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Leakage of CO_2 from Geological Storage and Its Impacts on Fresh Soil-Water Systems: A Review

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Abstract

Leakage of CO_2 from the geological storage is a serious issue for the sustainability of receiving fresh soil-water system. Subsurface water quality issues are no longer related to one type of pollution in many regions around the globe. Thus, an effort has been made to review studies performed to investigate supercritical CO_2 ($scCO_2$) and CO_2 enrich brine migration and leakage from geological storage formations. Further, the study also reviewed its impacts on fresh soil-water systems, soil microbes and vegetation. First part of the study discussed $scCO_2/CO_2$ enrich brine migration and its leakage from storage formations along with its impact on pore dynamics of hydrological regimes. Later, a state-of-the-art literature survey has been performed to understand the role of CO_2-brine leakage in groundwater dynamics and its quality along with soil microbes and plants. It is observed in the literature survey that most of the studies on CO_2-brine migration in storage formations reported significant CO_2-brine leakage due to over-pressurization through wells (injections and abandoned), fracture and faults during CO_2 injection. Thus, changes in the groundwater flow and water table dynamics can be the first impact of the CO_2-brine leakage. Subsequently three major alterations may also occur -i) drop in pH of subsurface water, ii) enhancement of organic compounds, and iii) mobilization of metals and metalloids. Geochemical alteration depends on the amount of CO_2 leaked and interactions with host rocks. Therefore, such alteration may significantly affect soil microbial dynamics and vegetation in and around CO_2 leakage sites. In-depth analysis of the available literature fortifies that a proper subsurface characterization along with the bio-geochemical analysis is extremely important and should be mandatory to predict the more accurate risk of CO_2 capture and storage activities on soil-water systems.

Keywords: CO_2 capture and storage, Leakage, Dissolution, Subsurface Pollution, Microbial Shifting

1.0 Introduction

CO_2 capture and storage (CCS) is emerging as an important tool for the mitigation of the greenhouse gas (GHG) emissions by deep cutting of the global atmospheric CO_2 concentration (Herzog, 2001; Bruant et al. 2002; Figueroa et al. 2008). Further, CCS projects were getting high interest globally not only to cut GHG emissions but also to enhance recovery of oil/gas (Michael et al. 2010). In early stage, the major attention was paid to develop economically acceptable techniques to capture CO_2 (Figueroa et al. 2008) and on estimations of potential geological sinks (Herzog, 2001). Herzog (2001) reported about the storage capacity of different geological units including ocean, saline formations, coal seams for future CCS activities. In 1990s, Alberta basin (Acid Gas) in Canada was the first geological sequestration project in which CO_2 was injected with H_2S for storage in deep zone. In early 2000s, the saline aquifer CO_2 storage (SACS) project, Sleipner in middle of the North Sea was a first commercial CCS project. This project established as an example for the global community gaining international acceptance and provided an option for CO_2 mitigation (Herzog, 2001; Torp and Gale, 2004). Since initial days, the tendency of CO_2

to escape from the storage zone to atmosphere via cap rock leakages was highlighted as a major concern for CCS project's success (Bruant et al. 2002; Zhou and Birkholzer, 2011; Lewicki et al. 2007).

Non-isothermal, two phase and multicomponent flow occurs once the supercritical (sc) CO_2/CO_2 enrich brine leaks from the storage zone to overlying aquifers (Birkholzer and Zhou, 2009). The dissolution of CO_2 in formation water significantly affect its migration in deep aquifers (Lions et al. 2014). Similarly, precipitation of the minerals is another dominating geochemical processes occurs due to introduction of CO_2. These geochemical processes significantly affect the pore water dynamics by dissolving host minerals and precipitations of other materials (Andre et al. 2007; Fritz et al. 2010; Jin et al. 2016). Thus, previous studies reported significant impacts of the CO_2 injection, migration and its leakage on groundwater table dynamics and on flow regimes (Nicot, 2008; Yamamoto et al. 2009).

Further, introduction of CO_2-brine in fresh groundwater zone may also cause three major geochemical changes, 1) drop in pH; 2) enrichment of organic compounds; 3) mobilization of metalloids. These changes were commonly found in previous studies as an impacts of CO_2/CO_2 enrich brine in fresh aquifer zones (Kharaka et al. 2010; 2017; Zheng and Spycher, 2018). Acidification of soil-water systems may significantly enhance the sorption of exiting pollutants, especially like arsenic (As); Lead (Pb), Iron (Fe) and Manganese (Mn) (Smyth et al. 2009; Lu et al. 2010; Humez et al. 2013). Studies considering impacts of CO_2-brine leakage on behaviors of metals and metalloids indicate that 1) one category of metals and metalloids (Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, Zn) rapidly increases its concentration then stabilize with time; 2) second category (Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) may increase it concentrations with the start of CO_2 flux for some time then decline with progress of time (Smyth et al. 2009; Lu et al. 2010). Likewise, some studies also reported increment in organic compounds like benzene, toluene, ethylbenzene and xylene (BTEX), Phenol and naphthalene (Siirila and Maxwell, 2012; Atchley et al. 2013). Furthermore, degradation of groundwater quality can also be expected once CO_2-brine leaked from storage formations (Newmark et al. 2010; Derakhshan-Nejad et al. 2019). Geochemical alteration due to the leakage of CO_2/CO_2 enrich brine may also affect the soil microbe, vegetation and ultimately human health. However, very little attention has been paid in past to understand potential impacts of CO_2-brine leakage on subsurface microbiological resources, and plants at CCS sites. Generally, the elevated CO_2 concentration in the vadose zone may negatively affect root water absorption, chlorophyll, starch content and total biomass. Furthermore, plants exposed to high CO_2 shows significant impacts on its growth by reducing plant height, root length, leaf number, leaf area, seed number, pod number (Al-Traboulsi et al. 2012; Wu et al. 2014) and by altering physiological stress (Zhao et al. 2017).

Groundwater resources are depleting with fast rate around the globe (Famiglietti, 2014). It's quality decreases day-by-day due to occurrence of large number of pollutants (Strokal et al. 2019). Thus, the production of safe groundwater resources for drinking purpose is key challenge for policy makers and scientists. In this highly demanding situation, one can't ignore the risk associated with CO_2 intrusion from geological storage or during geological sequestration and their impact on the groundwater quality. Therefore, analysis of the reasons for the deterioration of groundwater resources around the CCS sites may be the first step towards the better maintenance of CCS activities. Thus, an effort has been made to present current understanding and knowledge gaps in the areas of CO_2 leak from storage reservoirs and its geochemical interactions in the groundwater zone; its impact on groundwater quality, subsurface microbes, and plants. Figure 1 demonstrating the scope of this review article in which numbers in red circle indicating the scope of different section of this review manuscript.

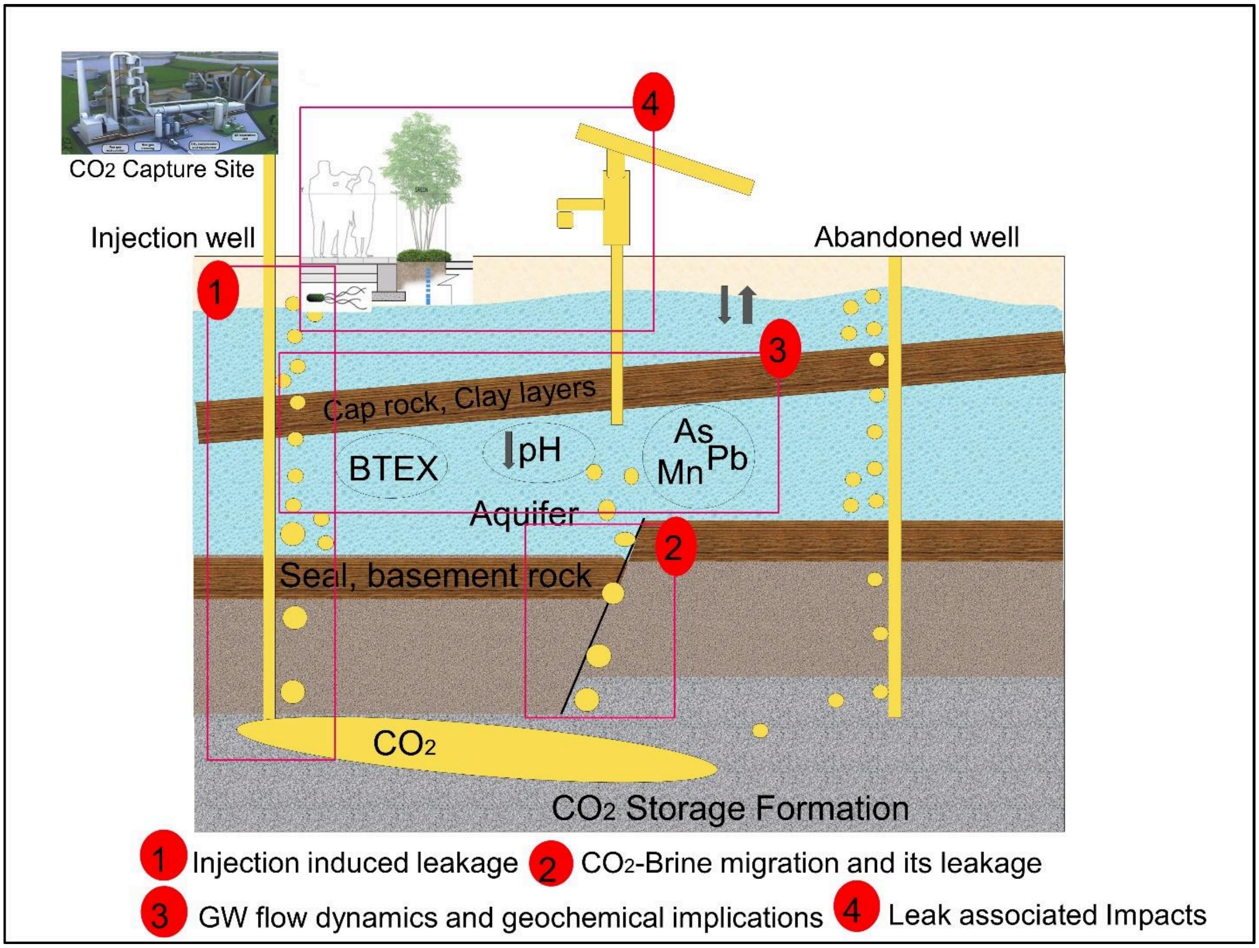


Figure 1: Schematic diagram of CO_2 leakage along faults, fracture, and wells (injection and abandoned) and its impact on the fresh soil-water system.

2.0 Experiencing CO_2 Leakage

Field scale CO_2 release experiments have been conducted in different regions of the world to understand the CO_2 leakage from subsurface/vadose zone (Table 1). An effort has been made by Roberts and Stalker, (2017) to list such field CO_2 release experiments. Nine studies (ASGARD-UK, QICS-UK, CO_2FieldLab-Norway, Grimsrud Farm-Norway, CO_2DEMO-France, PISCO$_2$-

Spain, Ginninderra-Australia, Ressacada Farm-Brazil, and ZERT-USA) out of 14 studies revealed the leakage of CO_2 at experimental sites as listed in table 1. In these experiments, the injection rate of CO_2 varies from 0.04 gs^{-1} [1.3 t(CO_2)pa] to 4.9 gs^{-1} [153.3 t(CO_2)pa] where 5% (CO_2FieldLab-Norway) to 90% (ZERT-USA) of CO_2 leaked from the release zone. In which, 34% of total CO_2 were seep at ASGARD site in England, 82% from Grimsrud Farm in Norway, 78% from CO_2-DEMO site in France, 82.3% from PISCO$_2$ site in Spain and 90% from ZERT in USA. Global data on CO_2 leakage has been discussed by Roberts and Stalker, (2017). They highlighted that the CO_2 flux was reported for 39 sites (70% of the dataset), seep rate at 49 sites (90% of the dataset) and both flux and seep rate measurements were reported for 30 sites (55% of the dataset).

These field scale CO_2 release experiments were performed either in top soil (Grimsrud Farm site), or vadose zone (PISCO$_2$; Ginninderra; CO_2-DEMO; ASGARD sites) or shallow saturated zone (QICS; CO_2 Field Lab; Vrøgum sites) to track the potential leakage and its pathways (table 1). Lassen et al. (2015) performed an experimental study in shallow aquifers formations at a site located in Vrøgum in the western Denmark where 45 kg gaseous CO_2 was injected at the depth of 8 m. CO_2 plume was monitored using cross-borehole ground penetrating radar (GPR). The results of this study demonstrates that several CO_2 gas pockets of gas saturation upto 0.3 formed below lower-permeable sand layers. This study conclude that the lateral migration of CO_2 gas was significant in case of the leakage from CCS site. Further, CO_2 leakage during its injection from the deep saline aquifer was investigated by Hu et al. (2016) using the pressure tomography. Results of this study show that the CO_2 migrate upward through the permeable seal and the leaky path with 0.62 and 0.86 CO_2 saturation level, respectively, into the overlying aquifer. In some cases, CO_2 plume was also observed at the upper aquifer due to the long injection and its leakage through leaky pathways. Likewise, a Shallow Injection Monitoring Experiment (SIMEx) was performed by injecting 550.6 t(CO_2)pa in 15 m deep shallow in 3.5 hours. At this site, no leakage was experienced but alternation in geochemical makeup was clearly demonstrated (Pezard et al. 2016).

At industrial scale, CCS projects have experienced CO_2 leakage from storage geological formations in past due to mechanical disturbance i.e. injection process, geochemical processes and or natural geological disturbances like earthquake (Zoback, and Gorelick, 2012). Generally, the supercritical CO_2 is injected in deep geological formations shallower than 3 km, where CO_2 would be stored. Mechanical disturbances may occur due to variations in operational parameters like injection pressures, which may further cause changes in dynamics flow regimes and the fracture in the heterogeneous cap-rocks. The injected CO_2 can also displace the brine and increases its flow velocity which results in high brine discharged rate to near the surface zone/lake or stream (Bergman and Winter, 1995). Similarly, Nicot (2008) described that the pressure pulse travels much faster than the mass of the CO_2 plume as injection progress, which has the potential to displace reservoir fluids swiftly. Over-pressurization/large-scale pressure build-up in response to the injection may cause fracture in the caprock and in the overlying subsurface zones (Zhou and Birkholzer, 2011). Such pressurization may also cause the upward movement of CO_2-brine through localized pathways. In conclusion, there were high experience of CO_2 leakage occurs through faults, fractures and rock discontinuities at natural sites and from operational wells due to cracked/corrosion well casing and or well blowout at industrial (Lewicki et al. 2007). Thus, a better understanding of CO_2 seep mechanisms, pathways, and associated risk is needed in and around CCS sites.

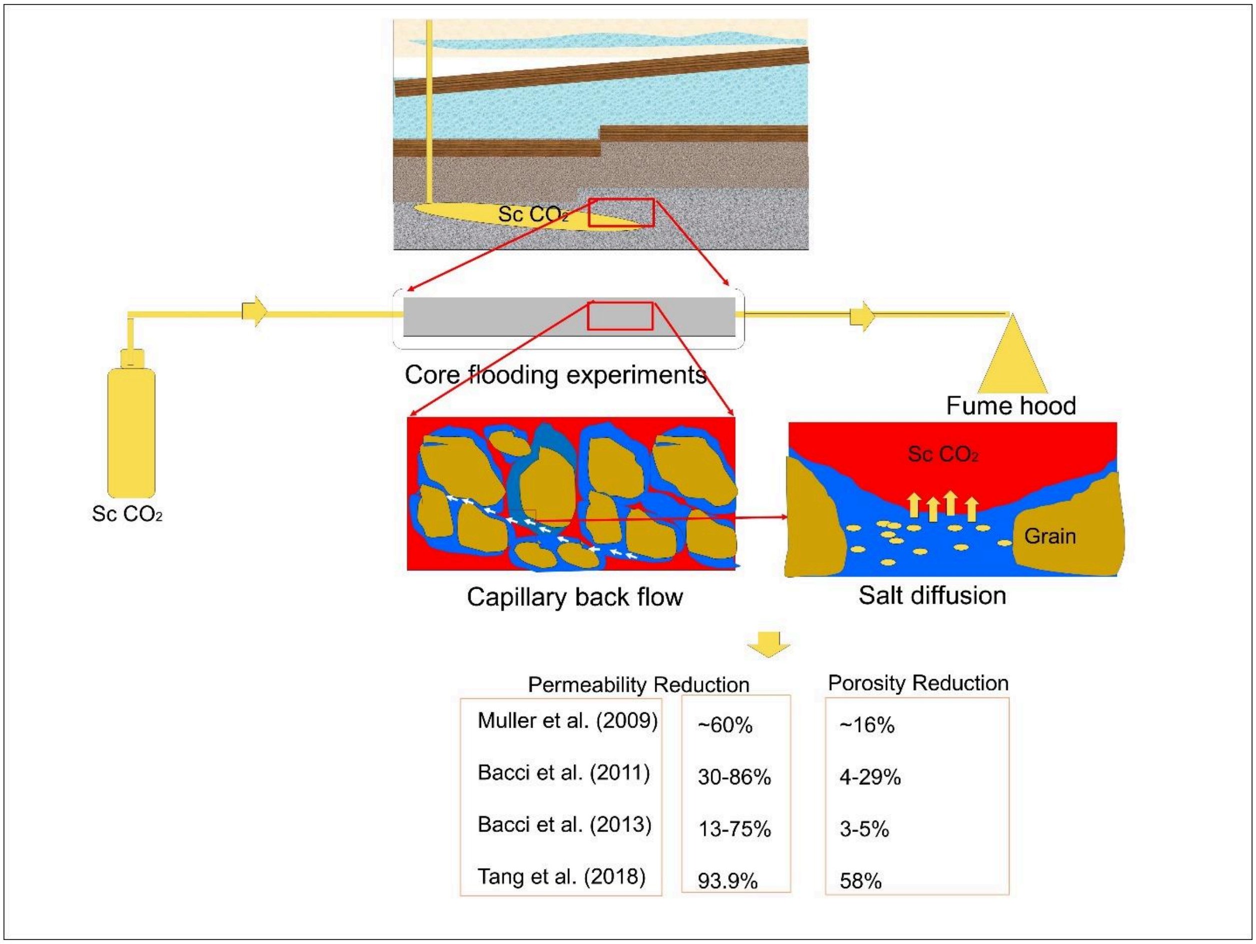
2.1 Effects on the porosity and permeability

Alternation in pore dynamics has been highlighted as first and direct effect of CO_2 injection. Further, changes in geochemical processes, especially mineral dissolution, have also been associated with CO_2 injection. It is also expected that complex geochemical reactions can occur due to fluid-rock interactions during the CO_2 injection and its storage. Such geochemical processes significantly affect pore dynamics by dissolving host minerals and other materials (Andre et al. 2007; Fritz et al. 2010; Jin et al. 2016). A study performed by Andre et al. (2007) to investigate rock-water interactions during the CO_2 injection in the Dogger aquifer (Paris Basin, France) suggests that the dissolution of carbonate by the acidic aqueous solution due to CO_2 injection significantly affects the porosity and permeability of media. Such changes in the porosity and permeability of media after injection of CO_2 causes significant variations in hydrodynamic regimes. Likewise, Fritz et al. (2010) performed experiment to investigate hydro-thermodynamics associated with CO_2 injections and their impacts on the porosity. This study fortifies that the hydrothermal circulation in granite increases the porosity of domain. A saturated high porosity zone can storage more energy than non-affected area which may create fractures and fault. Such factures may act as potential CO_2 leakage pathways to overlying subsurface zones. A study by Jin et al. (2016) highlights that the high risk can be observed in the area having dolomite due to its high dissolution rate in presence of CO_2. These studies clearly indicate that CO_2 induced dissolution significantly affect the hydrological conditions by altering the porosity and permeability of CO_2 storage zones which further increases the risk of CO_2 leakage.

2.2 Precipitation of salts and their effects on the pore dynamics

Precipitation of host or other minerals in salt form due to the injection of unsaturated CO_2 is another potential geochemical process which significantly affect the porosity and permeability of storage zones (Pruess, and Müller, 2009; Guyant et al. 2015; Guodong et al. 2016). In the reservoir, the pore water evaporates due to large volume of the dry supercritical CO_2 injection which enhance the concentration of salts in the brine and it will precipitate out as exceeds solubility limit under reservoir (thermodynamic) conditions (Miri and Hellevang, 2016). Such precipitated salts diffuse and occupy the available pore space which further alter the porosity and permeability of the domain (figure 2). A core flood experiment performed by Muller et al. (2009) in CO2SINK Project, a European Union research project, reported halite precipitation over the entire pore network of the Berea sandstone core which reduced the CO_2 permeability by approx. 60% and the porosity by approx. 16%. Bacci et al. (2011) performed a core flooding experiment on a St. Bees sandstone core to investigate porosity and permeability changes due to salt precipitation during the CO_2 injection. Results of this study indicates the porosity and permeability reduction ranged from ~4 to 29 % and 30 to 86% from the initial value. Another experiment performed by Bacci et al. (2013) indicates that the porosity reduction of about 3 - 5 % and the permeability reduction between 13 to 75 %. Likewise, Tang et al. (2018) reported a reduction in the porosity and permeability by 58% and 93.9%, respectively. Most of studies (Ott et al. 2010; 2013; Oh et al. 2013; Kim et al. 2013; Peysson et al. 2014; Nooraiepour et al. 2018) performed to investigate impacts of CO_2 injections on alternation of reservoir properties are reported a significant reduction in the porosity and the permeability of the host domain. Upward pressure is exerted on the caprock layer when the pore space reduced for large volume injections and or CO_2 changes its phase from supercritical to liquid or to gaseous form, after injection (Shukla et al. 2010). One can refer a review by Miri and Hellevang, (2016) for better understanding of the physics of salt precipitation during the CO_2 injection.

Risk of CO_2 leakage will intensify due to changes in hydrodynamics of pore space, however, very limited information is available on the role of salt precipitation and or dissolution of minerals on risk associated with CO_2 leakages during CCS activities. To the date, the geochemical impacts on alternation of the hydrodynamic due to the CO_2 injection has mainly been studied at near well conditions. Current knowledge clearly indicates that the variation in injection rate/style, improperly constructed well, fault and fracture zone can act as fast and direct conduits for CO_2 leakage from depth to the surface (Lewicki,et al. 2007). Qualitative estimation of the combined risk associated with CO_2 injections and geochemically induced leakage for reservoir scale and for basin scale will be needed for the accurate prediction. A better understanding the CO_2 flow mechanisms, magnitude of leakage, and steps to remedy leakage are important factors for the risk assessment and the risk management.



	Permeability Reduction	Porosity Reduction
Muller et al. (2009)	~60%	~16%
Bacci et al. (2011)	30-86%	4-29%
Bacci et al. (2013)	13-75%	3-5%
Tang et al. (2018)	93.9%	58%

Figure 2: Schematic illustration of core flooding experiment performed to estimate effects of salt precipitation on pore dynamics and different physical mechanisms contributing to the process of salt precipitation.

3.0 CO_2-Brine Migration and its Leakage

If CO_2 migrates upward through a fracture or an abandoned well, supercritical CO_2 changes their phase as liquid- CO_2, or gas- CO_2 to receiving aquifers under controlled temperature-pressure regimes (Wilkin and DiGiulio, 2010). Just after the CO_2-brine leakage, one can expect a highly non-isothermal, two-phase and multicomponent flow in the domain. A study by Birkholzer and Zhou (2009) performed simulation for the Illinois basin scale (570Km ×550Km), where CO_2 was injected at the rate of 5 million tonnes of CO_2 for 50 years. A three dimensional mesh (1.2 million grid-blocks and more than 3.7 million connections) was constructed to simulate the two-phase flow and the multi-component transport of CO_2-brine in the response to CO_2 injection under isothermal mode. Mount Simon Formation, the Eau Claire caprock and the weathered portion of the granite base rock were considered as lithofacies. CO_2 was injected in the high permeability and the high porosity part of the Mount Simon formation. The results of this study show that the shale-sandstone sequences of the Mount Simon help to retard upward migration of CO_2. The thickness of the Mount Simon and the slop of structural surfaces affect the shape of the CO_2 plume which elongate it to 6-8 km long lateral CO_2 plume. Discharge of the brine from top and lateral boundaries was observe equivalent to the Darcy flow velocity of 0.47 mm/year and 0.2m/year for 50 years, respectively. The cumulative volume of the brine released from different boundaries accounts 9% at 50 years and 86% at 200 years of the total displaced brine.

Another study was performed by Zhou et al. (2010) by incorporating 20 injection wells for the injection of CO_2 at the rate of 5 Mt CO_2/year/well for 50 years at the Illinois basin scale (570Km

×550Km). In this study, number of injection wells were considered twice and a five-fold more injection rate to Birkholzer and Zhou, (2009). A CO_2 plume of size 9-13.5 km was observed in the lateral direction which indicates slow migrations of CO_2. Displacement of the brine was significant in the injection area and thus a cumulative volume of 1.57×10^9 m^3 was predicted to leak in 200 years. The fraction of leakage rates increases from 0 to 0.22 in 50 years, which accounts 9.5 % and 62% of the total brine volume displaced at 50 and 200 years, respectively. After Birkholzer and Zhou, (2009) and Zhou et al. (2010), another Illinois basin scale modeling was performed to investigate basin scale hydrological impacts of CO_2 sequestration by Person et al. (2010) using the single and multiphase i.e. sharp-interface model. In this study, CO_2 was injected in 726 wells at the rate of 0.11 Mt CO_2/year/well for 100 years and then the fate of pressure and CO_2 plume was observed for next 100 years. They found that the CO_2 plume of size 0.5-2 km developed radially after 100 years of continuous injection. The calculated pressure anomaly in this study was 6 time high than reported pressure anomaly by Birkholzer and Zhou, (2009) i.e. 3MPa. This study indicates that pressure anomalies restricted to a distance of 25 Km from injection well while Zhou et al. (2010) indicates it reaching the limit of the basin. Upward displacement of the brine into the Eau Claires was also observed at slow migration rates. These studies indicate that numbers of well can significantly affects CO_2 plume size and directions. For example, the plume change from 6 - 8 km in study by Birkholzer and Zhou (2009) to 9 - 13.5 km in study by Zhou et al. (2010). Thus, it is important to investigate the role of factors as the thickness, number of well, the slope to the variation of direction and maximum size of the plume. In conclusion, the pressure buildup in the Mt. Simon has capability to push the brine upward through the Eau Claire caprock into overlying formations. However, this is unknown that at what extend this discharged volume will affects above-lying groundwater resources. One can improve this study by considering aquifers above the

Eau Claire caprock, as this study does not incorporate any groundwater zones to reduces the load on computation.

Likewise, a high performance supercomputer based numerical study performed by Yamamoto et al. (2009) to investigate the impact of two phase flow i.e. CO_2- groundwater migration on regional groundwater flow of an area of about 60km × 70km in Tokyo Bay using the multiphase flow simulator TOUGH2-MP/ECO2N. Ten injection wells were considered to inject CO_2 at a depth of 1 km under Tokyo Bay at the rate of 10 million tons/year for 100 years. The results indicate that the lateral plume appears in the injection layer extending over a range of 4-5 km. This study demonstrate that the dissolution of CO_2 plume gradually increases and finally becomes dominant in the domain. A large CO_2 plume-groundwater interaction area is the main driving factor to enhance dissolution of CO_2 into the surrounding groundwater. However, the vertical velocity of CO_2 plume was low because of the two-phase flow affected by the low relative permeability and the high capillary pressure in the deep groundwater zone. However, one can expect more local leakages of CO_2 from seal containing alternate layers of the sandstone and the mudstone which was not considered in this study. By developing a precise lithofacies model for the seal one can upscale this study for Tokyo Bay. Similarly, Pan et al. (2011) highlights a transient two-phase, non-isothermal flow of CO_2-water mixture after its leakage. This study also indicates that leakage dynamics is much more complicated than the simple quasi-steady-state flow.

Impacts of CO_2 leakage on groundwater depend on the formation permeability, if leakage occurs from the high permeability zone, it will result in high flow variations (Wainwright et al 2013). Zhao et al. (2012) investigated the CO_2 plume migration and the pressure buildup due to CO_2 injections at the rate of 3Mt CO_2/year/well for 50 years in five wells of the Sanzhao Depression, Songliao Basin, China. Results of this study indicate that a 7.8MPa pressure buildup in the high permeability zone of the formation while it can even reach to 10.5MPa in low permeability layers. CO_2 plume size in the formation was about 5.8Km at 100 years, while interference of CO_2 occurs at 200 years. CO_2 migrations toward the Southeast of the depression indicate a potential risk of freshwater pollution. This fortifies that the permeability of the storage formation is the main factor to control the pressure buildup, CO_2-brine migration and impact of CO_2 leakage on above-lying formations. Furthermore, the CO_2-brine flow in low permeability saline aquifers in the Ordos basin was studied by Xie et al. (2015a) and Xie et al. (2015b) using one injection well having different injection rates i.e. 5.42 Kg s^{-1} and 3.17 Kg s^{-1}, respectively. CO_2 migrate in the radially shape of size 658m, 913m, 1013m at 3.65, 53.65, and 103.65 years, respectively, after the beginning of the injection in the simulation domain of Xie et al. (2015a). While in Xie et al. (2015b), CO_2 plume moves 330, 550, 680, 780 m at 1,3,40, and 103 years respectively. Pressure buildup data matches well with the observed pressure profiles in both the studies. However, both studies indicate acceptable leakage of CO_2 i.e. 0.02 and 0.1% of injected CO_2 volume as the gas phase CO_2. Such a small fraction of the predicted CO_2 leakage was considered acceptable in this study as up to 2% of the injected volume was suggested valuable by van der Zwaan and Gerlagh, (2009). All these study clearly indicates that formation permeability is most important parameter which control the plume extension and risk of CO_2-brine leakage.

<Insert Table 1 here> Table 1: Summary of experimental studies reported CO_2 leakage at various sites around the globe.

4.0 CO_2-Brine Leakage and its Impact on Groundwater Flow Dynamics

The growing literature indicates that the variability in the pressure buildup, andCO_2-brine migration patterns in varying permeable zones of the storage formation causes significant leakage of pure/dissolved CO_2 and brine to shallow groundwater systems (Lions et al. 2014). A numerical study performed by Nicot (2008) to investigate impact of pressure build-up due to the CO_2 injection on the groundwater system in the Gulf Coast Basin. Two case studies were performed by incorporating 1Mt CO_2/year/well and 2Mt CO_2/year/well injection rates in 50 injection wells for 50 years in MODFLOW by incorporating site specific aquifer parameters along with the groundwater evapotranspiration condition. This study indicates that the CO_2 injection equivalent to 50 million tons of CO_2/year for 50 years resulted in an average increases of the water table by ~1m with significant increase in the groundwater evapotranspiration. While the base flow of surface water bodies did not increase significantly in case of the actual base condition, but could increases by two fold for the high injection rate condition. Finally, the groundwater flow direction was reversed during the CO_2 injection from the bottom of the basin. Similarly, in Tokyo Bay study by Yamamoto et al. (2009) upward groundwater migration due to the injection of CO_2 was observed with maximum vertical pore velocities of about 50mm/year. The groundwater flow direction before injection was from the mountainous area toward Tokyo Bay, however, CO_2 injection changed the flow direction, especially in and around the reservoir.

Another significant study was performed by Bricker et al. (2012) to investigate the effect of CO_2 injection on the shallow groundwater table in the Sherwood Sandstone aquifer, UK using a groundwater flow model ZOOMQ3D. Injection of 15 Mt/year of the CO_2 for 20 years was considered into the Sherwood Sandstone Group (SSG) underlying zone to the Mercia Mudstone Group (MMG) and the Chalk group of aquifers. Four leakage scenarios were simulated by considering leakage coefficients, C_z=0 (MMG as perfect seal), $C_z=10^{-7}$(Preferred leakage value), $C_z=10^{-6}$ (leakage increased by one order of magnitude), $C_z=10^{-8}$ (leakage reduced by one order of magnitude) and vertical hydraulic conductivity of 0, 10^{-6},10^{-5}, and 10^{-6} m/day, respectively (table 2). The results show that approximately 40Ml/day of saline water would leak out from the formation to MMG even in case of preferred leakage. In case of $C_z=10^{-7}$, an increase of 0.01-10m and <1m was observed in groundwater heads in the potable confined aquifer and in the unconfined aquifer, respectively, with a corresponding increase in river flows by 10-15%. Sensitivity analysis fortifies that one-fold increase in leakage magnitude results in reduction of the groundwater heads of (un-) confined aquifers by two fold. However, if the leakage co-efficient reduces by one fold then there will be a five-fold increase in groundwater heads of (un-) confined aquifers. This indicate that the degree of impact on shallow groundwater systems is highly sensitive to the vertical leakage assigned to the caprock. Groundwater head increases of this proportion could result in the groundwater flooding in and around the Humber Estuary of the study area.

<Insert Table 2 here> Table 2: Summery of parameters and conditions used to simulate groundwater model by Bricker et al. (2012) to understand CO_2 leakage scenarios.

The upper shallow aquifer formation was not assign in simulation domain of Yamamoto et al. (2009) and Bricker et al. (2012). One can improve results of these study by incorporating more precise lithofacies and by considering upper heterogeneous shallow soil-water systems. Other major limitation of these studies was the single phase model approach which may cause variance in the results as Nicot (2008) reported about 10% and less than 20% variation in results if simulated using single phase models. Although, these study indicate regional scale variations in groundwater flow dynamics, it hasn't demonstrated local variations of the groundwater system. Table 3 listed summery of studies addressing the field and plume scale hydrological impacts of CO_2 injection and storage. To frame management plan and to improve the groundwater quality, it is important to understand the local impacts of such CO_2-brine leakage in the near surface environment.

<Insert Table 3 here> Table 3: Summery of studies addressing the field and plume scale hydrological impact of CO_2 injection and storage.

5.0 Groundwater Quality Concerns

CO_2 leakage from deep storage reservoirs may induce geochemical reactions and lead to degradation of (ground-) water quality, which is likely the greatest concern associated with CO_2 migration from deep storage sites to the near-surface environment. In past, variations in the groundwater geochemistry due to CO_2 leakage has been considered as a monitoring tool. However, the assessment of leak magnitudes leading to endangerment of the drinking water is still an area of active research (Wilson et al. 2007). A better understanding of impacts of CO_2 leakage on the groundwater quality help to frame a better management and remediation plan at CCS sites.

5.1 Mixing of the CO_2/Brine-Fresh Groundwater and Changes in the Groundwater Chemistry

Leakage of the CO_2/CO_2-enriched brine to a fresh aquifer might directly affect the groundwater chemical state by modifying (i) the pH, (ii) the redox potential and (iii) mobilization of inorganic and organic contaminants (Harvey et al. 2012; Lions et al. 2014). In general, the chemical reactions between the fresh groundwater-formation materials or by mixing of fresh groundwater-saline/CO_2 enriched waters alter the pH and the redox potential of fresh zone groundwater (Lions et al. 2014).

Precipitation and dissolution of minerals are dominating geochemical processes occurs in aquifers once scCO_2/CO_2-enriched brine leaked. In table 4, the host rock-water-scCO_2/CO_2 enrich brine interactions occurs during CO2 injection, storage and its leakage are presented. Mixing of the CO_2/brine-fresh groundwater or dissolved CO_2 induced reactions forms H_2CO_3 (Reaction 2a) causing an imminent drop in the pH of the brine or the fresh groundwater. H_2CO_3 (acid) interact with minerals of the host rock like carbonate and rapidly buffer the pH (Reaction 2b). The bicarbonate ion may then dissociate to form the carbonic ion as in Reaction 4 (table 4) and later these Carbonate ion form minerals like calcite (5a); magnesite (5b); and dolomite (5c). At a low pH (~4), the production of H_2CO_3 dominates and at a mid pH (~6), production of HCO_3^- dominates. However, at a high pH (~9) CO_3^{2-} production dominates. Cui et al. (2017) performed a laboratory experiments using rock samples from typical sandstone and carbonate reservoirs. Experimental results show that CO_2 can lead to the dissolution of ankerite and clay minerals and the precipitation of plagioclase, which can result in increases of Ca^{2+} and Mg^{2+} in the formation water of sandstone test. While in case of the carbonate test, CO_2 can induce the dissolution of dolomite and the precipitation of ankerite and calcite. Subsequently, the changes in the pH influence the dissolution of soil minerals (e.g., calcite, dolomite, K-feldspar, and plagioclase) as highlighted in reaction 6-9 of table 4. Furthermore, the dissolution of minerals can extend to the silicates as well as carbonates with examples for albite (reaction 10 and 11) and Fe-rich chlorite (reaction 12). There is growing literature on rock-water interactions in the near-well high saline environment as a result of the dissolution and precipitation, but only few studied has been reported in case of low-salinity environments. Farquhar et al. (2015) investigated CO_2-water-rock interactions in a low-salinity reservoir system. This study indicates the partial dissolution and desorption of calcite, carbonates, chloritic clays and annite followed by the long term dissolutions of additional silicates, such as feldspars. Furthermore, the host mineral-dissolved CO_2 brine interaction in vadose zone or near surface environment has still not studied. Review article by Gaus (2010) present further details on rock-water interactions considering CO_2 injection and storage in formations.

<Insert Table 4 here> Table 4: Host rock-water-CO_2/CO_2 enrich brine interactions occurs during CO_2 injection, storage and its leakage.

5.2 Drop in pH

Introduction of CO_2 or CO_2-rich brines in the fresh groundwater enhance the dissolution of CO_2 ($CO_2(aq)$) resulting in increase of carbonic acid (H_2CO_3) concentrations, followed by its deprotonation and thus in turn decreasing the pH of fresh groundwater. However, decrease in the pH depends on the nature of water-rock system due to the proton interactions with various solid phases in the soil-water system during the precipitation/dissolution and adsorption/desorption processes (Lions et al. 2014). Low pH condition due to increase in bicarbonate ion concentrations ($HCO3^-$) could lead the high saturation of water with respect to carbonate minerals and to the precipitation of minerals (Druckenmiller and Maroto-Valer, 2005). Carbonate, clay, and feldspars minerals tend to buffer the pH and cause the brine to be less acidic. Reaction 2 of table 4, can rapidly reach equilibrium under suitable conditions however the dissolution of these minerals characterize by slow reaction kinetics. Previous research indicates that the CO_2/CO_2-enriched brine significantly drop the pH, especially in sandy soils as these are more sensitive to an increase in CO_2 concentrations due to the low buffering capacity than the clay-rich soil with a higher buffering capacity (Harvey et al. (2012); Derakhshan-Nejad et al. 2019). In modeling studies by Birkholzer et al. (2008), Carroll et al. (2009) and Zheng et al. (2009) with CO_2 injections rates of 2.36, 10^3-10^6, and 2.36 tons of CO_2/year, respectively in the carbonate sedimentary, confined non-carbonate, confined carbonate aquifer indicate a drop of pH of ~2, ~2 and ~1.5 units respectively. Likewise, *In-situ* CO_2 experiment performed by injecting 300 kg of CO_2 (30 days) in the alluvial deposit by Kharaka et al. (2010) indicates a pH drop of about 1-1.4 units. Similarly, Lu et al. (2010) performed a laboratory experiment with and without carbonates by applying CO_2 bubbling for 15 days and observed a drop in pH of ~1.5-2.5 and ~1.5-2.2, respectively. Zheng et al. (2012) model the unconfined sandy aquifer at the Montana State University Zero Emission Research and

Technology (MSU-ZERT) field site and observed a pH drop of ~1-1.7 in groundwater. Further, a field based study in which 5700 ppm dissolved CO_2 was injected (30 days) in confined sandy aquifer by Trautz et al. (2012) show a pH drop of ~2.4-2.9 units. Similarly, Peter et al. (2012) perform *in-situ* experiment by injecting 787 kg of CO_2 at a depth of 18 m below surface level into a quaternary sand aquifer close to the town of Wittstock in the Northeast Germany. The results show that the total inorganic carbon concentrations increased and the pH decreased to a level of 5.1 (drop of ~0.8-1.8 units) after injection of CO_2. Another *in-situ* experiment was performed by Cahill and Jakobsen (2013) in which 45Kg of CO_2 was injected at 10 m depth in Aeolian and glacial sands at the Vrøgum field site. They observed a plume of depressed pH ranging 5.6-4.7, which indicates a drop of ~1.5 pH units. The study has shown that the CO_2 and or CO_2 enrich brine can alter the pH of groundwater of fresh aquifer but CO_2 gas stream can also change the pH conditions. A batch and column scale study performed by Wang et al. (2016) by injecting CO_2 gas into oxidizing carbonate aquifer indicates a drop of pH by two units. As pH deceases with CO_2 leakage, one can consider the pH monitoring in initial phase of CO_2 risk analysis at CCS sites. Similarly, alkalinity might also be used as a monitoring parameter. However, for small CO_2 release, the pH variation might be less than the detection limits. Likewise, the alkalinity of a solution may not be necessarily modified by CO_2 leakage and can be the results of water-rock interactions (Lions et al. 2014). Although there are numbers of study highlighted a drop of pH in the groundwater due to CO_2 leakage (all phase), it is also important to see how such changes affect the vadose zone water quality and plume of exiting pollutants, if any, under site specific conditions.

5.3 Alteration of Dissolved Organic Carbon (DOC)

Soil acidification due to release of CO_2 from the deep subsurface may alter the dissolved organic carbon (DOC) concentrations. The host soil has some buffering capacity, and it will exchange extra H^+ with basic cations. This will lead to an increase in base cations in leachates and will further affect the quality of the water in the saturated zone. Organic soils have been found to have higher buffering capacity than the sub-surface mineral soils (Moonis et al. 2017). Composition is important because it is closely related to pH buffering, ion exchange, especially in case of mineral host soils (Lee et al. 2016). For example, Lime ($CaCO_3$) dominating host media may have high buffering capacity to against CO_2-induced acidity than sandy soils. The combined influences of buffering capacity, injection amount of CO_2, hydraulic characteristics may lead to alternation in the DOC concentration (Moonis et al. 2017). A study was performed by Kharaka et al. (2006; 2009), where 1600 tons of CO_2 was injected at 1500 m depth into a 24-m thick sandstone section of Frio Formation, US Gulf Coast. The DOC values obtained from the subarkosic fine-grained quartz and feldspar sandstone during the CO_2 injection increased moderately to 5–6 mg/L; the values however, increased unexpectedly by a factor of 100 in samples collected 20 days after injection stopped. Such variation in CO_2 injection induced DOC concentrations has high significance value to understand occurrence and fate of polar polycyclic aromatic hydrocarbons (PAHs) and BTEX compounds. Another study performed by Moonis et al. (2017) to investigate the impact of CO_2 leakage on DOC in different soils by applying 100% CO_2 for 32 days indicates that the DOC significantly increases in organic soil while decreases in mineral soil and alteration in DOC significantly affect mobilization of organics.

5.4 Mobilization of Polycyclic Aromatic Hydrocarbons (PAHs)

Leakage of the CO_2 in supercritical phase significantly mobilize non-to moderately PAHs compounds present in soil-water system as it is known to be an excellent solvent. For example, Hexane and benzene, small apolar and weakly monopolar PAHs have relatively the high solubility in the sc-CO_2 than small polar PAHs compounds such as acetic acid and phenol. Larger compounds, longer chain of alkanes, large PAHs with a molecular weight greater than 200g/mol, have the low solubility in the sc-CO_2 (Burant et al. 2012). However, the solubility of organic compounds in the sc-CO_2 plume depends upon temperature, pressure and salinity. A review article by Burant et al. (2012) can be referred by the readers for more details on the partitioning behavior of organic contaminants in carbon storage environments. In this direction, a study performed by Scherf et al. (2011) by injecting the sc-CO_2 into the sandstone at the CO_2SINK site near Ketzin, Germany observed free and ester-bound fatty acids, especially *n*-hexadecanoic acid, *n*-octadecanoic, isomeric *n*-octadecenoic and *n*-octadecadienoic acids. Additionally, acetate, propionate, butanoic and pentanoic acid as well as lactic, pyruvic, and glycolic and gluconic acid were also detected in varying amounts in certain samples. Since CO_2 injection started, concentrations of these organic compounds were detected in the downhole fluid samples from observation wells. Similarly, Kharaka et al. (2006; 2009) observed a high concentration of formate, acetate, oxalate and toluene after CO_2 injection, however VOCs and semi-VOCs concentrations were low near the zone of injection wells. Results of previous studies indicates that the sc-CO_2 in the formation may significantly enhance the mobilization of hydrocarbons. Therefore, the mobilization of hydrocarbons from non-oil bearing saline aquifers could have major implications for the groundwater quality concern. Low pH induced increment in DOC and PAHs may significantly alter the metals and metalloids as a result of de-sorption of fresh groundwater systems (Zheng and Spycher, 2018). Likewise, the drop of pH, high DOC, PAHs accelerates the dissolution of calcite, and then the increase in the concentration of Ca triggers a series of cation-exchange reactions that cause an increase in the concentrations of metals and metalloids (Zheng et al. 2016). Further study is required to understand the role of the near surface environment on the mobilization of wide range of organic compounds due to the leakage of sc-CO_2/dissolved CO_2 into fresh groundwater systems. Similarly, a better understanding of PAHs, n-alkane, MTBE and other organics on mobilization of metals and metalloids will help to predict future risk and planning related to management of CCS sites.

5.5 Mobilization of Metals and Metalloids

The mobilization of metals and metalloids are the major groundwater quality concern in case of CO_2 leakage from a storage site to the subsurface environment. The growing literature indicates that the presence of CO_2 and CO_2 enrich brine plume can modify the subsurface environment mainly by two mechanisms: (i) alteration of oxidation-reduction potential of the aquifer system and (ii) amending the sorption/desorption reactions. Unconfined aquifers can be either oxic in the upper part where redox potential is high, and anoxic at the bottom of the aquifer where redox potential is comparatively low and dynamic (Lions et al. 2014). The redox status of the groundwater system mainly controlled by two mechanisms: (i) dynamically fluctuating groundwater table conditions and/or (ii) contamination by oxidizing or reducing components such as O_2, organic matter, CH_4, and HS^- (McMahon and Chapelle, 2008; Lions et al. 2014). A rising water table towards unsaturated zone can replace the initial oxic condition by the anoxic condition leading to the decrease of redox potential in the saturated zone. In case of CO_2 injection or leakage, a rise in water table was reported by Nicot (2008) and other researchers (refer section 3.2). Thus, change in the redox status are expected due to introduction of oxidizing and/or reducing components due to the rise in the water table condition under the influence of CO_2 sequestration activities.

Leakage of brines significantly enhance the organic compounds (acetate, formate etc.) in the fresh groundwater zone (section 4.3) which serve as energy sources for the endogenous microorganisms in the aquifer zone. This energy induced microbial metabolic activity results in the reduced concentration of electron acceptors (oxygen) in the aerobic zone. While in the anaerobic zones increased concentrations of organic compounds may lead to the increased iron, sulphate reduction and or methanogenesis (Lions et al. 2014). Furthermore, the co-injected substances can also be strongly oxidizing (i.e. O_2, SO_2, NO_x) or reducing (i.e. H_2S) agents. Recently, Zhang et al. (2019) observed changes in the redox condition due to injections of the SO_2 in the saline sandstone formation and their significant impacts on native microbes under co-injected SO_2 in CO_2 storage formations. It is evident from the literature survey that inadequate studies have been performed to characterize the impact of the co-injected substances on redox status of overlaying aquifers. Thus, advancing the monitoring techniques based on redox status along with impact of- (i) dynamically fluctuating water table and (ii) co-injected chemicals are active area of research to mitigate the risk of CO_2 into fresh overlaying aquifers.

Impacts of CO_2 leakage on metals and metalloids fall into two categories: (i) metal(loid)s that are of health concern drinking-water (e.g. As, Cd, Cr, Hg, Ni, Pb, Se) and (ii) that are of low or zero health concern (e.g. Al, Ba, B, Cu, Fe, Mn, F, Zn, Sb) are the major risk to the groundwater quality associated with the CO_2 geological storage. Indeed, these chemicals can be present naturally in soil-water systems as geochemical background and their concentrations depending upon the lithology. Table 5 is presented with a summary of *in situ* field, laboratory and modeling studies performed to investigate the impact of CO_2 leakage on the mobilization of metal(loid)s.

<Insert Table 5 here> Table 5: Summery of studies investigated role of CO_2/CO_2 enrich brine on mobilization of metalloids in fresh groundwater zone.

Indeed, CO_2 leakage into groundwater system could enhance the release of the initially sorbed metal(loid)s and or accelerate dissolution of minerals that contain it. Smyth et al. (2009) and Lu et al. (2010) performed batch scale experiments by applying the high CO_2 to the aquifer media from the Texas Gulf Coast region. Results of these studies observed two types of response and then categories elements accordingly. Type-I: cations are Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, Zn, which showed a fast increasing concentrations at the start of the CO_2 injection that become steady before the end of the experiment. While in case of type-II cations (Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) initial increases in their concentrations were observed followed by a decreases to values less than background level. Similarly, Little and Jackson, (2010) performed laboratory experiment for the CO_2 infiltration under oxidizing conditions through the freshwater aquifer media. It was observed that two fold of concentration was increases in case of the alkali, alkaline, Mn, Cb, Ni and Fe. While, the uranium and barium concentration kept increasing throughout experimental durations. Other laboratory experiments (table 5) were performed by Druckenmiller and Maroto-Valer (2005), Wei et al. (2011), Viswanathan et al. (2012), Humez et al. (2013), Wunsch et al. (2014), Kirsch et al. (2014), Farquhar et al. (2015), Pearce et al. (2015), Shao et al. (2015) and Wang et al. (2016) to investigate the impacts of CO_2 leakage on the mobilization of different metal and metalloid contaminants. These experiments evaluated various types of aquifer media such as essentially carbonate free (Varadharajan et al. 2012), carbonate-dominated (Wunsch et al.2014) under the varying conditions in terms of redox state (Varadharajan et al. 2012) oxidizing (Little and Jackson, 2010) and pressure conditions (Varadharajan et al. 2012, Humez et al. 2013), with reaction times ranging from a couple of days to months. Most of these study observed two types of behaviours of metals and metalloids, first increases rapidly after CO_2 injection and then stabilize with the time or in late phase of experiments. While, second types of contaminants concentration increases with the CO_2 injection and then decreases with the time or as pH stabilize (Smyth et al. 2009; Lu et al. 2010). Commonly, all of the above studies have highlighted increases in metals mobilization after the CO_2 introduction but reported less concentrations than drinking water standards by the EPA or other agency (Kirsch et al. 2014). Dissolution of the host rock (for example calcite) or precipitation of minerals found to be the main driving mechanism of the high metals mobilization after the CO_2 introduction in laboratory setups. Although laboratory scale experiments enhance the understanding of the behavior of CO_2 on subsurface contaminants, they cannot accurately represent *in-situ* field conditions.

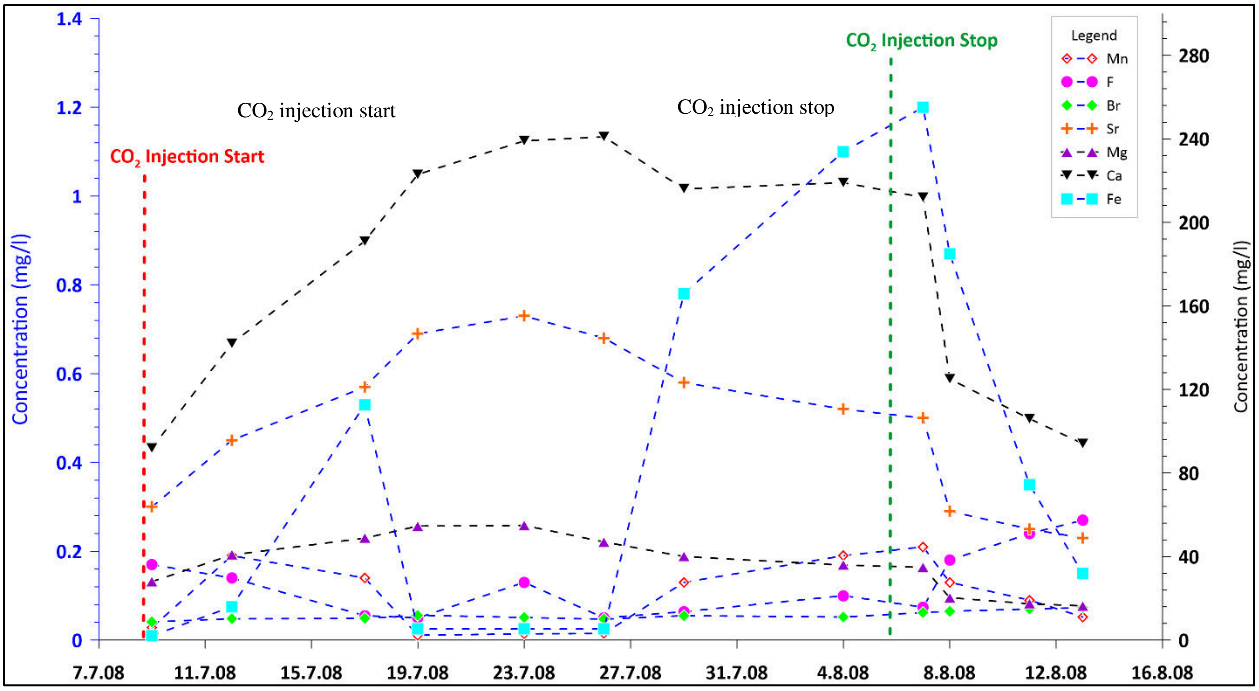


Figure 3: Concentrations of Mn, F, Br, Sr, Fe, Mg, and Ca in groundwater reported by Kharaka et al. (2010) from selected ZERT wells plotted as a function of time of sampling.

In field scale, Kharaka et al. (2010) performed CO_2 release test to investigate changes in the shallow groundwater at the ZERAT field site, where ~300 kg/day of CO_2 was injected. Groundwater samples were collected from 10 shallow monitoring wells for analysis of trace elements. It was observed that the concentrations of Ca, Mg, Fe, and Mn were increases significantly (Figure 3). Increases in Fe concentration was related to the dissolution of siderite (carbonate minerals) due to the acidification by the CO_2 injection. Fe and Mn are at the greatest abundance in the groundwater and increase rapidly after the injection of CO_2 but it can decrease with time in the oxiding zone. Likewise, Peter et al. (2012) observed water samples on a site where CO_2 was injected through three wells for 10 days at depth of 18 into aquifer in Northeast Germany. They showed a moderate increase (~15%-40%) in Ca, K, Mg and Fe and high increase (~120%-180%) in Al, Si, Mn in the groundwater. Similarly, an increase in concentrations of trace elements by ~260% and 320%~ for Ca and Mg, respectively were observed by Cahill and Jakobsen, (2013) at pilot test site (unconfined aquifer) in the Denmark. In this study, an increase of ~50% in Na and Si concentrations were observed along with ~730%, 370%, 330%, and 160% increment for Al, Ba, Sr, and Zn, respectively. In the Southern Norway, the groundwater assessment was performed by Gal et al. (2013) for a site where 6-day injection of CO_2 into a shallow glacio-fluvial aquifer at a depth of 20 m was done. They observed a significant increase in dissolved Ca and Si concentrations. A recent study by Choi, (2019) investigated the groundwater quality in the Chungcheong region (South Korea) where they studied leakage of CO_2 gas and CO_2-rich water into shallow aquifers. The study observed three different sites as-Group I (acidic CO_2-rich waters with low TDS), Group II (slightly acidic CO_2-rich waters with high TDS), and Group III (CO_2-poor waters with low TDS). Results of this study show that the concentration of trace elements (Al, Ba, Be, Cr, Cs, Fe, Mn, Ni, Rb, and U) in case of Group-I was is higher than Group-III. Whereas, concentration of Al, Mn (slightly) and Be (6.5 fold) exceeds the EPA drinking water limit. In addition, concentration of Fe and Mn exceed by 27.7 fold and 16.1 fold, respectively then the EPA drinking water limits. In conclusion, the understanding from both field and laboratory show an increase in the dissolved concentrations of metals and metalloids upon the CO_2 leakage into shallow aquifer zones. Mobilization of metals and metalloids especially As, Pb, Ba, Zn, Mn and Cd are more frequently in these studies. Although several studies have been performed to investigate potential impacts of CO_2 on the groundwater quality or on the mobilization of metals and metalloids in saturated zone, it has not been demonstrated that how these pollutants in the vadose zone or the unsaturated zone at CCS sites behaves. Furthermore, there is lack of information on the connectivity of dynamic hydrological responses of subsurface and the mobilization of metals and metalloids under different CO_2 leakage conditions.

6.0 Impacts on Soil Microbes and Vegetation

Previous section of this manuscript demonstrated that the leaked CO_2 could significantly alter groundwater quality of the fresh groundwater zone (Refer table 5). Thus, it is important to assess potential impacts of the CO_2 leakage on near surface microorganisms and vegetation including crops, to make sure these impacts could be tolerated. Thus, this section of manuscript is focused to understand the impact of the CO_2 leakage on soil microorganisms, vegetation and crops.

6.1 Shifts in Microbial Communities

Intrusion of CO_2 into the biosphere may alter microbial community composition, thus understanding their response to short and long-term changes is crucial for ecological balance. In this direction, only few research studies have been performed to investigate the impact of CO_2 leakage on the soil microbial community in natural analogues (Beaubien et al. 2008; Krüger et al. 2009, 2011; Oppermann et al. 2010; Frerichs et al. 2013; Zhao et al. 2017) and at artificial CO_2 release sites (He et al. 2019). Table 6 present summery of studies performed to see impacts of CO_2 leakage on soil microbes and plants. Beaubien et al. (2008) investigated the impact of CO_2 on the bacterial populations near a naturally occurring CO_2 gas vent located in Mediterranean pasture ecosystem, Central Italy. Extremely low bacterial cell counts were observed in area of vent core (>90% CO_2) having high CO_2 flux and low plant cover. Bacteria cell counts increase as moved away from the vent core. Likewise, Oppermann et al. (2010) investigated the compositions of microbial communities at the CO_2 vent (Beaubien et al. 2008) and at the reference site, using Q-PCR and observed that bacteria, archaea, and eukaryota decreased with increasing CO_2 concentration in the soil gas by 2-orders of magnitude. While, methanogens and SRB (anaerobic bacteria's) substantially increased in the CO_2-rich vent site. The family *Geobacteraceae* are anaerobes using Fe (III) were found less in two orders of magnitude at the CO_2 vent than at the reference site. Frerichs et al. (2013) observe that the bacterial sequences were affiliated to the *Betaproteobacteria*, *Acidobacteria* and *Bacilli*, while archaea to the *Thaumarchaeota.* They also report that the *Geobacteraceae* showed a significant decrease under high CO_2 concentrations. Likewise, Krüger et al. (2009, 2011) studied the impacts of CO_2 release from reservoir on abundance and diversity of microorganisms at a natural CO_2 vent at Laacher site in Germany and reported that the bacteria gene copies decrease from 9.6×10^9 g_{dw}^{-1} of soil at reference site to 8.7×10^8 g_{dw}^{-1} of soil towards the vent. While archaea were increased from control site towards the vent, with 7.7×10^6 and 6.5×10^7 gene copies g_{dw}^{-1} of soil. Similar trends were also observed by Ziogou et al. (2013) at a natural CO_2 vent in Florina, Greece.

At the ZERT field site, Morales and Holben, (2013) investigated the impacts of CO_2 leakage on microbial functional groups in surface and near-surface soils. A significant alteration in microbial communities was observed due to the elevated CO_2 at ZERT field site. Seasonal variations of the soil moisture and temperature also play important role in microbial shifting. A reduction in free living-nitrogen fixer community was also observed at the elevated CO_2 site. Likewise, 16S rRNA genes sequencing studies have also been carried out by de Miera et al. (2014) at the Campo de Calatrava natural CO_2 site in Spain. It was observed that the relative abundance of *Chloroflexi* increases while the relative abundance of *Acidobacteria, Verrucomicrobia* and

Gemmatiomonadetes phyla decreases as CO_2 flux increases. Within the *Chloroflexi* phylum, the genera *Thermogemmatispora, Ktedonobacter* and *Thermomicrobium* dominated bacterial communities sampled in sites with the highest CO_2 flux.

An artificial CO_2 release experiment was conducted on a farmland at the campus of China University of Mining and Technology, Xuzhou, China by Chen et al. (2017) to investigate the potential impacts on soil microbes. Fluxes of CO_2 were applied at different intensities (400-2000 g m^{-2} d^{-1}) and 16S rRNA genes sequencing was performed. It was observed that the relative abundance of *Bacteroidetes* phylum decreases while the relative abundance of *Firmicutes*, *Acidobacteria* and *Chloroflexi* phyla increases as CO_2 flux increased. The abundances of *Acidobacteria* increased with increasing CO_2 leakage, which indicated that they might be potentially important indicators for the detection and resolution of gas leakage (in-line with results of Oppermann et al. 2010). However, Ma et al. (2017) found that the abundance of *Acidobacteria* and *Chloroflexi* phylum decreased with increased CO2 flux, may be due to high abundance of *Proteobacteria* or other environmental conditions. Microbial shifting is not straightforward but these studies indicate that high molecular gene and microbiome sequencing can be an indicator to CO_2 leakage and risk evaluation. However, very little research has been focused towards the risk analysis of CO_2 seep at industrial CCS sites on soil archaea and bacteria from these environments.

<Insert Table 6 here> Table 6: Summery of studies performed to investigate impacts of the elevated CO_2 on soil microbes and vegetation.

6.2 Impacts on Vegetation

Like soil microbes, a better understanding of impacts of CO_2 leakage at CCS sites is important to evaluate risk, to restore sites and to manage resources. In this direction, Beaubien et al. (2008)

investigated the impact of CO_2 on the vegetation near a naturally occurring CO_2 gas vent located in Mediterranean pasture ecosystem, Central Italy. It was observed that vegetation distribution increases as we move away from the vent core. This fortifies that the high CO_2 flux significantly affects the biosphere at a site of naturally leaking CO_2. A study was performed by Male et al. (2010) to investigate the impact of CO_2 on vegetation using hyperspectral plant signatures during the 2008 ZERT CO_2 sequestration field experiment in Bozeman, Montana. During the experiment, the pure phase CO_2 was injected through a 100-m long horizontal well at a flow rate of 300 kg day^{-1}. On daily base from first day of injection, the spectral (visible-near infrared) signature of plants located inside and outside of CO_2 leakage zone was measured. Stress on plants was observed around the injection wells, which cover large area in the late phase of experiment. Similar observation was also reported by Krüger et al. (2011) at a terrestrial CO_2 vent at Laacher See, Germany. They observed that the dicotyledon is more sensitive than monocotyledon for CO_2 injection in a natural terrestrial CO_2 vent. Likewise, West et al. (2015) reported the impacts of elevated CO_2 on two different sites (Laacher See, Germany and Latera, Italy) located in the Mediterranean climatic zone. It was observed that *Agrostis capillaris L.* which is an acid tolerant grass starts growing on the edge of vent core. This indicate drop in pH, which support growth of such acid tolerant grass.

A field scale assessment of CO_2 leaking was performed by Zhao et al. (2017) at an experimental site in the Qinghai-Tibet Plateau and its impacts on the native vegetation, microorganisms, soil dwelling animals. Six sites as S002 (Blank), S03, S06, S10, S12 and S29 were selected for such analysis under the CO_2 leakage with different concentrations of 500ppm, 6000ppm, 18000ppm, 23000ppm, 12000ppm, and >112000ppm respectively. Plant quality under different CO_2 concentrations was determined by the soluble protein and the surge. Concentrations of other parameters like catalase (CAT), peroxidase (POD), superoxide dismutase (SOD) and proline (PRO), chlorophyll a, b and carotenoids were also determined. The plant distribution advocates that *Agropyron cristatum*, *Equisetum ramosissimum* and *Artemisia indica Willd*, *Herba lxeris* were increased in the high CO_2 concentration site, whereas *Agropyron cristatum* and *Plantago asiatica* were stable. However, the plant growth (total weight, stem length, number of leave and root length), except for *Herba lxeris* and *Equisetum ramosissimum*, was high at the site where the CO_2 concentration was 66400 ppm.

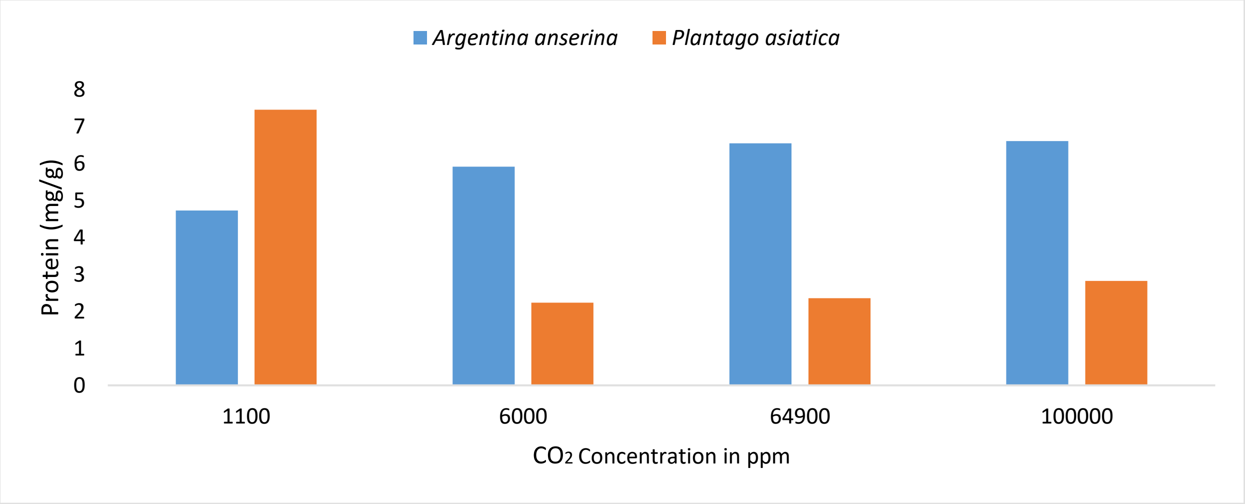


Figure 4: The effect of elevated CO_2 on protein contents in *Argentina anserine* and *Plantago asiatica* at CO_2 leaking site in the Qinghai-Tibet Plateau.

For evaluating impacts of elevated CO_2 on physiological system, *Argentina anserina* and Plantago asiatica were selected. It was observed that both plant indicates a high stress even in case of lower CO_2 concentrations possibly due to the soil acidification. Likewise, no trend was observed for photosynthetic pigments including chlorophyll a, chlorophyll b and carotenoid in this study. In *Argentina anserine*, sugar concentrations decrease sharply with the higher CO_2 concentration. Figure 4 indicates that the protein (mg/g) was high in case of *Argentina anserine* and low in case of *Plantago asiatica* located in plot having high CO_2 concentrations. This strengthens that the elevated CO_2 concentration significantly alter the protein contents of crop plant. Furthermore, it was also seen that starch content of wheat decreased from 70.93% to 61.75% in nearby farmlands. Very recently, He et al. (2019) performed a greenhouse experiment to investigate impact of high soil CO_2 on plant growth. A negative impact was observed on the root water absorption, chlorophyll, starch content and total biomass at the elevated CO_2. In conclusion, previous studies consistently reported that plants exposed to the high CO_2 showed significant impacts on its growth by reducing plant height, root length, leaf number, leaf area, seed number, pod number (Al-Traboulsi et al. 2012; Wu et al. 2014) and by altering physiological stress (Zhao et al. 2017). However, it is important to note that the most of these studies performed at natural analog, thus results of such studies may not be valid for assessment of the CO_2 leakage associated risks CCS sites.

7.0 Isotope and Geochemical Modeling for Assessing CO_2 Leakage

Geochemical modeling has been performed as monitoring tool for assessing $scCO_2$/CO_2-brine leakage and subsequently to understand hydrological and geochemical implications at natural analogue and industrial CO_2 geological storage sites (Gal et al. 2012). For geochemical studies, most commonly applied models are TOUGHREACT (Liu et al. 2019), TOUGH2/ECO2N (Zhou et al. 2010; Yamamoto et al. 2009), PHREEQC (Rillard et al. 2019), MODFLOW (Nicot, 2008), Sharp-interface model (Person et al. 2010), MINTEQA2 (Wang and Jaffe, 2004) and NUFT (Yang et al. 2019). These modelling tools were used to predict single and multiphase flow of CO_2 from different CCS sites, listed in table 3. Furthermore, such modeling approaches have also been applied for the predication of potential impact on fresh groundwater systems (Birkholzer et al. 2008; Zheng et al. 2009; Jones et al. 2015) and vadose zone. Recently, Liu et al. (2019) used

TOUGHREACT to predict the carbonates mineralization with CO_2 injection in unaltered and altered basalt formations. A good agreement between the computerized tomography (CT) scan results and TOUGHREACT modeling was observed which can reasonably describe the reaction of CO_2 and mineral carbonations. Similarly, Yang et al. (2019) successfully used Nonisothermal Unsaturated Flow and Transport (NUFT) code by coupling wellbore-leakage simulations to 3-D reactive, multi-phase flow of brine and CO_2 leakage plume migration in aquifers overlying the CO_2 storage reservoir. Results show that the carbonate alkalinity along with pressure monitoring can confirm CO_2 leakage more easily and help differentiate CO_2 seep from other sources. A detail review has been performed by Klusman (2011) to compare the surface and near-surface geochemical methods for detection of gas microseepage from CO_2 sequestration. Geochemical modeling based on isotopic analysis has also been a promising tool for CO2 leakage detection, pathway identification and impact assessment in and around CCS sites.

Isotopic test has been performed in past using the dynamic characteristics of C, H, and O isotopes of CO_2, carbonates, silicates and water molecules (Gal et al. 2012; Flude et al. 2016). A study by Choi (2019) evaluated the impact of leaking CO_2 gas and CO_2-rich waters on groundwater quality at Daepyeong and Daejeong sites in the Chungcheong region, South Korea. It was observed that the CO_2-rich waters at the Daepyeong site have δ13C- dissolved inorganic carbon values within the range of CO_2 from deep storage zone (ca. −1‰ to −8‰), which reveals that the CO_2 gas in CO_2- rich waters originated from deep source. Likewise, Kim et al. (2019) used carbon isotopic compositions to understand the flow path of CO_2 in Daepyeong area. A high soil CO_2 concentration (36%) flux (546.2 $g/m^2/d$) and relatively high δ13C-CO_2 (-5.7‰) revealed the origin of CO_2 to be deep-seated CO_2 and its pathway to be degassing from CO_2-rich water at the water table. Similar isotope study was performed at the Illinois Basin–Decatur Project carbon sequestration site (Shao et al. 2019). They also observed relatively high δ13C-CO_2 (~5‰) from deep formation. Recently, Amonette et al. (2019) performed column experiment to detect CO_2 leakage using noble-gas isotopes as tracer through a core collected from the proposed FutureGen 2.0 carbon storage site (Jacksonville, IL, USA). In which ratio of different noble-gas isotopes ($^{4}He/^{22}Ne$; $^{20}Ne/^{36}Ar$; $^{20}Ne/^{22}Ne$; $^{21}Ne/^{22}Ne$; $^{38}Ar/^{36}Ar$; $^{40}Ar/^{26}Ar$; $^{84}Kr/^{26}Ar$; $^{132}Xe/^{84}Kr$) in control site and atmosphere were used to understand leakage dynamics.

Even small leakage or microseepage can be detected using noble-gas isotopes tracer in field conditions (Klusman, 2011). Recently, Ju et al. (2019) used Kr, He, Ar as tracers to evaluate the CO_2 leakage at K-COSEM site, South Korea. PHREEQC was used to model pCO_2 using alkalinity, pH, temperature, major cation and anion concentrations as input parameters. They successfully demonstrated a relatively small amount of CO_2 saturated groundwater spiked with He and Kr tracers into a shallow aquifer. Readers can get further details on noble-gas isotopes application in CO_2 leakage and impact evaluation in following studies: Stalker et al. (2009); Myers et al. (2013); Amonette et al. (2014); Jenkins et al. (2015); McIntosh et al. (2018). Although it has been reported that noble-gas isotopes can be easily applied to detect CO_2 leakage, however in-depth investigations of its behaviors will also be required as some may not be completely conservative, for example Sulfur hexafluoride. In future, further work is required to develop more realistic frame-work for selection of appropriate geochemical modeling and isotope analysis approaches for groundwater and vadose zone as many soil biochemical processes creates noise in in measurements, especially in biogenic interferences.

8.0 Conclusive Remarks

An effort has been made to review literatures on the leakage of CO_2 and CO_2 enrich brine from the storage formation and its potential impacts on the groundwater quality, soil microbes and plants. It was observed that 1) a significant leakage of CO_2/CO_2 enrich brine through faults, fractures and wells (injection and abandoned) has been experienced by many CCS projects in past, 2) a non-isothermal, two-phase and multicomponent flow occurred once the CO_2 leak into fresh aquifers, 3) the leakage of CO_2/brine may significantly affect groundwater flow regimes, 4) the mixing of CO_2/brine and potable aquifer water may alter pH (generally drop of pH) and redox potential conditions, however such changes also depends on host rock conditions, 5) alteration of the DOC and mobilization of subsurface pollutants (organics and inorganics) has been experienced in previous studies, 6) two type of nature in cations were observed, one group increases once CO_2 leaked and remain stable while second group increases after CO_2 leakage and thereafter decreases with time, 7) the soil acidification due to the CO_2 leakage may significantly affect soil microbes by alternating their metabolic activities and the mutation, 8) the plant also gets affected by reducing plant height, root length, leaf number, leaf area, seed number and 9) the accelerated metalloids and organic compound (like BTEX) may increases the human health risk. Based on the knowledge developed by reviewing literature here, four main directions for future research have been listed as-

1) A proper subsurface characterization and demonstrative evaluation of impacts of CO_2 leakage is required before the implementation of large scale CCS projects. Subsurface characterizations must include- i) pilot/lab scale investigations of two phase/multiphase flow of CO_2 under varying subsurface conditions ii) incorporation of realistic groundwater table and flow dynamics iii) CO_2 flow behaviors in vadose zone iv) understanding of bio-geo chemical interactions of the (un)-saturated zone. While, in case of demonstrative evaluation of impacts of CO_2 leakage, realistic experimentations are required by conducting the controlled plot scale performance of CO_2 injection in subsurface.

2) There is a need to develop further understanding of behaviors of multi-pollutants under dynamically CO_2 leakage conditions by performing plot/lab scale experiments and numerical modeling.

3) More research is needed for the accurate prediction of risk of CO_2 and CO_2 enrich brine on soil microbes, plants and on human for the short and long time scale. In past, most of risk analysis were based on either small scale laboratory case or hypothetical case based on large number of assumptions. Only few studies have been reported on human health risk assessment, which needed further evaluation for realistic CCS sites.

4) Management and remediation of polluted resources in and around the CCS sites is an important topic of interest and strongly recommended for future research works. More research is needed to develop remediation technologies to reduce the risk of elevated metalloids and organic contaminations in highly acidic and saline subsurface environment.

Conflicts of Interest: No any

Data Availability

No data, models, or code were generated or used during the study (e.g., opinion or data-less paper).

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