

Capture, Storage and Use of CO₂ (CCUS)

CO₂ leakage and effects on the chemistry of aquatic systems
– monitoring and remediation

Rasmus Jakobsen

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Preface

Late 2019, GEUS was asked to lead research initiatives in 2020 related to technical barriers for Carbon Capture, Storage and Usage (CCUS) in Denmark and to contribute to establishment of a technical basis for opportunities for CCUS in Denmark. The task encompasses (1) the technical potential for the development of cost-effective CO₂ capture technologies, (2) the potentials for both temporary and permanent storage of CO₂ in the Danish subsurface, (3) mapping of transport options between point sources and usage locations or storage sites, and (4) the CO₂ usage potentials, including business case for converting CO₂ to synthetic fuel production (PtX). The overall aim of the research is to contribute to the establishment of a Danish CCUS research centre and the basis for 1-2 large-scale demonstration plant in Denmark.

The present report forms part of Work package 7 and focuses on the effects of a possible leakage of CO₂ to the aquatic environment, options for monitoring the aquatic environment and the possibilities of remediating a leak related to the injection infrastructure or the geology surrounding the geological CO₂ storage

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Resumé

De effekter på vandmiljøet som vil opstå hvis der siver CO₂ ud af et CO₂ lager skyldes at CO₂ opløses i vandet og danner kulsyre, og syren får pH til at falde. Er der urenheder i CO₂ gassen, så som NO_x'er og SO_x'er, kan det føre til lavere pH værdier. Ved lavere pH øges hastigheden for opløsningen af de fleste af de mineraler der befinder sig i de aflejringer som vandet er i kontakt med og der sker en ændring i ligevægten mellem mineraloverflader og de spormetaller som er bundet til dem. Det kan føre til højere koncentrationer i vandet af aluminium (Al), jern (Fe) og sporelementer som arsen (As) og nikkel (Ni), evt. til værdier der overskrider gældende grænseværdier for drikke- og/eller overfladevand. Aflejringer indeholder mange forskellige mineraler, men de fleste af dem reagerer langsomt, dette gælder imidlertid ikke karbonatmineraler som f.eks. kalcit (CaCO₃) og aluminiumhydroxider som f.eks. gibbsit (Al(OH)₃). Grundvandsmagasiner uden karbonatmineraler er derfor mest sårbare ift. forsurening, og eksperimenter har vist at der efter 5 måneders tilførsel af i alt 1600 kg CO₂ til et grundvandsmagasin kun var små effekter på vandkvaliteten, og kun stoffer der ville blive fjernet ved vandbehandling på vandværkerne, overskred grænseværdierne for drikkevand. I søer og vandløb kan lavere pH og forhøjede koncentrationer af opløst Al, Fe og sporelementer skade biologien og økologien i systemet. I meget næringsrige systemer hvor det kan være CO₂ der begrænser algevæksten, kan tilførsel af CO₂ forøge omfanget af en algeopblomstring.

På grund af den høje reaktivitet som kendetegner karbonatmineraler vil tilstedeværelsen af en karbonatrig aflejring mellem et CO₂ lager og et overliggende grundvandsmagasin eller overfladevandssystem kunne give en ekstra beskyttelse fordi en del af den undslupne CO₂ vil reagere og blive neutraliseret under passagen.

En kvalitativ forhåndsvurdering af tætheden af forseglingen over et muligt CO₂ lager kan opnås ved at måle koncentrationen af ⁴He indenfor og udenfor en geologiske struktur der potentielt kunne blive et lager. Ved naturligt radioaktivt henfald af uran og thorium dannes ⁴He, og hvis forseglingen er tæt og udvekslingen med omgivelserne lille vil der ophobes ⁴He under forseglingen.

Helt generelt er overvågning af vandmiljøet i relation til et CO₂ lager baseret på prøver fra enkelte "punkter" i form af borer eller bølger vanskelig, fordi prøverne normalt udgør et meget lille volumen i forhold til det store volumen hvori en udsivning kan opstå. Dette er især et problem hvis man gerne vil overvåge tæt på CO₂ lageret da man må forvente en mindre spredning tættere på lageret, på den anden side giver det en mulighed for en tidlig registrering af udsivningen. Det er muligt at oppumpe større vandmængder, men fortyndingen af påvirket vand med ikke-påvirket vand kan betyde at detektionsgrænsen bliver for høj. Søer, vandløb og marine systemer opsamler vand fra et stort område og øger chancen for at en prøve indeholder påvirket vand, men også her kan detektionsgrænsen blive for høj på grund af opblanding med ikke-påvirket vand. Hvis observationspunkter placeres strategisk, f.eks. hvor kortlægning af geologien peger på en højere mulighed for udsivning, eller hvor strømlinjerne i systemet løber sammen øges muligheden for at registrere en evt. udsivning. Ny teknologi, i form af kilometer lange sensorer bygget op omkring optiske fibre kan markant øge mulighederne for at detektere en udsivning i terrænnære grundvandsmagasiner. Der ser ud til at være mulighed for at sætte sporstoffer til den injicerede CO₂, det vil gøre det nemmere og mere entydigt at detektere et udslip. Den umættede zone, dvs. over grundvandsspejlet, vil i mange tilfælde have et netværk af drænledninger som potentielt kan udnyttes til overvågning.

Udsivning i forbindelse med borer kan ofte udbedres fordi systemet er kendt og i tilfælde hvor skaden ikke kan udbedres kan boringen lukkes helt af ved udfyldning. Udsivninger forårsaget af geologien kan være vanskelige at udbedre, men erfaringer fra naturgaslagre har vist at en udsivning kan stoppes ved at ændre trykfordelingen i systemet. Udsivning som når op til drikkevandsforekomster kan, hvis påvirkningen kræver det, udbedres med metoder kendt fra håndtering af grundvandsforurening f.eks. afværgepumpning. Udsivning til overfladevandssystemer kan sandsynligvis lokaliseres og lukkes til, men hvis kilden stadig er aktiv, er det sandsynligt at den udsivende CO₂ finder en anden vej op.

Summary

The effects of CO₂ leakage stem from the formation of carbonic acid which lowers the pH. Associated SO_x and NO_x may lead to lower pH values. A lower pH will increase rates of mineral dissolution and change the competition for sorption sites on mineral surfaces, thereby increasing concentrations of Al, Fe and trace elements, potentially to levels exceeding threshold levels for the drinking water and/or surface waters. An experiments in a carbonate free aquifer, most vulnerable to acidification, show that a 1600 kg leak lasting 5 months had minor effects on groundwater quality and only elements that are taken care of by standard water treatment exceeded the drinking water limits. In surface water systems the lowered pH as well as the increases in dissolved Al, Fe and trace elements can have detrimental effects on the biology and ecology of the system. In eutrophic systems where CO₂ is limiting increased levels of CO₂ can increase the magnitude of algal blooms.

Due to the high reactivity of carbonate minerals, the presence of carbonate rich formations above the storage, below any overlying drinking water reservoirs would use up part of any escaping CO₂, acting as an extra natural barrier protecting the surface water bodies as well as drinking water.

Preassessment of the efficiency of the seal over a reservoir by measuring ⁴He concentrations inside and outside the closure could give simple qualitative information on the exchange of water and gas below the seal and indicate whether the mapped geological closure will hold injected CO₂ for extended periods.

In general, monitoring for CO₂ leakage in aquatic systems based on samples from monitoring points could be difficult due to the small volumes that are normally sampled, especially at depth – on the other hand it bears the possibility of early notifications of a leak. The closer to the source of leakage, the smaller the chance of the observations intersecting the leakage. If large volumes are sampled, dilution may imply that the detection limit becomes too high. Surface waters integrate the signal from large volumes/areas, increasing the chance of intersecting effects of a leak, but again the detection limit may become too high. Placing monitoring points strategically, e.g. where mapping indicates higher probability of a leak or where streamlines in the system converge will increase the probability of detecting a leak. New developments such as long (km's) fiber optic sensors may improve the chances of detecting leaks in near-surface groundwater systems. The unsaturated zone may contain a distributed network of drainpipes that could potentially be exploited for monitoring purposes.

Leaks related to wells can often be remediated because the system is known, in cases where this is not possible the well can be plugged. Leaks related to the geology are difficult to repair, but experiences from natural gas storage have shown that leakage can be stopped by changing the pressure distribution in the system. Leaks that reach near-surface drinking water resource can, if the effects on groundwater quality requires it, be remediated using technologies from the environmental industry. Leaks that reach surface waters can presumably be located precisely and potentially be plugged but may reappear in new places if the source is still active.

1. Pathways and effects of CO₂ and associated components from CO₂ storage to the aquatic environment

Stored CO₂ may find its way, leak, into the aquatic environment through geological conduits such as fractures typically associated with fault zones or through man-made conduits in the form of wells (Fig.1).

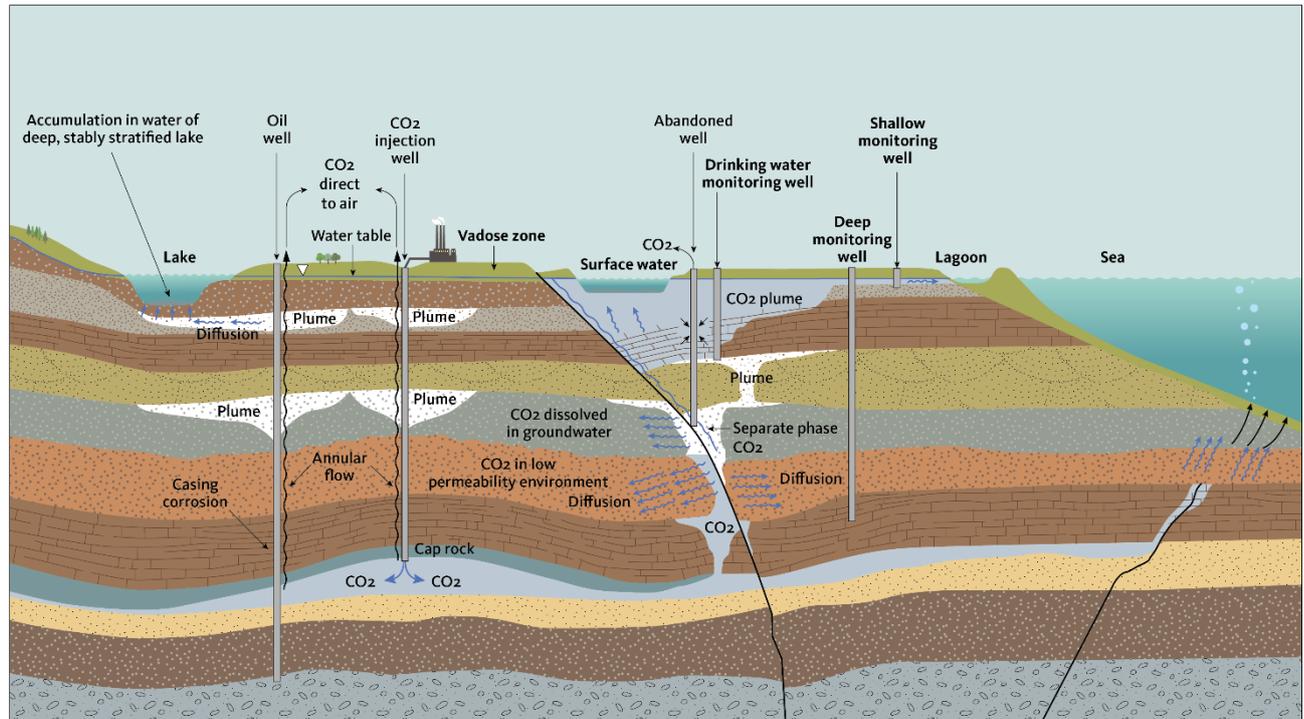


Figure 1. CO₂ leakage coming via anthropogenic (left) or via natural (right) conduits and monitoring targets (bold) in the aquatic environment.

The wells may be wells that are part of the storage system, made for injection or monitoring. The wells could also be existing wells made for hydrocarbon exploration or water production. There is also the possibility that geological conduits are connected to man-made conduits, e.g. that a fracture zone connected to the storage intersects a well. The leaking CO₂ will pass through water saturated sediments before reaching the surface. If the flux of leaking CO₂ exceeds the rate at which it can be adsorbed by dissolving in the water or reacting with minerals the leaking CO₂ may reach the surface as a gas and go into the atmosphere or emanate as bubbles into surface water bodies such as streams, lakes or the marine environment. The CO₂ may dissolve in the surface waters or, again if the flux is higher than the rate of dissolution, the CO₂ will reach the atmosphere as bursting bubbles. CO₂ that has dissolved in moving groundwater will also reach surface water bodies, and due to the drop in pressure as the groundwater moves up, part of the CO₂ reaching surface waters may form a gas phase and become bubbles. The only commercial scale CO₂ capture technology available in 2020, the amine absorption, produces 99.9% clean CO₂, but if the stored CO₂ contains other gases (SO_x, NO_x, H₂S etc.) these gases will also leak, if they have not reacted. Even if these associated gases leak, they may not necessarily reach the surface waters because they may dissolve in the water saturated sediments or, due to their high reactivity, may be used up in reactions within the sediment.

1.1 General effects of CO₂ leaking into aquatic systems; aquifers, streams and the marine environment and possible parameters affected by CO₂ and other possible major and/or minor gases present in the injected gas.

The effects on the geochemistry of a sediment-water system are summarized in Fig. 2. The overall effect of dissolving CO₂ in water is the production of acid, implying a lower pH value. When CO₂ dissolves in water part of the CO₂ combines with water to form carbonic acid (H₂CO₃), how much will depend on the pressure. The carbonic acid will dissociate forming H₃O⁺ and HCO₃⁻ ions, and the higher activity of H₃O⁺ ions implies that the pH of the water decreases and that the electrical conductivity of the water increases since the water contains more ions. If CO₂ bubbles through the water, it will carry O₂ dissolved in the water with it, changing the redox state of the groundwater. An example of these general effects is seen in Table 1 where the results are taken from an injection experiment (Cahill *et al.*, 2014).

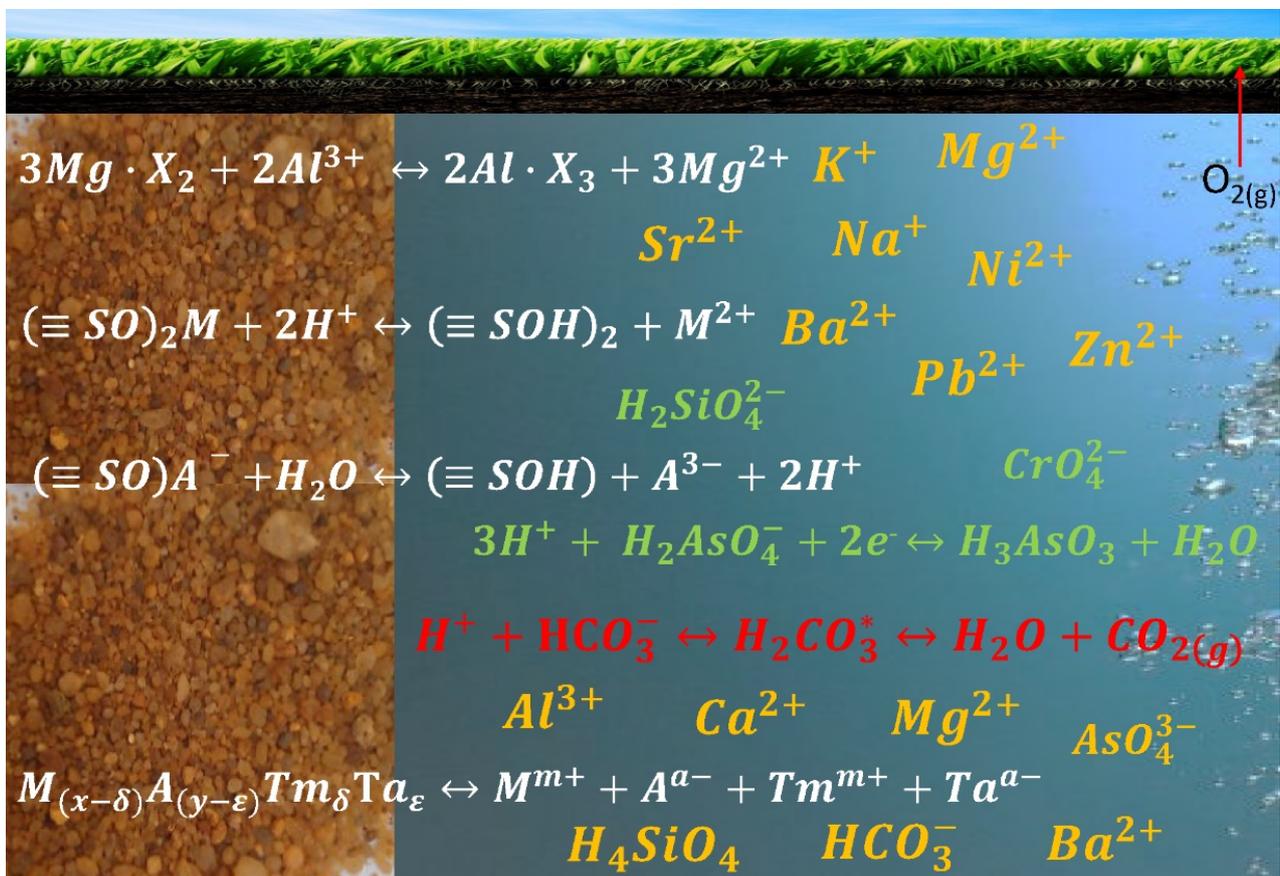


Figure 2 Schematic of the type of reactions that may occur due to the entrance of CO₂ into a sediment-water system. CO₂ dissolves in the water and forms carbonic acid. The acid may dissolve minerals releasing both the main ions and substituting trace element ions and these ions will exchange with other ions bound to sediment surfaces or as interlayer ions in clay minerals. The CO₂ may also remove O₂ from the system changing the redox state of the system thereby changing the mobility of some elements e.g. Mn and Fe that are more soluble in their reduced state (Mn(II) and Fe(II)), Cr which is less soluble in its reduced state (Cr(III)) and As which often sorbs more strongly in its oxic form (As(V)).

In groundwater, the lower pH and change of redox conditions will mean that the groundwater will no longer have a composition reflecting the previous equilibrium and/or steady state with the minerals in the sediment. Therefore, the changed state will most probably cause mineral dissolution and possibly

precipitation of other minerals, thereby changing the composition of the groundwater. Since many processes occurring in groundwater are mediated by microbes, the microbial community may also be affected by the lower pH and lower O₂ level.

Table 1: Basic effects of CO₂ contacting groundwater (Cahill et al., 2014)

	Natural groundwater	CO ₂ affected water
pH	5.4	5.1
Electrical conductivity [μ S/cm]	200	280
Dissolved oxygen [mg/l]	9	2-6
Alkalinity [meq/l]	0.08	0.5-1.0

In fresh surface waters the lower pH and possibly lower O₂ levels will likewise affect the equilibrium or steady state conditions between bottom sediments and the water. In addition to this the biological system will be affected since the biological life in the system is related to the pH and the oxygen level of the water. In flowing streams the magnitude of the effects will depend on the flux of CO₂ into the system compared to the water flux in the stream and likewise small lakes with no through-flow will be more affected than large lakes with large through-flow.

Similarly, sea water will also be affected, but due to the large buffering capacity of seawater as well as a faster exchange of water with the surroundings the effects will most likely be localized to very near the site where the leakage occurs. Gros *et al.* (2019) observed natural seeps of CO₂ at the sea bottom, and found that a lowered pH could only be observed ~40 m away.

Where the fresh and marine waters are fed by groundwater, there may be effects of the change in the chemical composition of the water due to dissolution/precipitation as well as microbiological process occurring in the groundwater. The effects could be related to the increase in total dissolved substances or related to specific compounds such as toxic trace metals released due to mineral dissolution.

The velocity of the water in the different aquatic systems can be very different implying that the effects will spread at very different velocities. Groundwater normally moves less than a meter pr. day, while stream water can move by several meters pr. second. The ratio between sediment and water is also very different. In groundwater the volume is dominated by sediment, while in surface waters, water is the dominating phase.

1.1.1 Relative risk of acidification of different freshwater aquifer formations to CO₂

The effects on the water chemistry and the volume of the aquifer affected will be determined by the minerals and the amounts that are present in the system. If a mineral such as calcite (CaCO₃), or gibbsite (Al(OH)₃), which react relatively rapidly when the pH is lowered, the effect will be development of a dissolution front where the mineral is dissolved. The front will move slower than the groundwater, how slow will depend on how much of the reactive mineral is present. The dissolution of calcite or gibbsite will release Ca²⁺ or Al³⁺. The released cations will lead to a new equilibrium between exchangeable cations on clay minerals and cations sorbed to surfaces of e.g. Fe- or Mn-oxides, this may lead to the release of Mg²⁺, Na⁺ and K⁺ but also trace elements such as Ni²⁺ and As. Trace

elements may also be released from dissolving minerals where trace elements substitute for the main ions in the minerals. If the oxygen is stripped out by the CO₂ some elements might change their oxidation state. These different processes will occur together (Fig. 2), and they are in general coupled, as mentioned, through ion exchange, but also through pH, e.g. the Al³⁺ released from dissolution of gibbsite will exchange with other cations on the sediment, this implies more gibbsite is dissolved, limiting the decrease in pH and thereby limiting the release of trace metals from surface complexes. Changes in the concentrations of major ions such as Ca²⁺, Mg²⁺ and Na⁺ will not be large enough to change the usability as drinking water, but the release of trace elements, where the allowed amounts in drinking water are low could be a problem. If an aquifer contains carbonate minerals it is normally in concentrations of 1% and normally more, and this will mean that the carbonic acid is neutralized, and the dissolution front moves very slowly. If there is no calcite, then the mineral buffering the pH decrease via dissolution is often gibbsite, which is normally present in much smaller amounts and therefore the dissolution front moves faster. The dissolution of gibbsite increases the Al³⁺ concentration, which again increases the amount of Al bound as exchangeable Al on the sediment. When the pH increases again the Al bound to the exchanger will reprecipitate as gibbsite, taking up hydroxyl ions and forming acid, thereby prolonging the acidification of the aquifer.

1.1.2 Leakage effects of CO₂ on groundwater chemistry in aquifers without carbonate

There have been a number of experiments where CO₂ gas or CO₂ rich water was discharged into aquifers without carbonate (e.g. Trautz *et al.*, 2013; Cahill *et al.*, 2014). The experiment by Cahill *et al.*, 2014 was carried out in Denmark (Vrøgum Plantage). Here 1600 kg of CO₂ was injected into the aquifer comprised of quaternary meltwater sand overlain by postglacial aeolian sand for a period of 72 days and the effects on the water chemistry was monitored closely for 189 days. Seven years after the injection, a final sampling of water and sediment at a position close to the injection was made, to see if there were still any effects related to the CO₂ injection (unpublished). Because the aquifer did not contain carbonate minerals gibbsite dissolved releasing Al³⁺ and buffered the pH so that it never dropped below 3, and mostly stayed above 4. The background pH value before the injection started was between 4.4 and 6.7. The released Al³⁺ from gibbsite dissolution exchanged with the major cations, especially Ca²⁺ on mineral surfaces and there were minor increases in Ba²⁺, Ni²⁺ and Zn²⁺ in the groundwater, but the concentrations did not exceed the limits for drinking water. The only parameter that exceeded the limit for drinking water was Al which went up to 3 mg/l in a few places, but most values were below the limit of 0.2 mg/l. Even if water with an Al concentration of 3 mg/l arrived at the water works, the normal treatment of the water would increase the pH and thereby lower the Al concentration. The samples taken 7 years after the CO₂ release showed that the water chemistry was now similar to the background chemistry before the injection. It was, however, possible to see slightly higher concentrations in the exchangeable cations, most notable Al³⁺ and Ca²⁺, 7 years after. It was also possible to see slightly elevated proportions of Al, Ba and some major cations in extractions targeting Fe-oxides, especially in the ascorbic acid extract which dissolves the more reactive Fe-oxides with large surface areas and sorption capacity. The results from the Trautz *et al.*, 2013 study, where CO₂ saturated water was injected for 5 months, in a Pliocene unconsolidated fluvial sand formation dominated by quartz, feldspars, clay minerals and some pyrite, were very similar. The CO₂ injection caused minor increases in trace elements along with increases in major cations but compared to the Vrøgum study there were very low Al concentrations (Zheng *et al.*, 2016). Actually, when modelled by Zheng *et al.* (2016) it is assumed that there are small amounts of calcite below the limit of detection. As for the Vrøgum study, drinking water limits were not exceeded. There are no data on the long term

(years) effects of the CO₂ injection from the Trautz *et al.*, 2013 study), but there are no indications that the long-term effects for that setting would be different from that of the Vrøgum study.

Both studies were characterized by a relatively short pulse of increase for many dissolved ions related to the dissolution of the most reactive minerals. This also results in a marked pulse of increased electrical conductivity of the water. Through modelling, the effects can be extrapolated as done for the Danish injection experiment (Cahill and Jakobsen, 2015). The model was used to simulate the effects of leakage at greater depth, resulting in the water equilibrating with a higher partial pressure of CO₂. This resulted in a pH of 3.4 for a depth of 100 m (10 bar) after the gibbsite was depleted. This would have the effect of increasing the dissolution rate of silicate minerals leading to higher concentrations of major as well as trace elements in the water. However, silicate dissolution was not included in the model. The effects on the water quality would be highly dependent on the aquifer material. At depth there are often carbonates present, implying that increased rates of silicate weathering would not be seen as long as the carbonate was not depleted. A similar but shorter CO₂ gas injection experiment was carried out in a carbonate free sandy aquifer in Northern Germany (Schulz *et al.*, 2012) where the $\delta^{13}\text{C}$ in the dissolved inorganic carbon (DIC) was sampled. In this system there was a clear breakthrough of $\delta^{13}\text{C}$ depleted DIC that matched the breakthrough in electrical conductivity, the added SF₆ tracer and pH, showing that it is possible to use $\delta^{13}\text{C}$ as a tracer. In a system with dissolving carbonates the shift in $\delta^{13}\text{C}$ would be disturbed by the ¹³C released from the carbonates, making $\delta^{13}\text{C}$ a less sensitive parameter for monitoring.

1.1.3 Leakage effects of CO₂ on groundwater chemistry in aquifers with carbonate

There are no published field experiments for aquifers containing carbonate as detailed as the studies described in the previous section, but there are a few e.g. Mickler *et al.* (2013) that have used push-pull tests (meaning the same well is used for injection and observation). In addition, there are several laboratory studies using various rock types containing carbonate. Most relevant for Danish conditions is the study by (Cahill *et al.*, 2013) that studied the release of ions after suspending 7 different Danish sediments in CO₂ saturated water. As suspected the effect on pH is much smaller compared to sediments without carbonate minerals. Like other studies on carbonate bearing materials (e.g. Wunsch *et al.*, 2014) it was found that higher levels of trace elements (found as impurities in the carbonate minerals) were observed in the groundwater when the carbonates dissolved. Similar results were found by Mickler *et al.* (2013) in their laboratory tests as well as their push-pull tests in sediments with very low carbonate contents. The push-pull tests showed reaction rates that were ~2 orders of magnitude lower than seen in their lab test. In the Cahill *et al.* (2013) the substantial release of trace elements was also seen for the samples containing clay. Due to the large capacity for neutralizing the carbonic acid, the elevated trace element concentrations related to carbonate dissolution would only occur close to the CO₂ leak and only spread very slowly as the carbonates dissolve. Because the clay sediments are impermeable the release from clays, even if these do not contain carbonate, should only occur from the interface of an aquifer in which the carbonic acid is transported. If leakage is long lasting, the effects may of course be seen in a larger volume of the aquifer, even in a carbonate aquifer (Bacon *et al.*, 2014). In the model study by Bacon *et al.* (2014) the effects of dissolving carbonate as well as desorption of trace metals from calcite surfaces and equilibrium with a large suite of minerals could be seen ~1000 meters from a well that had leaked CO₂ for 100 years.

1.1.4 Effects of possibly associated gases on freshwater aquifers

When combustion of carbon rich material takes place in an atmosphere with N₂, various nitrous oxide gases (NO_x) may be produced. If the combusted material contains sulfur compounds various sulfur oxide gases may form (SO_x). Depending on the source of CO₂ and how it is purified, the CO₂ injected into a storage facility may contain some NO_x and SO_x. The information on the effects of these associated gases on freshwater aquifers are limited, with no experimental data. Some information can be obtained from modelling studies. In one model study (Jacquemet *et al.*, 2011) water equilibrated with a gas containing 90.2% CO₂, 0.2% NO, 1.5% SO₂, 1.6% O₂ and the rest being Ar (5.6%) and N₂ (0.6%) reacted with a glauconitic sandstone. The effect was a local additional lowering of the pH of 1 unit (compared to pure CO₂) accompanied by local increases in Fe and Mn from dissolution of Fe- and Mn- oxides. Presumably also Al-oxyhydroxides would dissolve as described above referring to (Cahill *et al.*, 2014). If carbonate minerals are present these would also dissolve, as described above. The dissolution of Al-, Fe- and Mn-minerals as well as carbonates may lead to increases in trace element concentrations if these are either bound in or to the surface of the oxides. This was not tested in the model and it will also depend on the extent of sorbed and co-precipitated trace elements in the formation that the impure gas leaks into. The SO₂ was oxidized in the model leading to elevated sulfate concentrations. The model simulated a presumably unrealistic situation where the impurities in the injected CO₂ had not reacted, neither during storage nor during travelling up into the aquifer. Considering that the impurities in the gas are rather reactive it is quite likely that they would be present in much lower concentration, or even absent when the leaking gas reaches an aquifer, implying that the effects of the extra acidity related to SO_x and NO_x would be smaller and very local.

1.1.5 Effects of upwards migrating deep saline groundwater

The pressure changes caused by the injection itself could in principle lead to an upwards displacement of deep saline groundwater, though groundwater flow simulations (unpublished) based on pressure propagation from injection into the Vedsted structure ((Mbia *et al.*, 2014) has indicated that this is very unlikely. A generic study on possible effects (Murdoch *et al.*, 2015) indicated that there could be effects in the form of increasing salinities in aquifers above the CO₂ storage, but the actual effect depends highly on local conditions. Alternatively, saline groundwater in the lower parts of an aquifer could be more directly displaced by migrating CO₂, though this would require specific local conditions. In any case if saline water enters the aquifer the effects would be very similar to the effects observed when seawater intrusion occurs in near-coastal systems, typically due to over-exploitation of the aquifer. The primary detrimental effect is an increase in chloride making the water unfit for drinking. In addition the accompanying sodium ion will trigger ion exchange reactions that will change the content of especially Ca, Mg, and K and cause precipitation of calcite (e.g. Andersen *et al.*, 2005). In addition seawater intrusion has been found to trigger release of trace elements (Wong *et al.*, 2010; Mora *et al.*, 2020) though this will be highly dependent on the specific aquifer and the concentrations of trace metals bound in the aquifer sediment.

1.1.6 Effects of displacement of methane

If the reservoir used for the injection of CO₂ contains methane, the methane could be displaced or it could mix with the CO₂, and in the case of leakage be carried into the groundwater system. Methane is

much less soluble in water than CO₂ increasing the relative chance of methane migrating as bubbles. The methane is a reduced carbon compound and may therefore act as electron donor for methanotrophic bacteria in the groundwater system. An experiment where methane was leaked into an aquifer for 72 days (Forde *et al.*, 2019) showed very minor effects on the water quality and a later sampling 4.5 years after the simulated leak showed that the water as well as the sediment chemistry was very close to the concentrations measured prior to the experiment. Still if leakage containing methane persisted for a longer period the redox state of the system would eventually change completely and Fe- and Mn-oxides would be reduced by microbes oxidizing the methane. The reduction of Fe- and Mn-oxides could lead to increased concentrations of trace elements in the water, depending on the trace elements bound to the oxides.

1.1.7 Effects of CO₂ and possibly associated gases on lake and stream water

If the leak from storage is large enough, bubbles of CO₂ and possibly associated gases could make it into fresh surface waters, in other words lakes and streams. Laacher See is a lake in a volcanic area where CO₂ from the volcanic activity is entering the lake (Gal *et al.*, 2011). The pH of the water in the lake ranges from 7-9 with the lower values at depth where the CO₂ concentration is highest, reaching a P_{CO2} of 0.023 atm. Surfacing bubbles are seen, but except for the increase in P_{CO2} with depth, the effects on the water chemistry within the water column are not clear. This is explained by effects from ongoing photosynthesis on pH, CO₂ and O₂. The electrical conductivity was generally high, and rather constant over depth, close to 600 µS/cm. Lakes with water of lower electrical conductivities, without the presence of natural CO₂, would presumably be more sensitive to sudden changes in the CO₂ level and related effects on CO₂. Oligotrophic lakes have lower consumption of CO₂ from photosynthesis and therefore also a naturally lower pH. In such lakes the entrance of CO₂ would further decrease the pH and lead to release of trace metals bound in or on minerals in the bottom sediment. A study looking into effects of increasing CO₂ in the atmosphere (Verspagen *et al.*, 2014) have found that in eutrophicated freshwater systems, CO₂ may limit the growth of algae so that when extra CO₂ is available algal blooms may become more severe. A similar effect would be expected if CO₂ enters a surface water system from below. Stream water chemistry should also change if CO₂ was entering in a specific place along the stream, presumably implying lower pH, higher alkalinity and higher concentrations of ions released from bottom sediments. Presumably the effects of associated SO_x and NO_x would be similar to the effects in freshwater aquifers with increased sulfate concentration and lower pH than with only CO₂, increasing the risk of higher trace element concentrations. In addition, the NO_x would probably oxidize to nitrate which could cause or increase eutrophication of the surface water body.

1.1.8 Effects of CO₂ and possibly associated gases on the marine environment

CO₂ leakage into the marine environment may affect both the sea-bed sediments, as well as the water column. The magnitude of the effects will be very dependent on whether the marine system is a close lagoon or the open due to the very different rates of water exchange – which are again very dependent on the weather. In a set of experiments from the Norwegian Storefjord (Ishida *et al.*, 2013) with benthic chambers, where the seawater inside was enriched in CO₂ to ~5,000 µatm and ~20,000 µatm, showed an increase in number of archaea (part of which produce methane) especially in the ~5,000 µatm experiments, accompanied by an increase in methane production rates. The rate of sulfate reduction

was ~twice as high in the chamber with ~20,000 μatm of CO_2 compared to the control. ATP, an indicator for the total microbial metabolism, was generally higher in the CO_2 amended chambers. According to Ishida *et al.* the changes may indicate decreases in the predator populations, but it could also be that the increase in CO_2 makes CH_4 production energetically favorable and the increased CH_4 can act as electron donor for sulfate reduction. There are also negative effects of elevated CO_2 on larger creatures such as fish (Ishimatsu *et al.*, 2005) and in general water-breathing organisms are more susceptible to an increase in CO_2 than terrestrial organisms because the difference in the P_{CO_2} of the body fluid of e.g. fish and the ambient medium is small (~4000 μatm), ~10 times smaller than for terrestrial animals. In a deep sea experiment where pools of liquid CO_2 resulting in CO_2 enriched surroundings (Barry *et al.*, 2013). Echinoderms (e.g. sea urchins) were the most sensitive while molluscs and crustaceans were highly tolerant. In addition to the direct physiological effects of higher CO_2 on the ecosystem, interaction between elevated CO_2 concentrations will lead to the effects discussed for the other systems where lower pH leads to increased trace element concentrations due to dissolution of carbonates and desorption from Fe- and Mn-oxides and clay minerals as well as silicate dissolution (Lichtschlag *et al.*, 2015). Likewise bubbling of CO_2 through the sediment may strip dissolved oxygen from otherwise oxic sediment, which could lead to reduction of Fe- and Mn-oxides and release of bound trace elements. The effects of associated SO_x and NO_x would be similar to the effects in fresh surface waters, lower pH, risk of higher trace element concentrations and eutrophication level.

2. Baseline assessment, monitoring options and methods

2.1 Definition of baseline assessment and general consideration for meaningful monitoring of aquatic systems

To monitor changes in a system, caused by leakage of CO₂ the baseline or the natural state of the system needs to be known, and it needs to be known in enough detail in time and space to enable the discrimination of an effect due to leakage. A measurable set of parameters will show different dynamics, some may naturally fluctuate chaotically with high amplitude, making them less useful for monitoring, while others may vary but predictably periodic and some parameters may be close to constant. Predictable parameters are not necessarily well suited for monitoring, because the sensitivity to CO₂ leakage for the parameter could be low, but sensitive predictable parameters may be less suited for monitoring because of limitations in analytical precision, the price of the analyses or difficulties in acquiring representative samples. Ideally a sensitive monitoring parameter should be easy/cheap to sample and measure, preferably remotely, for long unattended periods with adequate precision relative to the expected signal to show small changes that could give an early warning of leakage. Even with an ideal monitoring parameter it is still necessary to measure in the right place at the right time. If there were very clear indications from e.g. seismic mapping, of where a possible leak from the storage reservoir might occur, it could indicate that it was perhaps not the best site. And, if it was known when infrastructure components would fail, they would be changed beforehand. This implies that ideally, the right place at the right time is everywhere - all the time. This is close to impossible when monitoring the aquatic systems that could be impacted by leakage. In addition to this it is preferable that a leak is detected as early as possible, meaning as close to the storage reservoir as possible. The closer to the leaking source you are the less likely it is that the leaking CO₂ has spread out. Close to the source could be at depths of e.g. 500 m, but wells to this depth are very expensive and unless they are pumped the monitored area/volume is very small. At shallow depths, the leaking CO₂ has likely spread to a larger volume, but the effects on the water chemistry might also have been diluted.

2.2 Early assessment of sub caprock groundwater

If monitoring is defined as observations looking for changes over time, then this is not strictly monitoring, but it could be a component in the general assessment of the suitability of the site for CO₂ storage. If the storage reservoir is under a tight seal, the flow of groundwater passing through the reservoir should be extremely slow and the groundwater therefore very old, This implies that determining the age of the groundwater in the reservoir prior to anything else should give a very good indication of just how well isolated the reservoir is with regards to the environment. There are a number of parameters that can be used to date very old groundwater (IAEA, 2013). The simplest is ⁴He which is formed when radioactive isotopes of e.g. uranium and thorium present in the rocks undergo α -decay where a ⁴He nucleus is ejected from the radioisotope. The ⁴He nucleus unites with two electrons from the surroundings forming an atom of very inert ⁴He. Because ⁴He is inert it accumulates in stagnant water over time and may form a gas phase or enter into an already present gas phase such as natural gas. If ⁴He is present in a gas phase it will accumulate at the top of the reservoir similarly to the stored CO₂. The amount of ⁴He formed within a given time will depend on the concentrations of radioisotopes that

emit α particles. If the concentrations of uranium and thorium are known, the rate of ^4He production can be derived and used for estimating the groundwater age. It turns out that in practice it can be rather difficult to unravel from what geological formations the accumulated ^4He comes from. On top of this there are several small-scale interferences that may play a role, e.g. time of diffusion through the grains and release of old trapped ^4He as minerals dissolve. All these factors make it difficult to use ^4He for providing a precise groundwater age. However, a comparison of the ^4He concentration inside the closure intended for storage, with the ^4He concentration outside the closure, in the part with the most similar geology and hydrogeology, will give a qualitative indication of whether the water inside the closure is considerably more stagnant than the water outside. If a suite of noble gases and their isotopes are measured a more sophisticated analysis can be made (IAEA, 2013). There are additional methods that can be applied for dating old groundwater, namely measurements of ^{81}Kr and ^{36}Cl , and ^{234}U and ^{238}U but the upper limit of these methods is ~ 1 mill. years, which relates to the methods relying on radioactive decay which reduces concentrations beyond the limit of detection over time. Other factors also make these methods less suited, e.g. because ^{81}Kr requires that very large volumes of water are sampled, ^{36}Cl is prone to interference from varying chloride concentrations and ^{234}U and ^{238}U are not inert species.

2.3 Monitoring of injected and reservoir CO_2 composition for possible tracer components – intrinsic or added

Regardless of where in the aquatic system monitoring of the storage site takes place, monitoring of the composition of the injected gas, during and if possible in the reservoir, could imply the option of monitoring the aquatic system for specific associated components found in the injected gas and/or the gas in the reservoir. The associated gases may be reactive (SO_x , NO_x , H_2S etc.), non-reactive gases (e.g. N_2 , He , Ne) and isotopes (e.g. ^{13}C , ^{18}O , ^{15}N , ^{34}S) – in principle anything that is present in concentrations high enough to provide measurements that can discriminate leakage. Currently the composition of the injected gas is not known, but when it is, these additional possibilities should be considered in planning a monitoring program. There is also the possibility of deliberately adding a tracer to the stored CO_2 . This has been done in some of the onshore injection experiments (e.g. Trautz *et al.*, 2013), but for these, experimental simplicity has been the focus. The use of geochemical tracers that are dissolved in the CO_2 for a full-scale storage have been discussed for offshore storage (Roberts *et al.*, 2017), but most of the ideas are generally applicable to aquatic systems, though there are differences between the systems, especially when it comes to sampling. Roberts *et al.* (2017) discuss several options and find that helium and xenon isotopes (particularly $^{124,129}\text{Xe}$), and artificial tracers such as PFCs and deuterated methane (CD_4) are the most suitable added tracers. They are inert (CD_4 can be oxidized but the deuterium would still be present), have low environmental impact and are relatively inexpensive. They also find that SF_6 (used in several experiments) and ^{14}C are not suitable tracers for CCS due to environmental issues (e.g. SF_6 is an extremely potent climate gas) and many other potential tracers are simply too expensive when large amounts are needed. In a lab-study (Kilgallon *et al.*, 2018) on the addition of tracers to injected CO_2 , it was found that Kr , Xe and SF_6 all moved more rapidly than CO_2 through a porous sandstone – indicating that addition of noble gases to the injected CO_2 could provide early warnings of leakage. Together the two studies indicate that it is worth pursuing the possibility of using Xe as added tracer. If the injected CO_2 contains a good tracer, added or present anyway, it also means that it will be less necessary to use resources for determining which parameter changes related to reactions with CO_2 are the most sensitive in a given system. In

addition the tracer can be used to obtain information on degassing and mixing along the path of CO₂ migration (Ju *et al.*, 2020)

2.4 Monitoring at intermediate depth (above caprock, below fresh aquifer) - baseline assessment and monitoring options

At depths above the caprock and below the fresh aquifer groundwater flow is likely to be slow and chemical changes occur very slowly because the water chemistry is likely in a quasi-steady state relative to the minerals in the system. This on the other hand means that it would require long term monitoring to be certain that the system is actually stable. Anyway, a low level of intrinsic dynamics should make it easier to detect changes in water chemistry, but due to the probable lack of spreading from the leak zone near the source, combined with limited sample volumes from wells, the probability of an “intersection” between the leak and the monitoring well is low. In principle the sample volume can be increased by pumping, but this will also delete whatever signal is created by the leak and add costs. Despite the difficulties, monitoring at intermediate depths have a possibility of detecting leakage at an early stage. Depending on the hydrogeology of the aquifer above it might be possible to establish a network of constantly pumping wells to cover a large area, but costs would be high and the problem with dilution would still be there. This means that monitoring of the water chemistry at intermediate depth is probably more suited to places in the system where e.g. seismics or other geophysical measurements have indicated a higher probability of a leak. This could be where the caprock is thin or in a fracture zones or other features that could be sources of leakage.

To optimize monitoring with regards to analytical costs and sensitivity, the parameters most likely to change in case of leakage should be determined – assuming there is no tracer present in the CO₂. This could be done by subjecting sediment/rock samples from the cap rock and the intermediate depth formations to CO₂ and measure what is released, as done by Cahill *et al.* (2013), preferable in an improved version with a water composition mimicking the formation water. As described above the parameters most likely to change should then be evaluated with regards to analytical sensitivity, taking the background solution and background fluctuations into account. Assuming the water chemistry is stable it is not necessary to have a high sampling frequency to be able to separate a signal generated by leakage from background fluctuations. Therefore, the choice of sampling frequency is more a question of how soon after a leakage you want to detect it, given the difficulties of actually intersecting water chemistry effects of a leakage with a given well.

2.5 Freshwater aquifers (drinking water reservoirs) baseline and monitoring options

Freshwater aquifers are nearer to the surface and are much more affected by changes in precipitation patterns and land use, leading to changes in flow patterns, and groundwater chemistry. Furthermore, groundwater flow is generally faster compared to deeper aquifers. Depending on the magnitude and frequency of these changes as well as the actual groundwater flow, it may imply that the groundwater does not have time to reach a quasi-steady-state of water chemistry and minerals. This means that the water chemistry in a given observation point is more dynamic than in deep aquifers, making it more difficult to establish a baseline and more difficult to identify small changes in the water chemistry related

to CO₂ leakage. This makes it very important that the most sensitive parameters are determined, it could be in simple closed batch systems (Cahill *et al.*, 2013) or given the more accessible depth, it could be done in small scale field experiments. To compensate for the natural fluctuations, monitoring would need to be more frequent than in the deeper systems to be able to discriminate effects of CO₂ leakage. The normally higher level of knowledge with regards to flow patterns could be exploited by placing monitoring points in volumes of the aquifer where flowlines from a larger area converge, though this of course implies that the detection level will increase due to dilution by non-affected water. A specific case of this would be production wells which, depending on the pumping rate relative to the groundwater flux, draw in groundwater from a larger area. Produced water is normally treated to remove dissolved Fe and Mn by oxidation and precipitation of Fe(III) and Mn(III/IV) oxides. The oxides will bind Al and trace elements, also the ones potentially released due to a CO₂ leak. The amounts could be monitored by extracting samples of the sludge generated when the filters at the water works are backwashed. This could be a way of monitoring a large volume of the aquifer, the question is if the sensitivity is high enough. Sensitivity would depend on background levels and variations over time, but for many trace elements they tend to sorb to the oxides. If changes are observed in the extracts the individual wells providing water to the water works should be tested. This is of course only feasible if there are waterworks placed above/downstream of the storage site.

In general most drinking water reservoirs contain carbonate minerals implying that the effects of a CO₂ leak will only affect a small volume of the aquifer due to the buffering of the pH by carbonate dissolution, unless it is a very long lasting leak. Even if the dissolution of the carbonates leads to release of trace elements, without a decrease in pH, the trace elements will be highly retarded. An indication of the inherent difficulties in intersecting effects of leakage comes from an Australian experiment (Michael *et al.*, 2020) where 38 tons of gaseous CO₂ was injected 336-342 mbs in a fault zone, but was not detected within two months in near surface observations above the injection, presumably because shale and clay layers above the fault zone stopped or diverted the CO₂.

2.6 Shallow groundwater not used for drinking water – baseline and monitoring options

At least some shallow aquifers are found above the acidification front in the groundwater system, meaning that carbonates have been leached out. This makes the aquifer much more sensitive to effects of a CO₂ leak. Without carbonates the background electrical conductivity (EC) of the groundwater is normally very low, making it possible to detect CO₂ leakage from a simple and robust measurement of the EC. On the other hand, the instability in the groundwater chemistry is presumably even higher than in deeper drinking water reservoir, which probably implies that higher sample frequencies are necessary. An example of this is that in shallow aquifers close to the sea there is a large amount of dry deposition (dried sea salt) which can lead to large fluctuations in the EC, underlining that if monitoring is to be carried out on water samples the most sensitive parameters relative to background values and their variation need to be determined for the specific system. Because shallow aquifers are further from the source of the leak the probability that the CO₂ and derived effects has been spread to a larger area/volume is higher. Furthermore, costs of installation of monitoring wells to shallow depths are considerably smaller. The shallow depth could also make it possible to deploy fiber optics CO₂ sensors (Alonso, 2016) where the entire length of the fiber (up to 3,000 m in length) is used as a sensor. So far it appears that this is a prototype, but it appears promising. As for the drinking water reservoirs, it may be possible to exploit knowledge of the groundwater flow by placing wells or optical fiber sensors in

areas of groundwater flow convergence. Because of the shallow depth it would also be feasible to carry out field injection experiments to determine how far from a leak it is possible to measure the effect and to what extent the effect is transversally dispersed. This knowledge could then be used in the dimensioning of a monitoring network of wells or optical fibers.

2.7 Vadose/Unsaturated zone - baseline and monitoring options

The part of the subsurface aquatic system above the water table is called the unsaturated zone to indicate that the pores are only partially filled with water, which also means that they are in contact with the soil atmosphere and also the atmosphere above. Due to the large seasonal fluctuations in the CO₂ content of the soil atmosphere combined with occasional advective transport due to atmospheric pressure changes the unsaturated zone could be a difficult monitoring target. One feature that could perhaps be exploited is that in many clay rich areas of Denmark the agricultural fields are drained. For many fields this means that a network of drainpipes with a 20 m spacing covers the entire field. Monitoring of the drain system could in principle be in the dry season monitoring the gas phase, perhaps with sensors, perhaps aided by pumping. It could also be monitored in the wet season, when the drains are flowing, measuring on the water coming out of the system. The sensitivity could be a challenge due to dilution and because drains are placed in clay the leaking CO₂ may well find a path around the clay evading detection. It has not been possible to find any studies that have tested the idea but considering the very large infrastructure that could potentially be exploited for monitoring it seems worth exploring further.

2.8 Groundwater fed streams - baseline and monitoring options

Another distributed system are the streams that run through the landscape. Streams have been used in relation to CH₄ (Woda *et al.*, 2020), but apparently not for CO₂. Most streams are in contact with the groundwater and some stretches of the streams will have a base flow coming from the groundwater up through the bottom of the stream. Especially in the dry season, groundwater makes up a very large part of the flow in the stream. In terms of monitoring, these periods will presumably also be the periods with a relative stable water chemistry. Because it is surface water there will be fluctuations in pH, O₂ and CO₂ depending on surface temperature and insolation that affect the primary production in the stream. The water chemistry will also depend on which stretches of the stream that are fed by groundwater, which again depends on the given groundwater level, which will fluctuate as a function of the weather. The effects of leaking CO₂ would be diluted, to what extent depends on how far downstream the stream is monitored. In spite of this, and the intrinsic instabilities it might be possible to monitor effects of CO₂ leakage in groundwater fed streams, though small leaks would probably not be detectable due to dilution by water from non-contaminated stretches of the stream. If feasible, the big advantage would be that effects happening within a large volume/area of the aquifer is collected in the stream water. As for the other parts of the aquatic system the most sensitive parameters relative to the background variation in the parameters need to be determined. Whether the method is applicable will depend on the hydrogeology and hydrology of the specific site.

2.9 Lakes - baseline and monitoring options

Many lakes have inflow from streams, implying that the water chemistry in the lake is to some extent an average of the inflowing water, but on top of this are processes occurring within the lake. Due to the volume in the lake there will be a delay before any effects go above the limit of detection. Still, as for the streams, though even more pronounced, lakes have the advantage of accumulating effects from a large volume/area, though unless it is a small lake, there are no periods where the water is almost exclusively groundwater. Some lakes do not have inflow of surface water but are exclusively fed by groundwater and at the end of the dry season may contain a large proportion of groundwater. These lakes could potentially show changes in water chemistry related to changes occurring in the inflowing groundwater due to effects of CO₂ leakage. Again, knowledge on the most sensitive parameters should be acquired, but even with this knowledge detection limits are probably high due to a probably high proportion of uncontaminated water. In cases where the leakage flux is large enough for bubbles to reach the surface of the lake, the leak is visible, much like a leak in a bicycle tire tube. However, in a study on Laacher See (Gal *et al.*, 2011), where natural CO₂ enters the system it is actually difficult to precisely locate where CO₂ and underwater springs are emerging. Considering how accessible a lake is, compared to an aquifer, it indicates just how difficult it can be to locate very local leakage in an aquifer. Apart from water chemistry and direct observations of bubbles reaching the surface, it is also possible to monitor the eco-system if it contains species that are sensitive to effects related to CO₂ leakage. Using sensitive species implies that natural background variations related to weather patterns, population dynamics etc., for these species need to be established beforehand. As mentioned above, one of the effects of CO₂ leakage could be larger algal blooms, but it could be difficult to establish a detection limit due to the many other factors involved, e.g. the influx of nutrients from agriculture, which is a function of precipitation and the timing of it.

2.10 Marine systems – baseline and monitoring options

Marine waters in general are very dynamic with waves and currents constantly moving the seawater around locally as well as regionally. Near-coastal regions, fjords and especially lagoons may be much less dynamic, even close to stagnant in periods without storms. This implies that any attempts of monitoring in a marine system needs to be tailored to the local conditions. Many proposed storage sites are off-shore in abandoned oil fields and therefore some considerations on monitoring the marine environment are published (Arts *et al.*, 2011; Blackford *et al.*, 2013, 2017; Graziani *et al.*, 2014; Hannis *et al.*, 2017). The offshore monitoring proposed in Arts *et al.* (2011) is related to the Vedsted structure, where the marine system is the shallow water of Limfjorden. Here it is proposed to use direct gas detection (a low cost sensor is described by Graziani *et al.* (2014)), changes in seabed morphology, pH measurements in seawater and an assessment of impacts on vertebrate, invertebrate and microbial communities. This would require that baselines can be established for these parameters. In terms of observations these could be made from ships, ROV's, and buoys, using video cameras, CTDs, sampling of water, sediment and biota and continuous gas monitoring stations. A monitoring frequency is suggested, but the optimal frequency of observations for a given parameter should be established based on the natural background observations. In a study on the North sea (Hvidevold *et al.*, 2015) it is shown that the use of a circulation model in planning sensor placement can double the chance of detecting a leak. This is similar to using knowledge of the groundwater flow pattern for positioning observations in an aquifer.

Like for the other aquatic environments the most sensitive parameters relative to the background should be determined, by laboratory tests or probably better through small scale field tests. The most sensitive parameters are not the same from system to system. In fresh carbonate-free groundwater systems, the electrical conductivity is a parameter that is very easy to measure and CO₂ leakage gives a very clear signal, but due to the high salinity of marine water, the pH, P_{CO2} and total inorganic carbon are probably more sensitive to changes in a marine system, but these parameters are also more demanding to monitor.

2.11 Water sampling, methods; passive, automated, flow-through etc.

An important aspect of the monitoring of an aquatic system is how samples are acquired. Here sampling is not only seen as taking some water, preserving it and taking it to the laboratory. Some parameters can be measured by sensors ranging in complexity from relatively simple temperature and electrical conductivity probes to fiber optical CO₂ sensors 1000's of meters long, while other parameters require that water is taken out of the system and brought to the laboratory without changing the parameter you want to measure. From the previous sections it should be clear that the needed frequency of sampling is an issue. There are, however, several sampling methods that integrate the concentration over time or flux. Devices such as Peepers (Teasdale *et al.*, 1995) or devices related to the DET (Davison *et al.*, 1991) rely on passive diffusive equilibration over time into water or a gel behind a membrane. The DGT (Davison and Zhang, 1994) also relies on diffusion but is more active due to the presence of a sorbent, which also increases sensitivity. In principle a DGT could be placed in a waterworks in the piping from the production wells to monitor changes in water chemistry integrated over time. The Sorbicell (De Jonge and Rothenberg, 2005) integrates over the flux by sorbing what passes through the Sorbicell and determining the flux by the extent of dissolution of a salt. If an integrating type of sampling is used the question of sampling frequency becomes a question of how often the samplers are exchanged. In the context of monitoring CO₂ leakage the time or flux integrating samplers could be an advantage in e.g. groundwater system where the direction of flow varies over time or in streams where the stretches of the stream that are in contact with the groundwater may change over time. This way the chance of catching effects of a leak could be increased without increasing the sampling frequency, given that the sensitivity is still high enough. In cases where the parameter can be measured continuously by a probe or another type of sensor the question of sampling frequency becomes a question of how often the sensor needs to be calibrated and/or serviced to remove precipitates and/or biofilm affecting the measurements. Samples can also be acquired by automatic samplers and with current technology even slightly complex procedures such as cleaning and calibration of electrodes or probes can be done by robots. Likewise, there are several ways of having instrumentation and measurements available online, reducing the time used for collecting samples and facilitating observation in remote locations. Decisions on what sampling methods to use and how to implement them still needs to be a function of which parameters are most sensitive and the natural variation of these in time and space.

3. Corrective measures and remediation of unintended leakage

Natural gas storage in geological formations in closures under caprocks has been going on for many years (Benson and Hepple, 2005) with very few incidents. This implies that most of the experiences with geological gas storage come from these operations. More recently the EU FP7 project MiReCOL (Brunner and Neele, 2017) (<https://www.mirecol-co2.eu/>) has examined options for remediating leaks. Once a leak is localized, corrective measures and remediation will depend on the nature of the leak. If the leak is a result of a failure in a man-made installation, e.g. a well or mine, the possibilities of remediation and corrective measures are different from a situation associated with the geology of the site, e.g. undetected windows in or failure of the caprock, or leakage outside the closure due to overfilling or an unexpected migration path of the injected CO₂. This is also the categories used in the MireCOL handbook (MiReCOL, 2017) and web tool (<https://tool.mirecol-co2.eu>).

3.1 Possible corrective measures related to engineered systems (wells)

The MireCOL handbook (MiReCOL, 2017) contains details on a range of methods for remediating leaking wells. The background for part of the MiReCOL project comes from a leakage related to a blow-out of a well at a natural CO₂ reservoir (Karas *et al.*, 2016). Here a number of fluids with several chemicals (silicate, polymer, urea, formaldehyde) were injected via a new well, eventually, successfully blocking the leak – demonstrated by declining CO₂ in monitoring wells. Other methods described in the handbook are a number of squeeze cement methods where cement is forced into the leaks to block them, pressure and temperature activated sealants and silicate based sealants. Small cracks in concrete may self-heal (Yang *et al.*, 2009) and experiments indicate that larger cracks can self-heal if polymers are added to the concrete (Lee *et al.*, 2016). In addition, there are more physical methods such as patching of casing and tubing replacement. Other more novel chemical techniques discussed involve induced (by adding CaCl₂) precipitation of carbonate in fractures, a feature also seen in natural analogues (Rochelle and Milodowski, 2013) as well as formation of silica gels. In case remediation by repair is not possible the well may be plugged completely and abandoned.

3.2 Possible corrective measures related to near-surface contamination resulting from leakage associated with the site geology

Depending on the geology and where within the closure the leakage is situated, it may be possible to change the pressure distribution in the system (pumping one place and injecting in another) and thereby stop the leakage as summarized by Benson and Hepple (2005) for the gas storage in Galesville, IL, USA that leaked into a groundwater reservoir above it. In other cases, changing injection pressures have been able to stop the leakage. There are no examples of stopping geologically related leakage from a CO₂ storage site by injecting sealants or using similar approaches and it would probably be difficult due to the probably large affected area and volume at considerable depth making precise positioning difficult. The expected large areal extent of CO₂ leakage once it reaches a near-surface systems is derived from a suite of natural analogues described in MireCOL (2017) report.

If the leak cannot be stopped remedial measures also used in relation to contamination of aquifers can be applied. The simplest of these are diversion of the flow by pumping, blocking by sheet piling, or variations on pump-and-treat where the water is pumped up and possibly reinjected after treatment. The aim is to stop the contamination, before it reaches a surface water recipient or a water supply well or anything else that could potentially be damaged by the arrival of the plume generated by the CO₂ leakage. More elaborate methods involve injecting reactants to neutralize or bind the contaminant, or installing permeable reactive barriers with reactants that neutralizes, degrades or traps/binds the contaminant as it flows into the barrier material.

If the leak affects surface water, marine or fresh, the leak may be visible via bubbles or morphological features in the bottom sediments (e.g. pock marks) and therefore possible to locate and it may therefore be possible to stop the leak. However, since the leak will presumably have taken the easiest path to the surface at first, plugging the conduit may lead to new leaks emerging later in other places.

4. Suggestions for supplementary investigations

It appears that sampling and measuring for ^4He to obtain an indication of the tightness of the seal over the reservoir has some potential, however it requires that samples in which the ^4He is intact can be obtained. Is this feasible, what does it require in terms of drilling techniques, sampling equipment and sample preservation?

Monitoring has so far not been carried out in streams, though there is a potential for monitoring a large area/volume due to the convergence of the groundwater towards the stream before entering the stream. What parameters are most sensitive and when is the optimal period for monitoring? Should monitoring comprise several stations along the stream measured together to enable location of small differences along the stream?

Another system that could potentially be exploited for monitoring is the enormous drainage system underlying agricultural fields in many clay rich areas. Could the gas phase of the drainage system be monitored in the dry season? What are the most sensitive parameters in the water phase and when is the optimal time for monitoring – seasonally – and relative to precipitation events.

How can groundwater models be used to optimize the placement of monitoring sites and is it possible to include dilution in the models so that dilution can be taken into account when positioning monitoring wells.

CO_2 detecting optical fibers up to 3000 m in length have been developed – are they as promising as it appears – where can they be used – in streams, drains, shallow aquifers, the unsaturated zone?

Monitoring in all systems should be optimized by determining the most sensitive parameters relative to background variations for the site/system, but what methods are optimal – batch-tests, should samples be fresh and preserved, should tests be aerobic, anaerobic, use pure water or formation water, are column tests, tank tests or small-scale field tests preferable?

The option of adding tracers to the injected CO_2 appears promising based on the literature. Some of the expenses of adding tracer may be compensated by lower costs for determining the most sensitive/efficient parameters for monitoring.

Waterworks pump water from a large volume of the aquifer compared to monitoring wells. The water chemistry as such could perhaps be used for monitoring changes related to CO_2 leakage in the catchment. Perhaps the Fe- and Mn-oxide sludge from backwashing the filters at water works can be used for monitoring effects of CO_2 leakage in the catchment of the production wells. The question is what the sensitivity is, but since this method will monitor trace elements, there could be substantial delays before these arrived at the waterworks.

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