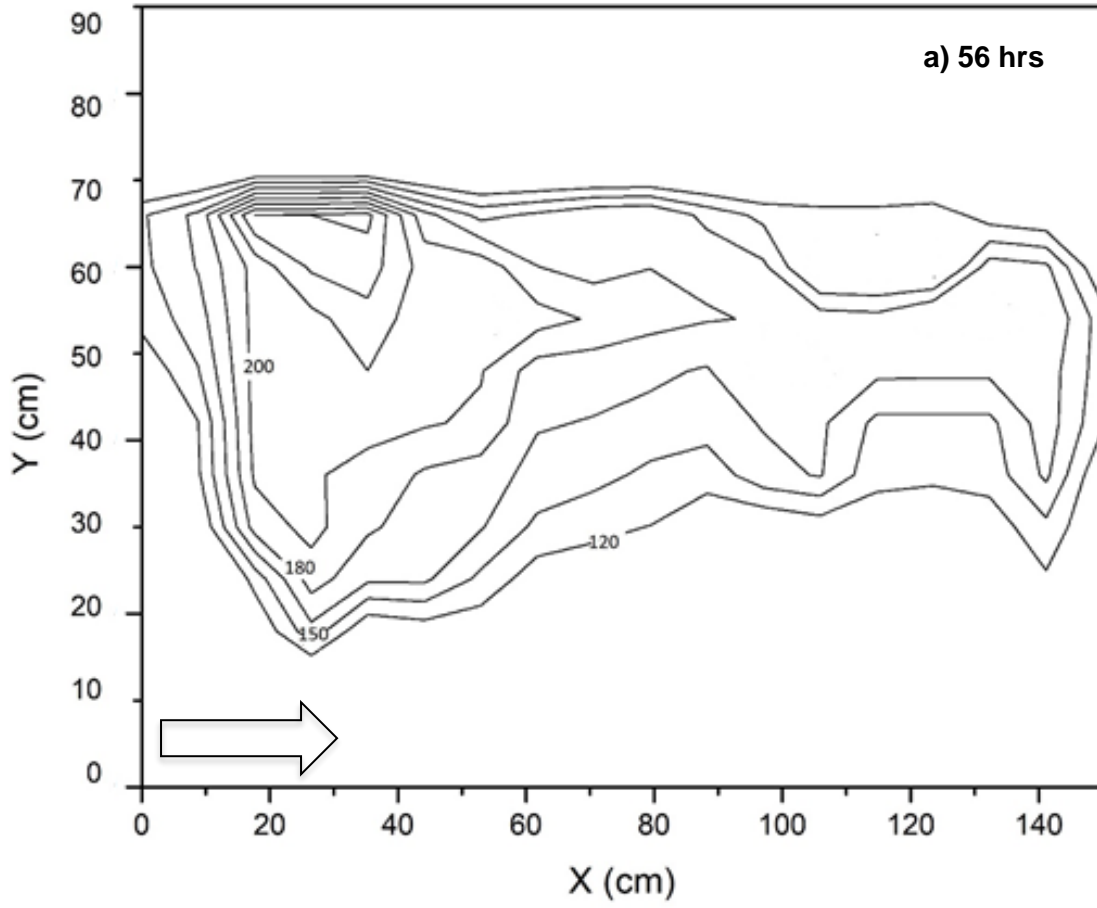
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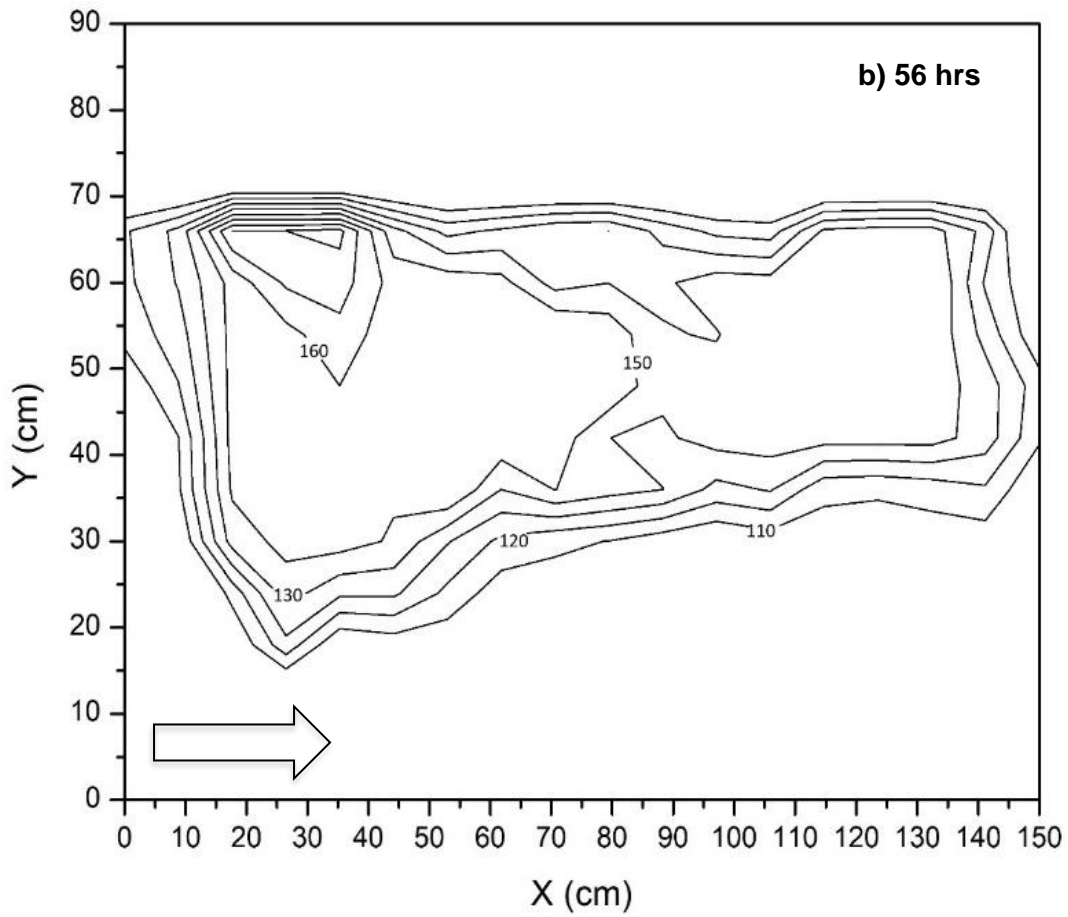
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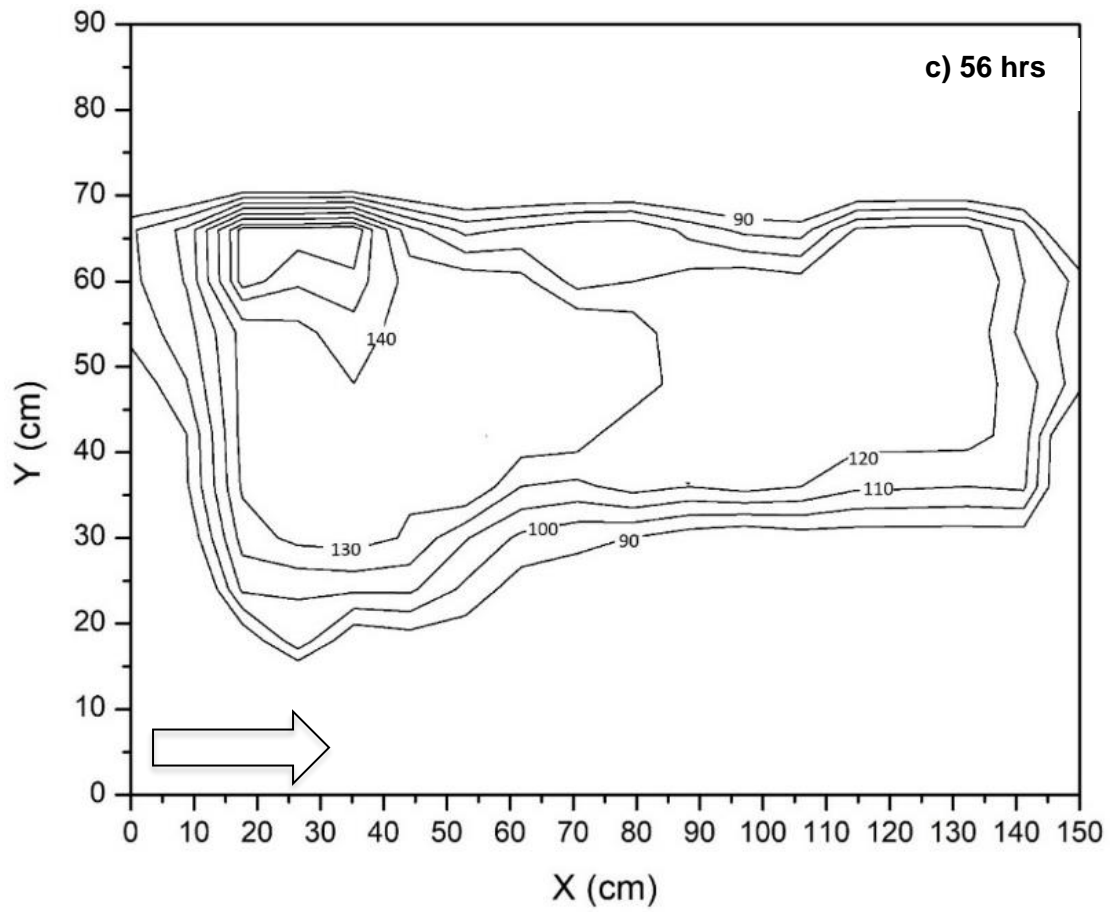


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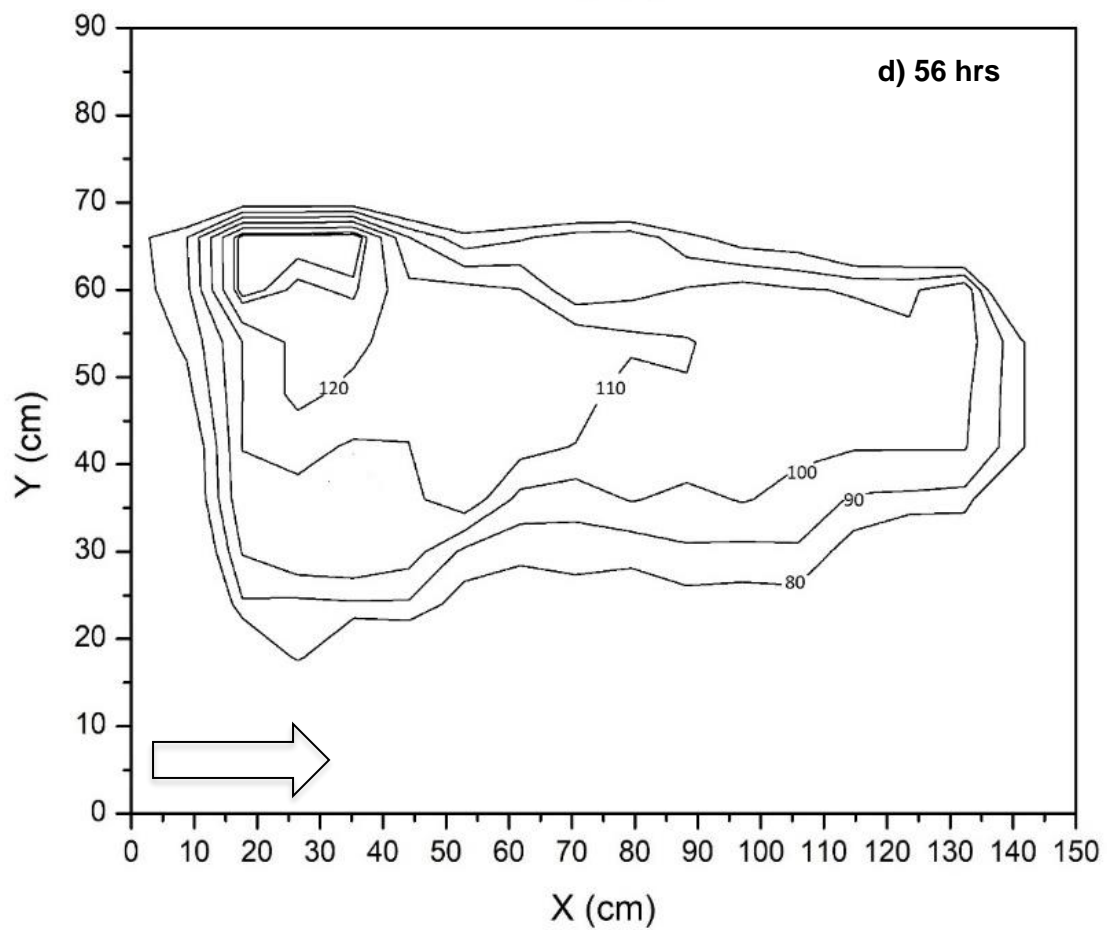


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500

501 Figure 8: Concentration isolines presenting the extension of dissolved LNAPL plume  
502 originated from pure phase source under a) rapid, b) general, c) slow and d) stable  
503 groundwater table fluctuation cases.  
504

#### 505 **4.4 Biodegradation under different groundwater table fluctuation conditions**

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

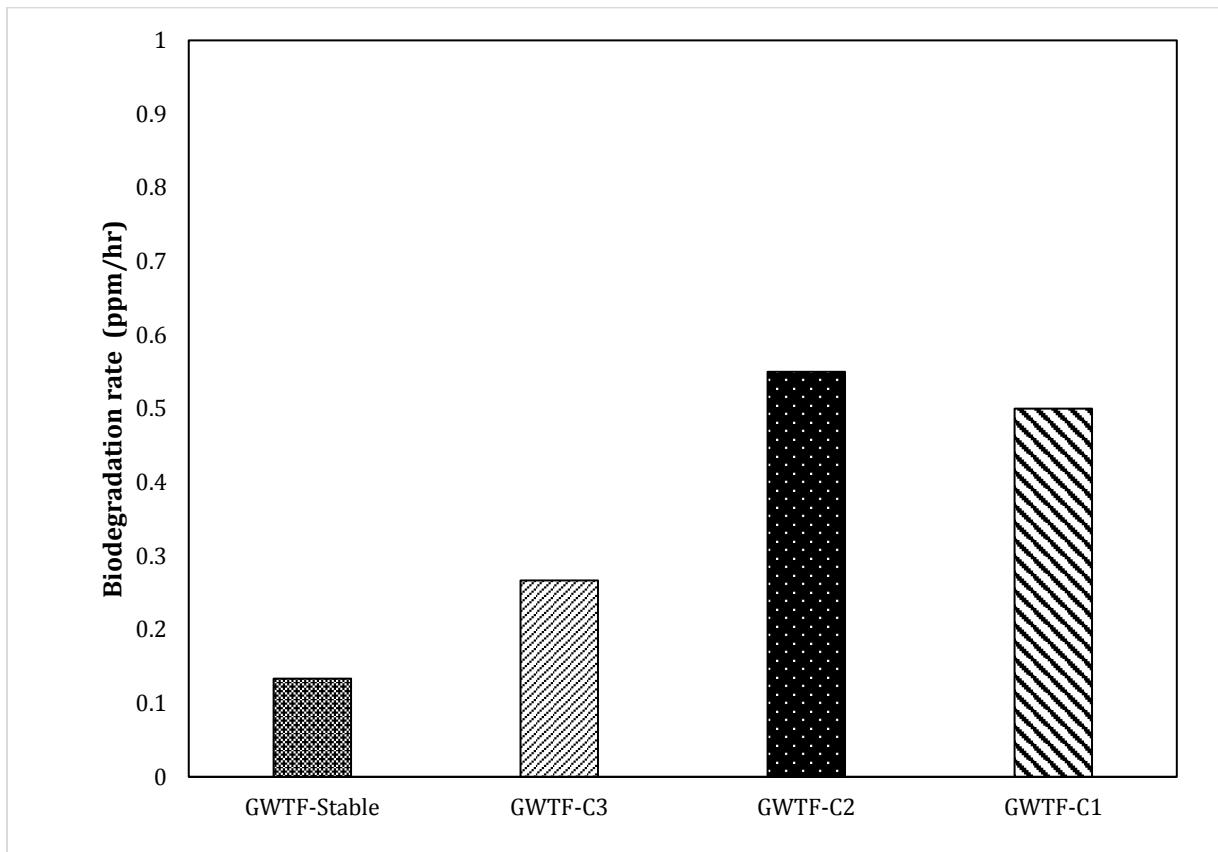
516 The biodegradation rate was found comparatively low in case of rapid fluctuation than general  
517 fluctuation because of large high concentration (>150 ppm) region which causes toxic effects  
518 on potential microbes lies in this region. While, the high biodegradation rate in case of general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

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

535 observed at upper and lower layer respectively. In GWTF-C1 case, the microbial count at port  
536 1 increases upto  $305 \times 10^4$  CFU/mL in 24 hours and then decreases to  $78 \times 10^4$  CFU/mL in 56  
537 hours. Similarly, at port 7, overgrowth was recorded after 24 hours thereafter decreases to  
538  $224 \times 10^4$  CFU/mL in 56 hours.

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

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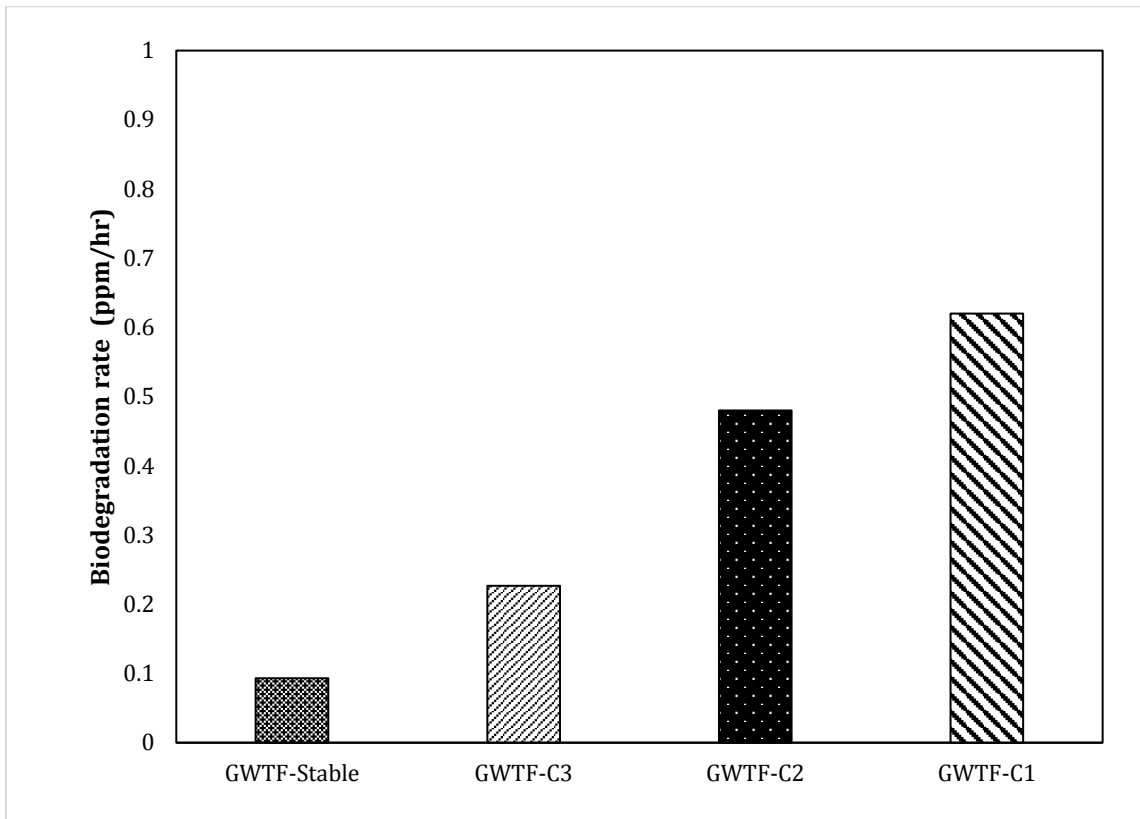
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(a)

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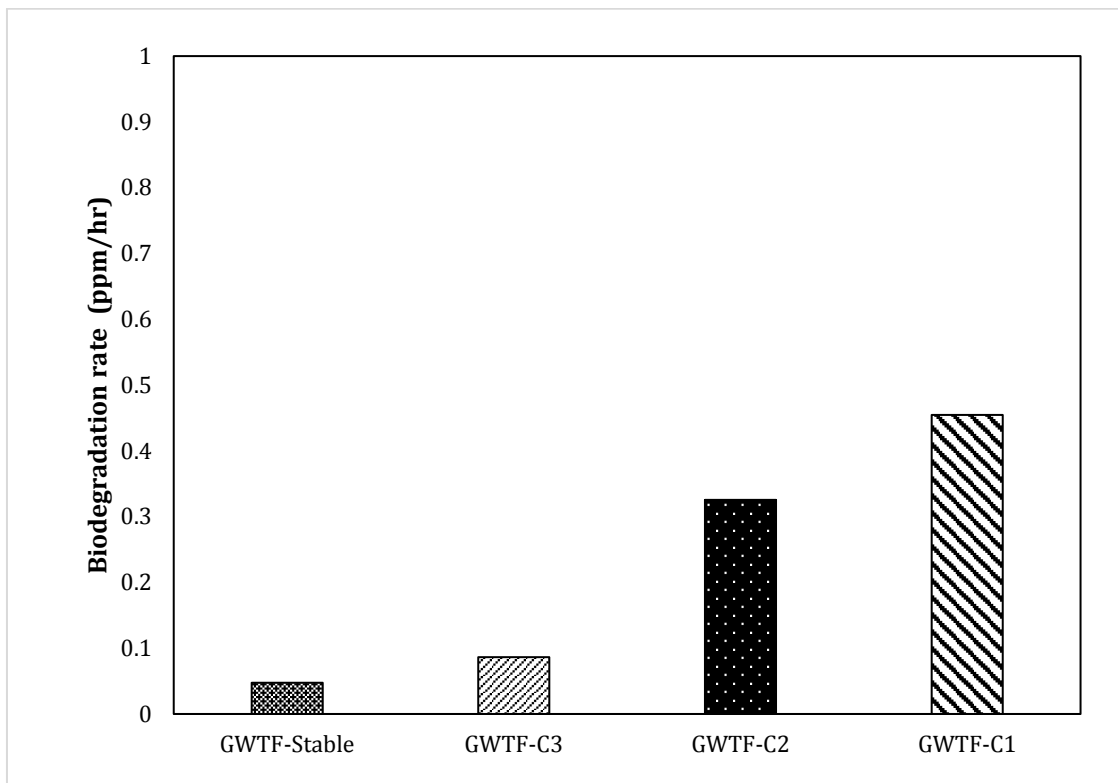


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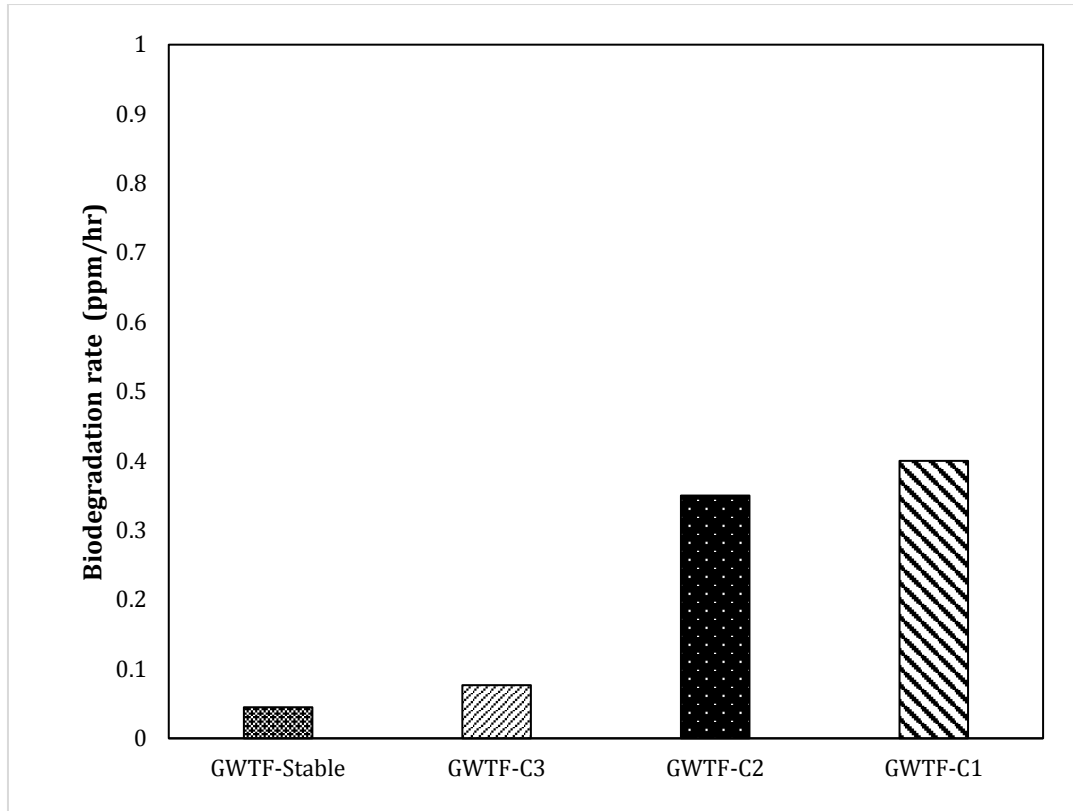
(b)



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(c)



(d)

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

566

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

569

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
GWFT-C1	254.5	305	78	258.0	O	224.5	147.2	165	135.4	142.5	145.8	165
GWFT-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

570 O= Overgrowth

571

572

573

574 **5. Conclusion**

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

598

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600

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604

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