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## ► To cite this version:

Amélie Cavelan, Fabrice Golfier, Stéfán Colombano, Hossein Davarzani, Jacques Deparis, et al.. A critical review of the influence of groundwater level fluctuations and temperature on LNAPL contaminations in the context of climate change. *Science of the Total Environment*, 2022, 806, pp.150412. 10.1016/j.scitotenv.2021.150412 . hal-03352335

**HAL Id: hal-03352335**

<https://hal.univ-lorraine.fr/hal-03352335v1>

Submitted on 23 Sep 2021

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1 **A critical review of the influence of groundwater level fluctuations and temperature on LNAPL**  
2 **contaminations in the context of climate change**

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9 **Abstract**

10 The intergovernmental panel on climate change (IPCC) predicts significant changes in  
11 precipitation patterns, an increase in temperature, and groundwater level variations by 2100. These  
12 changes are expected to alter light non-aqueous phase liquid (LNAPL) impacts since groundwater level  
13 fluctuations and temperature are known to influence both the mobility and release of LNAPL  
14 compounds to air and groundwater. Knowledge of these potential effects is currently dispersed in the  
15 literature, hindering a clear vision of the processes at play. This review aims to synthesize and discuss  
16 the possible effects of the increase in temperature and groundwater level fluctuations on the behavior of  
17 LNAPL and its components in a climate change context. In summary, a higher amplitude of groundwater  
18 table variations and higher temperatures will probably increase biodegradation processes, the LNAPL  
19 mobility, and spreading across the smear zone, favoring the release of LNAPL compounds to the  
20 atmosphere and groundwater but decreasing the LNAPL mass and its longevity. Outcomes will,  
21 nevertheless, vary greatly across arid, cold, or humid coastal environments, where different effects of  
22 climate change are expected. The effects of the climate change factors linked to soil heterogeneities,  
23 local conditions, and weathering processes will govern LNAPL behavior and need to be further clarified.

24 **Keywords:** Light non-aqueous phase liquids; Groundwater; Dissolution, Biodegradation;  
25 Volatilization.

## 26        **1. Introduction**

27        Over the last century, the development of chemical and petroleum industries has led to numerous  
28 accidental spills of petroleum products that have greatly affected the long-term quality of groundwater  
29 (Güler, 2019). Light non-aqueous phase liquids (LNAPLs), are one the most common source of  
30 groundwater pollution (Rivett et al., 2014). When released, LNAPLs redistribute by migrating through  
31 the saturated (SZ) and unsaturated zone (USZ) and interacting with groundwater. Redistribution of  
32 LNAPL and partitioning of its components cause significant groundwater and soil pollutions (Huntley  
33 and Beckett, 2002; Lee and Chrysikopoulos, 1998; McCarthy and Johnson, 1993; Mobile et al., 2012;  
34 Nambi and Powers, 2003; Oostrom et al., 2007; Patterson and Davis, 2009). Several petroleum LNAPL  
35 compounds are carcinogenic (e.g., benzene) affecting plants, microorganisms, animals, and human  
36 health, and making groundwater unsuitable for both agriculture and drinking water supply. Remediation  
37 of LNAPL contaminated sites can be prolonged and expensive since LNAPL fuels and oils are usually  
38 a complex multi-component mixture with variable physical properties (Newell, 1995). The processes  
39 controlling LNAPL remobilization and degradation at contaminated sites are numerous and the relation  
40 between them is not always clear (Garg et al., 2017; Sookhak Lari et al., 2019). Better understanding  
41 the controlling factors of LNAPL mobilization and remediation processes became, therefore, a major  
42 scientific goal these last decades (Alazaiza et al., 2020; Benioug et al., 2019; Chen et al., 2010; Dobson  
43 et al., 2007; Ismail et al., 2020; McAlexander and Sihota, 2019; Sookhak Lari et al., 2016b, 2020; Sun,  
44 2016; Werner and Höhener, 2002; Zeman et al., 2014).

45        Numerous laboratory, modeling, and field studies have demonstrated that seasonal or pump-  
46 induced groundwater level fluctuations may affect LNAPL migration and redistribution (Davis et al.,  
47 1993; Lenhard et al., 2019, 2018, 2017; Steffy et al., 1998, 1995), component dissolution rates (Davis  
48 et al., 1993; Kechavarzi et al., 2005; Lekmine et al., 2014; Lenhard et al., 2004; Mobile et al., 2012;  
49 Teramoto and Chang, 2017), volatilization (Davis et al., 2005; Guo et al., 2019; Illangasekare et al.,  
50 2014; McCarthy and Johnson, 1993; Picone et al., 2012; Qi et al., 2020; Soucy and Mumford, 2017;  
51 Werner and Höhener, 2002; Zhang et al., 2021), or biodegradation (Dobson et al., 2007; Gupta et al.,  
52 2019; Ismail et al., 2020; Rainwater et al., 1993). These works showed that fluctuating groundwater

53 level conditions and/or soil moisture changes affect the vertical dispersion and redistribution of the  
54 LNAPL compounds at the capillary fringe, modifying their release into the environment. However, the  
55 dynamic nature and the intensity of groundwater level variations may change significantly in the coming  
56 decades in response to climate change (Goderniaux et al., 2009; Green et al., 2011; Jarsjö et al., 2020;  
57 Smerdon, 2017). Depending on local climatic conditions, more intense groundwater level fluctuations  
58 may occur over the next century in response to variations in rainfall intensity and frequency and the  
59 increasing use of water resources (Christensen and Christensen, 2007; IPCC, 2014; Nygren et al., 2020).  
60 This context may strongly impact the LNAPL mobilization, the contamination lifetime, and the risk for  
61 receptors. Moreover, an increase in a few degrees in the mean surface and groundwater temperature is  
62 also expected (IPCC, 2014). This phenomenon may affect temperature-dependent mobilization and  
63 (bio)degradation processes (Knauss et al., 2000; McAlexander and Sihota, 2019; Yadav et al., 2012;  
64 Zeman et al., 2014), further modifying the LNAPL constituents partitioning and release into air and  
65 groundwater.

66 Here we review and link literature primarily from the last two decades to form a basis for the  
67 possible evolution of all the processes affecting LNAPL mobility, partitioning, and (bio)degradation in  
68 the context of climate change. We focus mainly on the two factors that may have the most significant  
69 effect on LNAPL: groundwater level variations and temperature changes. A better understanding of  
70 likely transitions in the magnitude of the dominant processes provides a basis for better management  
71 and mitigation of the risks associated with LNAPL contaminated sites.

## 72 **2. Historical View**

### 73 **2.1. LNAPL features**

74 Petroleum LNAPLs (e.g., diesel, gasoline, crude oil) can be long-term persistent sources of  
75 groundwater and soil pollution that reach the SZ and USZ upon release. The LNAPL is characterized  
76 by a hydrophobic and non-ionic nature in the presence of water and exhibits a lower density than water.  
77 While LNAPL can correspond to a single chemical compound such as benzene, it is often a complex  
78 mixture of several hundred components with different chemical properties (Güler, 2019; Gupta et al.,

79 2019). Branched and *n*-alkanes (mainly  $<C_{25}$ ), cycloalkanes, alkenes, cycloalkenes, acetylenes and,  
80 BTEX (benzene, toluene, ethylbenzene, xylenes) are common LNAPL components.

## 81 **2.2. LNAPL mobility, partitioning process, and biodegradation**

82 After the release of LNAPLs into the subsurface, the mobile phase infiltrates downward through  
83 the soil porosity (Fig. 1i). During migration through the USZ, a significant part of the pollution can be  
84 trapped as residual LNAPL ganglia by capillary forces or sorbed to soil grains. Many of these  
85 components have a high vapor pressure and can directly volatilize into soil gas to form potentially  
86 harmful VOC emissions (McCarthy and Johnson, 1993; Nambi and Powers, 2003; Patterson and Davis,  
87 2009). If a sufficient volume of LNAPL is released, mobile LNAPL can reach and accumulate at the  
88 water table (Illangasekare et al., 1995; Powers et al., 1994, 1992) (Fig. 1i). Mobile LNAPL then  
89 propagates laterally in the direction of decreasing hydraulic gradient in the capillary fringe, forming  
90 residual lenses (Schroth et al., 1995). Mobile and residual LNAPL provide a source of soluble  
91 hydrocarbons to water infiltrating through the soil and to surrounding groundwater, forming a dissolved  
92 plume of LNAPL constituents (Fig. 1i, Huntley and Beckett, 2002; Lee and Chrysikopoulos, 1998;  
93 Mobile et al., 2012). Mechanical dispersion and diffusion combined with the advective groundwater  
94 flux then lead to the transverse migration of dissolved phase constituents, increasing the risks to  
95 receptors (e.g. drinking water supply) where groundwater is discharged (Picone et al., 2013; Yadav and  
96 Hassanizadeh, 2011). It remains complex and challenging to predict the evolution of these LNAPL  
97 contaminated environments over time, and the effectiveness of remediation techniques (Newell, 1995).

98 The native microorganisms of the soil also contribute to these variations in degrading LNAPL  
99 components (Ortega-Calvo and Alexander, 1994; Zeman et al., 2014). The diversity of the microbial  
100 community, microbial processes, and thus hydrocarbon components biodegradation is complex and  
101 strongly varies with depth along with redox conditions, electron acceptors' availability, and LNAPL  
102 composition (Garg et al., 2017; Sookhak Lari et al., 2019). Biodegradation mediated by microorganisms  
103 often follows a redox succession: aerobic, anaerobic respiration, fermentation, or methanogenesis (Garg  
104 et al., 2017; Gupta et al., 2019; Irianni-Renno et al., 2016). Works to identify the nature of the  
105 microorganisms and the mechanisms controlling bacterial activity are in progress (Bruckberger et al.,

106 2021) and there is no doubt about their major contribution to the LNAPL natural attenuation rates (Rivett  
107 and Sweeney, 2019).

### 108 **2.3. Effect of groundwater table variations at LNAPL sites**

109 Under 'steady-state' water table conditions, dissolution, volatilization processes, and transverse  
110 migration of the dissolved LNAPL constituents are relatively limited because of the small vertical  
111 dispersion, and the slow diffusion of dissolved LNAPL compounds (Chompusri et al., 2002; Dobson et  
112 al., 2007; Gupta et al., 2019; Huntley and Beckett, 2002; Lenhard et al., 1993). Retention and mobility  
113 of LNAPL in a saturated porous medium depend on the saturation of each phase in the USZ (air, water,  
114 LNAPL). Hysteresis effect strongly driven by the variations of the water table level often occurs, as the  
115 mobile LNAPL phase moves vertically along with the groundwater fluctuations (Gatsios et al., 2018;  
116 ITRC, 2018; Kemplowski and Chiang, 1990; Steffy et al., 1998). Within the mobile LNAPL phase, the  
117 LNAPL saturation is high and water is restricted to smaller pores and exhibits a low relative permeability  
118 (Fig. 3). When the water table drops, the mobile LNAPL moves down with the water table level (Figs.  
119 1ii, 3ii, Ballesterro et al., 1994; Steffy et al., 1998), causing the redistribution of the LNAPL and the  
120 reconfiguration of the partitioning of LNAPL components between the different phases. A part of the  
121 LNAPL remains as discontinuous residual LNAPL ganglia in the USZ (Charbeneau, 2007; Jeong and  
122 Charbeneau, 2014; Kechavarzi et al., 2005; Kemplowski and Chiang, 1990; Lenhard et al., 1993). The  
123 most volatile and soluble compounds of the LNAPL can volatilize or be leached by successive water  
124 infiltration and contribute to the evolution of the dissolved plumes (Kechavarzi et al., 2005). The  
125 subsequent rise of the water table (Fig. 1iii, 3ii-iii) results in upward redistribution of mobile LNAPL,  
126 leaving behind some immobile entrapped LNAPL droplets in the SZ (Charbeneau, 2007; Lenhard and  
127 Parker, 1990). The zone of the water table and LNAPL fluctuation is often called the smear zone. During  
128 successive drainage/imbibition phases, the effect of capillary pressure, as well as the trapping of fluids  
129 in the SZ and USZ, continuously modify the water flow paths (Sookhak Lari et al., 2016a). These  
130 hysteresis effects accompanied by additional LNAPL-water interactions (groundwater and rainwater)  
131 favor the mobilization of the contaminants (Parker and Lenhard, 1987; Van Geel and Sykes, 1997).  
132 Hence, seasonal or pump-induced groundwater level fluctuations often lead to (i) significant

133 redistribution and spreading of the pollutants through the water table fluctuation zone (Fig. 1), (ii) a  
134 decrease in the average LNAPL saturation and mass of the mobile LNAPL remaining afterward (Fig. 3,  
135 Charbeneau, 2007; Kemblowski and Chiang, 1990; Lenhard et al., 1993; Lenhard and Parker, 1990;  
136 Newell, 1995; Reddi et al., 1998; Van Geel and Sykes, 1997), and (iii) a decrease in LNAPL recovery  
137 yield.

### 138 **3. Effects of groundwater table and temperature variations on LNAPL behavior**

#### 139 **3.1. Impact of climate change on groundwater**

140 Climate and groundwater flow systems are in constant dynamic balance. Changes in surface  
141 hydrological processes and vegetation cover in response to fluctuations of temperature and precipitation  
142 patterns expected in the coming decades will impact the magnitude and the quality of groundwater  
143 recharge. In consequence, groundwater levels will also be impacted (Illangasekare et al., 2015; Taylor  
144 et al., 2013). In most of the world, the IPCC predicts by the end of the century significant global  
145 warming, a decrease in precipitations in the mid-latitudes, and more intense and frequent extreme events  
146 (heatwaves, droughts, heavy precipitations, (IPCC, 2018). The mean surface temperature of the globe is  
147 expected to increase from 1.5°C to 2°C by 2100. However, the temperature can locally lead to much  
148 stronger variations (up to 9°C), this is why higher temperature variabilities were considered in this work.  
149 It has been shown that the mean shallow groundwater temperatures mimic variations of mean surface  
150 temperature (Menberg et al., 2014; Taylor and Stefan, 2009). An increase in the local surface  
151 temperature from 12°C to 20°C should, therefore, lead to a similar increase in mean shallow  
152 groundwater temperatures. This may significantly impact groundwater quality (Menberg et al., 2014;  
153 Taylor and Stefan, 2009) but also the soil moisture content, the microorganisms' activity, and thus, the  
154 LNAPL degradation (McAlexander and Sihota, 2019; Zeman et al., 2014) and mobilization (Margesin  
155 and Schinner, 2001; Picone et al., 2012; Yadav and Hassanizadeh, 2011).

156 The intensity and the temporal distribution of precipitation are expected to change around the  
157 world (IPCC, 2014). Precipitation is likely to be less frequent from spring to autumn in most parts of  
158 the world but will be probably more intense during winter (Dams et al., 2012; Goderniaux et al., 2011,

159 2009). In Europe (except in Scandinavia), a global decrease in the mean daily precipitations up to 23%  
160 in summer, and an increase of 12.3% in winter is expected (Christensen and Christensen, 2007). On the  
161 contrary, the duration and the intensity of meteorological droughts are expected to increase, as well as  
162 the frequency and intensity of extreme precipitation events (+ 25% in Europe by 2100, IPCC, 2014).  
163 These changes will affect both the dynamics and the quality of groundwater recharge, leading probably  
164 to an intensification of groundwater level variations, an increase in the capillary fringe thickness, and  
165 the occurrence of extremely high or low groundwater heads. More intensive pumping rates may also  
166 contribute to more rapid and intense variations in groundwater levels. In the southern aquifers of the  
167 western United States, the total recharge may decline by 20% by 2100 (Meixner et al., 2016). In Europe,  
168 a global decrease in groundwater heads of 8 m can locally occur (Dams et al., 2012; Goderniaux et al.,  
169 2011, 2009). Moreover, the rise in the mean surface temperature may cause an increase in irrigation and  
170 evapotranspiration rates enhancing decreased groundwater heads, especially during summer and drought  
171 events (Green et al., 2011). Such intensification of the groundwater-table fluctuations and global  
172 decrease in the mean groundwater heads may favor the trapping and spreading of the LNAPL across the  
173 smear zone, causing a greater exposure of the contaminant to attenuation and partitioning processes.  
174 The next section, therefore, proposes to summarize current knowledge on the global effect of  
175 groundwater level fluctuations and temperature on LNAPL behavior to discuss the potential evolution  
176 of LNAPL contaminated sites in this context.

### 177 **3.2. LNAPL source zone mobility, partitioning, and depletion**

178 The composition and physical-chemical properties of the LNAPL are temperature-dependent.  
179 Higher temperatures decrease the interfacial tensions, the viscosity, and the density of the LNAPL,  
180 modifying the distribution and the diffusion rate of the organic contaminants through the soil  
181 (Colombano et al., 2020; Sleep and Ma, 1997). A higher temperature also decreases the LNAPL soil-  
182 water partition coefficients and LNAPL/water interfacial tension, favoring LNAPL mobility (Imhoff et  
183 al., 1997; Sleep and Ma, 1997) and decreasing residual LNAPL saturations (Davis, 1994; Philippe et al.,  
184 2020; She and Sleep, 1998; Sinnokrot et al., 1971). The vapor diffusion coefficient of gas also increases  
185 with temperature (Davis, 1997; Knauss et al., 2000; Seager et al., 1963). In the context of climate change,



186 the earth's surface temperature could locally increase from 12°C to 20°C. The effect of this increase in  
187 temperature on the main properties and partitioning coefficients of oil and LNAPL compounds were  
188 calculated based on the available data of the literature and gathered in Tab. 1. The oil viscosity decreases  
189 up to 41% over this temperature range, increasing the LNAPL mobility (Tab. 1). On the contrary, the  
190 variation of the LNAPL density, soil-water partition coefficients, and LNAPL/water interfacial tensions  
191 appear to be negligible over this range of temperatures (Gaito et al., 2012; Imhoff et al., 1997; Sleep and  
192 Ma, 1997). Ten Hulscher and Cornelissen (1996) revealed that a decrease by 2-3% of the equilibrium  
193 sorption constant can be expected under this range of temperatures for most organic pollutants, probably  
194 favoring their desorption and remobilization into the air and water and making them more available for  
195 degrading microorganisms (McAlexander and Sihota, 2019; Yadav and Hassanizadeh, 2011). However,  
196 a striking opposite effect is, nevertheless, observed for BTEX (Tab. 1, David and Moldoveanu, 2019).  
197 The effect of temperature on the sorption trends of the contaminants remains thus, difficult to predict,  
198 especially because no information is available about the variations in  $K_{oc}$  (carbon-water partitioning  
199 coefficient) and  $K_{ow}$  (octanol-water partitioning coefficient) for the other LNAPL compounds in the  
200 investigated range of temperature (Tab. 1). A better understanding of these sorption processes between  
201 10-20°C is, therefore, required since they may significantly limit or delay the spreading of the dissolved  
202 constituents (Prommer et al., 2002). Calculations based on the literature data compilation show that such  
203 an increase in temperature may, nevertheless, strongly increase the saturated vapor pressure of most  
204 LNAPL compounds from 25% to 45% (Tab. 1), highly modifying their volatilization rates. In the light  
205 of these results, it is clear that the expected temperature rise will probably greatly increase gas and VOC  
206 surface emissions, and to a less extent the LNAPL mobility through the soil.

207 Changes in groundwater level also affect LNAPL volatilization and VOC emissions (Guo et al.,  
208 2019; Illangasekare et al., 2014; McCarthy and Johnson, 1993; Picone et al., 2012; Qi et al., 2020; Soucy  
209 and Mumford, 2017; Werner and Höhener, 2002). Rise and fall successions of the groundwater table  
210 level cause the shortening or the lengthening of gas transport pathways from the dissolved LNAPL  
211 plume to the surface (Fig. 1, Guo et al., 2019) and enhance mass transfers towards the dissolved LNAPL  
212 plume and the soil gas phase (McCarthy and Johnson, 1993). When the groundwater table level

213 decreases, the soil water enriched in dissolved LNAPL components is partially drained (Fig. 1ii). The  
214 dissolved LNAPL constituents in pore water are progressively exposed to an air phase, favoring the  
215 transfer of volatiles constituents to the vapor phase (McCarthy and Johnson, 1993; Qi et al., 2020). This  
216 increases VOC emissions and vapor intrusion risks, especially for shallow aquifers (Illangasekare et al.,  
217 2014; McCarthy and Johnson, 1993; Picone et al., 2012; Qi et al., 2020; Thomson et al., 1997; Werner  
218 and Höhener, 2002). Additionally, groundwater fluctuations can promote the advective transport of soil  
219 gases, accelerating the transport of the vapor phase through the USZ and their release into the  
220 atmosphere (Qi et al., 2020; Soucy and Mumford, 2017). During the rise of the groundwater, the increase  
221 in the soil water saturation reduces the soil gas/LNAPL interfacial area, reducing gas diffusivities and  
222 volatilization. Hence, low VOC emissions are sometimes temporarily observed (Petri et al., 2015; Yoon  
223 et al., 2002). However, while the drop in the water table level can create a “suction effect” limiting the  
224 flow of the gas, the upward movement of groundwater creates a “piston effect”, pushing the soil gases  
225 enriched in VOC towards the surface (Fig. 1iii, Boyle and Witherington, 2007). The air trapped at this  
226 moment with LNAPL ganglia in the smear zone below the water table creates a three-phase  
227 LNAPL/air/water system (Fig. 1iii, Lenhard et al., 1993; Fry et al., 1995; Van Geel and Sykes, 1997;  
228 Williams and Oostrom, 2000; Charbeneau, 2007; Dobson et al., 2007), further promoting the transfer of  
229 entrapped and dissolved LNAPL constituents toward the vapor phase in the early time after the upward  
230 movement of groundwater (Fig. 1iii, Soucy and Mumford, 2017). Given these studies, an intensification  
231 of the groundwater fluctuations will enhance volatilization. A global decrease in the average water table  
232 level in response to climate change will increase the global thickness of the USZ, probably favoring the  
233 exposure of the LNAPL constituents to volatilization processes and the enrichment of the soil gas in  
234 VOC. This may also significantly increase the exposure of the residual LNAPL compounds to the  
235 leaching/weathering process by infiltrated meteoric water. The modification of the dynamic moisture  
236 conditions induced by the infiltration of meteoric water resulting from rainfalls or irrigation causes the  
237 leaching/the desorption and the downward aqueous transport of LNAPL constituents (Lee et al., 2001;  
238 Newell, 1995). The increase in this leaching process may affect the chemical and the physical properties  
239 of the residual LNAPL in causing a faster depletion in the most soluble constituents. However, the  
240 contribution of this process also closely depends on the intensity and frequency of precipitation events

241 and will thus probably suffer severe local and temporal modifications in response to the expected change  
242 in precipitation patterns and heavy precipitation frequency (IPCC, 2014). Previous studies showed that  
243 the mobile LNAPL phase can be more subject to adsorption into the smear zone as the water level  
244 fluctuates, preventing the soluble contaminants to be washed away by groundwater level fluctuations  
245 (Yadav and Hassanizadeh, 2011; Yang et al., 2017). However, the influence of groundwater level  
246 fluctuations and temperature on sorption was too poorly documented to conclude.

### 247 **3.3. Dissolved LNAPL plume**

248 Higher temperatures increase the aqueous solubility of the LNAPL (Margesin and Schinner,  
249 2001). However, the aqueous solubility of most LNAPL components evolves only slightly over the 10-  
250 20°C temperature range, and in different ways (Tab. 1). The effect of temperature will thus probably  
251 remain limited since the water solubility of LNAPL remains low between 0 and 20°C (Tab. 1). On the  
252 contrary, the increase in Henry's law constant of the LNAPL compounds by up to 51% is expected in  
253 this range of temperature (Tab. 1), which will probably greatly favor the volatilization of most of the  
254 dissolved LNAPL constituents.

255 Under fluctuating water table conditions, spatial-temporal variations of the dissolved LNAPL  
256 constituents concentrations and the plume thickness are generally observed as a function of the increase  
257 and decrease in the groundwater level (Davis et al., 1999). Below the water table, the entrapped LNAPL  
258 ganglia form a thin continuous film of molecular thickness at the interface between gas and water in  
259 these three-phases systems (Fenwick and Blunt, 1998). These films exhibit higher LNAPL-water  
260 interfacial areas more available for dissolution than in a classical LNAPL/water system (Bradford et al.,  
261 1999; Shojib, 2015). This results in the faster dissolution of the entrapped LNAPL compounds under  
262 fluctuating groundwater table conditions (Shojib, 2015). Moreover, the advection is the dominant  
263 transport pathway for the dissolved LNAPL constituents under fluctuating groundwater conditions  
264 (Gupta et al., 2019). This enhances the depletion of the LNAPL source zone with the preferential  
265 dissolution of the most soluble compounds, leading to a more rapid decrease in the LNAPL source  
266 zone's longevity (Dobson et al., 2007; Gupta et al., 2019). However, this leads also to faster transport  
267 and spreading of the dissolved LNAPL constituents in groundwater along the vertical and the horizontal

268 direction (Davis et al., 1999; Gupta et al., 2019; Yadav and Hassanizadeh, 2011). The pollution thus  
269 reaches a more distant location, creating a larger polluted plume (Gupta et al., 2019; Sarikurt et al., 2017;  
270 Zhou et al., 2015).

271 Despite a probably limited effect of the higher temperatures on the contaminants' aqueous  
272 solubilities, more intense groundwater level fluctuations will probably greatly increase the  
273 water/air/LNAPL interfaces, favoring the spreading and the enrichment of the groundwater dissolved  
274 plume in LNAPL constituents in the climate change context. The increased contribution of the leaching  
275 of residual LNAPL droplets in the USZ, may also further contribute to the dissolved plume, especially  
276 for recent or not yet stabilized LNAPL, still rich in soluble compounds. Nevertheless, the correlation  
277 between the amplitude and the frequency of the water level variations and the enrichment of the  
278 dissolved and gaseous phase in LNAPL compounds is not clear enough (Davis et al., 1999; Eichert et  
279 al., 2017; McAlexander and Sihota, 2019). It remains, therefore, difficult to predict to which extent a  
280 rise or a drop of the water level of a known amplitude can affect dissolution and volatilization processes.  
281 Yet, understanding today the effect of the amplitude of these fluctuations (when they exist) on the  
282 LNAPL plume behavior on different sites could, therefore, help us to better predict the effects of climate  
283 change. The spatial variability between monitoring wells in the same site suggests that other effects may  
284 be at work such as local variations in the hydrogeological properties of the soil (soil heterogeneities), or  
285 in the height of water table variations. The low spatial and temporal resolution of field studies does not  
286 allow the conclusions to be drawn.

### 287 **3.4. Natural source zone depletion**

288 It has been demonstrated that the rise of temperature favors the (bio)degradation of the organic  
289 pollutants (Askarani, 2020; Dagois et al., 2016; Margesin and Schinner, 2001; McAlexander and Sihota,  
290 2019; Yadav et al., 2012; Yadav and Hassanizadeh, 2011; Zeman et al., 2014). Askarani (2020)  
291 demonstrated that monitoring subsurface temperature is a viable technique to resolve LNAPL  
292 attenuation rates for LNAPLs since both factors are correlated. Toluene biodegradation rates have been  
293 shown to double for every 10°C increase in temperature (Yadav et al., 2012). At higher temperatures,  
294 the permeability of the microbial cell membrane of LNAPL-degrading microorganisms is greater,

295 favoring the uptake of nutrients and organic components (Corseuil and Weber, 1994; Zeman et al.,  
296 2014). The toxicity of the contamination is also reduced for the microorganisms since the low molecular  
297 weight compounds are more easily and quickly volatilized at higher temperatures (Davis, 1997).

298 Comparison between experiments under steady-state and fluctuating water levels showed that  
299 successive rises and drops of the water level and the ensuing partitioning of LNAPL components  
300 strongly modify the LNAPL biodegradation rates (Dobson et al., 2007; Gupta et al., 2019; Ismail et al.,  
301 2020; Rainwater et al., 1993; Van De Ven et al., 2021). Experiments by Rainwater et al., (1993) revealed  
302 that a column subjected to cyclic water table variations (15 cm of variations each 48 h) exhibit 15% less  
303 residual fuel contamination after 9 weeks than a static water level column. The extent of the  
304 anaerobic/anoxic zones depends on redox conditions and the availability of electron acceptors, which  
305 suffer spatial and temporal variations as a function of the rises and drops of the groundwater level  
306 (Rezanezhad et al., 2014; Sinke et al., 1998; Van De Ven et al., 2021). Variations of the water table level  
307 also temporarily affect soil moisture, modifying the oxygen diffusion rates in the vadose zone, and thus  
308 aerobic biodegradation processes. This affects the biodegradability of the organic pollutants and the  
309 ensuing gaseous emissions (Davis et al., 2005; Dobson et al., 2007; Gupta et al., 2019; Van De Ven et  
310 al., 2021; Zhou et al., 2015). More generally, successive groundwater level variations naturally enhance  
311 (i) the diffusion of oxygen (Dobson et al., 2007; Gupta et al., 2019; Haberer et al., 2012; Lenhard et al.,  
312 1993; Vorenhout et al., 2004), (ii) the renewal of micronutrients through the soil and the water column  
313 by advective transport (Rezanezhad et al., 2014; Schimel et al., 2007), (iii) the evacuation of the reaction  
314 by-products accumulated during biodegradation (Nyer, 2000), (iv) the functional diversity and  
315 flexibility of microorganisms themselves (Zhou et al., 2015). This naturally enhances the biochemical  
316 and microbial dynamics, leading to higher microbial degradation rates of the dissolved, entrapped, and  
317 residual organic contaminants (Dobson et al., 2007; Fry et al., 1997; Rezanezhad et al., 2014; Suthersan  
318 et al., 2015). This process is further accentuated by the important spreading of the mobile LNAPL and  
319 dissolved LNAPL compounds across the soil and the water column, making the LNAPL compounds  
320 more available to the microorganisms (Dobson et al., 2007; Gupta et al., 2019; Zhou et al., 2015). The  
321 intensification of groundwater fluctuations in response to climate change may thus conduce to greater

322 availability of carbon and nutrients to soil microorganisms, sustaining biodegradation of the LNAPL.  
323 The global decrease in the mean groundwater heads and the ensuing increase in the USZ thickness may  
324 also favor the exposure of the residual LNAPL phase to the air, favoring aerobic LNAPL  
325 (bio)degradation processes.

326 It seems, therefore, relatively clear that an increase in temperature by a few degrees and an  
327 intensification of water table level fluctuations will be beneficial to the activity of the microorganisms  
328 at most contaminated sites, favoring the natural attenuation of contaminations. While this may reduce  
329 the risks associated with the residual and mobile LNAPL phase, this may, however, enhance surface  
330 emissions (mainly CO<sub>2</sub> and CH<sub>4</sub>) (Fig. 1ii, iii, Mayer, 2005; Amos and Mayer, 2006; Sihota et al., 2013).  
331 Indeed, the important source of gas resulting from the biodegradation of the dissolved LNAPL  
332 constituents in groundwater may also promote the ebullition of gas bubbles in the SZ (Amos and Mayer,  
333 2006; Rezaeehad et al., 2014; Sihota et al., 2013). This generates important vertical gas bubble flow  
334 from the groundwater at the origin of advection-dominated conditions in the USZ (Soucy and Mumford,  
335 2017). However, this “bubble-facilitated VOC transport” may probably have a limited impact on VOC  
336 emissions on the surface as many of these VOCs are likely to be degraded by the increased bacterial  
337 activity. Nevertheless, this could contribute to an increase in CO<sub>2</sub> and CH<sub>4</sub> surface emissions. These  
338 attenuation rates may, therefore, be faster in the coming decades at most of the contaminated sites.  
339 Intense biodegradation of the dissolved LNAPL constituent also sustains high concentration gradients,  
340 maintaining high dissolution processes over time (Davis et al., 1999). This may contribute to the faster  
341 natural attenuation of the contamination but without lowering the concentration of the dissolved  
342 compounds in the early years after the contamination (Dobson et al., 2007; Gupta et al., 2019).  
343 Moreover, above certain concentrations that depend on the bacterial strains and organic species, LNAPL  
344 components become toxic for the microorganisms, reducing the efficiency of biodegradation (Gupta et  
345 al., 2019). In some areas where important concentrations of dissolved LNAPL components are released,  
346 the biodegradation rates may thus remain limited. The biodegradability of certain LNAPL compounds  
347 exhibits also spatial-temporal variations depending on the availability of more easily biodegradable  
348 organic species and the accommodation time of the microbial community to the less biodegradable and

349 toxic compounds (Sinke et al., 1998). This incubation time varies greatly between LNAPL compounds  
350 (Wiedemeier et al., 1995). The extent of the effect of climate change on biodegradation rates may thus  
351 be very inconsistent across sites. Finally, the changes in the mass of the dissolved LNAPL constituents  
352 and the availability of electron acceptors are decreasing with the increasing sorption phenomenon (up  
353 to -30%) under a fluctuating water level. This may impact biodegradation rates (Prommer et al., 2002).  
354 A better understanding of the effects of climate change on these sorption effects is therefore crucial.  
355 However, this implies a better integration of the soil properties at sites including composition, sorption  
356 capacity, and soil heterogeneities. This is all the more important since the presence of soil  
357 heterogeneities (*i.e.* more or less compacted layers) influences not only sorption processes but also soil  
358 moisture contents, and gas diffusivities (Davis et al., 2005). These expected effects of climate change  
359 on LNAPL contaminated sites are summarized in Tab. 2.

#### 360 **4. Cases of different climatic conditions and contaminated sites properties**

361 Global climate models often give inconsistent predictions for precipitation patterns and  
362 groundwater recharge (Goderniaux et al., 2011; Meixner et al., 2016; Smerdon, 2017). Hence,  
363 uncertainties remain related to the difficulty to predict the effect of climate change on groundwater  
364 resources. There is a lack of knowledge about the future evolution of precipitations and extreme events'  
365 frequency and intensity and their consequences on the hydrological cycle, the anthropic activity  
366 (especially water consumption), and groundwater resources (Meixner et al., 2016; Smerdon, 2017).  
367 Furthermore, the effect of climate change on LNAPL may vary locally as a function of specific sites  
368 properties but also between arid, cold, or humid coastal environments, where different precipitation and  
369 groundwater recharge patterns are expected in the coming decades (Christensen and Christensen, 2007;  
370 IPCC, 2014; Meixner et al., 2016). This paragraph, therefore, proposes to discuss the possible effects of  
371 climate change on LNAPL with different climatic conditions. These expected effects of climate change  
372 on LNAPL contaminated sites under these particular climatic conditions are summarized in Tab. 3

##### 373 **4.1 Cold regions**

374 In cold environments (such as boreal environments), the environmental factors consist in low  
375 temperatures ( $<8^{\circ}\text{C}$ ), low soil nutrient contents and availability, and excess water distribution (rainfalls  
376  $> 900$  mm/year) which is often responsible for low soil oxygen diffusivities (Rayner et al., 2007). Hence,  
377 natural volatilization, dissolution, and biodegradation of petroleum hydrocarbons are generally reduced  
378 to nearly negligible rates (Boethling et al., 2009; Rayner et al., 2007). Hydrocarbon pollutants can,  
379 therefore, remain for long periods and be more damaging to the environment (Boethling et al., 2009). In  
380 the climate change context, these areas could experience greater global warming than the rest of the  
381 world ( $+5$  to  $+9^{\circ}\text{C}$ , IPCC, 2014). Moreover, the increase in winter precipitations ( $+ 30$ - $50\%$ , Christensen  
382 and Christensen, 2007; IPCC, 2014) and the reduction of the snow cover and soil frost can be expected  
383 to enhance the groundwater recharge, leading to a rise in groundwater levels in winter (Okkonen et al.,  
384 2010). On the contrary, warmer temperatures will enhance evapotranspiration rates, leading to a  
385 decrease in groundwater recharge and heads in summer (Okkonen et al., 2010). This may have several  
386 consequences on LNAPL. The increased temperature and snowmelt and decreased frost may contribute  
387 to oxygen-rich water inputs (Okkonen et al., 2010), enhancing the LNAPL-degrading microorganism's  
388 activity and biodegradation rates. Increased spreading of LNAPL across the soil and groundwater can  
389 be expected due to more intense water table fluctuations. The warmer temperatures will increase LNAPL  
390 viscosity (except for older contaminations where all soluble and volatile compounds have already been  
391 remobilized; in this case, the change will be minimal) and LNAPL compounds volatility and solubility  
392 (to a less extent). This may enhance the transfer of LNAPL constituents to the dissolved and the gaseous  
393 phase, decreasing the contamination lifetime. For example, the vapor pressure of benzene increases up  
394 to 70% between  $5^{\circ}\text{C}$  and  $15^{\circ}\text{C}$  (Sanemasa et al., 1982). It is also conceivable that more frequent flooding  
395 events and surface-water intrusion occur from wetlands, increasing the risk of groundwater exposure to  
396 new contaminations.

#### 397 **4.2. Arid and semi-arid zones**

398 Arid and semi-arid areas are characterized by specific extremes environmental conditions,  
399 including highly variable temperatures and important water table level and soil moisture content  
400 dynamics. These conditions are generally favorable to the mobilization and the biodegradation of the



401 LNAPL (McAlexander and Sihota, 2019; Yadav and Hassanizadeh, 2011). In the context of climate  
402 change, these arid regions are expected to become drier and warmer (IPCC, 2014). The expected  
403 increase in temperature (+4 to +7°C, IPCC, 2014) may lead to a net rise in the evapotranspiration rate,  
404 a strong decrease in soil moisture content, and a significant increase in the pressure on the groundwater  
405 resources for drinking water, agricultural or industrial activities (Meixner et al., 2016; Taylor et al.,  
406 2013). At the same time, the drop in precipitation in spring and summer and the declining snowpack  
407 (the major part of the water table recharge in mountainous areas) may drastically reduce the groundwater  
408 recharge (Meixner et al., 2016). Hence, a decrease in groundwater recharge up to -30% is expected in  
409 some arid lands by 2100 (e.g. San Pedro Basin AZ, Sonora Mexico, Meixner et al., 2016). Several  
410 consequences may, therefore, be expected for existing LNAPL contaminated sites: (i) greater spreading  
411 of LNAPL across both the USZ and the SZ due to global falling water levels and greater level variations  
412 tied with the encroachment catchment areas of pumping wells; (ii) greater volatility of LNAPL  
413 compounds and an increase in VOC emissions in response to higher temperatures and LNAPL/air  
414 surface areas in the SZ. The extremely hot temperatures in summer may also decrease nucleic acids,  
415 proteins, and the enzyme activity of soil microorganisms (Corseuil and Weber, 1994). The increase of  
416 droughts may dry the soil out, preventing the development of LNAPL-degrading microorganisms  
417 (Dagois et al., 2016). More intense drought events and heatwaves may thus take over the microbial  
418 population from the soil in these areas, decreasing significantly the LNAPL natural attenuation rates.  
419 The expected increase in extreme precipitation events' frequency and intensity may also lead to an  
420 increasing number of floods (IPCC, 2014). These events may accelerate riverbank erosion and damage  
421 LNAPL transport infrastructures, and storage tanks, causing important new LNAPL spills. For example,  
422 Colorado has more than 5,900 oil and gas wells within 500 feet of the state's rivers and streams. In 2013,  
423 severe flooding occurred, damaging more than 2,650 oil and gas facilities (wells and storage tanks),  
424 resulting in the spill of approximately 48,250 gallons of oil and condensate in the environment.

### 425 **4.3. Humid coastal areas**

426 Many LNAPL spills occurred in coastal environments (Gupta et al., 2019, 2018; Rice et al.,  
427 1995). In coastal regions, groundwater tables often suffer highly dynamic conditions due to tidal effects.

428 These environments are particularly vulnerable to climate change. In the climate change context, the sea  
429 level is expected to rise (1,7 mm/year) from 0.43 to 0.84 m by 2100 due to thermal expansion, melting  
430 ice sheets and glaciers, and land water storage changes (IPCC, 2014). Most coastal areas -are supposed  
431 to become wetter due to the increase in precipitations by the end of the century (Christensen and  
432 Christensen, 2007; IPCC, 2014). These phenomena are already at work. Between 1991 and 2012, coastal  
433 regions of the USA recorded an increase in precipitation and extreme precipitation events of 5-15% and  
434 5-71% respectively (USGCRP, 2014). The sea levels have risen by approximately 15 cm since 1960 in  
435 the western USA, and are now rising about 3,3 cm per decade (USGCRP, 2014). The increasing sea  
436 level and the more frequent extreme precipitation and storm frequency and intensity are expected to  
437 cause more frequent floods, which may greatly contribute to coastal erosion (IPCC, 2014). These  
438 phenomena may have important consequences on LNAPL contaminations. First, the recharge of  
439 adjacent coastal aquifer systems and average groundwater heads are expected to increase in coastal  
440 humid environments (IPCC, 2014). This may significantly reduce the vadose assimilation space, or even  
441 totally submerge residual LNAPL contaminants by groundwater flooding. This may limit VOC  
442 emissions but favor the dissolution and the dilution of LNAPL compounds in groundwater. It may also  
443 promote the spreading and the transfer of the dissolved contaminants and the mobile LNAPL to the sea  
444 or connected rivers. This may, however, decrease soil gas diffusivities. The rise of the sea level can also  
445 increase salt-water intrusion into groundwater (IPCC, 2014), impacting the microorganisms' activity and  
446 the biodegradation rates of LNAPL components (Rezanezhad et al., 2019). Moreover, most of the  
447 petroleum refineries and industries are located in coastal regions across the world (e.g of the California  
448 coast, USA Rice et al., 1995). Therefore, the floods caused by the rising sea level, heavy precipitations,  
449 and storms are expected to significantly damage infrastructures (Rahimi et al., 2020) such as petroleum  
450 industries' storage or transportation facilities. Thus, despite the precautions taken to better manage the  
451 risk of possible new spills or to stabilize existing contaminations in the last decades, new soil and  
452 groundwater contamination may occur.

## 453 **5. Conclusions and perspectives**

454 Predicting the effect of climate change on groundwater is complex and often limited to very  
455 local scales and particular climatic conditions. Climate change predictions on LNAPL sites are thus  
456 uncertain and depend on these inconsistent various numerical models. However, according to current  
457 global predictions, the higher amplitude of groundwater table variations and higher temperatures will  
458 probably increase biodegradation processes, the LNAPL mobility, and spreading across the smear zone,  
459 favoring the release of LNAPL compounds to the atmosphere and groundwater but decreasing the  
460 LNAPL mass and its longevity. Outcomes will, nevertheless, vary greatly across arid, cold, or humid  
461 coastal environments, where different effects of climate change are expected. For example, the expected  
462 drop of the water table levels and soil moisture contents may decrease biodegradation rates in arid lands,  
463 where extreme temperatures and droughts events are expected. In coastal areas, higher precipitations  
464 and groundwater levels may lead to the submersion and the dilution of the LNAPL compounds in  
465 groundwater and connected rivers. In colds areas, warmer temperatures may significantly increase the  
466 mobility of LNAPL, dissolution, and volatilization processes. The particularities of each site, need,  
467 therefore, to be considered.

468 Another difficulty comes from the differences between experimental, numerical, and field  
469 studies carried out on LNAPL, where the time scale, the amplitude of groundwater level variations, the  
470 porous medium type vary greatly between studies (Tab. 4, 5, Garg et al., 2017; Lari et al., 2016; Sookhak  
471 Lari et al., 2019). There are relatively few field studies (28%) compared to laboratory experiments and  
472 numerical modeling (Tab. 4). However, laboratory experiments and numerical works are simplified  
473 models that neglected the soil composition and heterogeneities, the LNAPL chemical complexity (Tab.  
474 5), or the amplitude of water table fluctuations. Although these properties are specific to each site, they  
475 can generate discrepancies between field observations and the results of numerical models or laboratory  
476 experiments. The amplitude of water table fluctuations may control the evolution of dissolved LNAPL  
477 constituents' concentration (Teramoto and Chang, 2017), soil moisture content, gas diffusivity, and thus,  
478 VOC fluxes (Qi et al., 2020). Variations in soil grain sizes, composition, or compaction determine the  
479 permeability which is one of the main parameters affecting rainfall infiltration, thermal-physical  
480 effective parameters, the migration path, the plume velocity, the entrapment, LNAPL saturation

481 distribution in the soil, gas soil moisture content, gaseous phase pathways, and gas diffusivities (Davis  
482 et al., 2005; Huntley and Beckett, 2002; Illangasekare et al., 1995b; Lehmann et al., 2012; Powers et al.,  
483 1998; Qi et al., 2020; Sarikurt et al., 2017; Sun, 2016). The behavior of an organic component in the  
484 single-component conditions of laboratory experiments and numerical models is not always  
485 representative of the behavior of the complex LNAPL mixtures present at most contaminated sites due  
486 to the interactions existing between different organic species that may affect the solubility of each  
487 compound (Lekmine et al., 2014; Vasudevan et al., 2016). This highlights the necessity of replacing the  
488 current compartmentalized vision of these three-phase systems with more dynamic/real-time monitoring  
489 of LNAPL integrated approaches that consider the full complexity of these contaminated sites.

490 Finally, the evolution of environmental standards and regulations over the last decades has led  
491 to a dramatic reduction in LNAPLs releases (ITRC, 2018b, 2009). Remediation efforts and precautions  
492 taken on industrial sites have stabilized and/or reduced the evolution and mobilization of the LNAPL  
493 compounds (Askarani and Sale, 2020). Many of these LNAPL sites will be only slightly affected by a  
494 slight increase in surface and groundwater temperature or higher water level variations. On the other  
495 hand, for coastal or riverside sites, the increased risk of flooding associated with rising sea levels and  
496 the frequency and intensity of extreme events could compromise these efforts and lead to the formation  
497 of new sources of contamination. A better understanding of these risks may help to prevent and mitigate  
498 their impacts. Understanding the effects of climate on current and future contaminated sites could  
499 therefore have great environmental and economic benefits.

#### 500 **Declaration of Competing Interest**

501 The authors declare that they have no known competing financial interests or personal relationships that  
502 could have appeared to influence the work reported in this paper.

#### 503 **Acknowledgments**

504 This work was supported by the French PIA project “Lorraine Université d’Excellence”, reference  
505 ANR-15-IDEX-04-LUE, and the BRGM (the French Geological Survey). The authors would like to  
506 thank Lorraine University and the BRGM. This work is included in the scientific program of the GISFI

507 research consortium dedicated to the knowledge and the development of remediation technologies for  
508 degraded and polluted lands (Groupement d'Intérêt Scientifique sur les Friches Industrielles -  
509 <http://www.gisfi.univ-lorraine.fr>).

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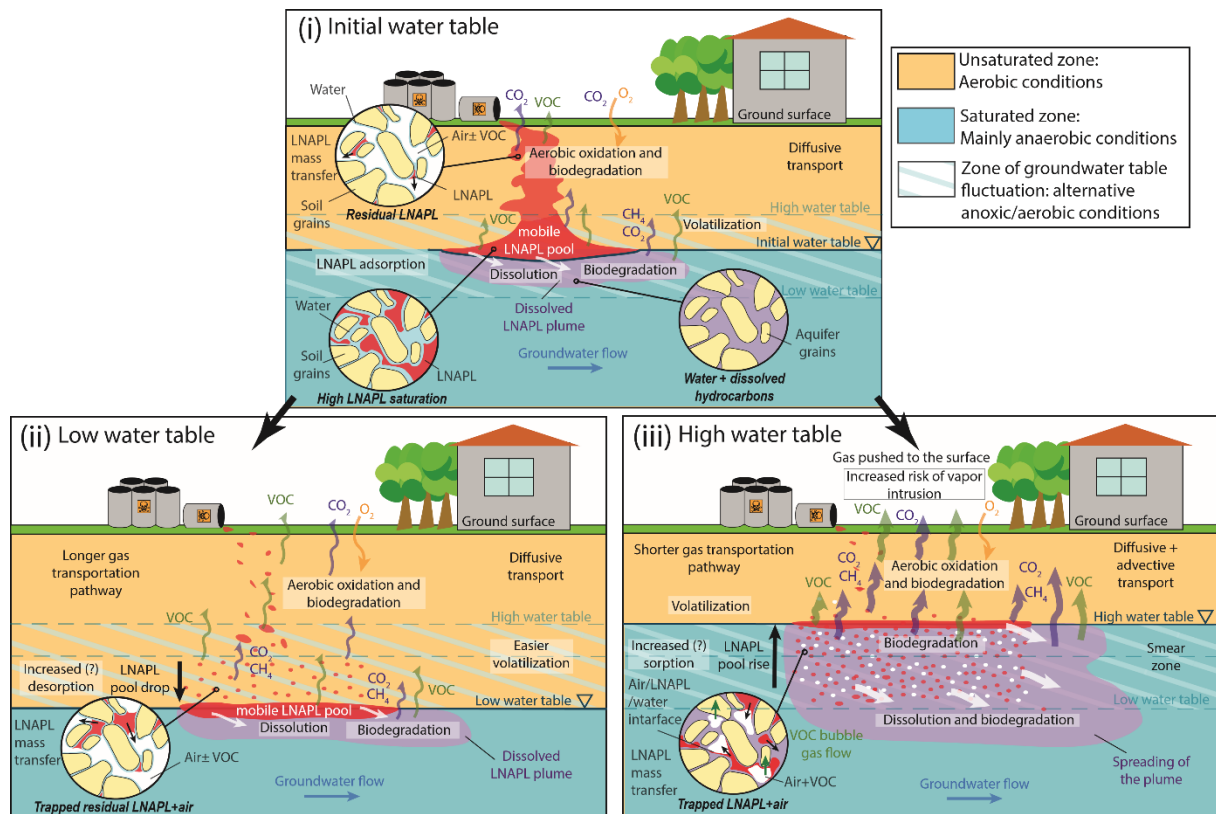
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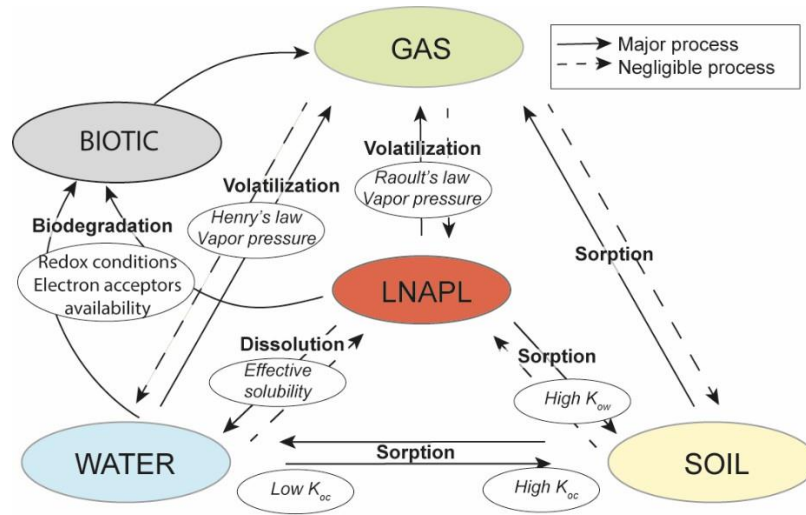
992 **Figures**



993

994 Fig. 1. Conceptual model showing LNAPL mobilization and transformation processes in a contaminated  
 995 site during water table fluctuations: (i) initial water table level during the oil spill; (ii) low water table  
 996 level (dry season); (iii) high water table level (wet season). VOC: volatile organic carbon.

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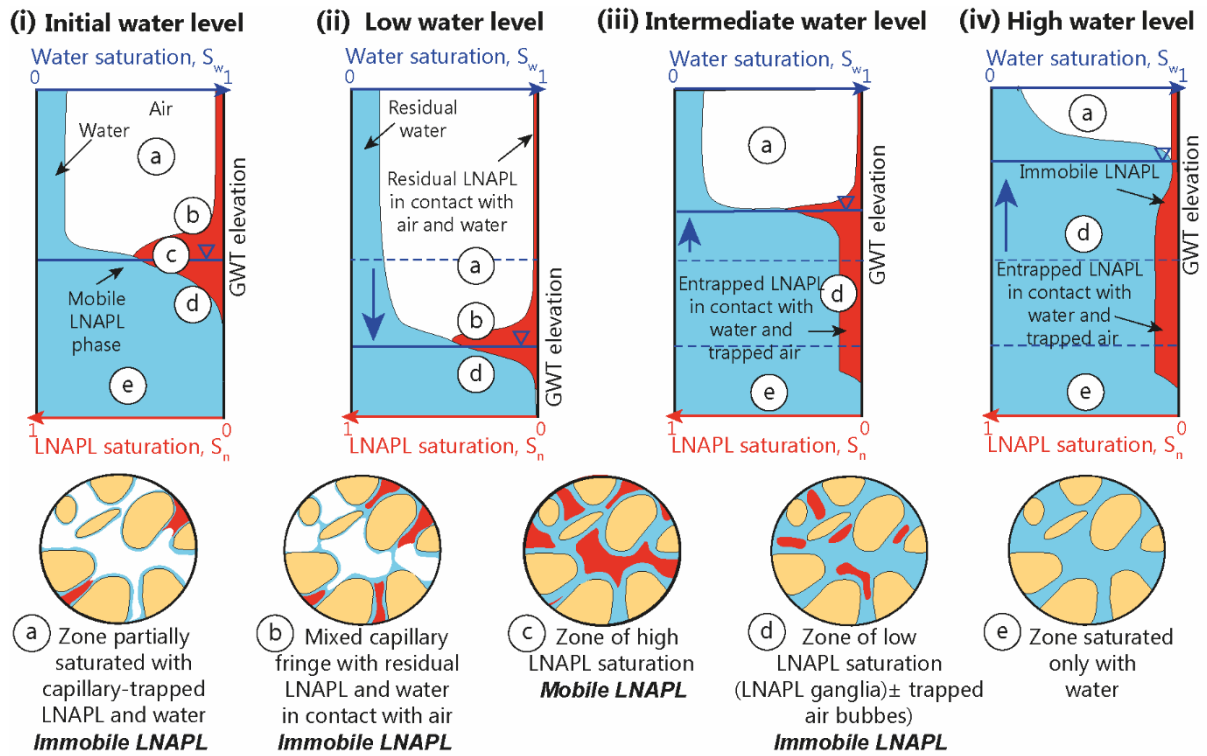


998

999 Fig. 2. Dominant processes involved in the LNAPL biodegradation and compounds partitioning between  
 1000 the phases potentially present in the saturated and unsaturated zone.  $K_{ow}$ : octanol-water partitioning  
 1001 coefficient.  $K_{oc}$ : carbon-water partitioning coefficient.

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1003

1004 Fig. 3. A conceptual representation of the fluctuations of LNAPL ( $S_n$ ) and water ( $S_w$ ) saturations of the  
 1005 soil during variations of the water table between (i) an initial, (ii) a low, (iii) an intermediate, and (iv) a  
 1006 high water table level (modified after ITRC, 2018; Rivett et al., 2014). The circular images a) to e) show  
 1007 the distribution and the mobility of the mobile LNAPL phase in the porosity. GTW: groundwater table.

1008

1009 **Tables**

1010 Tab. 1. Main properties and partitioning coefficients of oil and different LNAPL components between  
 1011 a temperature of 12 and 20°C.

Temperature (°C)	Vapor pressure (mmHg) <sup>a</sup>				Ref.
	12.0	14.0	17.0	20.0	
Benzene	50.4	55.9	64.9	75.1	(Willingham et al., 1945)
Toluene	13.9	15.6	18.4	21.7	(Pitzer and Scott, 1943)
m-Xylene	3.8	4.3	5.1	6.2	(Pitzer and Scott, 1943)
n-Hexane	83.8	92.1	105.9	121.4	(Willingham et al., 1945)
n-Heptane	22.4	25.0	29.5	34.7	(Carruth and Kobayashi, 1973; Willingham et al., 1945)
n-Decane	0.45	0.50	0.60	0.71	(Carruth and Kobayashi, 1973)
Cyclohexane	52.5	58.0	67.2	77.5	(Li et al., 1973)
Cyclopentane	185.0	201.8	229.2	259.6	(Willingham et al., 1945)
Henry's law constant (atm.m <sup>3</sup> /mol)					
Benzene	3.05E-03	3.38E-03	3.94E-03	4.60E-03	(Staudinger and Roberts, 2001)
Toluene	3.41E-03	3.79E-03	4.42E-03	5.14E-03	(Staudinger and Roberts, 2001)
m-Xylene	3.99E-03	4.43E-03	5.15E-03	5.97E-03	(Staudinger and Roberts, 2001)
n-Hexane	0.905	0.99	1.14	1.30	(Abraham and Matteoli, 1988)
n-Heptane	1.20	1.33	1.54	1.77	(Abraham and Matteoli, 1988)
n-Decane				5.15	(Clough, 2014)
Cyclohexane	0.11	0.12	0.13	0.15	(Ashworth et al., 1988)
Cyclopentane	9.03E-02	9.81E-02	0.11	0.13	(Hansen et al., 1993)
Solubility in water (mg/L)					
Benzene	1589.5	1581.7	1585.6	1597.3	(Sanemasa et al., 1982)
Toluene	510.6	512.9	516.5	520.1	(Sanemasa et al., 1982)
m-Xylene	156.6	157.4	158.7	160.0	(Sanemasa et al., 1982)
n-Hexane	10.4	10.5	9.4	10.6	<sup>b</sup>
n-Heptane	2.1	2.1	2.2	2.3	(Nelson and De Ligny, 1968)
n-Decane				9.0E-03	(Clough, 2014)
Cyclohexane	86.7	88.0	81.2	70.0	(Budantseva et al., 1976; Pierotti and Liabastre, 1972)
Cyclopentane	341.1	341.7	304.8	249.0	(Pierotti and Liabastre, 1972)
Log K <sub>oc</sub> (L/kg)					
Benzene	1.88	1.89	1.91	1.92	(Sabljic et al., 1995) <sup>c</sup>
Toluene	2.28	2.30	2.31	2.33	(Sabljic et al., 1995) <sup>c</sup>
m-Xylene				2.34	(Sabljic et al., 1995)
Hexane				3.34	ECHA <sup>d</sup>
Heptane				2.38	ECHA
Decane				4.16	ECHA
Cyclohexane					
Cyclopentane				2.53	ECHA
Log K <sub>ow</sub>					
Benzene	2.20	2.21	2.24	2.25	(David and Moldoveanu, 2019)
Toluene	2.69	2.71	2.73	2.75	(David and Moldoveanu, 2019)
m-Xylene				3.20	(Sabljic et al., 1995)
Hexane				3.90	(Hansch et al., 1985) (25°C)
Heptane				4.66	(Miller et al., 1985) (23°C)
Decane				5.01	(Coates et al., 1985)
Cyclohexane				3.44	(Hansch et al., 1985) (25°C)
Cyclopentane				3.00	(Hansch et al., 1985) (25°C)
Density (g/cm <sup>3</sup> )					
Oil (Voltesso 35)	0.859	0.859	0.858	0.858	(Sleep and Ma, 1997) <sup>e</sup>

Dynamic viscosity (cP)					
Oil (Voltesso 35)	33,5	29,0	23,7	19,6	(Sleep and Ma, 1997) <sup>f</sup>
Interfacial tension of oil-water system (mJ/m <sup>2</sup> )					
Oil (Voltesso 35)	44.3	43.8	43.1	42.4	(Sleep and Ma, 1997) <sup>g</sup>

1012 <sup>a</sup> Calculated using Antoine Equation Parameters using data of the cited references.

1013 <sup>b</sup> Calculated from Henry's law constant and the vapor pressure.

1014 <sup>c</sup> Calculated from the log  $K_{ow}$  after the equation of Sabljic et al. (1995):  $\log K_{oc} = 0.81 * \log K_{ow} + 0.10$ .<sup>dc</sup>

1015 <sup>d</sup> European Chemicals Agency (ECHA): <https://echa.europa.eu/fr/information-on-chemicals>. The data  
1016 of each parameter and compound at the different temperatures were determined according to the data  
1017 available in the respective references.

1018 <sup>e</sup> Calculated after the equation of Sleep and Ma (1997):  $\rho_{oil} = 0.8610 - 1.1750 * 10^{-4} * T - 2.7738 * 10^{-6} * T^2$

1019 <sup>f</sup> Calculated after the equation of Sleep and Ma (1997):  $\ln \mu_{oil} = 24.306 - 1.767 * 10^4 / T - 3.366 * 10^6 / T^2$

1020 <sup>g</sup> Calculated after the equation of Sleep and Ma (1997):  $\gamma_{oil} = 47.226 - 0.244 * T$

1021

1022 Tab. 2. Summary of the main expected global effects of the increase in temperature and groundwater  
 1023 table fluctuations on the LNAPL mobility, the dissolved plume, and natural attenuation rates under the  
 1024 climate change context.

	<b>Main effects of the increase in temperature from 12 to 20°C</b>	<b>Main effect of more intense groundwater level variations</b>	<b>Global expected effect of climate change</b>
LNAPL source zone mobility, partitioning, and depletion	<ul style="list-style-type: none"> <li>• Decreased LNAPL viscosity (up to 41%).</li> <li>• Sorption?</li> <li>• Increased saturated vapor pressures (up to 45%)</li> </ul>	<ul style="list-style-type: none"> <li>• Greater spreading of the LNAPL across the SZ and USZ</li> <li>• Greater exposure of the LNAPL to the air, meteoric water, and groundwater</li> <li>• Accelerated diffusion and advective transport of soil gas</li> </ul>	<ul style="list-style-type: none"> <li>• Increased global LNAPL mobility</li> <li>• Increased leaching of the residual LNAPL by infiltrated meteoric water</li> <li>• Increased volatilization from the mobile, residual LNAPL</li> <li>• Increased VOC surface emissions</li> </ul>
Dissolved plume	<ul style="list-style-type: none"> <li>• Low variation of the LNAPL compounds solubility</li> <li>• Increased Henry's law constant (up to 51%)</li> </ul>	<ul style="list-style-type: none"> <li>• Greater LNAPL- meteoric and groundwater interfacial areas</li> <li>• Easier dissolved phase transportation by advection</li> </ul>	<ul style="list-style-type: none"> <li>• Increased residual and entrapped LNAPL constituents' dissolution</li> <li>• Increased dissolved groundwater plume concentration</li> <li>• Greater spreading of the dissolved plume in groundwater</li> <li>• Increased volatilization from the dissolved phase</li> </ul>
Natural attenuation	<ul style="list-style-type: none"> <li>• Increased uptake of nutrients and organic components by microorganisms</li> <li>• Increased microorganisms' activity</li> </ul>	<ul style="list-style-type: none"> <li>• Greater availability and renewal of carbon, oxygen, and micronutrients through the soil and the water column</li> <li>• Better evacuation of the reaction by-products accumulated during biodegradation</li> <li>• Greater functional diversity and flexibility of microorganisms</li> </ul>	<ul style="list-style-type: none"> <li>• Increased LNAPL biodegradation and attenuation rates</li> <li>• Increased gaseous (CO<sub>2</sub>, CH<sub>4</sub>) surface emissions</li> <li>• Decreased LNAPL source zone longevity</li> <li>• Maintains strong dissolution processes</li> <li>• Increased short-term risks</li> <li>• Decreased long-term risks</li> </ul>

1025

1026 Tab. 3. Summary of the main expected effects of climate change on LNAPL contaminations under  
 1027 specific climatic conditions.

	<b>Main current properties <sup>a</sup></b>	<b>Main expected effect of climate change by 2100<sup>a</sup></b>	<b>Main expected effect of climate change on LNAPL</b>
Cold regions	<ul style="list-style-type: none"> <li>• Low temperatures (&lt;8°C)</li> <li>• Low soil nutrient contents and availability</li> <li>• Excess water distribution (rainfalls&gt; 900 mm/yr)</li> <li>• Low soil oxygen diffusivities</li> <li>• Very low LNAPL volatilization, dissolution, and biodegradation</li> </ul>	<ul style="list-style-type: none"> <li>• Increased temperature (+5-9°C) and rainfalls (up to +50%)</li> <li>• Reduced snow cover and soil frost</li> <li>• Increased groundwater recharge, and heads in winter</li> <li>• Increased evapotranspiration, decreased groundwater recharge, and heads in summer</li> <li>• Increased groundwater level fluctuations</li> <li>• Higher oxygen inputs and diffusion in the soil and water</li> <li>• Strongly enhanced soil microbial activity</li> </ul>	<ul style="list-style-type: none"> <li>• Strongly increased LNAPL viscosity, volatility, and solubility</li> <li>• Increased spreading of the pollution in the soil and water</li> <li>• Strongly enhanced LNAPL biodegradation</li> <li>• Higher VOC emissions and dissolved pollutants concentrations</li> <li>• Strongly decreased pollution longevity</li> </ul>
Arid/semi-arid zones	<ul style="list-style-type: none"> <li>• Highly variable and extremes temperatures (-10°C-60°C)</li> <li>• Scarce but intense rainfalls (mean rainfalls: 185-550 mm/yr)</li> <li>• Important water table level and soil moisture content fluctuations</li> <li>• High LNAPL mobilization and biodegradation</li> </ul>	<ul style="list-style-type: none"> <li>• Increased temperature (+4-7°C)</li> <li>• Decreased snowpack and precipitations in spring and summer</li> <li>• Strongly increased evapotranspiration and groundwater use</li> <li>• Strongly decreased groundwater recharge (up to -30%) and heads</li> <li>• Increased groundwater level variations tied with the encroachment catchment areas of pumping wells</li> <li>• Strongly decreased soil moisture content and soil microbial activity</li> <li>• Increase extreme precipitation events and floods frequency and intensity</li> </ul>	<ul style="list-style-type: none"> <li>• Increased LNAPL/air surface areas in the SZ</li> <li>• Increased LNAPL compounds volatility and VOC emissions</li> <li>• Increased spreading of the pollution in soil</li> <li>• Decreased LNAPL biodegradation</li> <li>• Increased risks of new LNAPL spills due to damage LNAPL transport and storage infrastructures during floods</li> </ul>
Humid coastal areas	<ul style="list-style-type: none"> <li>• High groundwater table dynamic due to tidal effects</li> </ul>	<ul style="list-style-type: none"> <li>• Increased sea level (0.43-0.84 mm/yr) due to thermal expansion, melting ice sheets, glaciers, and land water storage changes</li> <li>• Increased precipitations (+10-20%) and extreme precipitation events (+10-50%)</li> <li>• Increased coastal erosion, flood events frequency, and intensity</li> <li>• Increased coastal aquifer and groundwater heads</li> <li>• Increase salt-water intrusion and groundwater salinity</li> </ul>	<ul style="list-style-type: none"> <li>• Increase LNAPL/water surface contact</li> <li>• Increased pollutants dissolution and dilution in groundwater, connected rivers, and sea</li> <li>• Modification of some pollutants biodegradation rates due to changes in water salinity, soil moisture content, and the oxygen diffusivity</li> <li>• Increased risks of new LNAPL spills due to damage of coastal LNAPL transport and storage infrastructures during floods, storms</li> </ul>

1028 <sup>a</sup> Predictions from IPCC (2014), Meixner et al. (2016), USGCRP (2014).

1029 Tab. 4. Main research papers from 1993 to 2021 focusing on the effect of temperature or groundwater  
 1030 table fluctuations on the LNAPL transport and mobilization sorted according to the studied process and  
 1031 the scientific approach.

<b>Main process</b>	<b>References</b>	<b>Scientific approach</b>
<i>Dissolution, transport, sorption</i>	Alazaiza et al., 2020; Chompusri et al., 2002; David and Moldoveanu, 2019; Dobson et al., 2007; Gupta et al., 2019; Gupta and Yadav, 2020; Kechavarzi et al., 2005; Lekmine et al., 2014; Lenhard et al., 1993; Schroth et al., 1995; Shojib, 2015; Steffy et al., 1998; Sun, 2016; Van Geel and Sykes, 1997, 1994; Vasudevan et al., 2016; Yang et al., 2017	<i>Laboratory experiments</i>
	Davis et al., 1999; Gatsios et al., 2018; J.-Y. Lee et al., 2001; Steffy et al., 1995; Teramoto and Chang, 2017	<i>Field monitoring</i>
	Jeong and Charbeneau, 2014; Lari et al., 2016; Lenhard et al., 2004; Mobile et al., 2012; Reddi et al., 1998; Teramoto and Chang, 2017; Vasudevan et al., 2014	<i>Numerical modeling</i>
<i>Biodegradation/Attenuation</i>	Dobson et al., 2007; Gupta et al., 2019; Ismail et al., 2020; Picone et al., 2013; Rainwater et al., 1993; Rezanezhad et al., 2014; Sinke et al., 1998; Van De Ven et al., 2021; Yadav et al., 2012	<i>Laboratory experiments</i>
	Askarani, 2020; Eichert et al., 2017; C.-H. Lee et al., 2001; McAlexander and Sihota, 2019; Sihota et al., 2013; Wilson et al., 1995; Zeman et al., 2014; Zhou et al., 2015	<i>Field monitoring</i>
	Prommer et al., 2002	<i>Numerical modeling</i>
<i>Volatilization, gas transport</i>	Chen et al., 2010; McCarthy and Johnson, 1993; Soucy and Mumford, 2017	<i>Laboratory experiments</i>
	Baedecker et al., 2011; Guo, 2015; Patterson and Davis, 2009	<i>Field monitoring</i>
	Picone et al., 2012; Qi et al., 2020; Thomson et al., 1997	<i>Numerical modeling</i>

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1033 Tab. 5. Main relevant LNAPL laboratory experiments on soil columns and numerical studies from 1993  
 1034 to 2021 sorted according to the complexity of the porous media and LNAPL source composition used.

<b>LNAPL composition</b>		
LNAPL mixture complexity	Commonly used compounds	References
One component	Toluene, <i>n</i> -heptane, <i>n</i> -decane, or <i>n</i> -pentane	Chompusri et al., 2002; Gupta et al., 2019; Gupta and Yadav, 2020; Ismail et al., 2020; Picone et al., 2013; Shojib, 2015; Sinke et al., 1998; Soucy and Mumford, 2017; Steffy et al., 1998; Van Geel and Sykes, 1997, 1994; Yadav et al., 2012; Yang et al., 2017
2-4 components	BTEX, <i>n</i> -hexadecane, methylnaphthalene,	Chen et al., 2010; David and Moldoveanu, 2019; Dobson et al., 2007; Teramoto and Chang, 2017; Vasudevan et al., 2016; 2014
> 4 components	Fuel, isoparaffinic solvent, or mineral oils.	Alazaiza et al., 2020; Kechavarzi et al., 2005; Lekmine et al., 2014; Rainwater et al., 1993; Sun, 2016
<b>Porous media composition</b>		
Porous media complexity	Type	References
One homogeneous soil system /experiment	Fine, medium, or coarse silica/calcareous sand (90 µm-1,2 mm)	Alazaiza et al., 2020; Chompusri et al., 2002; Dobson et al., 2007; Gupta et al., 2019; Gupta and Yadav, 2020; Kechavarzi et al., 2005; McCarthy and Johnson, 1993; Rainwater et al., 1993; Schroth et al., 1995; Shojib, 2015; Sinke et al., 1998; Soucy and Mumford, 2017; Steffy et al., 1998; Van Geel and Sykes, 1997, 1994; Yadav et al., 2012; Yang et al., 2017.
	Mixture of clay, sand, and silt	Lenhard et al., 1993; Picone et al., 2013
	Natural homogenized soil	Chen et al., 2010; Ismail et al., 2020; Rezanezhad et al., 2014; Van De Ven et al., 2021
Heterogeneous soil system	Alternations of clay, fine to coarse silica sand layers	Huntley and Beckett, 2002; Illangasekare et al., 1995a; Jeong and Charbeneau, 2014; Powers et al., 1998; Qi et al., 2020; Sarikurt et al., 2017; Sun, 2016
	Fractured porous medium	Legout et al., 2009

1035