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

Amélie Cavelan, Fabrice Golfier, Stéfan Colombano, Hossein Davarzani, Jacques Deparis, Pierre Faure

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

Amélie CAVELAN [1]*, Fabrice GOLFIER [2], Stéfan COLOMBANO [3], Hossein DAVARZANI [3], Jacques DEPARIS [3], Pierre FAURE [1]

[1] Université de Lorraine, CNRS, LIEC, F-54000 Nancy, France

[2] Université de Lorraine, CNRS, GeoRessources, F-54000 Nancy, France

[3] BRGM (French Geological Survey), F-45100 Orléans, France

* Corresponding author: amelie.cavelan@univ-lorraine.fr

Abstract

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

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

1. Introduction

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

Numerous laboratory, modeling, and field studies have demonstrated that seasonal or pump-induced groundwater level fluctuations may affect LNAPL migration and redistribution (Davis et al., 1993; Lenhard et al., 2019, 2018, 2017; Steffy et al., 1998, 1995), component dissolution rates (Davis et al., 1993; Kechavarzi et al., 2005; Lekmine et al., 2014; Lenhard et al., 2004; Mobile et al., 2012; Teramoto and Chang, 2017), volatilization (Davis et al., 2005; Guo et al., 2019; Illangasekare et al., 2014; McCarthy and Johnson, 1993; Picone et al., 2012; Qi et al., 2020; Soucy and Mumford, 2017; Werner and Höhener, 2002; Zhang et al., 2021), or biodegradation (Dobson et al., 2007; Gupta et al., 2019; Ismail et al., 2020; Rainwater et al., 1993). These works showed that fluctuating groundwater level conditions and/or soil moisture changes affect the vertical dispersion and redistribution of the LNAPL compounds at the capillary fringe, modifying their release into the environment. However, the dynamic nature and the intensity of groundwater level variations may change significantly in the coming decades in response to climate change (Goderniaux et al., 2009; Green et al., 2011; Jarsjö et al., 2020; Smerdon, 2017). Depending on local climatic conditions, more intense groundwater level fluctuations may occur over the next century in response to variations in rainfall intensity and frequency and the increasing use of water resources (Christensen and Christensen, 2007; IPCC, 2014; Nygren et al., 2020). This context may strongly impact the LNAPL mobilization, the contamination lifetime, and the risk for receptors. Moreover, an increase in a few degrees in the mean surface and groundwater temperature is also expected (IPCC, 2014). This phenomenon may affect temperature-dependent mobilization and (bio)degradation processes (Knauss et al., 2000; McAlexander and Sihota, 2019; Yadav et al., 2012; Zeman et al., 2014), further modifying the LNAPL constituents partitioning and release into air and groundwater.

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

2. Historical View

2.1. LNAPL features

Petroleum LNAPLs (e.g., diesel, gasoline, crude oil) can be long-term persistent sources of groundwater and soil pollution that reach the SZ and USZ upon release. The LNAPL is characterized by a hydrophobic and non-ionic nature in the presence of water and exhibits a lower density than water. While LNAPL can correspond to a single chemical compound such as benzene, it is often a complex mixture of several hundred components with different chemical properties (Güler, 2019; Gupta et al., 2019). Branched and *n*-alkanes (mainly <C_{25}), cycloalkanes, alkenes, cycloalkenes, acetylenes and, BTEX (benzene, toluene, ethylbenzene, xylenes) are common LNAPL components.

2.2. LNAPL mobility, partitioning process, and biodegradation

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

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

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

2.3. Effect of groundwater table variations at LNAPL sites

Under 'steady-state' water table conditions, dissolution, volatilization processes, and transverse migration of the dissolved LNAPL constituents are relatively limited because of the small vertical dispersion, and the slow diffusion of dissolved LNAPL compounds (Chompusri et al., 2002; Dobson et al., 2007; Gupta et al., 2019; Huntley and Beckett, 2002; Lenhard et al., 1993). Retention and mobility of LNAPL in a saturated porous medium depend on the saturation of each phase in the USZ (air, water, LNAPL). Hysteresis effect strongly driven by the variations of the water table level often occurs, as the mobile LNAPL phase moves vertically along with the groundwater fluctuations (Gatsios et al., 2018; ITRC, 2018; Kemblowski and Chiang, 1990; Steffy et al., 1998). Within the mobile LNAPL phase, the LNAPL saturation is high and water is restricted to smaller pores and exhibits a low relative permeability (Fig. 3). When the water table drops, the mobile LNAPL moves down with the water table level (Figs. 1ii, 3ii, Ballestero et al., 1994; Steffy et al., 1998), causing the redistribution of the LNAPL and the reconfiguration of the partitioning of LNAPL components between the different phases. A part of the LNAPL remains as discontinuous residual LNAPL ganglia in the USZ (Charbeneau, 2007; Jeong and Charbeneau, 2014; Kechavarzi et al., 2005; Kemblowski and Chiang, 1990; Lenhard et al., 1993). The most volatile and soluble compounds of the LNAPL can volatilize or be leached by successive water infiltration and contribute to the evolution of the dissolved plumes (Kechavarzi et al., 2005). The subsequent rise of the water table (Fig. 1iii, 3ii-iii) results in upward redistribution of mobile LNAPL, leaving behind some immobile entrapped LNAPL droplets in the SZ (Charbeneau, 2007; Lenhard and Parker, 1990). The zone of the water table and LNAPL fluctuation is often called the smear zone. During successive drainage/imbibition phases, the effect of capillary pressure, as well as the trapping of fluids in the SZ and USZ, continuously modify the water flow paths (Sookhak Lari et al., 2016a). These hysteresis effects accompanied by additional LNAPL-water interactions (groundwater and rainwater) favor the mobilization of the contaminants (Parker and Lenhard, 1987; Van Geel and Sykes, 1997). Hence, seasonal or pump-induced groundwater level fluctuations often lead to (i) significant redistribution and spreading of the pollutants through the water table fluctuation zone (Fig. 1), (ii) a decrease in the average LNAPL saturation and mass of the mobile LNAPL remaining afterward (Fig. 3, Charbeneau, 2007; Kemblowski and Chiang, 1990; Lenhard et al., 1993; Lenhard and Parker, 1990; Newell, 1995; Reddi et al., 1998; Van Geel and Sykes, 1997), and (iii) a decrease in LNAPL recovery yield.

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

3.1. Impact of climate change on groundwater

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

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

3.2. LNAPL source zone mobility, partitioning, and depletion

The composition and physical-chemical properties of the LNAPL are temperature-dependent. Higher temperatures decrease the interfacial tensions, the viscosity, and the density of the LNAPL, modifying the distribution and the diffusion rate of the organic contaminants through the soil (Colombano et al., 2020; Sleep and Ma, 1997). A higher temperature also decreases the LNAPL soil-water partition coefficients and LNAPL/water interfacial tension, favoring LNAPL mobility (Imhoff et al., 1997; Sleep and Ma, 1997) and decreasing residual LNAPL saturations (Davis, 1994; Philippe et al., 2020; She and Sleep, 1998; Sinnokrot et al., 1971). The vapor diffusion coefficient of gas also increases with temperature (Davis, 1997; Knauss et al., 2000; Seager et al., 1963). In the context of climate change, the earth's surface temperature could locally increase from 12°C to 20°C. The effect of this increase in temperature on the main properties and partitioning coefficients of oil and LNAPL compounds were calculated based on the available data of the literature and gathered in Tab. 1. The oil viscosity decreases up to 41% over this temperature range, increasing the LNAPL mobility (Tab. 1). On the contrary, the variation of the LNAPL density, soil-water partition coefficients, and LNAPL/water interfacial tensions appear to be negligible over this range of temperatures (Gaito et al., 2012; Imhoff et al., 1997; Sleep and Ma, 1997). Ten Hulscher and Cornelissen (1996) revealed that a decrease by 2-3% of the equilibrium sorption constant can be expected under this range of temperatures for most organic pollutants, probably favoring their desorption and remobilization into the air and water and making them more available for degrading microorganisms (McAlexander and Sihota, 2019; Yadav and Hassanizadeh, 2011). However, a striking opposite effect is, nevertheless, observed for BTEX (Tab. 1, David and Moldoveanu, 2019). The effect of temperature on the sorption trends of the contaminants remains thus, difficult to predict, especially because no information is available about the variations in K_{oc} (carbon-water partitioning coefficient) and K_{ow} (octanol-water partitioning coefficient) for the other LNAPL compounds in the investigated range of temperature (Tab. 1). A better understanding of these sorption processes between 10-20°C is, therefore, required since they may significantly limit or delay the spreading of the dissolved constituents (Prommer et al., 2002). Calculations based on the literature data compilation show that such an increase in temperature may, nevertheless, strongly increase the saturated vapor pressure of most LNAPL compounds from 25% to 45% (Tab. 1), highly modifying their volatilization rates. In the light of these results, it is clear that the expected temperature rise will probably greatly increase gas and VOC surface emissions, and to a less extent the LNAPL mobility through the soil.

Changes in groundwater level also affect LNAPL volatilization and VOC emissions (Guo et al., 2019; Illangasekare et al., 2014; McCarthy and Johnson, 1993; Picone et al., 2012; Qi et al., 2020; Soucy and Mumford, 2017; Werner and Höhener, 2002). Rise and fall successions of the groundwater table level cause the shortening or the lengthening of gas transport pathways from the dissolved LNAPL plume to the surface (Fig. 1, Guo et al., 2019) and enhance mass transfers towards the dissolved LNAPL plume and the soil gas phase (McCarthy and Johnson, 1993). When the groundwater table level decreases, the soil water enriched in dissolved LNAPL components is partially drained (Fig. 1ii). The dissolved LNAPL constituents in pore water are progressively exposed to an air phase, favoring the transfer of volatiles constituents to the vapor phase (McCarthy and Johnson, 1993; Qi et al., 2020). This increases VOC emissions and vapor intrusion risks, especially for shallow aquifers (Illangasekare et al., 2014; McCarthy and Johnson, 1993; Picone et al., 2012; Qi et al., 2020; Thomson et al., 1997; Werner and Höhener, 2002). Additionally, groundwater fluctuations can promote the advective transport of soil gases, accelerating the transport of the vapor phase through the USZ and their release into the atmosphere (Qi et al., 2020; Soucy and Mumford, 2017). During the rise of the groundwater, the increase in the soil water saturation reduces the soil gas/LNAPL interfacial area, reducing gas diffusivities and volatilization. Hence, low VOC emissions are sometimes temporarily observed (Petri et al., 2015; Yoon et al., 2002). However, while the drop in the water table level can create a "suction effect" limiting the flow of the gas, the upward movement of groundwater creates a "piston effect", pushing the soil gases enriched in VOC towards the surface (Fig. 1iii, Boyle and Witherington, 2007). The air trapped at this moment with LNAPL ganglia in the smear zone below the water table creates a three-phase LNAPL/air/water system (Fig. 1iii, Lenhard et al., 1993; Fry et al., 1995; Van Geel and Sykes, 1997; Williams and Oostrom, 2000; Charbeneau, 2007; Dobson et al., 2007), further promoting the transfer of entrapped and dissolved LNAPL constituents toward the vapor phase in the early time after the upward movement of groundwater (Fig. 1iii, Soucy and Mumford, 2017). Given these studies, an intensification of the groundwater fluctuations will enhance volatilization. A global decrease in the average water table level in response to climate change will increase the global thickness of the USZ, probably favoring the exposure of the LNAPL constituents to volatilization processes and the enrichment of the soil gas in VOC. This may also significantly increase the exposure of the residual LNAPL compounds to the leaching/weathering process by infiltrated meteoric water. The modification of the dynamic moisture conditions induced by the infiltration of meteoric water resulting from rainfalls or irrigation causes the leaching/the desorption and the downward aqueous transport of LNAPL constituents (Lee et al., 2001; Newell, 1995). The increase in this leaching process may affect the chemical and the physical properties of the residual LNAPL in causing a faster depletion in the most soluble constituents. However, the contribution of this process also closely depends on the intensity and frequency of precipitation events and will thus probably suffer severe local and temporal modifications in response to the expected change in precipitation patterns and heavy precipitation frequency (IPCC, 2014). Previous studies showed that the mobile LNAPL phase can be more subject to adsorption into the smear zone as the water level fluctuates, preventing the soluble contaminants to be washed away by groundwater level fluctuations (Yadav and Hassanizadeh, 2011; Yang et al., 2017). However, the influence of groundwater level fluctuations and temperature on sorption was too poorly documented to conclude.

3.3. Dissolved LNAPL plume

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

Under fluctuating water table conditions, spatial-temporal variations of the dissolved LNAPL constituents concentrations and the plume thickness are generally observed as a function of the increase and decrease in the groundwater level (Davis et al., 1999). Below the water table, the entrapped LNAPL ganglia form a thin continuous film of molecular thickness at the interface between gas and water in these three-phases systems (Fenwick and Blunt, 1998). These films exhibit higher LNAPL-water interfacial areas more available for dissolution than in a classical LNAPL/water system (Bradford et al., 1999; Shojib, 2015). This results in the faster dissolution of the entrapped LNAPL compounds under fluctuating groundwater table conditions (Shojib, 2015). Moreover, the advection is the dominant transport pathway for the dissolved LNAPL constituents under fluctuating groundwater conditions (Gupta et al., 2019). This enhances the depletion of the LNAPL source zone with the preferential dissolution of the most soluble compounds, leading to a more rapid decrease in the LNAPL source zone's longevity (Dobson et al., 2007; Gupta et al., 2019). However, this leads also to faster transport and spreading of the dissolved LNAPL constituents in groundwater along the vertical and the horizontal direction (Davis et al., 1999; Gupta et al., 2019; Yadav and Hassanizadeh, 2011). The pollution thus reaches a more distant location, creating a larger polluted plume (Gupta et al., 2019; Sarikurt et al., 2017; Zhou et al., 2015).

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

3.4. Natural source zone depletion

It has been demonstrated that the rise of temperature favors the (bio)degradation of the organic pollutants (Askarani, 2020; Dagois et al., 2016; Margesin and Schinner, 2001; McAlexander and Sihota, 2019; Yadav et al., 2012; Yadav and Hassanizadeh, 2011; Zeman et al., 2014). Askarani (2020) demonstrated that monitoring subsurface temperature is a viable technique to resolve LNAPL attenuation rates for LNAPLs since both factors are correlated. Toluene biodegradation rates have been shown to double for every 10°C increase in temperature (Yadav et al., 2012). At higher temperatures, the permeability of the microbial cell membrane of LNAPL-degrading microorganisms is greater, favoring the uptake of nutrients and organic components (Corseuil and Weber, 1994; Zeman et al., 2014). The toxicity of the contamination is also reduced for the microorganisms since the low molecular weight compounds are more easily and quickly volatilized at higher temperatures (Davis, 1997).

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

It seems, therefore, relatively clear that an increase in temperature by a few degrees and an intensification of water table level fluctuations will be beneficial to the activity of the microorganisms at most contaminated sites, favoring the natural attenuation of contaminations. While this may reduce the risks associated with the residual and mobile LNAPL phase, this may, however, enhance surface emissions (mainly CO_2 and CH_4) (Fig. 1ii, iii, Mayer, 2005; Amos and Mayer, 2006; Sihota et al., 2013). Indeed, the important source of gas resulting from the biodegradation of the dissolved LNAPL constituents in groundwater may also promote the ebullition of gas bubbles in the SZ (Amos and Mayer, 2006; Rezanezhad et al., 2014; Sihota et al., 2013). This generates important vertical gas bubble flow from the groundwater at the origin of advection-dominated conditions in the USZ (Soucy and Mumford, 2017). However, this "bubble-facilitated VOC transport" may probably have a limited impact on VOC emissions on the surface as many of these VOCs are likely to be degraded by the increased bacterial activity. Nevertheless, this could contribute to an increase in CO_2 and CH_4 surface emissions. These attenuation rates may, therefore, be faster in the coming decades at most of the contaminated sites. Intense biodegradation of the dissolved LNAPL constituent also sustains high concentration gradients, maintaining high dissolution processes over time (Davis et al., 1999). This may contribute to the faster natural attenuation of the contamination but without lowering the concentration of the dissolved compounds in the early years after the contamination (Dobson et al., 2007; Gupta et al., 2019). Moreover, above certain concentrations that depend on the bacterial strains and organic species, LNAPL components become toxic for the microorganisms, reducing the efficiency of biodegradation (Gupta et al., 2019). In some areas where important concentrations of dissolved LNAPL components are released, the biodegradation rates may thus remain limited. The biodegradability of certain LNAPL compounds exhibits also spatial-temporal variations depending on the availability of more easily biodegradable organic species and the accommodation time of the microbial community to the less biodegradable and toxic compounds (Sinke et al., 1998). This incubation time varies greatly between LNAPL compounds (Wiedemeier et al., 1995). The extent of the effect of climate change on biodegradation rates may thus be very inconsistent across sites. Finally, the changes in the mass of the dissolved LNAPL constituents and the availability of electron acceptors are decreasing with the increasing sorption phenomenon (up to -30%) under a fluctuating water level. This may impact biodegradation rates (Prommer et al., 2002). A better understanding of the effects of climate change on these sorption effects is therefore crucial. However, this implies a better integration of the soil properties at sites including composition, sorption capacity, and soil heterogeneities. This is all the more important since the presence of soil heterogeneities (*i.e.* more or less compacted layers) influences not only sorption processes but also soil moisture contents, and gas diffusivities (Davis et al., 2005). These expected effects of climate change on LNAPL contaminated sites are summarized in Tab. 2.

4. Cases of different climatic conditions and contaminated sites properties

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

4.1 Cold regions

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

4.2. Arid and semi-arid zones

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

LNAPL (McAlexander and Sihota, 2019; Yadav and Hassanizadeh, 2011). In the context of climate change, these arid regions are expected to become drier and warmer (IPCC, 2014). The expected increase in temperature (+4 to +7°C, IPCC, 2014) may lead to a net rise in the evapotranspiration rate, a strong decrease in soil moisture content, and a significant increase in the pressure on the groundwater resources for drinking water, agricultural of industrial activities (Meixner et al., 2016; Taylor et al., 2013). At the same time, the drop in precipitation in spring and summer and the declining snowpack (the major part of the water table recharge in mountainous areas) may drastically reduce the groundwater recharge (Meixner et al., 2016). Hence, a decrease in groundwater recharge up to -30% is expected in some arid lands by 2100 (*e.g.* San Pedro Basin AZ, Sonora Mexico, Meixner et al., 2016). Several consequences may, therefore, be expected for existing LNAPL contaminated sites: (i) greater spreading of LNAPL across both the USZ and the SZ due to global fallings water levels and greater level variations tied with the encroachment catchment areas of pumping wells; (ii) greater volatility of LNAPL compounds and an increase in VOC emissions in response to higher temperatures and LNAPL/air surface areas in the SZ. The extremely hot temperatures in summer may also decrease nucleic acids, proteins, and the enzyme activity of soil microorganisms (Corseuil and Weber, 1994). The increase of droughts may dry the soil out, preventing the development of LNAPL-degrading microorganisms (Dagois et al., 2016). More intense drought events and heatwaves may thus take over the microbial population from the soil in these areas, decreasing significantly the LNAPL natural attenuation rates. The expected increase in extreme precipitation events' frequency and intensity may also lead to an increasing number of floods (IPCC, 2014). These events may accelerate riverbank erosion and damage LNAPL transport infrastructures, and storage tanks, causing important new LNAPL spills. For example, Colorado has more than 5,900 oil and gas wells within 500 feet of the state's rivers and streams. In 2013, severe flooding occurred, damaging more than 2,650 oil and gas facilities (wells and storage tanks), resulting in the spill of approximately 48.250 gallons of oil and condensate in the environment.

4.3. Humid coastal areas

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

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

5. Conclusions and perspectives

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

Another difficulty comes from the differences between experimental, numerical, and field studies carried out on LNAPL, where the time scale, the amplitude of groundwater level variations, the porous medium type vary greatly between studies (Tab. 4, 5, Garg et al., 2017; Lari et al., 2016; Sookhak Lari et al., 2019). There are relatively few field studies (28%) compared to laboratory experiments and numerical modeling (Tab. 4). However, laboratory experiments and numerical works are simplified models that neglected the soil composition and heterogeneities, the LNAPL chemical complexity (Tab. 5), or the amplitude of water table fluctuations. Although these properties are specific to each site, they can generate discrepancies between field observations and the results of numerical models or laboratory experiments. The amplitude of water table fluctuations may control the evolution of dissolved LNAPL constituents' concentration (Teramoto and Chang, 2017), soil moisture content, gas diffusivity, and thus, VOC fluxes (Qi et al., 2020). Variations in soil grain sizes, composition, or compaction determine the permeability which is one of the main parameters affecting rainfall infiltration, thermal-physical effective parameters, the migration path, the plume velocity, the entrapment, LNAPL saturation distribution in the soil, gas soil moisture content, gaseous phase pathways, and gas diffusivities (Davis et al., 2005; Huntley and Beckett, 2002; Illangasekare et al., 1995b; Lehmann et al., 2012; Powers et al., 1998; Qi et al., 2020; Sarikurt et al., 2017; Sun, 2016). The behavior of an organic component in the single-component conditions of laboratory experiments and numerical models is not always representative of the behavior of the complex LNAPL mixtures present at most contaminated sites due to the interactions existing between different organic species that may affect the solubility of each compound (Lekmine et al., 2014; Vasudevan et al., 2016). This highlights the necessity of replacing the current compartmentalized vision of these three-phase systems with more dynamic/real-time monitoring of LNAPL integrated approaches that consider the full complexity of these contaminated sites.

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

Declaration of Competing Interest

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

Acknowledgments

This work was supported by the French PIA project “Lorraine Université d’Excellence”, reference ANR-15-IDEX-04-LUE, and the BRGM (the French Geological Survey). The authors would like to thank Lorraine University and the BRGM. This work is included in the scientific program of the GISFI research consortium dedicated to the knowledge and the development of remediation technologies for degraded and polluted lands (Groupement d'Intérêt Scientifique sur les Friches Industrielles - http://www.gisfi.univ-lorraine.fr).

References

Abraham, M.H., Matteoli, E., 1988. The temperature variation of the hydrophobic effect. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases 84, 1985–2000.

Alazaiza, M.Y.D., Ramli, M.H., Copty, N.K., Sheng, T.J., Aburas, M.M., 2020. LNAPL saturation distribution under the influence of water table fluctuations using simplified image analysis method. Bull Eng Geol Environ 79, 1543–1554. https://doi.org/10.1007/s10064-019-01655-3

Amos, R.T., Mayer, K.U., 2006. Investigating the role of gas bubble formation and entrapment in contaminated aquifers: Reactive transport modelling. Journal of contaminant hydrology 87, 123–154.

Ashworth, R.A., Howe, G.B., Mullins, M.E., Rogers, T.N., 1988. Air-water partitioning coefficients of organics in dilute aqueous solutions. Journal of Hazardous Materials 18, 25–36.

Askarani, K.K., 2020. DISSERTATION THERMAL MONITORING OF NATURAL SOURCE ZONE DEPLETION. https://doi.org/10.13140/RG.2.2.29924.53129

Askarani, K.K., Sale, T.C., 2020. Thermal estimation of natural source zone depletion rates without background correction. Water Research 169, 115245. https://doi.org/10.1016/j.watres.2019.115245

Baedecker, M.J., Eganhouse, R.P., Bekins, B.A., Delin, G.N., 2011. Loss of volatile hydrocarbons from an LNAPL oil source. Journal of Contaminant Hydrology 126, 140–152. https://doi.org/10.1016/j.jconhyd.2011.06.006

Ballestero, T.P., Fiedler, F.R., Kinner, N.E., 1994. An investigation of the relationship between actual and apparent gasoline thickness in a uniform sand aquifer. Groundwater 32, 708–718.

Benioug, M., Golfier, F., Fischer, P., Oltean, C., Buès, M.A., Yang, X., 2019. Interaction between biofilm growth and NAPL remediation: A pore-scale study. Advances in water resources 125, 82–97.

Boethling, R., Fenner, K., Howard, P., Klečka, G., Madsen, T., Snape, J.R., Whelan, M.J., 2009. Environmental persistence of organic pollutants: guidance for development and review of POP risk profiles. Integrated Environmental Assessment and Management: An International Journal 5, 539–556.

Boyle, R., Witherington, P., 2007. Guidance on evaluation of development proposals on sites where methane and carbon dioxide are present. NHBC and RSK Guidance on methane and carbon dioxide 4, 1–87.

Bradford, S.A., Vendlinski, R.A., Abriola, L.M., 1999. The entrapment and long-term dissolution of tetrachloroethylene in fractional wettability porous media. Water Resources Research 35, 2955–2964.

Bruckberger, M.C., Gleeson, D.B., Bastow, T.P., Morgan, M.J., Walsh, T., Rayner, J.L., Davis, G.B., Puzon, G.J., 2021. Unravelling Microbial Communities Associated with Different Light Non-Aqueous Phase Liquid Types Undergoing Natural Source Zone Depletion Processes at a Legacy Petroleum Site. Water 13, 898.

Budantseva, L.S., Lesteva, T.M., Nemstov, M.S., 1976. Deposited Doc. Zhurnal Fizicheskoi Khimii, VINITI 50, 437–476.

Carruth, G.F., Kobayashi, R., 1973. Vapor pressure of normal paraffins ethane through n-decane from their triple points to about 10 mm mercury. Journal of Chemical and Engineering Data 18, 115–126.

Charbeneau, R., 2007. LNAPL Distribution and Recovery Model. Distribution and Recovery of Petroleum Hydrocarbon Liquids in Porous Media. Vol. 1. API Publication 4760.

Chen, W., Tong, L., Zheng, X., Li, M., 2010. Influencing Factors of BTEX Volatilization, in: 2010 4th International Conference on Bioinformatics and Biomedical Engineering. Presented at the 2010 4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE), IEEE, Chengdu, China, pp. 1–5. https://doi.org/10.1109/ICBBE.2010.5516007

Chompusri, S., Rivett, M.O., Mackay, R., 2002. LNAPL redistribution on a fluctuating water table: column experiments. IAHS PUBLICATION 225–234.

Christensen, J.H., Christensen, O.B., 2007. A summary of the PRUDENCE model projections of changes in European climate by the end of this century. Climatic Change 81, 7–30. https://doi.org/10.1007/s10584-006-9210-7

Clough, S.R., 2014. Decane, in: Encyclopedia of Toxicology (Third Edition). Academic Press, pp. 1144–1146.

Coates, M., Connell, D.W., Barron, D.M., 1985. Aqueous solubility and octan-1-ol-water partition coefficients of aliphatic hydrocarbons. Environmental science & technology 19, 628–632.

Colombano, S., Davarzani, H., van Hullebusch, E.D., Ignatiadis, I., Huguenot, H., Zornig, C., Guyonnet, D., 2020. In Situ Thermal Treatments and Enhancements: Theory and Case Study, in: van Hullebusch, E.D., Huguenot, D., Pechaud, Y., Simonnot, M.-O., Colombano, S. (Eds.), Environmental Soil Remediation and Rehabilitation. Springer International Publishing, Cham, pp. 149–209. https://doi.org/10.1007/978-3-030-40348-5_3

Corseuil, H.X., Weber, W.J., 1994. Potential biomass limitations on rates of degradation of monoaromatic hydrocarbons by indigenous microbes in subsurface soils. Water Research 28, 1415–1423.

Dagois, R., Schwartz, C., Coussy, S., Lorgeoux, C., Ouvrard, S., Faure, P., 2016. Climatic influence on mobility of organic pollutants in Technosols from contrasted industrial activities. Journal of soils and sediments 16, 1306–1315.

Dams, J., Salvadore, E., Van Daele, T., Ntegeka, V., Willems, P., Batelaan, O., 2012. Spatio-temporal impact of climate change on the groundwater system. Hydrology and Earth System Sciences 16, 1517–1531.

David, V., Moldoveanu, S.C., 2019. Variation with temperature of octanol/water partition coefficient for the homologous series from benzene to propylbenzene. Separation Science Plus 2, 457–464.

Davis, E.L., 1997. How heat can enhance in-situ soil and aquifer remediation: important chemical properties and guidance on choosing the appropriate technique. U.S. EPA Issue paper 540/S–97/502.

Davis, E.L., 1994. Effect of temperature and pore size on the hydraulic properties and flow of a hydrocarbon oil in the subsurface. Journal of Contaminant Hydrology 16, 55–86.

Davis, G.B., Barber, C., Power, T.R., Thierrin, J., Patterson, B.M., Rayner, J.L., Wu, Q., 1999. The variability and intrinsic remediation of a BTEX plume in anaerobic sulphate-rich groundwater. Journal of Contaminant Hydrology 36, 265–290. https://doi.org/10.1016/S0169-7722(98)00148-X

Davis, G.B., Johnston, C.D., Thierrin, J., Power, T.R., Patterson, B.M., 1993. Characterizing the distribution of dissolved and residual NAPL petroleum hydrocarbons in unconfined aquifers to effect remediation. AGSO Journal of Geology and Geophysics 14, 89–94.

Davis, G.B., Rayner, J.L., Trefry, M.G., Fisher, S.J., Patterson, B.M., 2005. Measurement and Modeling of Temporal Variations in Hydrocarbon Vapor Behavior in a Layered Soil Profile. Vadose Zone Journal 4, 225–239. https://doi.org/10.2136/vzj2004.0029

Dobson, R., Schroth, M.H., Zeyer, J., 2007. Effect of water-table fluctuation on dissolution and biodegradation of a multi-component, light nonaqueous-phase liquid. Journal of Contaminant Hydrology 94, 235–248. https://doi.org/10.1016/j.jconhyd.2007.07.007

Eichert, J., McAlexander, B., Lyverse, M., Michalski, P., Sihota, N., 2017. Spatial and temporal variation in natural source zone depletion rates at a former oil refinery. Vadose Zone Journal 16, 1–16.

Fenwick, D.H., Blunt, M.J., 1998. Three-dimensional modeling of three phase imbibition and drainage. Advances in water resources 21, 121–143.

Fry, N.K., Fredrickson, J.K., Fishbain, S., Wagner, M., Stahl, D.A., 1997. Population structure of microbial communities associated with two deep, anaerobic, alkaline aquifers. Applied and environmental microbiology 63, 1498–1504. https://doi.org/10.1128/AEM.63.4.1498-1504.1997

Fry, V.A., Istok, J.D., Semprini, L., O'Reilly, K.T., Buscheck, T.E., 1995. Retardation of dissolved oxygen due to a trapped gas phase in porous media. Ground water 33, 391–399.

Gaito, S., Maki, M., Peters, C., 2012. LNAPL remediation technology bench-scale testing report. (Technical report No. B0064410), Revitalizing Auto Communities Environmental Response Trust (RACER). ARCADIS G&M of Michigan, LLC, Brighton, MI.

Garg, S., Newell, C.J., Kulkarni, P.R., King, D.C., Adamson, D.T., Renno, M.I., Sale, T., 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Groundwater Monitoring & Remediation 37, 62–81. https://doi.org/10.1111/gwmr.12219

Gatsios, E., García-Rincón, J., Rayner, J.L., McLaughlan, R.G., Davis, G.B., 2018. LNAPL transmissivity as a remediation metric in complex sites under water table fluctuations. Journal of Environmental Management 215, 40–48. https://doi.org/10.1016/j.jenvman.2018.03.026

Goderniaux, P., Brouyère, S., Blenkinsop, S., Burton, A., Fowler, H.J., Orban, P., Dassargues, A., 2011. Modeling climate change impacts on groundwater resources using transient stochastic climatic scenarios. Water Resources Research 47. https://doi.org/10.1029/2010WR010082

Goderniaux, P., Brouyère, S., Fowler, H.J., Blenkinsop, S., Therrien, R., Orban, P., Dassargues, A., 2009. Large scale surface–subsurface hydrological model to assess climate change impacts on groundwater reserves. Journal of Hydrology 373, 122–138. https://doi.org/10.1016/j.jhydrol.2009.04.017

Green, T.R., Taniguchi, M., Kooi, H., Gurdak, J.J., Allen, D.M., Hiscock, K.M., Treidel, H., Aureli, A., 2011. Beneath the surface of global change: Impacts of climate change on groundwater. Journal of Hydrology 405, 532–560.

Güler, C., 2019. Organic (Hydrocarbon) Contamination: Nonaqueous Phase Liquids, in: GIS and Geostatistical Techniques for Groundwater Science. Elsevier, pp. 251–268. https://doi.org/10.1016/B978-0-12-815413-7.00018-3

Guo, Y., 2015. Vapor intrusion at a site with an alternative pathway and a fluctuating groundwater table. Arizona State University.

Guo, Y., Holton, C., Luo, H., Dahlen, P., Johnson, P.C., 2019. Influence of Fluctuating Groundwater Table on Volatile Organic Chemical Emission Flux at a Dissolved Chlorinated-Solvent Plume Site. Groundwater Monitoring & Remediation 39, 43–52.

Gupta, G.P.K., Yadav, B., Yadav, B.K., 2019. Assessment of LNAPL in Subsurface under Fluctuating Groundwater Table Using 2D Sand Tank Experiments. Journal of Environmental Engineering 145, 04019048. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001560

Gupta, P.K., Ranjan, S., Kumar, D., 2018. Groundwater pollution by emerging industrial pollutants and its remediation techniques. Chapter 2. Recent advances in environmental management, CRC Press Taylor & Francis Group 1.

Gupta, P.K., Yadav, B.K., 2020. Three-dimensional laboratory experiments on fate and transport of LNAPL under varying groundwater flow conditions. Journal of Environmental Engineering 146, 04020010.

Haberer, C.M., Rolle, M., Cirpka, O.A., Grathwohl, P., 2012. Oxygen transfer in a fluctuating capillary fringe. Vadose Zone Journal 11, vzj2011.0056.

Hansch, C., Leo, A., Hoekman, D., 1985. Exploring QSAR hydro-phobic, electronic, and steric constants., American Chemical Society. ed. Washington, DC.

Hansen, K.C., Zhou, Z., Yaws, C.L., Aminabhavi, T.M., 1993. Determination of Henry's law constants of organics in dilute aqueous solutions. Journal of Chemical and Engineering Data 38, 546–550.

Huntley, D., Beckett, G.D., 2002. Persistence of LNAPL sources: relationship between risk reduction and LNAPL recovery. Journal of Contaminant Hydrology 59, 3–26. https://doi.org/10.1016/S0169-7722(02)00073-6

Illangasekare, T.H., Armbruster, E.J., Yates, D.N., 1995a. Non-Aqueous-Phase Fluids in Heterogeneous Aquifers—Experimental Study. Journal of Environmental Engineering 121, 571–579. https://doi.org/10.1061/(ASCE)0733-9372(1995)121:8(571)

Illangasekare, T.H., Petri, B., Fucik, R., Sauck, C., Shannon, L., Sakaki, T., Smits, K., Cihan, A., Christ, J., Schulte, P., 2014. Vapor intrusion from entrapped NAPL sources and groundwater plumes:

Process understanding and improved modeling tools for pathway assessment (Final report No. SERDP Project ER-1687). COLORADO SCHOOL OF MINES GOLDEN.

Illangasekare, T.H., Ramsey, J.L., Jensen, K.H., Butts, M.B., 1995b. Experimental study of movement and distribution of dense organic contaminants in heterogeneous aquifers. Journal of Contaminant Hydrology 20, 1–25. https://doi.org/10.1016/0169-7722(95)00045-W

Illangasekare, T.H., Smits, K.M., Fučík, R., Davarzani, H., 2015. From Pore to the Field: Upscaling Challenges and Opportunities in Hydrogeological and Land–Atmospheric Systems, in: Pore Scale Phenomena: Frontiers in Energy and Environment. World Scientific, pp. 163–202.

Imhoff, P.T., Frizzell, A., Miller, C.T., 1997. Evaluation of thermal effects on the dissolution of a nonaqueous phase liquid in porous media. Environmental science & technology 31, 1615–1622.

IPCC, 2018. Global Warming of 1.5°C. IPCC.

IPCC, 2014. IPCC fifth assessment synthesis report-climate change 2014 synthesis report. Intergovernmental Panel on Climate Change: Geneva, Switzerland.

Irianni-Renno, M., Akhbari, D., Olson, M.R., Byrne, A.P., Lefèvre, E., Zimbron, J., Lyverse, M., Sale, T.C., De Long, S.K., 2016. Comparison of bacterial and archaeal communities in depth-resolved zones in an LNAPL body. Appl Microbiol Biotechnol 100, 3347–3360. https://doi.org/10.1007/s00253-015-7106-z

Ismail, R., Shafieiyoun, S., Al-Raoush, R.I., 2020. Influence of Water Table Fluctuation on Natural Source Zone Depletion in Hydrocarbon Contaminated Subsurface Environments, in: Proceedings of the International Conference on Civil Infrastructure and Construction (CIC 2020). Presented at the The International Conference on Civil Infrastructure and Construction, Qatar University Press, pp. 654–658. https://doi.org/10.29117/cic.2020.0084

ITRC, 2018a. LNAPL site management: LCSM evolution, decision process, and remedial technologies. LNAPL-3. Interstate Technology & Regulatory Council., Washington, DC.

ITRC, 2018b. LNAPL site management: LCSM evolution, decision process, and remedial technologies. LNAPL-3. Interstate Technology & Regulatory Council., Washington, DC.

ITRC, 2009. Evaluating LNAPL remedial technologies for achieving project goals. Interstate Technology and Regulatory, Washington, DC.

Jarsjö, J., Andersson-Sköld, Y., Fröberg, M., Pietroń, J., Borgström, R., Löv, Å., Kleja, D.B., 2020. Projecting impacts of climate change on metal mobilization at contaminated sites: Controls by the groundwater level. Science of The Total Environment 712, 135560. https://doi.org/10.1016/j.scitotenv.2019.135560

Jeong, J., Charbeneau, R.J., 2014. An analytical model for predicting LNAPL distribution and recovery from multi-layered soils. Journal of Contaminant Hydrology 156, 52–61. https://doi.org/10.1016/j.jconhyd.2013.09.008

Kechavarzi, C., Soga, K., Illangasekare, T.H., 2005. Two-dimensional laboratory simulation of LNAPL infiltration and redistribution in the vadose zone. Journal of Contaminant Hydrology 76, 211–233. https://doi.org/10.1016/j.jconhyd.2004.09.001

Kemblowski, M.W., Chiang, C.Y., 1990. Hydrocarbon Thickness Fluctuations in Monitoring Wells. Groundwater 28, 244–252. https://doi.org/10.1111/j.1745-6584.1990.tb02252.x

Knauss, K.G., Dibley, M.J., Leif, R.N., Mew, D.A., Aines, R.D., 2000. The aqueous solubility of trichloroethene (TCE) and tetrachloroethene (PCE) as a function of temperature. Applied Geochemistry 15, 501–512.

Lari, S.K., Davis, G.B., Johnston, C.D., 2016. Incorporating hysteresis in a multi-phase multi-component NAPL modelling framework; a multi-component LNAPL gasoline example. Advances in Water Resources 96, 190–201. https://doi.org/10.1016/j.advwatres.2016.07.012

Lee, C.-H., Lee, J.-Y., Cheon, J.-Y., Lee, K.-K., 2001. Attenuation of petroleum hydrocarbons in smear zones: A case study. Journal of Environmental Engineering 127, 639–647.

Lee, J.-Y., Cheon, J.-Y., Lee, K.-K., Lee, S.-Y., Lee, M.-H., 2001. Factors affecting the distribution of hydrocarbon contaminants and hydrogeochemical parameters in a shallow sand aquifer. Journal of contaminant Hydrology 50, 139–158.

Lee, K.Y., Chrysikopoulos, C.V., 1998. NAPL pool dissolution in stratified and anisotropic porous formations. Journal of Environmental Engineering 124, 851–862.

Legout, C., Molenat, J., Hamon, Y., 2009. Experimental and Modeling Investigation of Unsaturated Solute Transport with Water-Table Fluctuation. Vadose Zone Journal 8, 21–31. https://doi.org/10.2136/vzj2007.0182

Lehmann, P., Neuweiler, I., Vanderborght, J., Vogel, H.-J., 2012. Dynamics of Fluid Interfaces and Flow and Transport across Material Interfaces in Porous Media—Modeling and Observations. Vadose Zone Journal 11, vzj2012.0105.

Lekmine, G., Bastow, T.P., Johnston, C.D., Davis, G.B., 2014. Dissolution of multi-component LNAPL gasolines: The effects of weathering and composition. Journal of Contaminant Hydrology 160, 1–11. https://doi.org/10.1016/j.jconhyd.2014.02.003

Lenhard, R.J., Johnson, T.G., Parker, J.C., 1993. Experimental observations of nonaqueous-phase liquid subsurface movement. Journal of Contaminant Hydrology 12, 79–101. https://doi.org/10.1016/0169-7722(93)90016-L

Lenhard, R.J., Oostrom, M., Dane, J.H., 2004. A constitutive model for air–NAPL–water flow in the vadose zone accounting for immobile, non-occluded (residual) NAPL in strongly water-wet porous media. Journal of Contaminant Hydrology 71, 261–282. https://doi.org/10.1016/j.jconhyd.2003.10.014

Lenhard, R.J., Parker, J.C., 1990. Estimation of free hydrocarbon volume from fluid levels in monitoring wells. Groundwater 28, 57–67.

Lenhard, R.J., Rayner, J.L., Davis, G.B., 2017. A practical tool for estimating subsurface LNAPL distributions and transmissivity using current and historical fluid levels in groundwater wells: Effects of entrapped and residual LNAPL. Journal of Contaminant Hydrology 205, 1–11. https://doi.org/10.1016/j.jconhyd.2017.06.002

Lenhard, R.J., Rayner, J.L., García-Rincón, J., 2019. Testing an analytical model for predicting subsurface LNAPL distributions from current and historic fluid levels in Monitoring Wells: A preliminary test considering hysteresis. Water 11, 2404.

Lenhard, R.J., Sookhak Lari, K., Rayner, J.L., Davis, G.B., 2018. Evaluating an analytical model to predict subsurface LNAPL distributions and transmissivity from current and historic fluid levels in groundwater wells: comparing results to numerical simulations. Groundwater Monitoring & Remediation 38, 75–84.

Li, I.P., Lu, B.C., Chen, E.C., 1973. Vapor-Liquid equilibriums of binary systems containing n-hexane, cyclohexane, and benzene at low temperatures. Journal of Chemical and Engineering Data 18, 305–309.

Margesin, R., Schinner, F., 2001. Biodegradation and bioremediation of hydrocarbons in extreme environments. Applied microbiology and biotechnology 56, 650–663.

Mayer, A.S., 2005. Soil and Groundwater Contamination: Nonaqueous Phase Liquids. American Geophysical Union.

McAlexander, B., Sihota, N., 2019. Influence of Ambient Temperature, Precipitation, and Groundwater Level on Natural Source Zone Depletion Rates at a Large Semiarid LNAPL Site. Groundwater Monitoring & Remediation 39, 54–65. https://doi.org/10.1111/gwmr.12309

McCarthy, K.A., Johnson, R.L., 1993. Transport of volatile organic compounds across the capillary fringe. Water Resources Research 29, 1675–1683.

Meixner, T., Manning, A.H., Stonestrom, D.A., Allen, D.M., Ajami, H., Blasch, K.W., Brookfield, A.E., Castro, C.L., Clark, J.F., Gochis, D.J., Flint, A.L., Neff, K.L., Niraula, R., Rodell, M., Scanlon, B.R., Singha, K., Walvoord, M.A., 2016. Implications of projected climate change for groundwater recharge in the western United States. Journal of Hydrology 534, 124–138. https://doi.org/10.1016/j.jhydrol.2015.12.027

Menberg, K., Blum, P., Kurylyk, B.L., Bayer, P., 2014. Observed groundwater temperature response to recent climate change. Hydrology and Earth System Sciences 18, 4453–4466. https://doi:10.5194/hess-18-4453-2014

Miller, M.M., Wasik, S.P., Huang, G.L., Shiu, W.Y., Mackay, D., 1985. Relationships between octanol-water partition coefficient and aqueous solubility. Environmental science & technology 19, 522–529.

Mobile, M.A., Widdowson, M.A., Gallagher, D.L., 2012. Multicomponent NAPL Source Dissolution: Evaluation of Mass-Transfer Coefficients. Environ. Sci. Technol. 46, 10047–10054. https://doi.org/10.1021/es301076p

Nambi, I.M., Powers, S.E., 2003. Mass transfer correlations for nonaqueous phase liquid dissolution from regions with high initial saturations. Water Resources Research 39. https://doi.org/10.1029/2001WR000667

Nelson, H.D., De Ligny, C.L., 1968. The determination of the solubilities of some n-alkanes in water at different temperatures, by means of gas chromatography. Recueil des Travaux Chimiques des Pays-Bas 87, 528–544.

Newell, C.J., 1995. Light Nonaqueous Phase Liquids. United States Environmental Protection Agency, Office of Research and Development, [and] Office of Solid Waste and Emergency Response.

Nyer, E.K., 2000. In situ treatment technology. CRC Press.

Nygren, M., Giese, M., Kløve, B., Haaf, E., Rossi, P.M., Barthel, R., 2020. Changes in seasonality of groundwater level fluctuations in a temperate-cold climate transition zone. Journal of Hydrology X 8, 100062.

Okkonen, J., Jyrkama, M., Klöve, B., 2010. A conceptual approach for assessing the impact of climate change on groundwater and related surface waters in cold regions (Finland). Hydrogeology Journal 18, 429–439. https://doi.org/10.1007/s10040-009-0529-9

Oostrom, M., Dane, J.H., Wietsma, T.W., 2007. A review of multidimensional, multifluid, intermediate-scale experiments: Flow behavior, saturation imaging, and tracer detection and quantification. Vadose Zone Journal 6, 610–637.

Ortega-Calvo, J.-J., Alexander, M., 1994. Roles of bacterial attachment and spontaneous partitioning in the biodegradation of naphthalene initially present in nonaqueous-phase liquids. Appl. Environ. Microbiol. 60, 2643–2646.

Parker, J.C., Lenhard, R.J., 1987. A model for hysteretic constitutive relations governing multiphase flow: 1. Saturation-pressure relations. Water Resources Research 23, 2187–2196. https://doi.org/10.1029/WR023i012p02187

Patterson, B.M., Davis, G.B., 2009. Quantification of vapor intrusion pathways into a slab-on-ground building under varying environmental conditions. Environmental science & technology 43, 650–656.

Petri, B.G., Fučík, R., Illangasekare, T.H., Smits, K.M., Christ, J.A., Sakaki, T., Sauck, C.C., 2015. Effect of NAPL source morphology on mass transfer in the vadose zone. Groundwater 53, 685–698.

Philippe, N., Davarzani, H., Colombano, S., Dierick, M., Klein, P.-Y., Marcoux, M., 2020. Experimental study of the temperature effect on two-phase flow properties in highly permeable porous media: Application to the remediation of dense non-aqueous phase liquids (DNAPLs) in polluted soil. Advances in Water Resources 146, 103783.

Picone, S., Grotenhuis, T., van Gaans, P., Valstar, J., Langenhoff, A., Rijnaarts, H., 2013. Toluene biodegradation rates in unsaturated soil systems versus liquid batches and their relevance to field conditions. Applied microbiology and biotechnology 97, 7887–7898.

Picone, S., Valstar, J., van Gaans, P., Grotenhuis, T., Rijnaarts, H., 2012. Sensitivity analysis on parameters and processes affecting vapor intrusion risk. Environmental Toxicology and Chemistry 31, 1042–1052.

Pierotti, R.A., Liabastre, A.A., 1972. The structure and properties of water solutions.

Pitzer, K.S., Scott, D.W., 1943. The thermodynamics and molecular structure of benzene and its methyl derivatives1. Journal of the American Chemical Society 65, 803–829.

Powers, S.E., Abriola, L.M., Weber Jr, W.J., 1994. An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: Transient mass transfer rates. Water Resources Research 30, 321–332.

Powers, S.E., Abriola, L.M., Weber Jr, W.J., 1992. An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: Steady state mass transfer rates. Water Resources Research 28, 2691–2705.

Powers, S.E., Nambi, I.M., Curry Jr, G.W., 1998. Non–aqueous phase liquid dissolution in heterogeneous systems: Mechanisms and a local equilibrium modeling approach - Powers - 1998 - Water Resources Research - Wiley Online Library. Water Resources Research 34, 3293–3302.

Prommer, H., Barry, D.A., Davis, G.B., 2002. Modelling of physical and reactive processes during biodegradation of a hydrocarbon plume under transient groundwater flow conditions. Journal of Contaminant Hydrology 59, 113–131. https://doi.org/10.1016/S0169-7722(02)00078-5

Qi, S., Luo, J., O'Connor, D., Cao, X., Hou, D., 2020. Influence of groundwater table fluctuation on the non-equilibrium transport of volatile organic contaminants in the vadose zone. Journal of Hydrology 580, 124353. https://doi.org/10.1016/j.jhydrol.2019.124353

Rahimi, R., Tavakol-Davani, H., Graves, C., Gomez, A., Fazel Valipour, M., 2020. Compound Inundation Impacts of Coastal Climate Change: Sea-Level Rise, Groundwater Rise, and Coastal Watershed Precipitation. Water 12, 2776.

Rainwater, K., Mayfield, M.P., Heintz, C., Claborn, B.J., 1993. Enhanced in situ Biodegradation of Diesel Fuel by Cyclic Vertical Water Table Movement: Preliminary Studies. Water Environment Research 65, 717–725.

Rayner, J.L., Snape, I., Walworth, J.L., Harvey, P.McA., Ferguson, S.H., 2007. Petroleum–hydrocarbon contamination and remediation by microbioventing at sub-Antarctic Macquarie Island. Cold Regions Science and Technology 48, 139–153. https://doi.org/10.1016/j.coldregions.2006.11.001

Reddi, L.N., Han, W., Banks, M.K., 1998. Mass loss from LNAPL pools under fluctuating water table conditions. Journal of Environmental Engineering 124, 1171–1177.

Rezanezhad, F., Couture, R.-M., Kovac, R., O'Connell, D., Van Cappellen, P., 2014. Water table fluctuations and soil biogeochemistry: An experimental approach using an automated soil column system. Journal of Hydrology 509, 245–256. https://doi.org/10.1016/j.jhydrol.2013.11.036

Rezanezhad, F., Shafieiyoun, S., Al-Raoush, R.I., Ismail, R.E., Ngueleu, S.K., Van Cappellen, P., 2019. Influence of Salinity and NAPL Composition on Sulfate Application in the Contaminated Subsurface Systems. AGU Fall Meeting Abstracts 21.

Rice, D.W., Grose, R.D., Michaelsen, J.C., Dooher, B.P., MacQueen, D.H., Cullen, S.J., Kastenberg, W.E., Everett, L.G., Marino, M.A., 1995. California leaking underground fuel tank (LUFT) historical case analyses. California State Water Resources Control Board.

Rivett, M., Sweeney, R., 2019. An introduction to natural source zone depletion at LNAPL sites. (technical bulletin). University of Strathclyde, Glasgow.

Rivett, M.O., Tomlinson, D.W., Thornton, S.F., Thomas, A.O., Leharne, S.A., Wealthall, G.P., 2014. An Illustrated Handbook of LNAPL Transport and Fate in the Subsurface, Civil And Environmental Engineering. London.

Sabljić, A., Güsten, H., Verhaar, H., Hermens, J., 1995. QSAR modelling of soil sorption. Improvements and systematics of log KOC vs. log KOW correlations. Chemosphere 31, 4489–4514. https://doi.org/10.1016/0045-6535(95)00327-5

Sanemasa, I., Araki, M., Deguchi, T., Nagai, H., 1982. Solubility measurements of benzene and the alkylbenzenes in water by making use of solute vapor. Bulletin of the Chemical Society of Japan 55, 1054–1062.

Sarikurt, D.A., Gokdemir, C., Copty, N.K., 2017. Sherwood correlation for dissolution of pooled NAPL in porous media. Journal of Contaminant Hydrology 206, 67–74. https://doi.org/10.1016/j.jconhyd.2017.10.001

Schimel, J., Balser, T.C., Wallenstein, M., 2007. Microbial stress-response physiology and its implications for ecosystem function. Ecology 88, 1386–1394.

Schroth, M.H., Istok, J.D., Ahearn, S.J., Selker, J.S., 1995. Geometry and position of light nonaqueous-phase liquid lenses in water-wetted porous media. Journal of Contaminant Hydrology 19, 269–287. https://doi.org/10.1016/0169-7722(95)00023-O

Seager, S.L., Geertson, L.R., Giddings, J.C., 1963. Temperature Dependence of Gas and Vapor Diffusion Coefficients. Journal of Chemical and Engineering Data 8, 168–169.

She, H.Y., Sleep, B.E., 1998. The effect of temperature on capillary pressure-saturation relationships for air-water and perchloroethylene-water systems. Water Resources Research 34, 2587–2597.

Shojib, M., 2015. Dissolution of Trapped Light Non-Aqueous Phase Liquid in the Presence of Trapped Gas (thesis).

Sihota, N.J., Mayer, K.U., Toso, M.A., Atwater, J.F., 2013. Methane emissions and contaminant degradation rates at sites affected by accidental releases of denatured fuel-grade ethanol. Journal of Contaminant Hydrology 151, 1–15. https://doi.org/10.1016/j.jconhyd.2013.03.008

Sinke, A.J.C., Dury, O., Zobrist, J., 1998. Effects of a fluctuating water table: column study on redox dynamics and fate of some organic pollutants. Journal of Contaminant Hydrology 33, 231–246. https://doi.org/10.1016/S0169-7722(98)00072-2

Sinnokrot, A.A., Ramey Jr, H.J., Marsden Jr, S.S., 1971. Effect of temperature level upon capillary pressure curves. Society of Petroleum Engineers Journal 11, 13–22.

Sleep, B.E., Ma, Y., 1997. Thermal variation of organic fluid properties and impact on thermal remediation feasibility. Soil and Sediment Contamination 6, 281–306.

Smerdon, B.D., 2017. A synopsis of climate change effects on groundwater recharge. Journal of Hydrology 555, 125–128. https://doi.org/10.1016/j.jhydrol.2017.09.047

Sookhak Lari, K., Davis, G.B., Johnston, C.D., 2016a. Incorporating hysteresis in a multi-phase multi-component NAPL modelling framework; a multi-component LNAPL gasoline example. Advances in Water Resources 96, 190–201. https://doi.org/10.1016/j.advwatres.2016.07.012

Sookhak Lari, K., Davis, G.B., Rayner, J.L., Bastow, T.P., Puzon, G.J., 2019. Natural source zone depletion of LNAPL: A critical review supporting modelling approaches. Water research 157, 630–646.

Sookhak Lari, K., Johnston, C.D., Davis, G.B., 2016b. Gasoline multiphase and multicomponent partitioning in the vadose zone: Dynamics and risk longevity. Vadose Zone Journal 15, 1–15.

Sookhak Lari, K., Rayner, J.L., Davis, G.B., Johnston, C.D., 2020. LNAPL Recovery Endpoints: Lessons Learnt Through Modeling, Experiments, and Field Trials. Groundwater Monitoring & Remediation 40, 21–29.

Soucy, N.C., Mumford, K.G., 2017. Bubble-Facilitated VOC Transport from LNAPL Smear Zones and Its Potential Effect on Vapor Intrusion. Environ. Sci. Technol. 51, 2795–2802. https://doi.org/10.1021/acs.est.6b06061

Staudinger, J., Roberts, P.V., 2001. A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. Chemosphere 44, 561–576.

Steffy, D.A., Johnston, C., Barry, D.A., 1995. A field study of the vertical immiscible displacement of LNAPL associated with a fluctuating water table. Presented at the Groundwater Quality: Remediation and Protection, International Association of Hydrological Sciences, Prague, Czech Republic.

Steffy, D.A., Johnston, C.D., Barry, D.A., 1998. Numerical simulations and long-column tests of LNAPL displacement and trapping by a fluctuating water table. Journal of Soil contamination 7, 325–356.

Sun, S., 2016. Transient water table influence upon Light Non-Aqueous Phase Liquids (LNAPLs) redistribution: laboratory and modelling studies. University of Birmingham.

Suthersan, S., Koons, B., Schnobrich, M., 2015. Contemporary management of sites with petroleum LNAPL presence. Groundwater Monitoring & Remediation 35, 23–29.

Taylor, C.A., Stefan, H.G., 2009. Shallow groundwater temperature response to climate change and urbanization. Journal of Hydrology 375, 601–612.

Taylor, R.G., Scanlon, B., Döll, P., Rodell, M., van Beek, R., Wada, Y., Longuevergne, L., Leblanc, M., Famiglietti, J.S., Edmunds, M., Konikow, L., Green, T.R., Chen, J., Taniguchi, M., Bierkens, M.F.P., MacDonald, A., Fan, Y., Maxwell, R.M., Yechieli, Y., Gurdak, J.J., Allen, D.M., Shamsudduha, M., Hiscock, K., Yeh, P.J.-F., Holman, I., Treidel, H., 2013. Ground water and climate change. Nature Climate Change 3, 322–329. https://doi.org/10.1038/nclimate1744

ten Hulscher, Th.E.M., Cornelissen, G., 1996. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants - a review. Chemosphere 32, 609–626. https://doi.org/10.1016/0045-6535(95)00345-2

Teramoto, E.H., Chang, H.K., 2017. Field data and numerical simulation of btex concentration trends under water table fluctuations: Example of a jet fuel-contaminated site in Brazil. Journal of Contaminant Hydrology 198, 37–47. https://doi.org/10.1016/j.jconhyd.2017.01.002

Thomson, N.R., Sykes, J.F., Van Vliet, D., 1997. A numerical investigation into factors affecting gas and aqueous phase plumes in the subsurface. Journal of Contaminant Hydrology 28, 39–70.

USGCRP, 2014. Climate change impacts in the United States. (U.S. Global Change Research Program).

Van De Ven, C.J., Scully, K.H., Frame, M.A., Sihota, N.J., Mayer, K.U., 2021. Impacts of water table fluctuations on actual and perceived natural source zone depletion rates. Journal of Contaminant Hydrology 238, 103771.

Van Geel, P.J., Sykes, J.F., 1997. The importance of fluid entrapment, saturation hysteresis and residual saturations on the distribution of a lighter-than-water non-aqueous phase liquid in a variably saturated sand medium. Journal of Contaminant Hydrology 25, 249–270. https://doi.org/10.1016/S0169-7722(96)00038-1

Van Geel, P.J., Sykes, J.F., 1994. Laboratory and model simulations of a LNAPL spill in a variably-saturated sand, 1. Laboratory experiment and image analysis techniques. Journal of Contaminant Hydrology 17, 1–25. https://doi.org/10.1016/0169-7722(94)90075-2

Vasudevan, M., Johnston, C.D., Bastow, T.P., Lekmine, G., Rayner, J.L., Nambi, I.M., Suresh Kumar, G., Ravi Krishna, R., Davis, G.B., 2016. Effect of compositional heterogeneity on dissolution of non-ideal LNAPL mixtures. Journal of Contaminant Hydrology 194, 10–16. https://doi.org/10.1016/j.jconhyd.2016.09.006

Vasudevan, M., Suresh Kumar, G., Nambi, I.M., 2014. Numerical study on kinetic/equilibrium behaviour of dissolution of toluene under variable subsurface conditions. European Journal of Environmental and Civil Engineering 18, 1070–1093. https://doi.org/10.1080/19648189.2014.922902

Vorenhout, M., van der Geest, H.G., van Marum, D., Wattel, K., Eijsackers, H.J., 2004. Automated and continuous redox potential measurements in soil. Journal of environmental quality 33, 1562–1567.

Werner, D., Höhener, P., 2002. The influence of water table fluctuations on the volatilisation of contaminants from groundwater. Groundwater Quality: Natural and enhanced restoration of groundwater polltuion, Sheffield. IAHS Publ 275.

Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N., Hansen, J.E., 1995. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater. Volume II. PARSONS ENGINEERING SCIENCE INC DENVER CO.

Williams, M.D., Oostrom, M., 2000. Oxygenation of anoxic water in a fluctuating water table system: an experimental and numerical study. Journal of Hydrology 230, 70–85. https://doi.org/10.1016/S0022-1694(00)00172-4

Willingham, C.B., Taylor, W.J., Pignocco, J.M., Rossini, F.D., 1945. Vapor pressures and boiling points of some paraffin, alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons. Journal of Research of the National Bureau of Standards 35, 219–244.

Wilson, J.T., Sewell, G.W., Caron, D., Doyle, G., Miller, R.N., 1995. Intrinsic bioremediation of jet fuel contamination at George Air Force Base, in: Intrinsic Bioremediation.

Yadav, B.K., Hassanizadeh, S.M., 2011. An overview of biodegradation of LNAPLs in coastal (semi)-arid environment. Water, Air, & Soil Pollution 220, 225–239.

Yadav, B.K., Shrestha, S.R., Hassanizadeh, S.M., 2012. Biodegradation of Toluene Under Seasonal and Diurnal Fluctuations of Soil-Water Temperature. Water Air Soil Pollut 223, 3579–3588. https://doi.org/10.1007/s11270-011-1052-x

Yang, Y.S., Li, P., Zhang, X., Li, M., Lu, Y., Xu, B., Yu, T., 2017. Lab-based investigation of enhanced BTEX attenuation driven by groundwater table fluctuation. Chemosphere 169, 678–684. https://doi.org/10.1016/j.chemosphere.2016.11.128

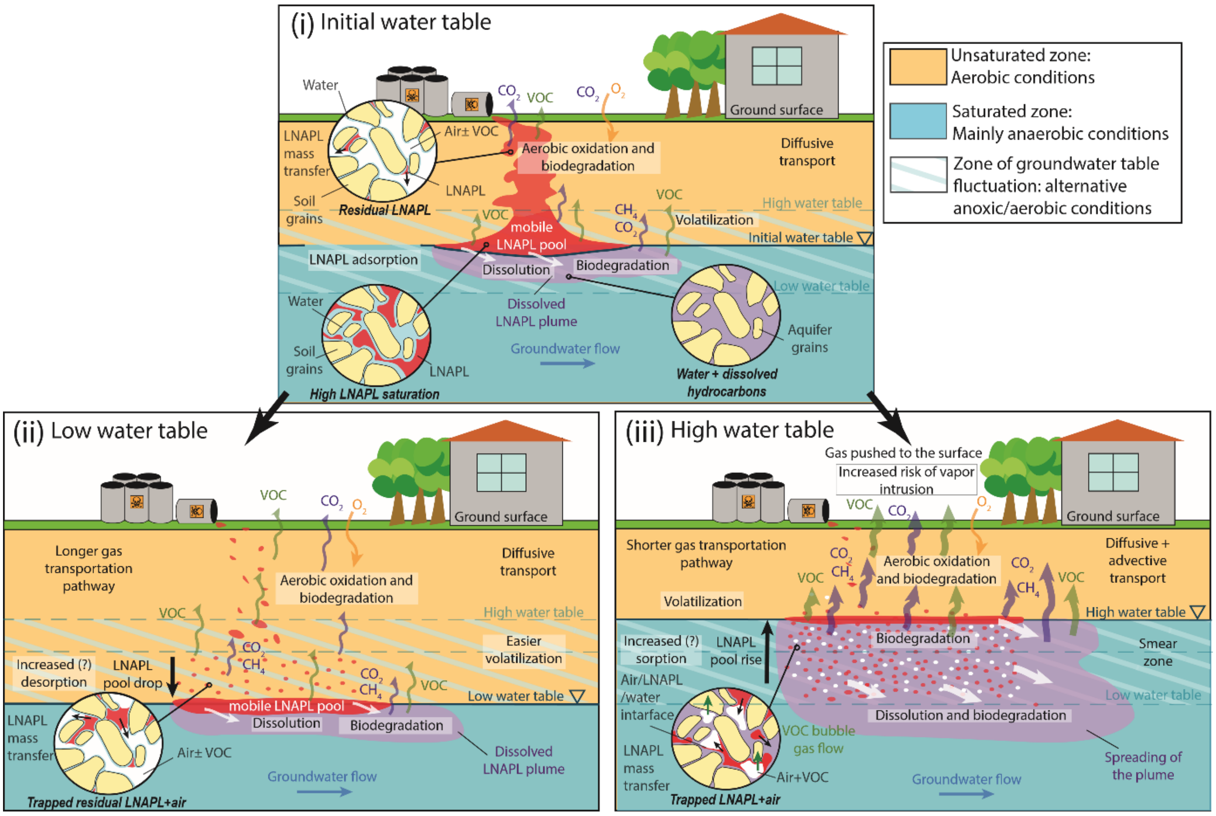
Yoon, H., Kim, J.H., Liljestrand, H.M., Khim, J., 2002. Effect of water content on transient nonequilibrium NAPL–gas mass transfer during soil vapor extraction. Journal of Contaminant Hydrology 54, 1–18.

Zeman, N.R., Irianni Renno, M., Olson, M.R., Wilson, L.P., Sale, T.C., De Long, S.K., 2014. Temperature impacts on anaerobic biotransformation of LNAPL and concurrent shifts in microbial community structure. Biodegradation 25, 569–585. https://doi.org/10.1007/s10532-014-9682-5

Zhang, H., Ye, Y., Yang, X., 2021. How Does the Periodic Groundwater Table Fluctuation Impact on Chlorinated Vapor Intrusion? Geofluids 2021.

Zhou, A., Zhang, Y., Dong, T., Lin, X., Su, X., 2015. Response of the microbial community to seasonal groundwater level fluctuations in petroleum hydrocarbon-contaminated groundwater. Environ Sci Pollut Res 22, 10094–10106. https://doi.org/10.1007/s11356-015-4183-6

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.

997

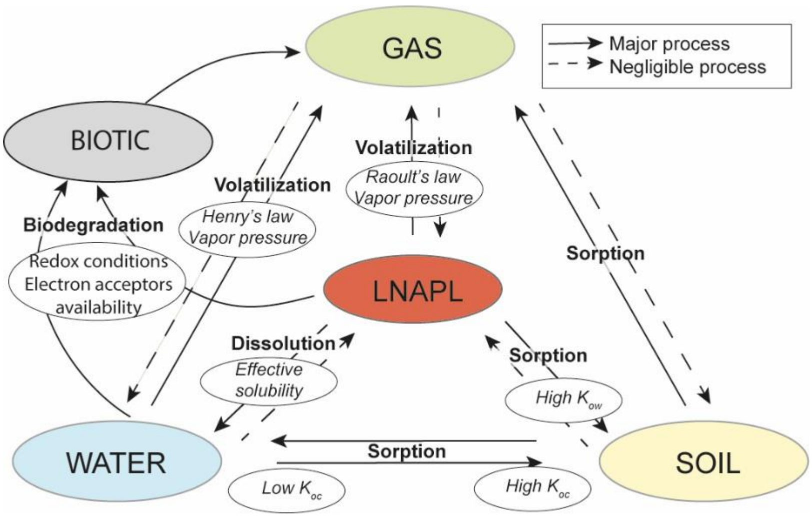
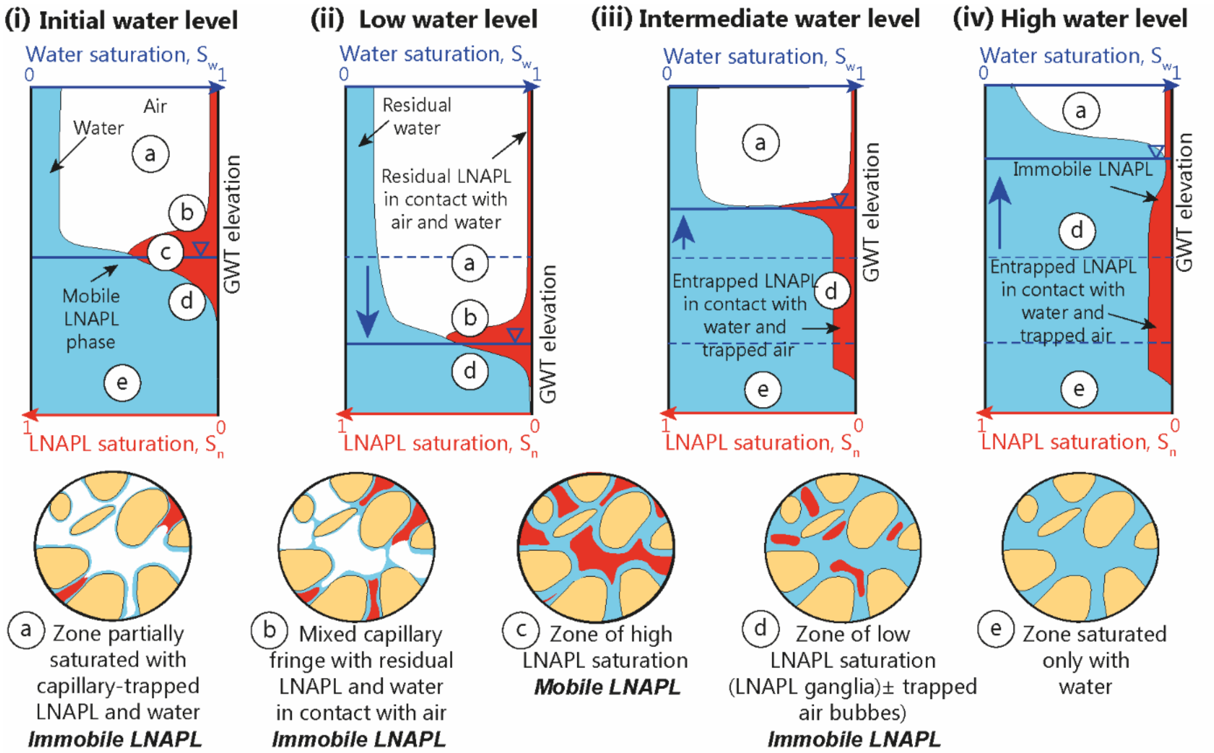


Fig. 2. Dominant processes involved in the LNAPL biodegradation and compounds partitioning between the phases potentially present in the saturated and unsaturated zone. K_{ow}: octanol-water partitioning coefficient. K_{oc}: carbon-water partitioning coefficient.

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

Tables

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

			Vapor pressure (mmHg)[a]		
Temperature (°C)	12.0	14.0	17.0	20.0	Ref.
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^3/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	[b]
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_{oc} (L/kg)		
Benzene	1.88	1.89	1.91	1.92	(Sabljić et al., 1995)[c]
Toluene	2.28	2.30	2.31	2.33	(Sabljić et al., 1995)[c]
m-Xylene				2.34	(Sabljić et al., 1995)
Hexane				3.34	ECHA[d]
Heptane				2.38	ECHA
Decane				4.16	ECHA
Cyclohexane					
Cyclopentane				2.53	ECHA
			Log K_{ow}		
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	(Sabljić 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^3)		
Oil (Voltesso 35)	0.859	0.859	0.858	0.858	(Sleep and Ma, 1997)[e]

Dynamic viscosity (cP)					
Oil (Voltesso 35)	33,5	29,0	23,7	19,6	(Sleep and Ma, 1997)[f]
Interfacial tension of oil-water system (mJ/m²)					
Oil (Voltesso 35)	44.3	43.8	43.1	42.4	(Sleep and Ma, 1997)[g]

[a] Calculated using Antoine Equation Parameters using data of the cited references.
[b] Calculated from Henry's law constant and the vapor pressure.
[c] Calculated from the log K_{ow} after the equation of Sabljić et al. (1995): log K_{oc}=0.81 log K_{ow}+0.10.*[dc]
[d] European Chemicals Agency (ECHA): https://echa.europa.eu/fr/information-on-chemicals. The data of each parameter and compound at the different temperatures were determined according to the data available in the respective references.
*[e] Calculated after the equation of Sleep and Ma (1997): ρ_{oil}= 0.8610-1.1750*10^{-4}*T-2.7738*10^{-6}*T^2*
*[f] Calculated after the equation of Sleep and Ma (1997): ln μ_{oil} = 24.306-1.767*$l0^4$/T-3.366*$l0^6$/T^2*
*g Calculated after the equation of Sleep and Ma (1997): γ_{oil}= 47.226-0.244*T*

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

	Main effects of the increase in temperature from 12 to 20°C	**Main effect of more intense groundwater level variations**	**Global expected effect of climate change**
LNAPL source zone mobility, partitioning, and depletion	• Decreased LNAPL viscosity (up to 41%). • Sorption? • Increased saturated vapor pressures (up to 45%)	• Greater spreading of the LNAPL across the SZ and USZ • Greater exposure of the LNAPL to the air, meteoric water, and groundwater • Accelerated diffusion and advective transport of soil gas	• Increased global LNAPL mobility • Increased leaching of the residual LNAPL by infiltrated meteoric water • Increased volatilization from the mobile, residual LNAPL • Increased VOC surface emissions
Dissolved plume	• Low variation of the LNAPL compounds solubility • Increased Henry's law constant (up to 51%)	• Greater LNAPL- meteoric and groundwater interfacial areas • Easier dissolved phase transportation by advection	• Increased residual and entrapped LNAPL constituents' dissolution • Increased dissolved groundwater plume concentration • Greater spreading of the dissolved plume in groundwater • Increased volatilization from the dissolved phase
Natural attenuation	• Increased uptake of nutrients and organic components by microorganisms • Increased microorganisms' activity	• Greater availability and renewal of carbon, oxygen, and micronutrients through the soil and the water column • Better evacuation of the reaction by-products accumulated during biodegradation • Greater functional diversity and flexibility of microorganisms	• Increased LNAPL biodegradation and attenuation rates • Increased gaseous (CO2, CH4) surface emissions • Decreased LNAPL source zone longevity • Maintains strong dissolution processes • Increased short-term risks • Decreased long-term risks

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

	Main current properties [a]	Main expected effect of climate change by 2100[a]	Main expected effect of climate change on LNAPL
Cold regions	• Low temperatures (<8°C) • Low soil nutrient contents and availability • Excess water distribution (rainfalls> 900 mm/yr) • Low soil oxygen diffusivities • Very low LNAPL volatilization, dissolution, and biodegradation	• Increased temperature (+5-9°C) and rainfalls (up to +50%) • Reduced snow cover and soil frost • Increased groundwater recharge, and heads in winter • Increased evapotranspiration, decreased groundwater recharge, and heads in summer • Increased groundwater level fluctuations • Higher oxygen inputs and diffusion in the soil and water • Strongly enhanced soil microbial activity	• Strongly increased LNAPL viscosity, volatility, and solubility • Increased spreading of the pollution in the soil and water • Strongly enhanced LNAPL biodegradation • Higher VOC emissions and dissolved pollutants concentrations • Strongly decreased pollution longevity
Arid/ semi-arid zones	• Highly variable and extremes temperatures (-10°C-60°C) • Scarce but intense rainfalls (mean rainfalls: 185-550 mm/yr) • Important water table level and soil moisture content fluctuations • High LNAPL mobilization and biodegradation	• Increased temperature (+4-7°C) • Decreased snowpack and precipitations in spring and summer • Strongly increased evapotranspiration and groundwater use • Strongly decreased groundwater recharge (up to -30%) and heads • Increased groundwater level variations tied with the encroachment catchment areas of pumping wells • Strongly decreased soil moisture content and soil microbial activity • Increase extreme precipitation events and floods frequency and intensity	• Increased LNAPL/air surface areas in the SZ • Increased LNAPL compounds volatility and VOC emissions • Increased spreading of the pollution in soil • Decreased LNAPL biodegradation • Increased risks of new LNAPL spills due to damage LNAPL transport and storage infrastructures during floods
Humid coastal areas	• High groundwater table dynamic due to tidal effects	• Increased sea level (0.43-0.84 mm/yr) due to thermal expansion, melting ice sheets, glaciers, and land water storage changes • Increased precipitations (+10-20%) and extreme precipitation events (+10-50%) • Increased coastal erosion, flood events frequency, and intensity • Increased coastal aquifer and groundwater heads • Increase salt-water intrusion and groundwater salinity	• Increase LNAPL/water surface contact • Increased pollutants dissolution and dilution in groundwater, connected rivers, and sea • Modification of some pollutants biodegradation rates due to changes in water salinity, soil moisture content, and the oxygen diffusivity • Increased risks of new LNAPL spills due to damage of coastal LNAPL transport and storage infrastructures during floods, storms

[a] *Predictions from IPCC (2014), Meixner et al. (2016), USGCRP (2014).*

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

Main process	**References**	**Scientific approach**
Dissolution, transport, sorption	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	*Laboratory experiments*
	Davis et al., 1999; Gatsios et al., 2018; J.-Y. Lee et al., 2001; Steffy et al., 1995; Teramoto and Chang, 2017	*Field monitoring*
	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	*Numerical modeling*
Biodegradation/ Attenuation	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	*Laboratory experiments*
	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	*Field monitoring*
	Prommer et al., 2002	*Numerical modeling*
Volatilization, gas transport	Chen et al., 2010; McCarthy and Johnson, 1993; Soucy and Mumford, 2017	*Laboratory experiments*
	Baedecker et al., 2011; Guo, 2015; Patterson and Davis, 2009	*Field monitoring*
	Picone et al., 2012; Qi et al., 2020; Thomson et al., 1997	*Numerical modeling*

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

LNAPL composition		
LNAPL mixture complexity	Commonly used compounds	References
One component	Toluene, *n*-heptane, *n*-decane, or *n*-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, *n*-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
Porous media composition		
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