

Leakage of CO₂ from Geological Storage and Its Impacts on Fresh Soil-Water Systems: A Review

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Abstract

Leakage of CO₂ 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 CO₂ (scCO₂) and CO₂ 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 scCO₂/CO₂ 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 CO₂-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 CO₂-brine migration in storage formations reported significant CO₂-brine leakage due to over-pressurization through wells (injections and abandoned), fracture and faults during CO₂ injection. Thus, changes in the groundwater flow and water table dynamics can be the first impact of the CO₂-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 CO₂ leaked and interactions with host rocks. Therefore, such alteration may significantly affect soil microbial dynamics and vegetation in and around CO₂ 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 CO₂ capture and storage activities on soil-water systems.

Keywords: CO₂ capture and storage, Leakage, Dissolution, Subsurface Pollution, Microbial Shifting

1.0 Introduction

CO₂ 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 CO₂ 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 CO₂ (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 CO₂ was injected with H₂S for storage in deep zone. In early 2000s, the saline aquifer CO₂ 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 CO₂ mitigation (Herzog, 2001; Torp and Gale, 2004). Since initial days, the tendency of CO₂

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) CO₂/CO₂ enrich brine leaks from the storage zone to overlying aquifers (Birkholzer and Zhou, 2009). The dissolution of CO₂ 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 CO₂. 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 CO₂ injection, migration and its leakage on groundwater table dynamics and on flow regimes (Nicot, 2008; Yamamoto et al. 2009).

Further, introduction of CO₂-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 CO₂/CO₂ 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 CO₂-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 its concentrations with the start of CO₂ 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 CO₂-brine leaked from storage formations (Newmark et al. 2010; Derakhshan-Nejad et al. 2019). Geochemical alteration due to the leakage of CO₂/CO₂ 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 CO₂-brine leakage on subsurface microbiological resources, and plants at CCS sites. Generally, the elevated CO₂ concentration in the vadose zone may negatively affect root water absorption, chlorophyll, starch content and total biomass. Furthermore, plants exposed to high CO₂ 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 CO₂ 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 CO₂ 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.

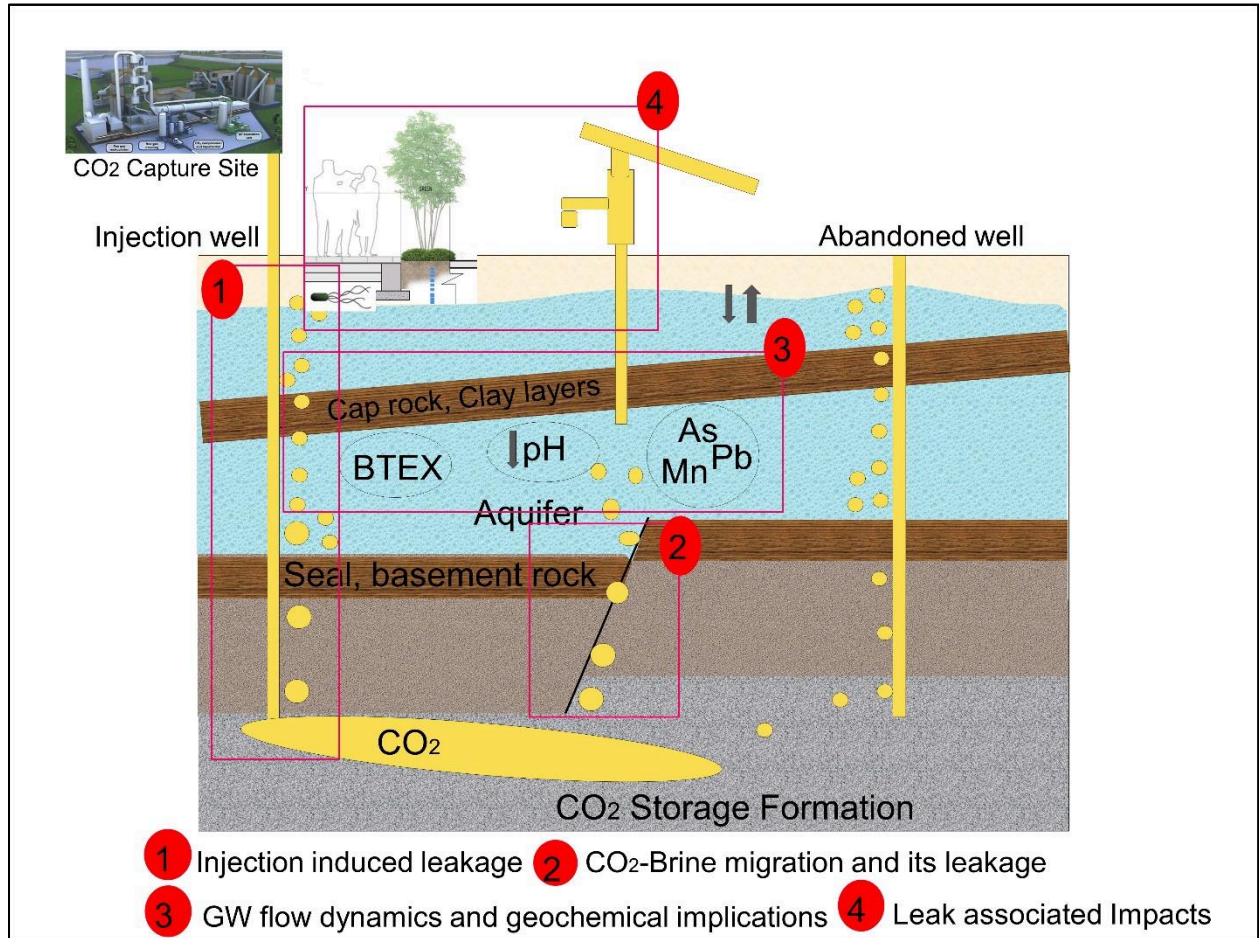


Figure 1: Schematic diagram of CO₂ leakage along faults, fracture, and wells (injection and abandoned) and its impact on the fresh soil-water system.

2.0 Experiencing CO₂ Leakage

Field scale CO₂ release experiments have been conducted in different regions of the world to understand the CO₂ leakage from subsurface/vadose zone (Table 1). An effort has been made by Roberts and Stalker, (2017) to list such field CO₂ release experiments. Nine studies (ASGARD-UK, QICS-UK, CO₂FieldLab-Norway, Grimsrud Farm-Norway, CO₂DEMO-France, PISCO₂-

Spain, Ginninderra-Australia, Ressacada Farm-Brazil, and ZERT-USA) out of 14 studies revealed the leakage of CO₂ at experimental sites as listed in table 1. In these experiments, the injection rate of CO₂ varies from 0.04 gs⁻¹ [1.3 t(CO₂)pa] to 4.9 gs⁻¹ [153.3 t(CO₂)pa] where 5% (CO₂FieldLab-Norway) to 90% (ZERT-USA) of CO₂ leaked from the release zone. In which, 34% of total CO₂ were seep at ASGARD site in England, 82% from Grimsrud Farm in Norway, 78% from CO₂-DEMO site in France, 82.3% from PISCO₂ site in Spain and 90% from ZERT in USA. Global data on CO₂ leakage has been discussed by Roberts and Stalker, (2017). They highlighted that the CO₂ 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 CO₂ release experiments were performed either in top soil (Grimsrud Farm site), or vadose zone (PISCO₂; Ginninderra; CO₂-DEMO; ASGARD sites) or shallow saturated zone (QICS; CO₂ 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 CO₂ was injected at the depth of 8 m. CO₂ plume was monitored using cross-borehole ground penetrating radar (GPR). The results of this study demonstrates that several CO₂ gas pockets of gas saturation upto 0.3 formed below lower-permeable sand layers. This study conclude that the lateral migration of CO₂ gas was significant in case of the leakage from CCS site. Further, CO₂ 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 CO₂ migrate upward through the permeable seal and the leaky path with 0.62 and 0.86 CO₂ saturation level, respectively, into the overlying aquifer. In some cases, CO₂ 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(CO₂)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 CO₂ 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 CO₂ is injected in deep geological formations shallower than 3 km, where CO₂ 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 CO₂ 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 CO₂ 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 CO₂-brine through localized pathways. In conclusion, there were high experience of CO₂ 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 CO₂ 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 CO₂ injection. Further, changes in geochemical processes, especially mineral dissolution, have also been associated with CO₂ injection. It is also expected that complex geochemical reactions can occur due to fluid-rock interactions during the CO₂ 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 CO₂ injection in the Dogger aquifer (Paris Basin, France) suggests that the dissolution of carbonate by the acidic aqueous solution due to CO₂ injection significantly affects the porosity and permeability of media. Such changes in the porosity and permeability of media after injection of CO₂ causes significant variations in hydrodynamic regimes. Likewise, Fritz et al. (2010) performed experiment to investigate hydro-thermodynamics associated with CO₂ 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 fractures may act as potential CO₂ 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 CO₂. These studies clearly indicate that CO₂ induced dissolution significantly affect the hydrological conditions by altering the porosity and permeability of CO₂ storage zones which further increases the risk of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ injection.

Risk of CO₂ 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 CO₂ leakages during CCS activities. To the date, the geochemical impacts on alternation of the hydrodynamic due to the CO₂ 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 CO₂ leakage from depth to the surface (Lewicki,et al. 2007). Qualitative estimation of the combined risk associated with CO₂ injections and geochemically induced leakage for reservoir scale and for basin scale will be needed for the accurate prediction. A better understanding the CO₂ flow mechanisms, magnitude of leakage, and steps to remedy leakage are important factors for the risk assessment and the risk management.

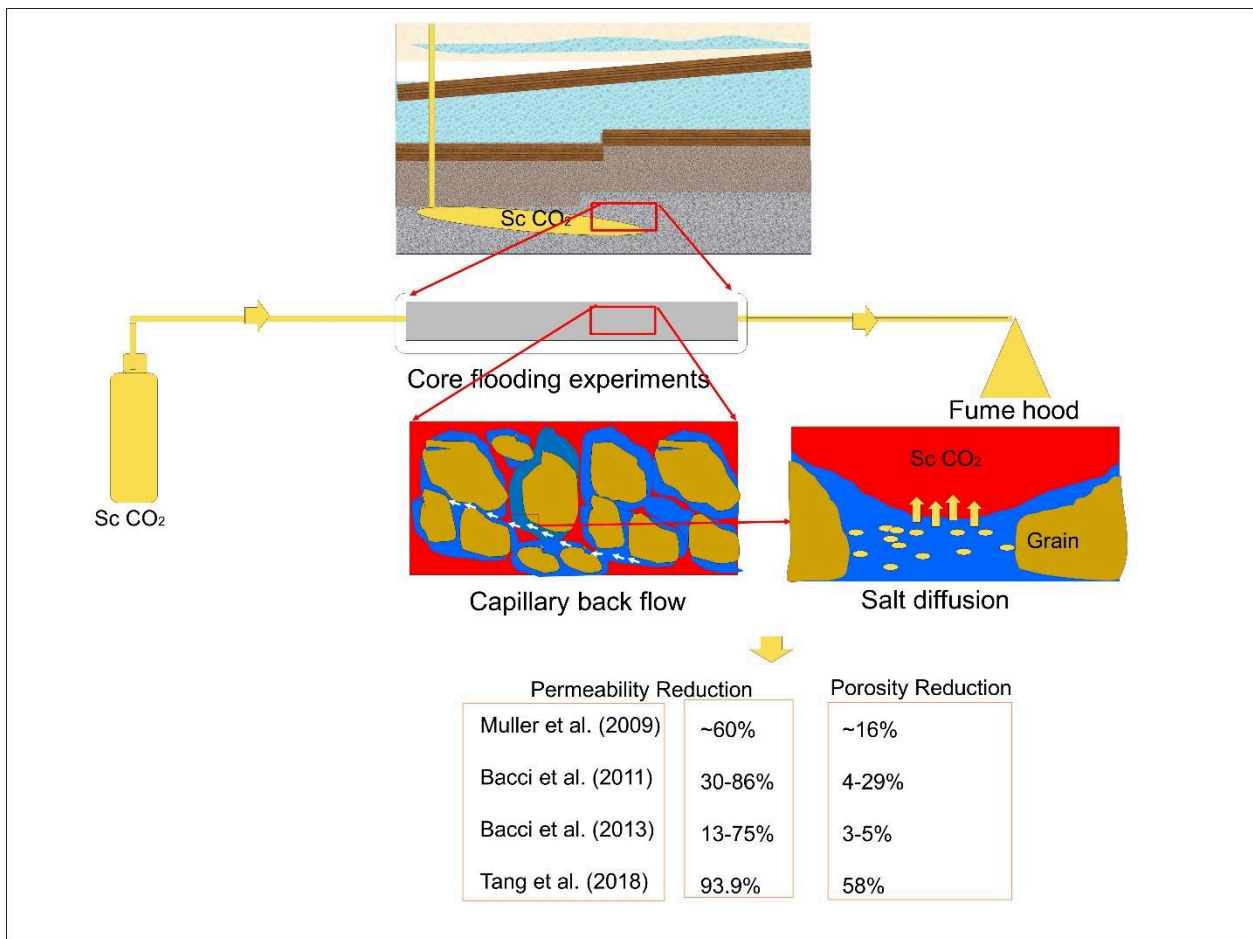


Figure 2: Schematic illustration of core flooding experiment performed to estimate effects of salt precipitation on pore dynamics and different physical mechanisms contributing to the process of salt precipitation.

3.0 CO₂-Brine Migration and its Leakage

If CO₂ migrates upward through a fracture or an abandoned well, supercritical CO₂ changes their phase as liquid- CO₂, or gas- CO₂ to receiving aquifers under controlled temperature-pressure regimes (Wilkin and DiGiulio, 2010). Just after the CO₂-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 CO₂ was injected at the rate of 5 million tonnes of CO₂ 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 CO₂-brine in the response to CO₂ injection under isothermal mode. Mount Simon Formation, the Eau Claire caprock and the weathered portion of the granite base rock were considered as lithofacies. CO₂ 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 CO₂. The thickness of the Mount Simon and the slop of structural surfaces affect the shape of the CO₂ plume which elongate it to 6-8 km long lateral CO₂ 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 CO₂ at the rate of 5 Mt CO₂/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 CO₂ plume of size 9-13.5 km was observed in the lateral direction which indicates slow migrations of CO₂. Displacement of the brine was significant in the injection area and thus a cumulative volume of $1.57 \times 10^9 \text{ m}^3$ 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 CO₂ sequestration by Person et al. (2010) using the single and multiphase i.e. sharp-interface model. In this study, CO₂ was injected in 726 wells at the rate of 0.11 Mt CO₂/year/well for 100 years and then the fate of pressure and CO₂ plume was observed for next 100 years. They found that the CO₂ 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 CO₂ 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

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

256 Likewise, a high performance supercomputer based numerical study performed by Yamamoto et
257 al. (2009) to investigate the impact of two phase flow i.e. CO₂- groundwater migration on regional
258 groundwater flow of an area of about 60km × 70km in Tokyo Bay using the multiphase flow
259 simulator TOUGH2-MP/ECO2N. Ten injection wells were considered to inject CO₂ at a depth of
260 1 km under Tokyo Bay at the rate of 10 million tons/year for 100 years. The results indicate that
261 the lateral plume appears in the injection layer extending over a range of 4-5 km. This study
262 demonstrate that the dissolution of CO₂ plume gradually increases and finally becomes dominant
263 in the domain. A large CO₂ plume-groundwater interaction area is the main driving factor to
264 enhance dissolution of CO₂ into the surrounding groundwater. However, the vertical velocity of
265 CO₂ plume was low because of the two-phase flow affected by the low relative permeability and
266 the high capillary pressure in the deep groundwater zone. However, one can expect more local
267 leakages of CO₂ from seal containing alternate layers of the sandstone and the mudstone which
268 was not considered in this study. By developing a precise lithofacies model for the seal one can
269 upscale this study for Tokyo Bay. Similarly, Pan et al. (2011) highlights a transient two-phase,
270 non-isothermal flow of CO₂-water mixture after its leakage. This study also indicates that leakage
271 dynamics is much more complicated than the simple quasi-steady-state flow.

272 Impacts of CO₂ leakage on groundwater depend on the formation permeability, if leakage
273 occurs from the high permeability zone, it will result in high flow variations (Wainwright et al
274 2013). Zhao et al. (2012) investigated the CO₂ plume migration and the pressure buildup due to
275 CO₂ injections at the rate of 3Mt CO₂/year/well for 50 years in five wells of the Sanzhao
276 Depression, Songliao Basin, China. Results of this study indicate that a 7.8MPa pressure buildup

277 in the high permeability zone of the formation while it can even reach to 10.5MPa in low
278 permeability layers. CO₂ plume size in the formation was about 5.8Km at 100 years, while
279 interference of CO₂ occurs at 200 years. CO₂ migrations toward the Southeast of the depression
280 indicate a potential risk of freshwater pollution. This fortifies that the permeability of the storage
281 formation is the main factor to control the pressure buildup, CO₂-brine migration and impact of
282 CO₂ leakage on above-lying formations. Furthermore, the CO₂-brine flow in low permeability
283 saline aquifers in the Ordos basin was studied by Xie et al. (2015a) and Xie et al. (2015b) using
284 one injection well having different injection rates i.e. 5.42 Kg s⁻¹ and 3.17 Kg s⁻¹, respectively.
285 CO₂ migrate in the radially shape of size 658m, 913m, 1013m at 3.65, 53.65, and 103.65 years,
286 respectively, after the beginning of the injection in the simulation domain of Xie et al. (2015a).
287 While in Xie et al. (2015b), CO₂ plume moves 330, 550, 680, 780 m at 1,3,40, and 103 years
288 respectively. Pressure buildup data matches well with the observed pressure profiles in both the
289 studies. However, both studies indicate acceptable leakage of CO₂ i.e. 0.02 and 0.1% of injected
290 CO₂ volume as the gas phase CO₂. Such a small fraction of the predicted CO₂ leakage was
291 considered acceptable in this study as up to 2% of the injected volume was suggested valuable by
292 van der Zwaan and Gerlagh, (2009). All these study clearly indicates that formation permeability
293 is most important parameter which control the plume extension and risk of CO₂-brine leakage.

294 <Insert Table 1 here> Table 1: Summary of experimental studies reported CO₂ leakage at various
295 sites around the globe.

296 **4.0 CO₂-Brine Leakage and its Impact on Groundwater Flow Dynamics**

297 The growing literature indicates that the variability in the pressure buildup, andCO₂-brine
298 migration patterns in varying permeable zones of the storage formation causes significant leakage
299 of pure/dissolved CO₂ and brine to shallow groundwater systems (Lions et al. 2014). A numerical

300 study performed by Nicot (2008) to investigate impact of pressure build-up due to the CO₂
301 injection on the groundwater system in the Gulf Coast Basin. Two case studies were performed
302 by incorporating 1Mt CO₂/year/well and 2Mt CO₂/year/well injection rates in 50 injection wells
303 for 50 years in MODFLOW by incorporating site specific aquifer parameters along with the
304 groundwater evapotranspiration condition. This study indicates that the CO₂ injection equivalent
305 to 50 million tons of CO₂/year for 50 years resulted in an average increases of the water table by
306 ~1m with significant increase in the groundwater evapotranspiration. While the base flow of
307 surface water bodies did not increase significantly in case of the actual base condition, but could
308 increase by two fold for the high injection rate condition. Finally, the groundwater flow direction
309 was reversed during the CO₂ injection from the bottom of the basin. Similarly, in Tokyo Bay study
310 by Yamamoto et al. (2009) upward groundwater migration due to the injection of CO₂ was
311 observed with maximum vertical pore velocities of about 50mm/year. The groundwater flow
312 direction before injection was from the mountainous area toward Tokyo Bay, however, CO₂
313 injection changed the flow direction, especially in and around the reservoir.

314 Another significant study was performed by Bricker et al. (2012) to investigate the effect
315 of CO₂ injection on the shallow groundwater table in the Sherwood Sandstone aquifer, UK using
316 a groundwater flow model ZOOMQ3D. Injection of 15 Mt/year of the CO₂ for 20 years was
317 considered into the Sherwood Sandstone Group (SSG) underlying zone to the Mercia Mudstone
318 Group (MMG) and the Chalk group of aquifers. Four leakage scenarios were simulated by
319 considering leakage coefficients, $C_z=0$ (MMG as perfect seal), $C_z=10^{-7}$ (Preferred leakage value),
320 $C_z=10^{-6}$ (leakage increased by one order of magnitude), $C_z=10^{-8}$ (leakage reduced by one order of
321 magnitude) and vertical hydraulic conductivity of 0, 10^{-6} , 10^{-5} , and 10^{-6} m/day, respectively (table
322 2). The results show that approximately 40MI/day of saline water would leak out from the

323 formation to MMG even in case of preferred leakage. In case of $C_z=10^{-7}$, an increase of 0.01-10m
324 and <1m was observed in groundwater heads in the potable confined aquifer and in the unconfined
325 aquifer, respectively, with a corresponding increase in river flows by 10-15%. Sensitivity analysis
326 fortifies that one-fold increase in leakage magnitude results in reduction of the groundwater heads
327 of (un-) confined aquifers by two fold. However, if the leakage co-efficient reduces by one fold
328 then there will be a five-fold increase in groundwater heads of (un-) confined aquifers. This
329 indicate that the degree of impact on shallow groundwater systems is highly sensitive to the vertical
330 leakage assigned to the caprock. Groundwater head increases of this proportion could result in the
331 groundwater flooding in and around the Humber Estuary of the study area.

332 <Insert Table 2 here> Table 2: Summery of parameters and conditions used to simulate
333 groundwater model by Bricker et al. (2012) to understand CO₂ leakage scenarios.

334 The upper shallow aquifer formation was not assign in simulation domain of Yamamoto et al.
335 (2009) and Bricker et al. (2012). One can improve results of these study by incorporating more
336 precise lithofacies and by considering upper heterogeneous shallow soil-water systems. Other
337 major limitation of these studies was the single phase model approach which may cause variance
338 in the results as Nicot (2008) reported about 10% and less than 20% variation in results if simulated
339 using single phase models. Although, these study indicate regional scale variations in groundwater
340 flow dynamics, it hasn't demonstrated local variations of the groundwater system. Table 3 listed
341 summery of studies addressing the field and plume scale hydrological impacts of CO₂ injection
342 and storage. To frame management plan and to improve the groundwater quality, it is important to
343 understand the local impacts of such CO₂-brine leakage in the near surface environment.

344 <Insert Table 3 here> Table 3: Summery of studies addressing the field and plume scale
345 hydrological impact of CO₂ injection and storage.

346 **5.0 Groundwater Quality Concerns**

347 CO₂ leakage from deep storage reservoirs may induce geochemical reactions and lead to
348 degradation of (ground-) water quality, which is likely the greatest concern associated with CO₂
349 migration from deep storage sites to the near-surface environment. In past, variations in the
350 groundwater geochemistry due to CO₂ leakage has been considered as a monitoring tool. However,
351 the assessment of leak magnitudes leading to endangerment of the drinking water is still an area
352 of active research (Wilson et al. 2007). A better understanding of impacts of CO₂ leakage on the
353 groundwater quality help to frame a better management and remediation plan at CCS sites.

354 **5.1 Mixing of the CO₂/Brine-Fresh Groundwater and Changes in the Groundwater** 355 **Chemistry**

356 Leakage of the CO₂/CO₂-enriched brine to a fresh aquifer might directly affect the groundwater
357 chemical state by modifying (i) the pH, (ii) the redox potential and (iii) mobilization of inorganic
358 and organic contaminants (Harvey et al. 2012; Lions et al. 2014). In general, the chemical reactions
359 between the fresh groundwater-formation materials or by mixing of fresh groundwater-saline/CO₂
360 enriched waters alter the pH and the redox potential of fresh zone groundwater (Lions et al. 2014).

361 Precipitation and dissolution of minerals are dominating geochemical processes occurs in
362 aquifers once scCO₂/CO₂-enriched brine leaked. In table 4, the host rock-water-scCO₂/CO₂ enrich
363 brine interactions occurs during CO₂ injection, storage and its leakage are presented. Mixing of
364 the CO₂/brine-fresh groundwater or dissolved CO₂ induced reactions forms H_2CO_3 (Reaction 2a)
365 causing an imminent drop in the pH of the brine or the fresh groundwater. H_2CO_3 (acid) interact
366 with minerals of the host rock like carbonate and rapidly buffer the pH (Reaction 2b). The
367 bicarbonate ion may then dissociate to form the carbonic ion as in Reaction 4 (table 4) and later

368 these Carbonate ion form minerals like calcite (5a); magnesite (5b); and dolomite (5c). At a low
369 pH (~4), the production of H_2CO_3 dominates and at a mid pH (~6), production of HCO_3^-
370 dominates. However, at a high pH (~9) CO_3^{2-} production dominates. Cui et al. (2017) performed a
371 laboratory experiments using rock samples from typical sandstone and carbonate reservoirs.
372 Experimental results show that CO_2 can lead to the dissolution of ankerite and clay minerals and
373 the precipitation of plagioclase, which can result in increases of Ca^{2+} and Mg^{2+} in the formation
374 water of sandstone test. While in case of the carbonate test, CO_2 can induce the dissolution of
375 dolomite and the precipitation of ankerite and calcite. Subsequently, the changes in the pH
376 influence the dissolution of soil minerals (e.g., calcite, dolomite, K-feldspar, and plagioclase) as
377 highlighted in reaction 6-9 of table 4. Furthermore, the dissolution of minerals can extend to the
378 silicates as well as carbonates with examples for albite (reaction 10 and 11) and Fe-rich chlorite
379 (reaction 12). There is growing literature on rock-water interactions in the near-well high saline
380 environment as a result of the dissolution and precipitation, but only few studied has been reported
381 in case of low-salinity environments. Farquhar et al. (2015) investigated CO_2 -water-rock
382 interactions in a low-salinity reservoir system. This study indicates the partial dissolution and
383 desorption of calcite, carbonates, chloritic clays and annite followed by the long term dissolutions
384 of additional silicates, such as feldspars. Furthermore, the host mineral-dissolved CO_2 brine
385 interaction in vadose zone or near surface environment has still not studied. Review article by
386 Gaus (2010) present further details on rock-water interactions considering CO_2 injection and
387 storage in formations.

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

390 5.2 Drop in pH

391 Introduction of CO₂ or CO₂-rich brines in the fresh groundwater enhance the dissolution of CO₂
392 (CO₂(aq)) resulting in increase of carbonic acid (H₂CO₃) concentrations, followed by its
393 deprotonation and thus in turn decreasing the pH of fresh groundwater. However, decrease in the
394 pH depends on the nature of water-rock system due to the proton interactions with various solid
395 phases in the soil-water system during the precipitation/dissolution and adsorption/desorption
396 processes (Lions et al. 2014). Low pH condition due to increase in bicarbonate ion concentrations
397 (HCO₃⁻) could lead the high saturation of water with respect to carbonate minerals and to the
398 precipitation of minerals (Druckenmiller and Maroto-Valer, 2005). Carbonate, clay, and feldspars
399 minerals tend to buffer the pH and cause the brine to be less acidic. Reaction 2 of table 4, can
400 rapidly reach equilibrium under suitable conditions however the dissolution of these minerals
401 characterize by slow reaction kinetics. Previous research indicates that the CO₂/CO₂-enriched
402 brine significantly drop the pH, especially in sandy soils as these are more sensitive to an increase
403 in CO₂ concentrations due to the low buffering capacity than the clay-rich soil with a higher
404 buffering capacity (Harvey et al. (2012); Derakhshan-Nejad et al. 2019). In modeling studies by
405 Birkholzer et al. (2008), Carroll et al. (2009) and Zheng et al. (2009) with CO₂ injections rates of
406 2.36, 10³-10⁶, and 2.36 tons of CO₂/year, respectively in the carbonate sedimentary, confined non-
407 carbonate, confined carbonate aquifer indicate a drop of pH of ~2, ~2 and ~1.5 units respectively.
408 Likewise, *In-situ* CO₂ experiment performed by injecting 300 kg of CO₂ (30 days) in the alluvial
409 deposit by Kharaka et al. (2010) indicates a pH drop of about 1-1.4 units. Similarly, Lu et al. (2010)
410 performed a laboratory experiment with and without carbonates by applying CO₂ bubbling for 15
411 days and observed a drop in pH of ~1.5-2.5 and ~1.5-2.2, respectively. Zheng et al. (2012) model
412 the unconfined sandy aquifer at the Montana State University Zero Emission Research and

413 Technology (MSU-ZERT) field site and observed a pH drop of ~1-1.7 in groundwater. Further, a
414 field based study in which 5700 ppm dissolved CO₂ was injected (30 days) in confined sandy
415 aquifer by Trautz et al. (2012) show a pH drop of ~2.4-2.9 units. Similarly, Peter et al. (2012)
416 perform *in-situ* experiment by injecting 787 kg of CO₂ at a depth of 18 m below surface level into
417 a quaternary sand aquifer close to the town of Wittstock in the Northeast Germany. The results
418 show that the total inorganic carbon concentrations increased and the pH decreased to a level of
419 5.1 (drop of ~0.8-1.8 units) after injection of CO₂. Another *in-situ* experiment was performed by
420 Cahill and Jakobsen (2013) in which 45Kg of CO₂ was injected at 10 m depth in Aeolian and
421 glacial sands at the Vrøgum field site. They observed a plume of depressed pH ranging 5.6-4.7,
422 which indicates a drop of ~1.5 pH units. The study has shown that the CO₂ and or CO₂ enrich brine
423 can alter the pH of groundwater of fresh aquifer but CO₂ gas stream can also change the pH
424 conditions. A batch and column scale study performed by Wang et al. (2016) by injecting CO₂ gas
425 into oxidizing carbonate aquifer indicates a drop of pH by two units. As pH decreases with CO₂
426 leakage, one can consider the pH monitoring in initial phase of CO₂ risk analysis at CCS sites.
427 Similarly, alkalinity might also be used as a monitoring parameter. However, for small CO₂
428 release, the pH variation might be less than the detection limits. Likewise, the alkalinity of a
429 solution may not be necessarily modified by CO₂ leakage and can be the results of water-rock
430 interactions (Lions et al. 2014). Although there are numbers of study highlighted a drop of pH in
431 the groundwater due to CO₂ leakage (all phase), it is also important to see how such changes affect
432 the vadose zone water quality and plume of exiting pollutants, if any, under site specific conditions.

433 **5.3 Alteration of Dissolved Organic Carbon (DOC)**

434 Soil acidification due to release of CO₂ from the deep subsurface may alter the dissolved organic
435 carbon (DOC) concentrations. The host soil has some buffering capacity, and it will exchange

436 extra H⁺ with basic cations. This will lead to an increase in base cations in leachates and will
437 further affect the quality of the water in the saturated zone. Organic soils have been found to have
438 higher buffering capacity than the sub-surface mineral soils (Moonis et al. 2017). Composition is
439 important because it is closely related to pH buffering, ion exchange, especially in case of mineral
440 host soils (Lee et al. 2016). For example, Lime (CaCO₃) dominating host media may have high
441 buffering capacity to against CO₂-induced acidity than sandy soils. The combined influences of
442 buffering capacity, injection amount of CO₂, hydraulic characteristics may lead to alternation in
443 the DOC concentration (Moonis et al. 2017). A study was performed by Kharaka et al. (2006;
444 2009), where 1600 tons of CO₂ was injected at 1500 m depth into a 24-m thick sandstone section
445 of Frio Formation, US Gulf Coast. The DOC values obtained from the subarkosic fine-grained
446 quartz and feldspar sandstone during the CO₂ injection increased moderately to 5–6 mg/L; the
447 values however, increased unexpectedly by a factor of 100 in samples collected 20 days after
448 injection stopped. Such variation in CO₂ injection induced DOC concentrations has high
449 significance value to understand occurrence and fate of polar polycyclic aromatic hydrocarbons
450 (PAHs) and BTEX compounds. Another study performed by Moonis et al. (2017) to investigate
451 the impact of CO₂ leakage on DOC in different soils by applying 100% CO₂ for 32 days indicates
452 that the DOC significantly increases in organic soil while decreases in mineral soil and alteration
453 in DOC significantly affect mobilization of organics.

454 **5.4 Mobilization of Polycyclic Aromatic Hydrocarbons (PAHs)**

455 Leakage of the CO₂ in supercritical phase significantly mobilize non-to moderately PAHs
456 compounds present in soil-water system as it is known to be an excellent solvent. For example,
457 Hexane and benzene, small apolar and weakly monopolar PAHs have relatively the high solubility
458 in the sc-CO₂ than small polar PAHs compounds such as acetic acid and phenol. Larger

459 compounds, longer chain of alkanes, large PAHs with a molecular weight greater than 200g/mol,
460 have the low solubility in the sc-CO₂ (Burant et al. 2012). However, the solubility of organic
461 compounds in the sc-CO₂ plume depends upon temperature, pressure and salinity. A review article
462 by Burant et al. (2012) can be referred by the readers for more details on the partitioning behavior
463 of organic contaminants in carbon storage environments. In this direction, a study performed by
464 Scherf et al. (2011) by injecting the sc-CO₂ into the sandstone at the CO₂SINK site near Ketzin,
465 Germany observed free and ester-bound fatty acids, especially *n*-hexadecanoic acid, *n*-
466 octadecanoic, isomeric *n*-octadecenoic and *n*-octadecadienoic acids. Additionally, acetate,
467 propionate, butanoic and pentanoic acid as well as lactic, pyruvic, and glycolic and gluconic acid
468 were also detected in varying amounts in certain samples. Since CO₂ injection started,
469 concentrations of these organic compounds were detected in the downhole fluid samples from
470 observation wells. Similarly, Kharaka et al. (2006; 2009) observed a high concentration of formate,
471 acetate, oxalate and toluene after CO₂ injection, however VOCs and semi-VOCs concentrations
472 were low near the zone of injection wells. Results of previous studies indicates that the sc-CO₂ in
473 the formation may significantly enhance the mobilization of hydrocarbons. Therefore, the
474 mobilization of hydrocarbons from non-oil bearing saline aquifers could have major implications
475 for the groundwater quality concern. Low pH induced increment in DOC and PAHs may
476 significantly alter the metals and metalloids as a result of de-sorption of fresh groundwater systems
477 (Zheng and Spycher, 2018). Likewise, the drop of pH, high DOC, PAHs accelerates the dissolution
478 of calcite, and then the increase in the concentration of Ca triggers a series of cation-exchange
479 reactions that cause an increase in the concentrations of metals and metalloids (Zheng et al. 2016).
480 Further study is required to understand the role of the near surface environment on the mobilization
481 of wide range of organic compounds due to the leakage of sc-CO₂/dissolved CO₂ into fresh

482 groundwater systems. Similarly, a better understanding of PAHs, n-alkane, MTBE and other
483 organics on mobilization of metals and metalloids will help to predict future risk and planning
484 related to management of CCS sites.

485 **5.5 Mobilization of Metals and Metalloids**

486 The mobilization of metals and metalloids are the major groundwater quality concern in case of
487 CO₂ leakage from a storage site to the subsurface environment. The growing literature indicates
488 that the presence of CO₂ and CO₂ enrich brine plume can modify the subsurface environment
489 mainly by two mechanisms: (i) alteration of oxidation-reduction potential of the aquifer system
490 and (ii) amending the sorption/desorption reactions. Unconfined aquifers can be either oxic in the
491 upper part where redox potential is high, and anoxic at the bottom of the aquifer where redox
492 potential is comparatively low and dynamic (Lions et al. 2014). The redox status of the
493 groundwater system mainly controlled by two mechanisms: (i) dynamically fluctuating
494 groundwater table conditions and/or (ii) contamination by oxidizing or reducing components such
495 as O₂, organic matter, CH₄, and HS⁻ (McMahon and Chapelle, 2008; Lions et al. 2014). A rising
496 water table towards unsaturated zone can replace the initial oxic condition by the anoxic condition
497 leading to the decrease of redox potential in the saturated zone. In case of CO₂ injection or leakage,
498 a rise in water table was reported by Nicot (2008) and other researchers (refer section 3.2). Thus,
499 change in the redox status are expected due to introduction of oxidizing and/or reducing
500 components due to the rise in the water table condition under the influence of CO₂ sequestration
501 activities.

502 Leakage of brines significantly enhance the organic compounds (acetate, formate etc.) in
503 the fresh groundwater zone (section 4.3) which serve as energy sources for the endogenous
504 microorganisms in the aquifer zone. This energy induced microbial metabolic activity results in

505 the reduced concentration of electron acceptors (oxygen) in the aerobic zone. While in the
506 anaerobic zones increased concentrations of organic compounds may lead to the increased iron,
507 sulphate reduction and or methanogenesis (Lions et al. 2014). Furthermore, the co-injected
508 substances can also be strongly oxidizing (i.e. O₂, SO₂, NO_x) or reducing (i.e. H₂S) agents.
509 Recently, Zhang et al. (2019) observed changes in the redox condition due to injections of the SO₂
510 in the saline sandstone formation and their significant impacts on native microbes under co-
511 injected SO₂ in CO₂ storage formations. It is evident from the literature survey that inadequate
512 studies have been performed to characterize the impact of the co-injected substances on redox
513 status of overlaying aquifers. Thus, advancing the monitoring techniques based on redox status
514 along with impact of- (i) dynamically fluctuating water table and (ii) co-injected chemicals are
515 active area of research to mitigate the risk of CO₂ into fresh overlaying aquifers.

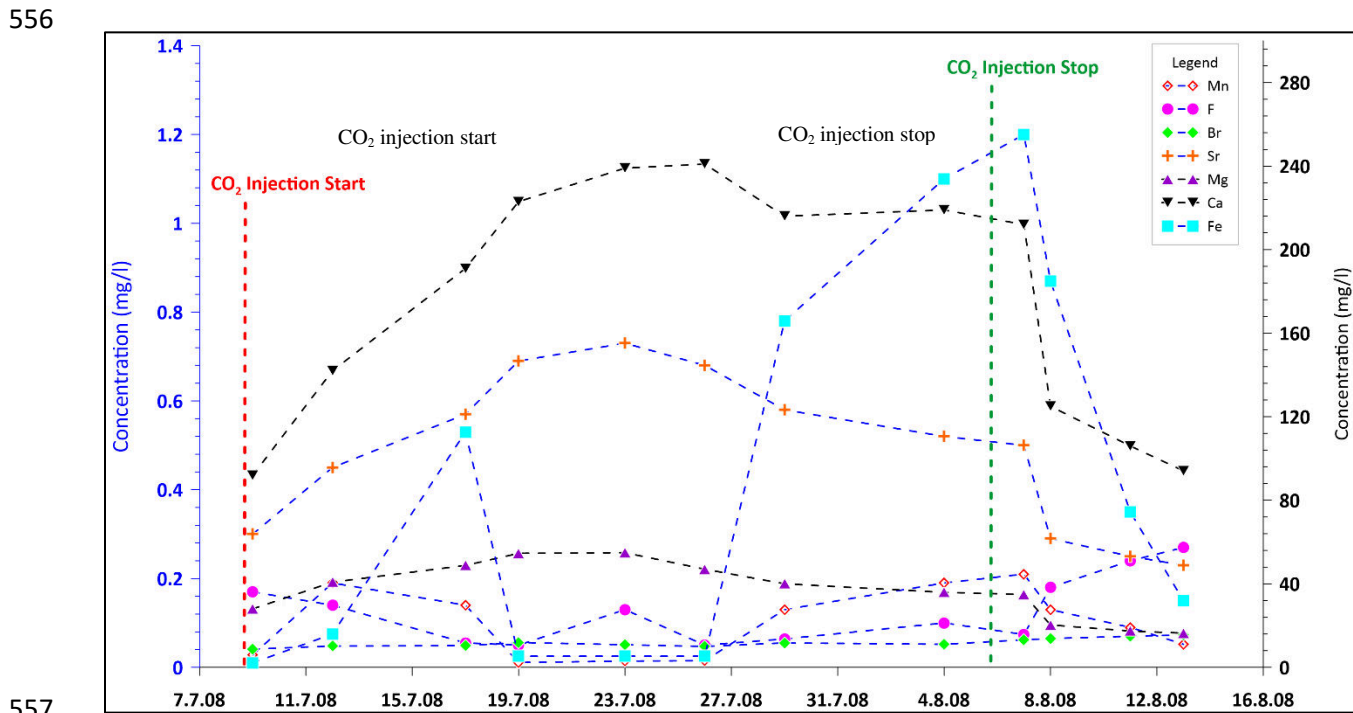
516 Impacts of CO₂ leakage on metals and metalloids fall into two categories: (i) metal(loid)s that are
517 of health concern drinking-water (e.g. As, Cd, Cr, Hg, Ni, Pb, Se) and (ii) that are of low or zero
518 health concern (e.g. Al, Ba, B, Cu, Fe, Mn, F, Zn, Sb) are the major risk to the groundwater quality
519 associated with the CO₂ geological storage. Indeed, these chemicals can be present naturally in
520 soil-water systems as geochemical background and their concentrations depending upon the
521 lithology. Table 5 is presented with a summary of *in situ* field, laboratory and modeling studies
522 performed to investigate the impact of CO₂ leakage on the mobilization of metal(loid)s.

523 <Insert Table 5 here> Table 5: Summary of studies investigated role of CO₂/CO₂ enrich brine on
524 mobilization of metalloids in fresh groundwater zone.

525 Indeed, CO₂ leakage into groundwater system could enhance the release of the initially
526 sorbed metal(loid)s and or accelerate dissolution of minerals that contain it. Smyth et al. (2009)
527 and Lu et al. (2010) performed batch scale experiments by applying the high CO₂ to the aquifer

528 media from the Texas Gulf Coast region. Results of these studies observed two types of response
529 and then categories elements accordingly. Type-I: cations are Ca, Mg, Si, K, Sr, Mn, Ba, Co, B,
530 Zn, which showed a fast increasing concentrations at the start of the CO₂ injection that become
531 steady before the end of the experiment. While in case of type-II cations (Fe, Al, Mo, U, V, As,
532 Cr, Cs, Rb, Ni and Cu) initial increases in their concentrations were observed followed by a
533 decreases to values less than background level. Similarly, Little and Jackson, (2010) performed
534 laboratory experiment for the CO₂ infiltration under oxidizing conditions through the freshwater
535 aquifer media. It was observed that two fold of concentration was increases in case of the alkali,
536 alkaline, Mn, Cb, Ni and Fe. While, the uranium and barium concentration kept increasing
537 throughout experimental durations. Other laboratory experiments (table 5) were performed by
538 Druckenmiller and Maroto-Valer (2005), Wei et al. (2011), Viswanathan et al. (2012), Humez et
539 al. (2013), Wunsch et al. (2014), Kirsch et al. (2014), Farquhar et al. (2015), Pearce et al. (2015),
540 Shao et al. (2015) and Wang et al. (2016) to investigate the impacts of CO₂ leakage on the
541 mobilization of different metal and metalloid contaminants. These experiments evaluated various
542 types of aquifer media such as essentially carbonate free (Varadharajan et al. 2012), carbonate-
543 dominated (Wunsch et al.2014) under the varying conditions in terms of redox state (Varadharajan
544 et al. 2012) oxidizing (Little and Jackson, 2010) and pressure conditions (Varadharajan et al. 2012,
545 Humez et al. 2013), with reaction times ranging from a couple of days to months. Most of these
546 study observed two types of behaviours of metals and metalloids, first increases rapidly after CO₂
547 injection and then stabilize with the time or in late phase of experiments. While, second types of
548 contaminants concentration increases with the CO₂ injection and then decreases with the time or
549 as pH stabilize (Smyth et al. 2009; Lu et al. 2010). Commonly, all of the above studies have
550 highlighted increases in metals mobilization after the CO₂ introduction but reported less

551 concentrations than drinking water standards by the EPA or other agency (Kirsch et al. 2014).
 552 Dissolution of the host rock (for example calcite) or precipitation of minerals found to be the main
 553 driving mechanism of the high metals mobilization after the CO₂ introduction in laboratory setups.
 554 Although laboratory scale experiments enhance the understanding of the behavior of CO₂ on
 555 subsurface contaminants, they cannot accurately represent *in-situ* field conditions.



557
 558 Figure 3: Concentrations of Mn, F, Br, Sr, Fe, Mg, and Ca in groundwater reported by Kharaka et
 559 al. (2010) from selected ZERT wells plotted as a function of time of sampling.

560 In field scale, Kharaka et al. (2010) performed CO₂ release test to investigate changes in the
 561 shallow groundwater at the ZERAT field site, where ~300 kg/day of CO₂ was injected.
 562 Groundwater samples were collected from 10 shallow monitoring wells for analysis of trace
 563 elements. It was observed that the concentrations of Ca, Mg, Fe, and Mn were increases
 564 significantly (Figure 3). Increases in Fe concentration was related to the dissolution of siderite
 565 (carbonate minerals) due to the acidification by the CO₂ injection. Fe and Mn are at the greatest

566 abundance in the groundwater and increase rapidly after the injection of CO₂ but it can decrease
567 with time in the oxidizing zone. Likewise, Peter et al. (2012) observed water samples on a site where
568 CO₂ was injected through three wells for 10 days at depth of 18 into aquifer in Northeast Germany.
569 They showed a moderate increase (~15%-40%) in Ca, K, Mg and Fe and high increase (~120%-
570 180%) in Al, Si, Mn in the groundwater. Similarly, an increase in concentrations of trace elements
571 by ~260% and 320%~ for Ca and Mg, respectively were observed by Cahill and Jakobsen, (2013)
572 at pilot test site (unconfined aquifer) in the Denmark. In this study, an increase of ~50% in Na and
573 Si concentrations were observed along with ~730%, 370%, 330%, and 160% increment for Al, Ba,
574 Sr, and Zn, respectively. In the Southern Norway, the groundwater assessment was performed by
575 Gal et al. (2013) for a site where 6-day injection of CO₂ into a shallow glacio-fluvial aquifer at a
576 depth of 20 m was done. They observed a significant increase in dissolved Ca and Si
577 concentrations. A recent study by Choi, (2019) investigated the groundwater quality in the
578 Chungcheong region (South Korea) where they studied leakage of CO₂ gas and CO₂-rich water
579 into shallow aquifers. The study observed three different sites as-Group I (acidic CO₂-rich waters
580 with low TDS), Group II (slightly acidic CO₂-rich waters with high TDS), and Group III (CO₂-
581 poor waters with low TDS). Results of this study show that the concentration of trace elements
582 (Al, Ba, Be, Cr, Cs, Fe, Mn, Ni, Rb, and U) in case of Group-I was is higher than Group-III.
583 Whereas, concentration of Al, Mn (slightly) and Be (6.5 fold) exceeds the EPA drinking water
584 limit. In addition, concentration of Fe and Mn exceed by 27.7 fold and 16.1 fold, respectively then
585 the EPA drinking water limits. In conclusion, the understanding from both field and laboratory
586 show an increase in the dissolved concentrations of metals and metalloids upon the CO₂ leakage
587 into shallow aquifer zones. Mobilization of metals and metalloids especially As, Pb, Ba, Zn, Mn
588 and Cd are more frequently in these studies. Although several studies have been performed to

589 investigate potential impacts of CO₂ on the groundwater quality or on the mobilization of metals
590 and metalloids in saturated zone, it has not been demonstrated that how these pollutants in the
591 vadose zone or the unsaturated zone at CCS sites behaves. Furthermore, there is lack of
592 information on the connectivity of dynamic hydrological responses of subsurface and the
593 mobilization of metals and metalloids under different CO₂ leakage conditions.

594 **6.0 Impacts on Soil Microbes and Vegetation**

595 Previous section of this manuscript demonstrated that the leaked CO₂ could significantly alter
596 groundwater quality of the fresh groundwater zone (Refer table 5). Thus, it is important to assess
597 potential impacts of the CO₂ leakage on near surface microorganisms and vegetation including
598 crops, to make sure these impacts could be tolerated. Thus, this section of manuscript is focused
599 to understand the impact of the CO₂ leakage on soil microorganisms, vegetation and crops.

600 **6.1 Shifts in Microbial Communities**

601 Intrusion of CO₂ into the biosphere may alter microbial community composition, thus
602 understanding their response to short and long-term changes is crucial for ecological balance. In
603 this direction, only few research studies have been performed to investigate the impact of CO₂
604 leakage on the soil microbial community in natural analogues (Beaubien et al. 2008; Krüger et al.
605 2009, 2011; Oppermann et al. 2010; Frerichs et al. 2013; Zhao et al. 2017) and at artificial CO₂
606 release sites (He et al. 2019). Table 6 present summary of studies performed to see impacts of CO₂
607 leakage on soil microbes and plants. Beaubien et al. (2008) investigated the impact of CO₂ on the
608 bacterial populations near a naturally occurring CO₂ gas vent located in Mediterranean pasture
609 ecosystem, Central Italy. Extremely low bacterial cell counts were observed in area of vent core
610 (>90% CO₂) having high CO₂ flux and low plant cover. Bacteria cell counts increase as moved

611 away from the vent core. Likewise, Oppermann et al. (2010) investigated the compositions of
612 microbial communities at the CO₂ vent (Beaubien et al. 2008) and at the reference site, using Q-
613 PCR and observed that bacteria, archaea, and eukaryota decreased with increasing CO₂
614 concentration in the soil gas by 2-orders of magnitude. While, methanogens and SRB (anaerobic
615 bacteria's) substantially increased in the CO₂-rich vent site. The family *Geobacteraceae* are
616 anaerobes using Fe (III) were found less in two orders of magnitude at the CO₂ vent than at the
617 reference site. Frerichs et al. (2013) observe that the bacterial sequences were affiliated to the
618 *Betaproteobacteria*, *Acidobacteria* and *Bacilli*, while archaea to the *Thaumarchaeota*. They also
619 report that the *Geobacteraceae* showed a significant decrease under high CO₂ concentrations.
620 Likewise, Krüger et al. (2009, 2011) studied the impacts of CO₂ release from reservoir on
621 abundance and diversity of microorganisms at a natural CO₂ vent at Laacher site in Germany and
622 reported that the bacteria gene copies decrease from 9.6×10^9 g_{dw}⁻¹ of soil at reference site to 8.7
623 $\times 10^8$ g_{dw}⁻¹ of soil towards the vent. While archaea were increased from control site towards the
624 vent, with 7.7×10^6 and 6.5×10^7 gene copies g_{dw}⁻¹ of soil. Similar trends were also observed by
625 Ziogou et al. (2013) at a natural CO₂ vent in Florina, Greece.

626 At the ZERT field site, Morales and Holben, (2013) investigated the impacts of CO₂
627 leakage on microbial functional groups in surface and near-surface soils. A significant alteration
628 in microbial communities was observed due to the elevated CO₂ at ZERT field site. Seasonal
629 variations of the soil moisture and temperature also play important role in microbial shifting. A
630 reduction in free living-nitrogen fixer community was also observed at the elevated CO₂ site.
631 Likewise, 16S rRNA genes sequencing studies have also been carried out by de Miera et al. (2014)
632 at the Campo de Calatrava natural CO₂ site in Spain. It was observed that the relative abundance
633 of *Chloroflexi* increases while the relative abundance of *Acidobacteria*, *Verrucomicrobia* and

634 *Gemmatimonadetes* phyla decreases as CO₂ flux increases. Within the *Chloroflexi* phylum, the
635 genera *Thermogemmatispora*, *Ktedonobacter* and *Thermomicrobium* dominated bacterial
636 communities sampled in sites with the highest CO₂ flux.

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

651 <Insert Table 6 here> Table 6: Summary of studies performed to investigate impacts of the
652 elevated CO₂ on soil microbes and vegetation.

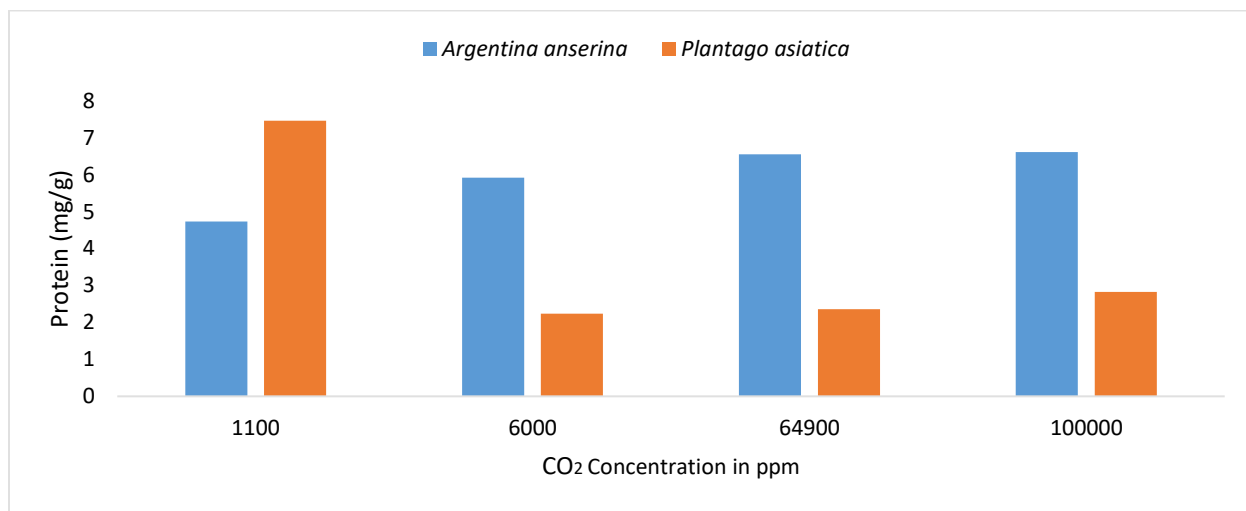
653 **6.2 Impacts on Vegetation**

654 Like soil microbes, a better understanding of impacts of CO₂ leakage at CCS sites is important to
655 evaluate risk, to restore sites and to manage resources. In this direction, Beaubien et al. (2008)

656 investigated the impact of CO₂ on the vegetation near a naturally occurring CO₂ gas vent located
657 in Mediterranean pasture ecosystem, Central Italy. It was observed that vegetation distribution
658 increases as we move away from the vent core. This fortifies that the high CO₂ flux significantly
659 affects the biosphere at a site of naturally leaking CO₂. A study was performed by Male et al.
660 (2010) to investigate the impact of CO₂ on vegetation using hyperspectral plant signatures during
661 the 2008 ZERT CO₂ sequestration field experiment in Bozeman, Montana. During the experiment,
662 the pure phase CO₂ was injected through a 100-m long horizontal well at a flow rate of 300 kg
663 day⁻¹. On daily base from first day of injection, the spectral (visible-near infrared) signature of
664 plants located inside and outside of CO₂ leakage zone was measured. Stress on plants was observed
665 around the injection wells, which cover large area in the late phase of experiment. Similar
666 observation was also reported by Krüger et al. (2011) at a terrestrial CO₂ vent at Laacher See,
667 Germany. They observed that the dicotyledon is more sensitive than monocotyledon for CO₂
668 injection in a natural terrestrial CO₂ vent. Likewise, West et al. (2015) reported the impacts of
669 elevated CO₂ on two different sites (Laacher See, Germany and Latera, Italy) located in the
670 Mediterranean climatic zone. It was observed that *Agrostis capillaris L.* which is an acid tolerant
671 grass starts growing on the edge of vent core. This indicate drop in pH, which support growth of
672 such acid tolerant grass.

673 A field scale assessment of CO₂ leaking was performed by Zhao et al. (2017) at an
674 experimental site in the Qinghai-Tibet Plateau and its impacts on the native vegetation,
675 microorganisms, soil dwelling animals. Six sites as S002 (Blank), S03, S06, S10, S12 and S29
676 were selected for such analysis under the CO₂ leakage with different concentrations of 500ppm,
677 6000ppm, 18000ppm, 23000ppm, 12000ppm, and >112000ppm respectively. Plant quality under
678 different CO₂ concentrations was determined by the soluble protein and the surge. Concentrations

679 of other parameters like catalase (CAT), peroxidase (POD), superoxide dismutase (SOD) and
 680 proline (PRO), chlorophyll a, b and carotenoids were also determined. The plant distribution
 681 advocates that *Agropyron cristatum*, *Equisetum ramosissimum* and *Artemisia indica Willd*, *Herba*
 682 *laxeris* were increased in the high CO₂ concentration site, whereas *Agropyron cristatum* and
 683 *Plantago asiatica* were stable. However, the plant growth (total weight, stem length, number of
 684 leave and root length), except for *Herba laxeris* and *Equisetum ramosissimum*, was high at the site
 685 where the CO₂ concentration was 66400 ppm.



686
 687 Figure 4: The effect of elevated CO₂ on protein contents in *Argentina anserine* and *Plantago*
 688 *asiatica* at CO₂ leaking site in the Qinghai-Tibet Plateau.

689 For evaluating impacts of elevated CO₂ on physiological system, *Argentina anserina* and *Plantago*
 690 *asiatica* were selected. It was observed that both plant indicates a high stress even in case of lower
 691 CO₂ concentrations possibly due to the soil acidification. Likewise, no trend was observed for
 692 photosynthetic pigments including chlorophyll a, chlorophyll b and carotenoid in this study. In
 693 *Argentina anserine*, sugar concentrations decrease sharply with the higher CO₂ concentration.
 694 Figure 4 indicates that the protein (mg/g) was high in case of *Argentina anserine* and low in case

695 of *Plantago asiatica* located in plot having high CO₂ concentrations. This strengthens that the
696 elevated CO₂ concentration significantly alter the protein contents of crop plant. Furthermore, it
697 was also seen that starch content of wheat decreased from 70.93% to 61.75% in nearby farmlands.
698 Very recently, He et al. (2019) performed a greenhouse experiment to investigate impact of high
699 soil CO₂ on plant growth. A negative impact was observed on the root water absorption,
700 chlorophyll, starch content and total biomass at the elevated CO₂. In conclusion, previous studies
701 consistently reported that plants exposed to the high CO₂ showed significant impacts on its growth
702 by reducing plant height, root length, leaf number, leaf area, seed number, pod number (Al-
703 Traboulsi et al. 2012; Wu et al. 2014) and by altering physiological stress (Zhao et al. 2017).
704 However, it is important to note that the most of these studies performed at natural analog, thus
705 results of such studies may not be valid for assessment of the CO₂ leakage associated risks CCS
706 sites.

707 **7.0 Isotope and Geochemical Modeling for Assessing CO₂ Leakage**

708 Geochemical modeling has been performed as monitoring tool for assessing scCO₂/CO₂-brine
709 leakage and subsequently to understand hydrological and geochemical implications at natural
710 analogue and industrial CO₂ geological storage sites (Gal et al. 2012). For geochemical studies,
711 most commonly applied models are TOUGHREACT (Liu et al. 2019), TOUGH2/ECO2N (Zhou
712 et al. 2010; Yamamoto et al. 2009), PHREEQC (Rillard et al. 2019), MODFLOW (Nicot, 2008),
713 Sharp-interface model (Person et al. 2010), MINTEQA2 (Wang and Jaffe, 2004) and NUFT (Yang
714 et al. 2019). These modelling tools were used to predict single and multiphase flow of CO₂ from
715 different CCS sites, listed in table 3. Furthermore, such modeling approaches have also been
716 applied for the predication of potential impact on fresh groundwater systems (Birkholzer et al.
717 2008; Zheng et al. 2009; Jones et al. 2015) and vadose zone. Recently, Liu et al. (2019) used

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

730 Isotopic test has been performed in past using the dynamic characteristics of C, H, and O
731 isotopes of CO₂, carbonates, silicates and water molecules (Gal et al. 2012; Flude et al. 2016). A
732 study by Choi (2019) evaluated the impact of leaking CO₂ gas and CO₂-rich waters on groundwater
733 quality at Daepyeong and Daejeong sites in the Chungcheong region, South Korea. It was observed
734 that the CO₂-rich waters at the Daepyeong site have $\delta^{13}\text{C}$ - dissolved inorganic carbon values
735 within the range of CO₂ from deep storage zone (ca. -1‰ to -8‰), which reveals that the CO₂
736 gas in CO₂- rich waters originated from deep source. Likewise, Kim et al. (2019) used carbon
737 isotopic compositions to understand the flow path of CO₂ in Daepyeong area. A high soil CO₂
738 concentration (36%) flux (546.2 g/m²/d) and relatively high $\delta^{13}\text{C}$ -CO₂ (-5.7‰) revealed the origin
739 of CO₂ to be deep-seated CO₂ and its pathway to be degassing from CO₂-rich water at the water
740 table. Similar isotope study was performed at the Illinois Basin–Decatur Project carbon

741 sequestration site (Shao et al. 2019). They also observed relatively high $\delta^{13}\text{C}-\text{CO}_2$ (~5‰) from
742 deep formation. Recently, Amonette et al. (2019) performed column experiment to detect CO_2
743 leakage using noble-gas isotopes as tracer through a core collected from the proposed FutureGen
744 2.0 carbon storage site (Jacksonville, IL, USA). In which ratio of different noble-gas isotopes
745 ($^4\text{He}/^{22}\text{Ne}$; $^{20}\text{Ne}/^{36}\text{Ar}$; $^{20}\text{Ne}/^{22}\text{Ne}$; $^{21}\text{Ne}/^{22}\text{Ne}$; $^{38}\text{Ar}/^{36}\text{Ar}$; $^{40}\text{Ar}/^{26}\text{Ar}$; $^{84}\text{Kr}/^{26}\text{Ar}$; $^{132}\text{Xe}/^{84}\text{Kr}$) in control
746 site and atmosphere were used to understand leakage dynamics.

747 Even small leakage or microseepage can be detected using noble-gas isotopes tracer in
748 field conditions (Klusman, 2011). Recently, Ju et al. (2019) used Kr, He, Ar as tracers to evaluate
749 the CO_2 leakage at K-COSEM site, South Korea. PHREEQC was used to model $p\text{CO}_2$ using
750 alkalinity, pH, temperature, major cation and anion concentrations as input parameters. They
751 successfully demonstrated a relatively small amount of CO_2 saturated groundwater spiked with He
752 and Kr tracers into a shallow aquifer. Readers can get further details on noble-gas isotopes
753 application in CO_2 leakage and impact evaluation in following studies: Stalker et al. (2009); Myers
754 et al. (2013); Amonette et al. (2014); Jenkins et al. (2015); McIntosh et al. (2018). Although it has
755 been reported that noble-gas isotopes can be easily applied to detect CO_2 leakage, however in-
756 depth investigations of its behaviors will also be required as some may not be completely
757 conservative, for example Sulfur hexafluoride. In future, further work is required to develop more
758 realistic frame-work for selection of appropriate geochemical modeling and isotope analysis
759 approaches for groundwater and vadose zone as many soil biochemical processes creates noise in
760 in measurements, especially in biogenic interferences.

761 **8.0 Conclusive Remarks**

762 An effort has been made to review literatures on the leakage of CO_2 and CO_2 enrich brine from
763 the storage formation and its potential impacts on the groundwater quality, soil microbes and

764 plants. It was observed that 1) a significant leakage of CO₂/CO₂ enrich brine through faults,
765 fractures and wells (injection and abandoned) has been experienced by many CCS projects in past,
766 2) a non-isothermal, two-phase and multicomponent flow occurred once the CO₂ leak into fresh
767 aquifers, 3) the leakage of CO₂/brine may significantly affect groundwater flow regimes, 4) the
768 mixing of CO₂/brine and potable aquifer water may alter pH (generally drop of pH) and redox
769 potential conditions, however such changes also depends on host rock conditions, 5) alteration of
770 the DOC and mobilization of subsurface pollutants (organics and inorganics) has been experienced
771 in previous studies, 6) two type of nature in cations were observed, one group increases once CO₂
772 leaked and remain stable while second group increases after CO₂ leakage and thereafter decreases
773 with time, 7) the soil acidification due to the CO₂ leakage may significantly affect soil microbes
774 by alternating their metabolic activities and the mutation, 8) the plant also gets affected by reducing
775 plant height, root length, leaf number, leaf area, seed number and 9) the accelerated metalloids and
776 organic compound (like BTEX) may increases the human health risk. Based on the knowledge
777 developed by reviewing literature here, four main directions for future research have been listed
778 as-

779 1) A proper subsurface characterization and demonstrative evaluation of impacts of CO₂ leakage
780 is required before the implementation of large scale CCS projects. Subsurface characterizations
781 must include- i) pilot/lab scale investigations of two phase/multiphase flow of CO₂ under varying
782 subsurface conditions ii) incorporation of realistic groundwater table and flow dynamics iii) CO₂
783 flow behaviors in vadose zone iv) understanding of bio-geo chemical interactions of the (un)-
784 saturated zone. While, in case of demonstrative evaluation of impacts of CO₂ leakage, realistic
785 experimentations are required by conducting the controlled plot scale performance of CO₂
786 injection in subsurface.

787 2) There is a need to develop further understanding of behaviors of multi-pollutants under
788 dynamically CO₂ leakage conditions by performing plot/lab scale experiments and numerical
789 modeling.

790 3) More research is needed for the accurate prediction of risk of CO₂ and CO₂ enrich brine on soil
791 microbes, plants and on human for the short and long time scale. In past, most of risk analysis were
792 based on either small scale laboratory case or hypothetical case based on large number of
793 assumptions. Only few studies have been reported on human health risk assessment, which needed
794 further evaluation for realistic CCS sites.

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

799 **Conflicts of Interest:** No any

800 **Data Availability**

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

802 **Acknowledgement:** Helps from Writing and Communication Center and the library of University
803 of Waterloo are well acknowledged. Author would like to thank the Editor-in-Chief and
804 anonymous reviewer for the valuable comments that enabled much improvement to this paper.

805

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2020-03-03

Attribution-NonCommercial 4.0 International

Gupta PK, Yadav B. (2020) Leakage of CO₂ from geological storage and its impacts on fresh soil–water systems: a review. *Environmental Science and Pollution Research*, Volume 27, April 2020, pp. 12995-13018

<https://doi.org/10.1007/s11356-020-08203-7>

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