POTENTIAL IMPACTS ON GROUNDWATER RESOURCES OF CO_2 GEOLOGICAL STORAGE

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POTENTIAL IMPACTS ON GROUNDWATER RESOURCES OF GEOLOGICAL STORAGE

Background to the Study

Groundwater resources for potable supply represent a major potential environmental receptor in the context of risk mitigation for the geological storage of as a greenhouse gas, especially for onshore and near shore storage scenarios. Many of the onshore and near shore sedimentary basins around the world that hold significant potential for storage in deep saline formations (DSF), depleted hydrocarbon fields and coal beds may also contain important potable groundwater resources at shallower depths.

Potable groundwater resources represent a key risk receptor for geological storage schemes, particularly in onshore locations. Potential impacts on groundwater resources could be negative or positive.

Negative impacts could result as a consequence of the following potential mechanisms:

- Leakage of buoyant, free-phase from the storage site into potable aquifers – impacts could include acidification and mobilisation/increased concentration of other substances;
- Displacement of high salinity groundwater (‘brine’) from deeper storage formations into potable aquifers;
- Disruption of aquifer flow systems and groundwater discharge patterns (natural and artificial) by pressure perturbations due to geological storage.

It is also possible that geological storage could induce positive impacts. For example, pressurisation and brine displacement could support and improve abstraction rates in aquifers that have previously been over-exploited, or affected by drought. In this context, consideration would need to be given as to whether the increased groundwater pressure heads are temporary i.e. as free phase progressively dissolves in formation waters and/or is trapped by geochemical reactions, does the groundwater system return to pre-injection conditions?

The Association was commissioned by IEAGHG in February 2010 to provide a thorough review of existing information and published research on the potential impact of storage on groundwater resources. The study also aimed to highlight the current state of knowledge and/or gaps and recommend further research priorities on these topics.

Scope of Work

The study, comprising a literature review and desk-based assessment, aimed to produce a ‘high level’ overview of potential impacts on groundwater resources from storage operations, concentrating on DSF storage across a range of typical regional settings. The study also highlighted the current state of knowledge and/or gaps, recommending further research priorities where appropriate.

The study reviewed the potential global scale of the issue by considering the likely juxtaposition of geological storage schemes and shallow potable groundwater resources, taking into account both existing abstraction profiles and future groundwater resource potential. This review focussed on world regions where widespread carbon dioxide capture and storage (CCS) is likely to be implemented at an early juncture, such as the USA, Canada, Europe and Australia. However, developing countries with high industrial emissions and therefore CCS potential were also considered, e.g. China and India.

The study then addressed potential impacts associated with storage in DSF, since these provide the largest theoretical global storage capacity and could impact shallower groundwater resources via either direct leakage of stored or displacement of brine or increased pressure heads. The potential chemical and physical effects of (including impurities) and brine on shallow groundwater were considered. The review also assessed the possible relevance of information from natural or industrial analogues and long term oil-gas field operations, especially where gas or brine has been injected and/or where contamination of potable groundwater has occurred. The review included a review of actual or likely regulatory restrictions, in the various world regions, on storage operations that relate to groundwater protection.

The study considered case study examples of storage in a DSF, where preliminary modelling or assessment of potential leakage, pressurisation or brine displacement rates could be used to gauge potential risks (or benefits) to shallower groundwater resources. Mitigation and remediation options should also be assessed.

The contractor was asked to refer to the following recent IEAGHG reports relevant to this study, to avoid obvious duplication of effort and to ensure that the reports issued by the programme provide a reasonably coherent output:

- Development Issues for Saline Aquifer Storage, CO2CRC, 2008/12.
- Storage Capacity Coefficients, EERC, 2009/13
- Injection Strategies for Storage Sites, CO2CRC, 2010/04
- Pressurisation and Brine Displacement Issues for Storage in Deep Saline Formations, 2010/15
- Potential Effects of Impurities on Geological Storage, final report due 2011/04

Findings of the Study

Geographical Overlap of Storage and Groundwater Resources

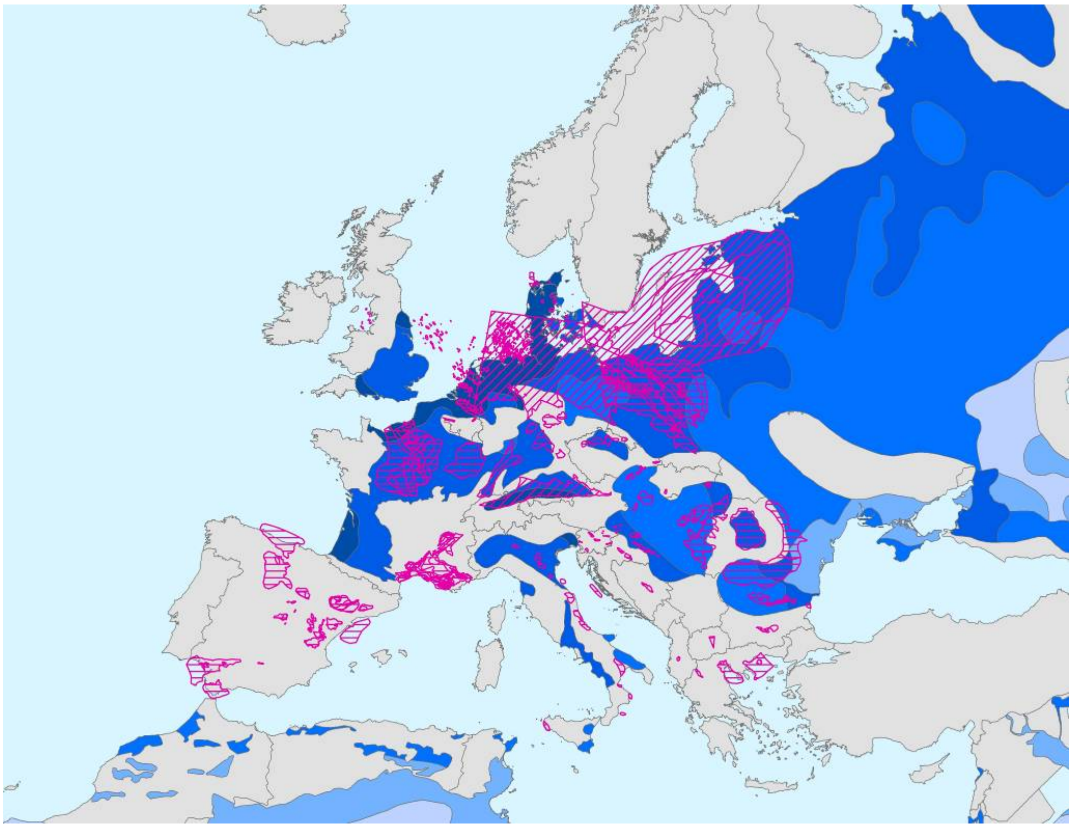
Data availability for DSF differs over different regions in the world, so instead of producing a worldwide map a regional approach was used. A GIS-based approach was used to look at the geographical overlap of resources by combining available storage atlases with information from the worldwide hydrogeological mapping and assessment programme, WHYMAP. This work focuses on Europe and North America, where detailed storage atlases are available, but also looks at areas where assessment is less fully developed, such as in Australia and China.

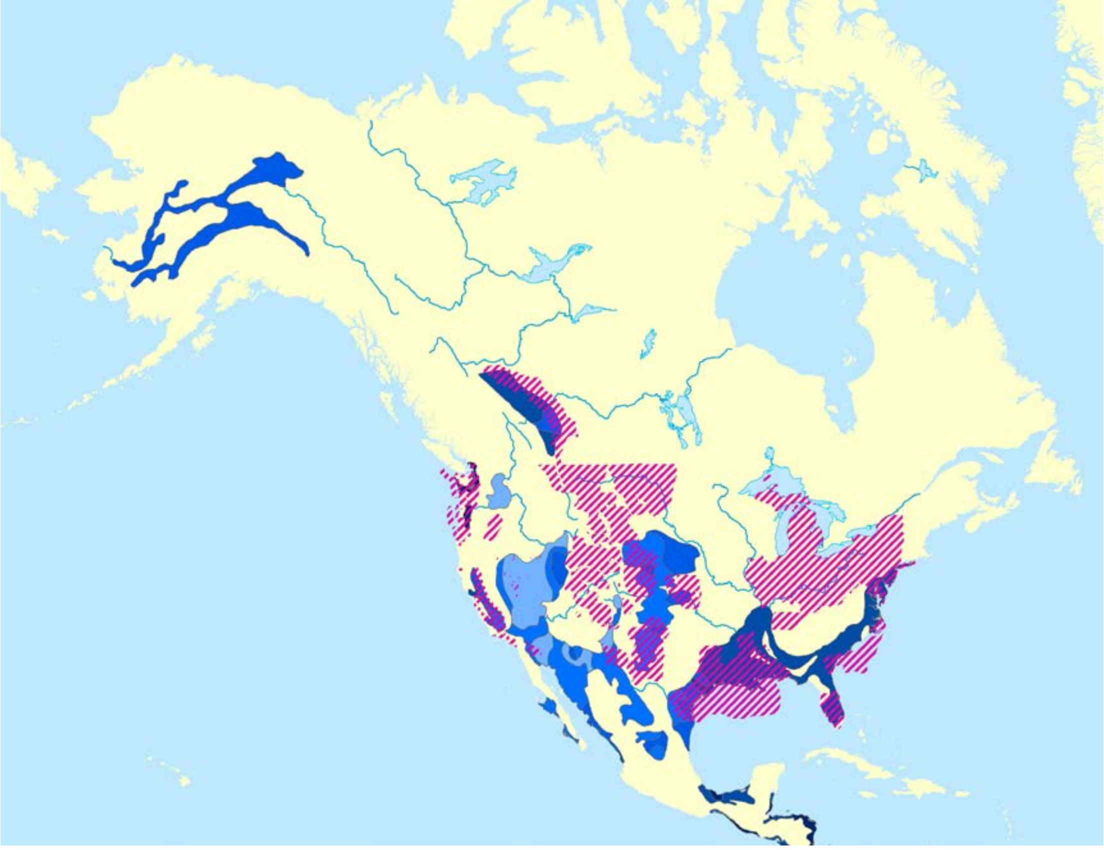
WHYMAP distinguishes between different types of aquifer:

- Large and rather uniform groundwater basins (aquifers and aquifer systems usually in large sedimentary basins that may offer good conditions for groundwater exploitation);
- Hydrogeological environments of complex structure where productive aquifers (including karst aquifers) may occur in close vicinity to non-aquifer strata;
- Areas with local and shallow aquifers in which low-porosity bedrock is exposed to the surface. In these areas, groundwater is limited to the alteration zone of the bedrock and overlying shallow layers of weathered bedrock.

Three maps were created for each area, showing the overlap of storage resources with each of the three types of potable aquifer system. Figure 1 shows the overlap with deep saline formations (DSF) and large uniform aquifers for Europe using data from the Geocapacity project and WHYMAP and Figure 2 shows the same for North America.

Figures 1and 2 Combining GEOCAPACITY (fig.1) and NatCarb (fig. 2) data on potential DSF, (indicated by hatched areas in **pink**) with WHYMAP thematic layers representing large, uniform freshwater aquifers (indicated by **blue** colours. The shades of blue represent different recharge rates).





This shows geographical overlap in central Europe of storage sites with large uniform freshwater aquifers; for some of these there are known to be impermeable layers between DSF and the shallower groundwater, but with deeper freshwater aquifers there is the potential for conflict with storage. Also important to note is that the WHYMAP data does not have any depth information, so whether or not there may actually be a conflict with the use of pore space will not be known until there is more site specific information.

The same analysis was carried out for North America, using information from the carbon sequestration atlas of the United States and Canada. The major difference between Europe and North America is that in North America DSF mostly coincide with ‘complex‘ freshwater systems as opposed to large, uniform freshwater aquifers.

Other regions were considered though detailed maps were not produced. In China where GeoCapacity data are available, the western and north-eastern basins identified as potential areas for storage coincide with large groundwater basins. In other areas, potential storage formations are found in areas with no groundwater resources identified or in areas of complex hydrogeological structure that contain important freshwater resources.

In Australia, the major onshore prospects for storage coincide with ‘major groundwater basins’ on WHYMAP, including the Great Artesian Basin. Here fresh groundwater is found at great depth and storage of in fresh groundwater is being investigated.

A typology of hydrogeological settings was developed based on the comparison of the storage and groundwater resources maps. These are meant to act as a general guideline that may be used in the selection and evaluation process of suitable storage areas, however on a local scale, the geological complexity and relative positions and depths of aquifers will determine the degree of potential impact. The typologies are:

a) areas with large and rather uniform freshwater, both shallow and deep aquifers overlying DSF;

b) areas with more complex hydrogeological structures where productive freshwater aquifers (including karst aquifers) may occur in close vicinity to non-aquiferous strata overlying DSF;

c) areas with DSF underlying areas with only local/shallow aquifers;

d) areas with formations containing saline groundwater in the vicinity or overlying DSF;

e) areas of over-exploited groundwater resources overlying DSF.

f) areas with no DSF suitable for storage.

The typologies can be used on a regional scale as a guideline to assess the types of impacts and potential conflicts to be considered in the site selection process. Analysis for selected countries Europe has been tabulated (Table 1) and map of location of typologies has been produced (Figure 2). The areas represented on the map coincide with all potential onshore

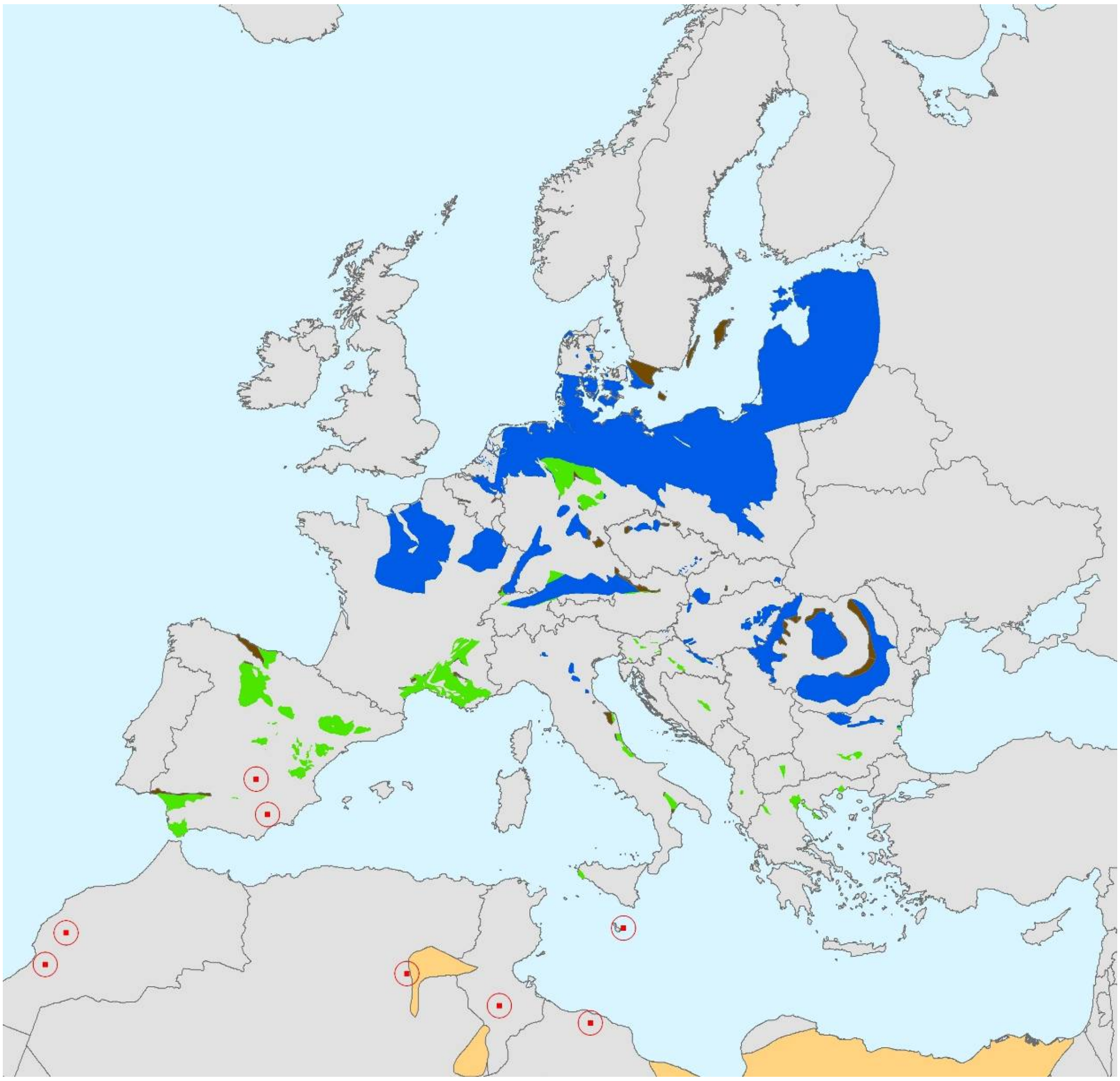
DSF from the Geocapacity project. The map of typologies does not infer whether storage is or is not possible, but is only what considerations of potential impacts need to be taken into account.

Table 1 Application of GEOCAPACITY and WHYMAP mapping to determine potential impacts of storage in DSF on potable groundwater resources.

GeoCapacity mapping	WHYMAP Basin	Geocapacity and WHYMAP identify potential conflict	Hydrogeological typology	Investigation of potential impacts on groundwater resources
United Kingdom				
Only offshore storage sites in oil and gas reservoirs are identified by GeoCapacity mapping. The Sherwood Sandstone Group (SSG) offshore offers the best prospect for storage.	WHYMAP identifies the entire southeast of England as a major aquifer basin. In reality only the Sherwood Sandstone Group and the Chalk are major basins. Only the SSG basins exceed 1000 m in depth over extensive areas to be suitable for CCS.	No, the offshore extension of the SSG was not identified by the GeoCapacity project.	a) Freshwater aquifer (Chalk) overlying deep saline formation in the Sherwood Sandstone Group. Onshore near outcrop this is freshwater but becomes saline where confined and offshore.	The CASSEM project investigated the impact of injection offshore in the Sherwood Sandstone group on shallow onshore groundwater systems. The groundwater model identifies possible impacts on fresh groundwaters.
FRANCE				
Three sedimentary basin (Paris, Aquitaine, Southeast) Geocapacity mapping identified Paris basin offering the best formations capacity for storage	Paris basin and Aquitaine Basin are identified as major groundwater bodies localized in sedimentary basins (clastic and carbonate formations). South east contains complex hydrological structure	The potential conflicts are mainly for the Paris Basin. The Aquitaine Basin has not been mapped because it has not been investigated for this purpose: (low industrial emitters and data on deep formations not available)	a) In the Paris Basin b) In southeast but low storage capacity f) in the Aquitaine Basin	Investigation on potential impacts of storage in Dogger formations on Albian shallow aquifer are conducted. Low permeable layers seems to be sufficient to avoid overpressure and leakage through natural pathways
GERMANY				
Onshore: sedimentary basins with a minimum depth of 1000 m (regional aquifers); offshore:	WHYMAP identifies majority of the sedimentary basins in Germany as “large and rather uniform groundwater basins”	Onshore, regional aquifers potentially suitable for storage largely coincide with areas of large rather uniform	a)In the North German Basin, the Franconian Basin, the Upper Rhine Graben and the South German Molasse Basin;	BGR is currently mapping distribution, thickness, and properties of the Oligocene Rupelium clay in North Germany,

potential storage structures (detailed aquifers)		freshwater aquifers as indicated in the Groundwater resources of the World Map	b) in the Thuringian Basin and in southern parts of the North German Basin; c) only locally.	the main barrier between fresh groundwater and DSF.
DENMARK				
On and offshore storage sites in both oil and gas reservoirs and aquifer structures with closure have been identified. Five regional formations offer prospects; the most widespread of which is the Bunter Sandstone Formation	Denmark is classified as large uniform freshwater aquifers and no local shallow aquifers. This is the case for the Pre-Quaternary chalk, limestone, marl, sand succession, but not for the glacial Quaternary aquifers	Offshore conflicts would be due to hydrocarbons in offshore structures, which is unlikely. Onshore there may be a conflict with the interest for the fresh groundwater resource.	Typology only applies to onshore a) In the main part of the country. b) In the Quaternary aquifers in Eastern Jutland. c), d) and e) only occur locally	Potential impacts have been investigated for the Vedsted structure (onshore).

Figure 2 Map of different typologies in Europe. Blue: overlap with large and rather uniform freshwater aquifers. Green: overlap with more complex hydrogeological structures coinciding with deep saline formations. Brown: overlap with local/shallow aquifers coinciding with deep saline aquifers. Grey: overlap with no deep saline formations suitable for storage. Orange: overlap with areas of saline surface water. Red symbols: areas of heavy groundwater abstraction/ overexploitation



Mechanisms of Potential Impact on Shallow Water

There are many possible impacts of storage on potable groundwater resources. This can be directly from the introduced media; and impurities from capture processes. Other substances may be produced from the interaction of and impurities with the reservoir rocks and overburden. The saline formation waters and any reaction products may be displaced into the groundwater source. There may also be immiscible hydrocarbons present, which may become altered and mobilised by . Then there are indirect pressure effects due to injection of into the subsurface.

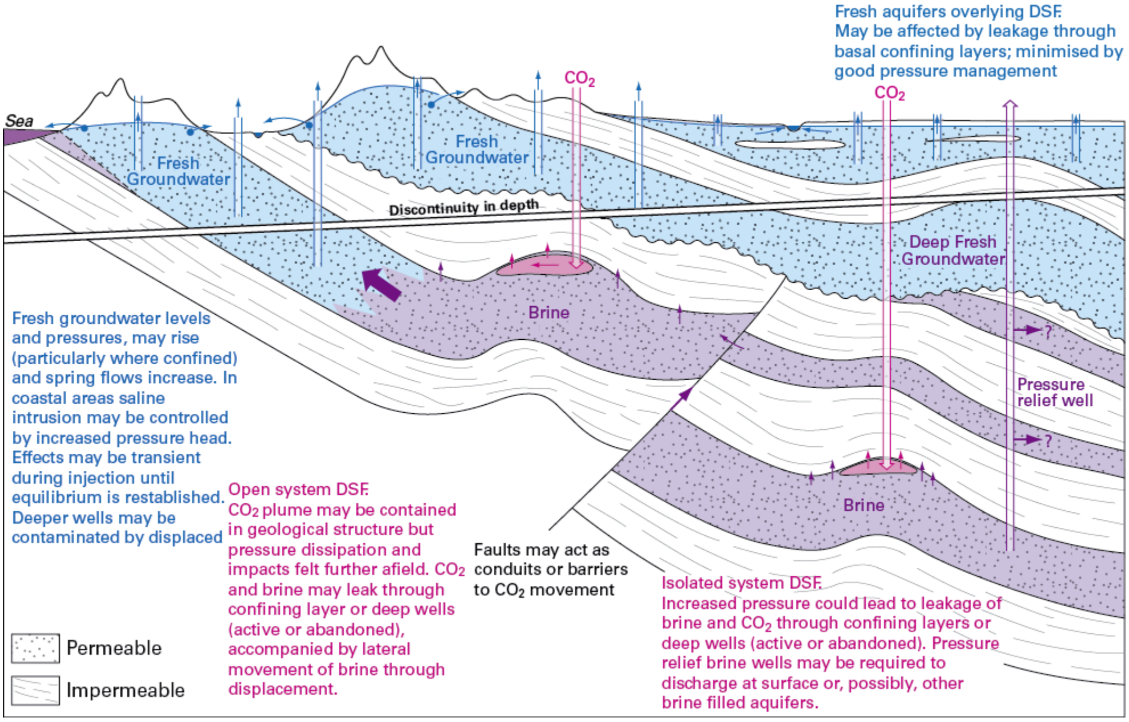
These impacts may all potentially affect groundwater, which may in turn react and interact with the shallow aquifer rocks and biota contained within them. Impacts resulting from these interactions may relate to groundwater availability and quality.

Natural analogues are used to show hydrodynamic and chemical affects caused by natural seeps as well as potential impacts based on laboratory experiments and thermodynamic computer simulations.

Analogues considered when looking at pressure effects are natural gas storage sites as this will correlate with an effectively instantaneous injection of compared to the gradual accumulation seen in natural accumulations of

Leakage mechanisms are described in Figure 3. Mechanisms related to closed or isolated systems are distinctly different from open systems, although a gradational spectrum between the two is likely.

Figure 3 Potential leakage mechanisms and impacts of storage on shallow groundwater.



Fresh aquifers overlying DSF. May be affected by leakage through basal confining layers; minimised by good pressure management

Fresh groundwater levels and pressures, may rise (particularly where confined) and spring flows increase. In coastal areas saline intrusion may be controlled by increased pressure head. Effects may be transient during injection until equilibrium is restablished. Deeper wells may be contaminated by displaced

Open system DSF. CO_2 plume may be contained in geological structure but pressure dissipation and impacts felt further afield. CO_2 and brine may leak through confining layer or deep wells (active or abandoned), accompanied by lateral movement of brine through displacement.

Faults may act as conduits or barriers to CO_2 movement

Isolated system DSF. Increased pressure could lead to leakage of brine and CO_2 through confining layers or deep wells (active or abandoned). Pressure relief brine wells may be required to discharge at surface or, possibly, other brine filled aquifers.

In closed systems, pressure management, through pressure relief wells may be needed to avoid creation of leakage pathways through fracturing of confining layers or reactivating existing fractures. Disposal of resulting saline water may be environmentally problematical and disposal in other saline formations will raise similar pressure management issues. Any leakage that might occur could be captured by overlying confining layers, possibly accompanied by a change of state from supercritical to gaseous , and corresponding large increase in volume, as it moves up the sequence.

Similar issues are considered in an open system, though lateral migration of and brine displacement are likely to be more dominant. Pressure effects have a much larger footprint than the plume and pressure dissipation may manifest itself with rising groundwater levels, both fresh and saline, and may result in increased spring discharges. An additional benefit in coastal regions may be pushing back of the saline/freshwater interface.

If migrates from the storage formation or if brine is displaced into an overlying aquifer as a result of pressure changes, it may potentially impact on groundwater by modification of pressure head, increased salinity and acidity as well as mobilisation of metals and other impurities.

When considering the chemical processes that may take place in the event of leakage into groundwater, natural analogues considered are laboratory experiments, industrial analogues: such as acid-gas injection, -EOR and brine injection; and natural accumulations. Laboratory experiments may show what reactions may take place, but are of limited use as the reaction rates are several orders of magnitude higher compared to field conditions. Natural accumulations are not considered a useful analogue for storage as they exist mostly in fractured volcanic regions; however, they are useful as an analogue for potential leakage into potable groundwater.

Arrival of to a balanced system may cause changes in the physical and chemical conditions, thereby modifying water-rock equilibrium. In fresh groundwater, the geochemical reactions occur under circumstances where only minor chemical reactions (e.g. mineral dissolution, ion desorption) could potentially affect the water quality. In DSF chemical reactivity with the host rock around injection points are not analogous to potential effects on fresh groundwater because of differences in brine chemistry, pressure conditions, and the rate of injection.

In the case of a release of into a freshwater aquifer, the most important chemical processes are considered to be:

- Modifications in flow, which plays a role in the transport of elements, and a contribution of constituents from brines seeping through matrix or along faults;
- Migration of dissolved organic compounds enriched in , as is an excellent solvent for organic compounds;
- Mineral dissolution increasing the mineralisation of the water and the release of associated trace elements;
- Precipitation of carbonates and other secondary minerals resulting from rock alteration
- Co-precipitation and sorption of metals, which may act as either a contaminant trap or source
- Changes in microbiological activity
- Aqueous complexation of cations that can promote the solubility (organic, chloride, bicarbonate complexes)

All the above mechanisms are interdependent, each affecting the others. The processes depend on physicochemical conditions of the aquifer (temperature, pH, Eh), flow directions and behaviour of pollutants and may potentially alter water quality. Therefore the exact effect would be very site specific, showing the need for specific case studies over the most realistic time scale possible to exemplify the combined effects that could occur.

Modelling Case Studies

A review of modelling studies was carried out, looking at chemical modelling, hydrodynamic modelling and modelling limitations.

There are a limited number of studies dealing with the effect on groundwater, as most deal only with reactivity within the storage reservoir, however, an analogy with mechanisms associated with leakage into a shallow groundwater aquifer is possible. The geochemical models take into account the initial mineralogy, the possible thermochemical reactions, the kinetic rate of the reactions and surface complexation. The chemical impacts considered are acidification and the release of solutes (possibly hazardous trace elements). These effects are extremely site specific, for example a serious problem could be the dissolution of pyrite, caused by acidification, with the consequent release of arsenic.

Hydrodynamic models show the effect of pressurisation, to be over a much larger area than the associated plume, however, brine displacement was found to be only over a very small distance and not likely to affect groundwater resources. Brine displacement through the caprock would be possible with permeabilities greater than 10^{-18} , though pore velocity is extremely slow. The largest risk to shallow groundwater would be through fast flow conduits, if they exist in the system, such as faults.

Also to be noted is that most models assess geochemical and hydrogeological effects separately and that the modelling of reactive transport for multiphase flow is still under active research and development.

Regulatory Constraints

A number of countries have developed dedicated storage regulations, including the European Union, the United States and Australia. Some measures relate in particular to groundwater protection in addition to more general measures such as prevention of any potential leakage. The most recurrent are dedicated characterisation and monitoring of surrounding fresh groundwater. The regulations for each of the countries considered are summarised in the report.

Existing groundwater protection rules show that there could be some legal barriers against the storage of in deep saline aquifers. Such barriers would need to be amended to allow the injection of such as in the European Directive for storage. Alternatively, injection is likely to depend on an authorisation or permit by authorities in charge of the protection of groundwater.

Mitigation and Remediation Options

Assessing the risk of leakage associated with the geological storage of is vital for the long-term fate of the stored as well as for the public acceptance of this concept as a means of reducing greenhouse gas emissions. storage projects should be carefully designed to minimise any need for remediation and mitigation options, however mitigation and remediation strategies need to identified.

The report gives a comprehensive review of the current state-of-the-art in leakage mitigation and remediation strategies. Table 2 shows examples of mitigation options for shallow groundwater

Table 2 Examples of mitigation options for shallow groundwater potentially affected by geological storage projects (non-exhaustive list)

	Options	Methods / Requirements
intrusion	Stop the injection of	Immediate implementation
	Extract -rich water from shallow GW and purify	Extractions wells, degassing, Injection wells
	Inject water in shallow GW to enhance the dissolution of and residual trapping	Injection wells
	Treat the contaminants dissolved in GW	'Pump and treat' methods (fluid extraction); flow-through system (reactive barrier); additives-based
	Place a hydraulic barrier to immobilize the contaminated plume	Injection wells
	Place a hydraulic barrier to stop the leak by increasing the pressure upstream	Injection wells
	Place a chemical barrier to stop the leak	Create a chemical sealant barrier upstream of the leak
	Consume by the biomass	Passive method: Natural biogeochemical process
	Extract (gas or dissolved) from shallow GW or directly the reservoir	Extraction wells - require drilling wells that intersect the plume
Pressure increase	Extract water from shallow GW	Extraction wells
Wellbore leak	Repair of wellbore leaks (active, monitoring, or abandoned well)	Immediate implementation
	Plug the leaking well	Cement plugs or chemical sealants
	Implement well intervention/recompletion techniques	Partial isolation and/or side-tracking of an existing well
	Place an external sealing	Cement plugs or chemical sealants
Lateral migration	Stop the injection of	Immediate implementation
	Remove stored	Extraction wells

	Place hydraulic barriers by water injection upstream	Extraction wells

For lateral migration of or brines, some remedial options include the use of hydraulic barriers by injecting water upstream or removing some of the stored and reinjecting it into another zone.

In the case of contamination of groundwater resources, “pump and treat’ methods could be employed. For , this could include both gas phase pumping and groundwater extraction. Other possible methods are additive-based, flow-through treatment barriers for removal of trace elements mobilized by groundwater acidification and hydraulic barriers to contain the plume of contaminated water.

From leakage mitigation scenarios examined, the results indicate that the combination of saline aquifer pressure reduction and groundwater pressure increase is the best mitigation strategy against leakage. In addition, having more than one well for controlling leakage can help continue to prevent/reduce leakage in the event that one of the well fails, although this approach has a cost implication.

Pressurising groundwater to reduce or stop leakage and flow from the DSF has the advantage of increasing the pressure and the supply of potable water, but the question remains as to the availability, treatment and compatibility of the injected water with the water in situ to avoid altering the water quality. If these conditions are met, then this strategy may be preferable compared to reducing the saline aquifer pressure, as production of brine from the DSF is associated with production of either dissolved or free (plume). Reducing the injection rate will prolong the injection phase of the project; this may necessitate the use of multiple wells distributed within the field and further simulation in order to understand dynamics and leakage in this situation.

Research is currently ongoing on various aspects of leakage, including possible leakage paths, impacts of leakage on the surrounding environment and possible mitigation and remediation methods. Numerical simulations as well as semi-analytical and analytical modelling techniques have been used to predict or estimate cross-formational leakage rates of and to model various leakage and remediation scenarios.

Careful design of storage operations should be conducted to minimise any need for remediation and mitigation options, as these depend on a range of site-specific conditions, which are difficult to obtain. Restoring certain sites may not be possible due to hydrogeological limitations.

Expert Review Comments

Expert comments were received from 6 reviewers, representing industry (corporate sponsors of IEAGHG) and academia. The overall response was positive and highlighted a significant contribution to this area of storage research.

Key technical suggestions made by reviewers included more information in the typology section and following the review a typology map for Europe was produced. It was suggested that there be included more information on Australian issues as the geology and situation is very different from North America and Europe; this includes deeper freshwater sources as found in the Great Artesian Basin. When looking at natural analogues it was suggested that the limitations of this approach as well as specific correlations with storage could be made clearer. All of these issues were addressed in the final report.

Conclusions

Areas of geographical overlap between potential DSF storage and overlying fresh water aquifers have been identified by combining available datasets to map the global and regional juxtaposition of groundwater resources and potential storage sites. A classification scheme has been developed for the various geological settings in which overlap may occur. This was then tested for Europe where groundwater resources and potential storage sites are relatively well documented and understood. In central Europe, potential storage areas coincide with areas of large, uniform potable aquifers and this could lead to potential conflicts in instances where potable aquifers extend to considerable depth, or low permeability caprock layers are scarce. In southern Europe, more complex aquifer systems (e.g. limestone karst) tend to coincide with potential storage resources. In North America it is the reversed situation, with the majority of geographical overlap occurring between complex aquifer systems and DSF and in Australia, there is overlap with deep freshwater aquifers. The situation in Australia is interesting to note as deep freshwater may coincide with potential DSF.

Two approaches have been used to address potential impact mechanisms of storage projects on the hydrodynamics and chemistry of shallow groundwater. The first approach classifies and synthesises observations of water quality changes obtained in natural or industrial analogues, and in laboratory experiments. The second approach reviews hydrodynamic and geochemical models, including coupled multiphase flow and reactive transport, with the aim of linking leakage scenarios to possible impacts on groundwater resources.

The findings of the study emphasise the current state-of-the-art regarding potential groundwater resource impacts to be based largely on theoretical considerations. Selection of appropriately characterised and risked storage sites should negate concerns over potential impacts on groundwater resources. Nevertheless, further research is required to better characterise potential leakage mechanisms and impacts, to inform the risk assessments required by regulators.

Possible mitigation options to stop or control leakage have been discussed. In particular, the effect of pressure in the host DSF and potential effects on shallow fresh water aquifers have been examined. In the literature, such options are mainly addressed through modelling approaches. Techniques for proper and effective mitigation of the impact of stored on fresh water resources have been identified. These include: interception and extraction of from the plume or brine from the storage reservoir; increase in pressure in formations above the leak; isolation or shut-off of leaks in accessible locations; creation of hydraulic barriers within the reservoir; and treatment of contamination caused by leakage, either in-situ or by ‘pump and treat’ technologies. Increased monitoring and investigation can also be regarded as an effective mitigation option in some instances.

Formulation of a credible mitigation strategy may form an important element of regulatory requirements for commercial scale storage sites. Also to be noted is that there is currently limited practical experience of storage on the industrial scale and knowledge of managing potential impacts is largely theoretical based on modelling studies.

Recommendations

Potential impacts on groundwater will continue to be of importance at the majority of storage sites, especially onshore. As CCS projects progress, more data on groundwater monitoring as well as any adverse effects will become available. IEAGHG should ensure that adequate attention is paid to these topics through future storage network meetings and by the study programme. Further work is needed in the area of mitigation and remediation, which could be covered as part of a future IEAGHG study.

The European Network of Excellence on the Geological Storage of
Association

POTENTIAL IMPACTS ON GROUNDWATER RESOURCES OF STORAGE

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List of acronyms

BHP:	Bottom Hole Pressure
CCS:	Carbon Capture and Storage
CCSD:	Directive on the geological storage of
DIC:	Dissolved Inorganic Carbon
DSF:	Deep Saline Formation
ELD:	Environmental Liability Directive
MCL:	Maximum Contaminant Level
IPCC:	Intergovernmental Panel on Climate Change
SC-:	Supercritical
SDWA:	Safe Drinking Water Act
TDS:	Total Dissolved Solutes
UIC:	Underground Injection Control
USDW:	Underground Source of Drinking Water
US EPA:	United States of America - Environmental Protection Agency
VEF:	Vulnerability Evaluation Framework
WFD:	Water Framework Directive
WHYMAP:	World-wide Hydrogeological Mapping and Assessment Programme

Executive summary

OBJECTIVES OF THE PRESENT STUDY

The IEA Greenhouse Gas R&D Programme (IEAGHG) commissioned the Association to undertake a literature review on potential impacts on groundwater resources of storage, with the aim of summarizing state-of-the-art knowledge and identifying knowledge gaps and research priorities in this field. This study is based on work undertaken by various members for the IEAGHG study contract.

In order to reduce atmospheric emissions of from human activities, Carbon dioxide Capture and Storage (CCS) is considered as one of the promising options. One of the main concerns associated with the geological storage of is that may leak from the intended storage formation, migrate to the near-surface environment, and eventually escape from the ground. This is a concern because such leakage may affect existing energy, mineral and groundwater resources and it may pose a hazard once at the ground surface. Even low but continued leakage is undesirable and would undermine the purpose of CCS by releasing the greenhouse gas back into the atmosphere.

The potential impacts of storage on shallow groundwater[1] are the object of current investigations because freshwater aquifers located above possible geological storage sites may be used for drinking water, industry and agriculture.

Leakage of in supercritical and gaseous form from onshore or near-shore deep saline aquifers or of the associated brines is frequently cited as a risk for the overlying or neighbouring potable groundwater resources. To date, the impact of storage has mainly been studied at near-well and reservoir scale, whereas risks in the larger context of regional multi-layered groundwater systems have not yet been widely assessed. Only recently, studies have focused on multi-aquifer systems comprising both deep saline formations (DSF) and potable groundwater resources using hydrodynamic and hydrochemical modelling. These studies and reviews have identified several mechanisms that can potentially lead to negative impacts on groundwater quantity and/or quality.

The main objectives of the present study are therefore (1) to identify geological settings with potential juxtaposition of shallow potable groundwater resources and storage sites, (2) to provide an overview of potential mechanisms of quantitative and qualitative impacts of storage schemes on adjacent aquifers, (3) to assess the relevance of those mechanisms through the analysis of results obtained on natural and industrial analogues, (4) to demonstrate the relevance of the potential impacts as identified/quantified by modelling approaches, (5) to address the relevance of potential impacts with respect to current regulation on storage and on water protection and

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[1] *Shallow aquifers* are here understood to be the groundwater bodies that contain fresh, potable groundwater (usually shallow), whereas *Deep Saline Formations* (DSF) are the loci of underground storage in deep underground rock formations composed of permeable materials and containing highly saline fluids deeper than 800 m to avoid CO$_2$ in gaseous phase (IPCC Glossary).

environmental impact assessment regulations, and (6) to discuss the remedial actions that can be implemented if leakage of or brine is detected.

This study is based on existing published and unpublished original works and reviews. The present report summarizes the state-of-the-art, and identifies knowledge gaps and research needs in this field.

JUXTAPOSITION OF POTABLE GROUNDWATER RESOURCES AND STORAGE SITES

In order to establish a guideline to assess the types of potential impacts of storage on freshwater resources on a regional scale, this study investigated the juxtaposition of deep saline formations (DSF), potentially suitable for geological storage, and potable groundwater resources.

Identifying the distribution and extent of geological reservoirs potentially suitable for storage of has been undertaken in some regions, but not in others. Focussing on the big industrial carbon emitting nations this study has collected data compilations from around the world, and where publically available, regional scale GIS representations of the distribution of potential reservoirs – GEOCAPACITY for Europe (and China) and NATCARB for North America.

At the global scale, the extent and nature of groundwater resources have been illustrated in the “World-wide Hydrogeological Mapping and Assessment Programme (WHYMAP)” launched in 2000 (.whymap.), and groundwater maps widely exist. However, the WHYMAP groundwater resources maps currently do not include information on multi-aquifer systems, i.e. the depth of freshwater aquifers and their juxtaposition to deep saline formations with potential for storage.

Comparison of the WHYMAP and the GEOCAPACITY datasets reveals that, in Central Europe, most deep saline formations suitable for storage onshore coincide with areas of “large, uniform freshwater aquifers” present in the major sedimentary basins. In some of these areas, DSFs are clearly separated from shallow aquifers by impermeable strata. However in other areas, deep freshwater resources exist where conflict could occur with deep storage projects. Lateral extensions of deep saline formations into freshwater aquifers are also found where potential for storage exists. In Southern Europe, deep saline formations identified coincide with more “complex freshwater aquifer systems”, including karstic systems. In parts of Scandinavia GEOCAPCITY data do indicate potential for storage, where WHYMAP identifies the presence of “local/shallow aquifers”.

Overlaying WHYMAP information on groundwater resources in North America with data of the “Carbon Sequestration Atlas of the United States and Canada” reveals a major difference to Europe. Whereas in Europe regions with deep saline formations suitable for storage mostly coincide with areas of large, uniform freshwater aquifers, in the U.S. and in Canada deep saline formations often coincide with areas with “complex” freshwater aquifer systems.

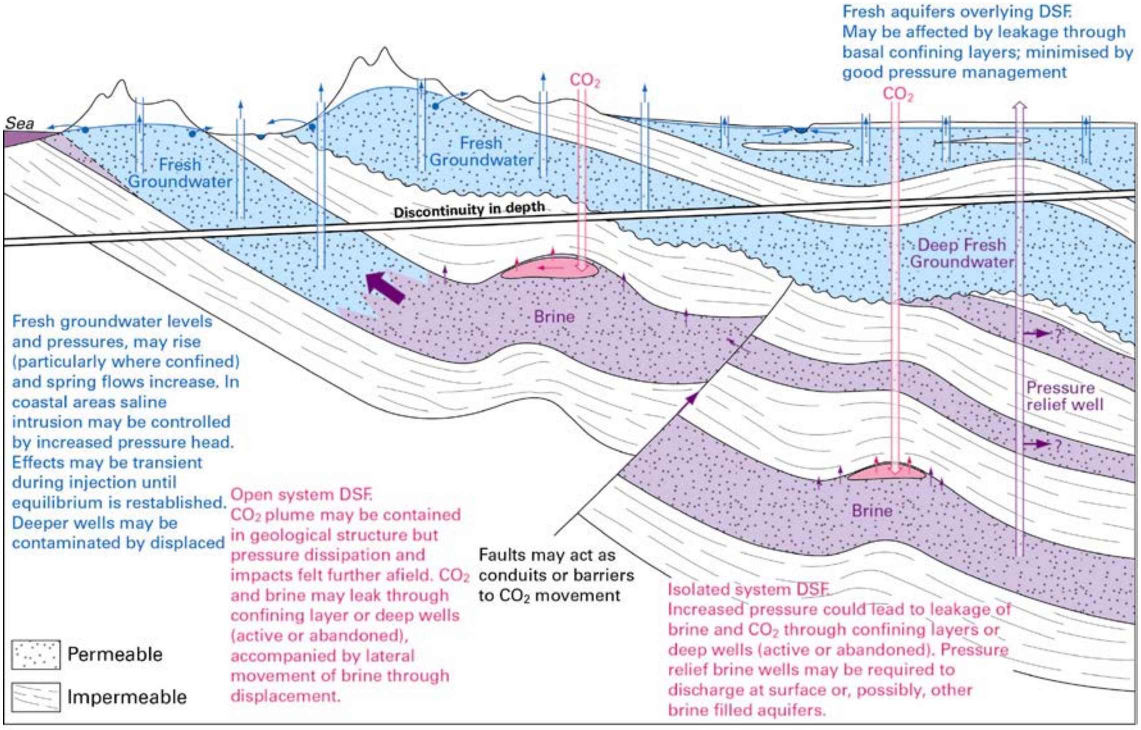
In China where GEOCAPACITY data are available, the western and north-eastern basins identified as potential areas for storage coincide with large groundwater basins. In other areas, potential storage formations are found in areas with no groundwater resources identified or in areas of complex hydrogeological structure that contain important freshwater resources.

A typology of hydrogeological settings was developed as a general guideline that may be used in the selection and evaluation process of suitable storage areas. However, on a local scale each site's geological complexity and the relative positions and depths of deep saline and freshwater aquifers will determine the degree of potential impacts.

POSSIBLE LEAKAGE & IMPACTS MECHANISMS

migration outside of the limits of the storage formation can potentially occur either in the vertical or lateral directions. In the first case, moves vertically upward either along a fault in the overlying geological strata or through a poorly sealed well (abandoned, monitoring, active). The second case relates to the lateral confinement of the storage structure and refers to the migration of the injected from the injection site/well through the formation either to the surface or until it reaches a confining structure.

Potential leakage mechanisms and impacts are shown schematically in Figure 1. Here isolated system DSF is distinct from open system DSF, although a gradational spectrum between the two is likely.



Fresh aquifers overlying DSF. May be affected by leakage through basal confining layers; minimised by good pressure management

Fresh groundwater levels and pressures, may rise (particularly where confined) and spring flows increase. In coastal areas saline intrusion may be controlled by increased pressure head. Effects may be transient during injection until equilibrium is restablished. Deeper wells may be contaminated by displaced

Open system DSF. CO_2 plume may be contained in geological structure but pressure dissipation and impacts felt further afield. CO_2 and brine may leak through confining layer or deep wells (active or abandoned), accompanied by lateral movement of brine through displacement.

Faults may act as conduits or barriers to CO_2 movement

Isolated system DSF. Increased pressure could lead to leakage of brine and CO_2 through confining layers or deep wells (active or abandoned). Pressure relief brine wells may be required to discharge at surface or, possibly, other brine filled aquifers.

Figure 1: Schematic representation of potential leakage mechanisms and impacts of storage on fresh groundwater (not to scale).

In isolated systems, pressure management will be important to avoid creation of leakage pathways via the fracturing of confining layers or the activation of existing fractures. This may need to be done through pressure relief wells discharging to the surface or into other saline formations. Disposal of this saline water may be environmentally problematical and disposal in other saline formations may raise similar pressure management issues unless it is managed in a more disseminated manner. Any leakage that might occur could be captured by overlying confining layers, possibly accompanied by a change of state from supercritical to gaseous (and large increase in volume) as it moves up the sequence.

Similar issues need to be considered in an open system DSF but lateral migration of the and brine displacement will play a more dominant role. Pressure effects will be felt many kilometres distant even if the plume is effectively constrained. Pressure dissipation may manifest itself with rising groundwater levels, both fresh and saline, and may result in increased spring discharges. An additional benefit in coastal regions may be the pushing back of the saline/freshwater interface.

If escapes from the storage formation (DSF) or if brine is displaced into an overlying aquifer as a result of pressure changes, it may potentially have impacts on groundwater, including modification of pressure head, increased salinity and acidity (reduced pH) as well as mobilization of metals and transport of contaminants with the , such as dissolved organic compounds. The processes behind all these potential impacts, which may affect groundwater resources (quality and quantity), must be understood to assess correctly the potential impacts on fresh groundwater resources.

The arrival of in a balanced system may cause changes in the physicochemical conditions, thereby modifying the water-rock equilibrium. In fresh groundwater (potable water), the geochemical reactions occur under circumstances where only minor chemical reactions (e.g. mineral dissolution, ion desorption) could potentially affect the water quality. Conversely, the chemical reactivity with the host rock around injection points in deep saline formations are not analogous to potential effects on fresh groundwater because of differences in brine chemistry, pressure conditions, and the rate of industrial injection.

Natural analogues and field experiments supplement geochemical understanding and predictions for the assessments of potential impacts in the long-term based on laboratory experiments and thermodynamic computer simulations.

Following an accidental migration of into freshwater aquifers, the most important changes would potentially be:

- *Modifications in flow,* which plays a role in the transport of solutes, and a contamination from brines seeping through leaking wells, the matrix or along faults;
- *Migration of dissolved organic compounds*, as supercritical is an excellent solvent for organic compounds;
- *Mineral dissolution* increasing the mineralization of the water and the release of associated trace elements;
- *Precipitation of carbonates and other secondary minerals* resulting in alteration of rock and aquifer characteristics;
- *Co-precipitation and sorption of metals*, which may act as either a contaminant trap or, if conditions subsequently change, a source;
- *Changes in microbiological activity;*

- *Aqueous complexation* (organic compound, chloride, bicarbonate complexes) that can promote the solubility.

All these mechanisms are interdependent, each affecting the others. The processes depend on the physicochemical conditions of the aquifer (mineralogy, temperature, pH, Eh etc.), and transport of mobilized elements which may potentially alter water quality. The interaction of these processes and mechanisms will give a relevant and broad understanding of potential impacts of leakage but the weight with which the different processes will interplay will be case dependent.

NUMERICAL MODELLING AS A PREDICTIVE TOOL

Assessing the impact of injection on the storage formation and potentially on the overlying aquifers requires the understanding of complex hydrogeological and hydrogeochemical systems. Basin scale modelling require the gathering of a large amount of data, often limited for a precise characterization and therefore involving modelling assessment through sensitivity analysis and multiple-run scenarios. One of the main difficulties for modelling impacts of storage on shallow groundwater is to handle both the changes of the hydrodynamics of the geological formations and the associated fluid-rock interactions. In fact, in the literature these two disciplines (hydrodynamics and geochemistry) are often assessed separately for providing modelling estimates. Thus, the modelling of reactive transport for multiphase flow systems is still under active research and development.

The limited number of geochemical simulations assessing water quality alteration due to leakage confirms that acidification will lead to trace element release from dissolution of metal-bearing sulfides. This release may potentially exceed standards according to the leakage assumptions (flow rate, pressure) and the geochemical parameters (mineralogy, buffering capacity, water composition). Processes of sorption are not systematically implemented in all modelling codes but, when taken into account, these sorption processes can significantly reduce metal mobility. Availability of data from field observations and experiments are crucial for model calibration in order to realize the complexity of these processes.

The potential hydrodynamic impacts of storage are based on different modelling approaches. In a single phase modelling approach injected water will provide an approximation of injection for an analogue pressure pulse. This allows for the use of numerical codes originally dedicated to hydrogeological issues and able to properly incorporate corresponding data. Alternatively a reservoir flow simulator may account for the gas phase in the over-pressured injection zone. Although a reservoir flow simulator is preferable for the prediction of gas propagation and mixing, such codes are often not suited for complete incorporation of hydrogeological features. As a second alternative, analytical modelling using a simplified geometry of the hydrogeological system may allow a quick estimate of overpressure and the associated fluid movement.

Predictions of pressure increases and associated fluid displacements related to injection of demonstrate that the pressure footprint will rapidly attain a large areal extent (up to 100 or 200 km) within the storage formation, but with a sharp decline in pressure away from the injection point. This pressure footprint is largely controlled by the total amount of injected and the permeability of the sealing rock. The pressure in the vicinity of the injection well can reach values of several tens of bars, while the impact on the head pressure in surface outcrops is in general predicted to not be of a particular concern. It differs according to the size and the boundary limits of the storage formation. Water table changes do not exceed few millimeters for fresh aquifers overlying DSF and are of the same order of magnitude as seasonal and inter-annual variations for lateral fresh groundwater in open system DSF. In some specific conditions to be more fully explored numerical estimates can reach up to few meters. Strongly controlled by the cap rock permeability, predictions of brine fluxes through shale are of the order of millimeters per year while the reservoir fluxes are meters per year.

REGULATION

Recently, a number of countries have developed dedicated storage regulations. Among them are the European Union, the United States of America, and Australia. A number of measures in these texts relate in particular to groundwater protection in addition to more general measures such as the prevention of any potential leakage. The most recurrent of these specific measures are dedicated characterization and monitoring of the adjacent fresh groundwater.

From the study of existing groundwater protection rules, it appears that there could be some legal barriers to the storage of in deep saline formations. Such barriers must be amended to allow the injection of such as in the European Directive for storage. Permitting the injection of is likely to rest with the authorities in charge of the protection of groundwater.

It is recommended that the “water regulation authorities” participate in every step in the qualification process of a storage project. They will provide an additional expertise to the one provided by the authorities regulating the storage of .

REMEDIATION

If CCS is to be accepted as an effective and reliable measure to combat increased concentrations in the atmosphere, the potential risk of leakage of stored will have to be properly addressed by putting in place effective measures to intervene in case of a leakage. A number of approaches have been suggested for mitigating leakage from reservoirs. These include:

- *Reduction of the pressure in the storage reservoir*. This is not a straightforward task, and would involve the removal of from the reservoir, consequently creating disposal challenges, and negating the original aims of geological storage of .
- *Interception and extraction of the plume from the reservoir* before it leaks out of the storage structure. This requires accurate information on the location of the plume, the potential need to drill new deep wells, and also the use of sophisticated techniques and equipment to extract the plume. Again disposal and cost challenges are faced, negating the original aims of geological storage.
- *Interception of the pressure plume in the brine, outside the plume itself and extraction of brine from the reservoir.* Brine disposal would also face environmental and cost challenges.
- *Increase of the pressure in the formation into which leakage is occurring*. This would be a very complicated exercise, as it would require information on the specific target area, amount and type of fluid and an accurate monitoring program.

- *Isolation (shut-off) of leaks in identified and accessible locations*, for example within wells using existing technologies (cement, polymer gels, mechanical means, etc.) or newly emerging technologies, thereby to stop leakage out of the storage formation.

For lateral migration of or brines, remedial options would include the use of hydraulic barriers or removing some of the stored and reinjecting it into another zone.

In the potential case of groundwater contamination by hazardous components, "pump and treat' methods could be employed, involving extraction of the contaminated groundwater, its treatment above ground to remove the unwanted impurities and then its discharge into surface waters or re-injection underground. Other possible methods include flow-through treatment barriers for removal of contaminants and hydraulic barriers to contain the plume of contaminated waters.

All the leak mitigation methods described above require, in the first place, information on the type, extent and location of the leak prior to implementing any of the corresponding remedial work. There may be a relatively large delay from when a leak occurs, to when it is detected, and to the point by which a mitigation or remediation method can be put in place.

Careful design and management of the store should be conducted to minimize any need for remediation and mitigation options, as these depend on a range of site-specific conditions, which are difficult to obtain. At certain sites, it may not be possible to restore aquifers due to hydrogeological constraints.

KNOWLEDGE GAPS AND RESEARCH PRIORITIES

From this review, the potential mechanisms associated with geological storage of that could impact adjacent groundwater resources are clearly identified. However, the levels/ranges of the impacts in relation to the effects associated with storage and potential leakage are not well defined. Thus, the mechanisms and processes expected are well-known as groundwater quality and availability are topics that have been subject to much of research during the last five decades. This knowledge needs to be applied to DSFs and deep groundwater resources to assess the impacts on groundwater in a storage context (impacts of a pressure head variation; impact of an acidification of water, impact of an intrusion of in natural analogues etc.).

However, some gaps remain and, currently, it is still difficult to quantify the impacts of storage with confidence. Therefore, more studies are required to correctly assess the relevance of the potential mechanisms of quantitative and qualitative impacts of storage on adjacent aquifers in the following areas:

- *Laboratory and pilot scale experiments* in several geological and chemical settings are required to evaluate the potential impacts on groundwater quality.

- *Large scale basin studies* are required to correctly assess the hydrodynamic impacts for specific sites (e.g. to characterize the connection between deep saline formations and overlying fresh groundwater, to determine the depth of freshwater aquifers and their proximity to storage complex).

- *High performance computing* is becoming an important support for improving the numerical modelling assessment of storage in general but also more specifically the impacts of CCS on groundwater. The coupling of multiphase flow with reactive transport modelling is very demanding in CPU time and memory, which often limits the proposed scenario (single phase approach, 2D or 1D modelling, homogeneous properties, reduction of chemical processes and data, etc.). Nevertheless, being able to simulate a complex 3D heterogeneous system, including all complexity of the mineralogy and water composition, cannot predict pertinent scenarios without being compared with real field data. Calibration of the modelling and development of thermodynamic and kinetic data bases is therefore a crucial need to ensure continued progress in modelling prediction.

- *Monitoring technology development.* If leakage of does occur, and most likely at depths of several hundred meters, it may not impact aquifers that are being utilized or reach the surface for decades, centuries or millennia. Detecting leakage and monitoring for impacts is therefore difficult and methods, including development of new technology, are needed to rapidly and accurately identify leakage positions.

1. Introduction

OBJECTIVES AND CONTENT OF THE PRESENT STUDY

Research into carbon dioxide () geological storage has been carried out over two decades, as part of studies to evaluate the feasibility of Carbon Dioxide Capture and Storage (CCS). Recently, there has been an increasing focus on potential impacts to surrounding geological formations and in particular, shallow aquifers and associated potable groundwater resources. Potential leakage of in both supercritical and gaseous form, from onshore or near shore deep saline formations[2] (DSF) or leakage of the associated formation brines, is frequently cited as a key risk scenario for overlying or neighbouring potable groundwater reservoirs. To date, the potential impact of storage has mainly been studied at the near-well and reservoir scale, whereas risks in the context of regional multi-layered groundwater systems have not yet been systematically assessed. Recent studies have begun to address this topic, using hydrodynamic and geochemical modelling approaches, through which several mechanisms have been identified that could potentially lead to negative impacts on groundwater quantity and/or quality.

The IEA Greenhouse Gas R&D Programme (IEAGHG) recently commissioned the Association to undertake a literature review on this topic, with the aim of summarizing state-of-the-art knowledge as well as identifying knowledge gaps and research priorities in this field. This study is also based on work undertaken by various consortium members for the IEAGHG study contract.

The main objective of the present study is therefore (1) to identify geological settings with potential juxtaposition of potable groundwater resources and storage sites, (2) to provide an overview of potential mechanisms of quantitative and qualitative impacts of storage schemes on overlying aquifers, (3) to assess the relevance of those mechanisms through the analysis of results obtained on natural and industrial analogues, (4) to demonstrate the relevance of the potential impacts as identified/quantified by modelling approaches, (5) to address the relevance of potential impacts with respect to current regulation on storage and on water protection and environmental impact assessment regulations and (6) to discuss the remedial actions that can be implemented once the leakage of or brine is detected.

BACKGROUND TO GEOLOGICAL STORAGE IMPACTS

In order to reduce atmospheric emissions of from human activities, innovative capture and storage strategies have to be applied to produced by the combustion of fossil fuels. Among currently proposed storage techniques, carbon dioxide capture and storage (CCS) is considered as one of the options. Geological storage of involves injecting the underground, for example in depleted oil and gas reservoirs, deep saline formations and unminable coal beds. becomes secured in a similar way to hydrocarbons that have remained naturally trapped in hydrocarbon fields for millions of years.

Carbon dioxide () injection in geological formations has been practiced since the early 1970's in the context of - Enhanced Oil Recovery projects. More recently, industrial and test sites have been developed strictly with the goal of storage. Both of these approaches have

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[2] *Shallow aquifers* are here understood to be the groundwater bodies that contain fresh, potable groundwater (usually shallow), whereas *Deep Saline Formations* (DSF) are the loci of underground storage in deep underground rock formations composed of permeable materials and containing highly saline fluids deeper than 800 m to avoid CO$_2$ in gaseous phase (IPCC Glossary).

demonstrated that it is feasible to safely store in geological formations. Storage of is currently being demonstrated at a commercial scale at several sites: the offshore Sleipner natural gas processing project in Norway; the Weyburn Enhanced Oil Recovery (EOR) project in Canada (which stores captured in the United States) and the In Salah natural gas project in Algeria.

Storage of in deep saline formations shall be undertaken only where all site exploration and risk assessment data indicate that will be safely trapped and potable groundwater will not be affected to an unacceptable extent. That said, a clear understanding of potential leakage and migration pathways and potential impacts on freshwater aquifers must be assessed to develop response protocols and to address stakeholder concerns.

 geological storage is generally expected to take place at depths below 800 m, where the is stored as a supercritical phase fluid (pressure and temperature higher than 71 bar and 32°C). Under these conditions, the density of will range from 50 to 80% of the density of water and will occupy considerably less volume than in the gas phase.

When injected underground, the compresses and fills the pore space by partially displacing the *in situ* fluids. Injecting into geological formations will result in increases of pressure that could lead to the migration of either through existing pathways (cap rock seal, active or abandoned wells, faults and natural fractures) or induce well fracturing or fault reactivation. Due to buoyancy forces tends to migrate upwards and to mix with the *in situ* fluids. Where constrained vertically, lateral migration of the injected may occur from the injection site/well through the formation either to the surface or until it reaches a confining structure. Consequently, an effective cap rock over the selected storage reservoir is important to ensure that remains trapped underground. Anticlinal geological formations containing a sealing cap rock are therefore the primary targets envisaged for insuring safe storage, although spatially extensive, sub-horizontal porous beds may also provide important storage reservoirs if capped by impermeable units (e.g. Sleipner in the North Sea). The complex behaviour, effects and reactions of stored in the subsurface are given in an overview by Friedman (2007) and in review of modelling approaches by Gaus *et al.* (2008).

 migration (leakage) outside of the limits of the storage formation can potentially occur either in the vertical or lateral directions.

REPORT STRUCTURE

This report is subdivided into five main sections. The first section (Chapter 2) introduces potential areas of impacts of storage on shallow potable water aquifers on a regional scale. The approach is based on combining available regional datasets to visualize on a single map the juxtaposition of groundwater resources and areas potentially suitable for storage. A typology of geological settings where impacts could occur is developed and tested in Europe where groundwater resources and DSF potentially suitable for storage are reasonably well understood.

In the second and third sections, literature relating to mechanisms of potential hydrodynamic and chemical impacts on shallow groundwater is reviewed. Chapter 3 focuses on evidence of these impacts as observed in natural or industrial analogues and experiments. Complementing this, Chapter 4 reviews the different modelling approaches used to study possible impacts of stored on groundwater resources. These results are based on scenarios and do not give evidence. The review discusses various approaches that can be used, including multiphase flow modelling combined with reactive transport models. The advantages and limitations of each approach, as well as the main conclusions obtained from case studies, are discussed.

The fourth section (Chapter 5) provides a review of storage-specific regulations in the main countries where CCS is being evaluated and researched. The review aims to identify the constraints imposed by existing regulations on the protection of groundwater resources via identification of (1) potential receptors constraints; (2) risk assessment constraints; (3) monitoring constraints; (4) remediation constraints; (5) geographical constraints; (6) construction requirements. The review includes existing regulations on water protection and/or Environmental Impact Assessment and how storage is considered within these regulations or further amendments. The main objective is to highlight the inconsistencies and the gaps between carbon storage regulations and Water Protection regulations. Recommendations and best practices for regulations (storage regulations versus groundwater protection or water and environment regulations versus storage operations) are proposed.

The last section, Chapter 6, describes possible mitigation options to stop or control potential leakage and release in a variety of scenarios. In particular, the effect of the increased pressure of the in the host deep saline formation (DSF) and the groundwater resource is examined. In the literature such methods are mainly addressed through modelling approaches. Techniques for effective mitigation of the impacts of stored on freshwater resources are identified.

2. GIS-based approach to assess potential impacts of geological storage on groundwater resources

In this chapter, available literature and data have been reviewed to give an overview of the current understanding of the distribution and relationship of deep saline formations (DSF) and freshwater aquifers on a regional scale. The potential impacts on freshwater aquifers will depend on the hydraulic properties of the aquifers and the confining layers that separate them from the deep saline formations being targeted for carbon dioxide storage, as well as their relative juxtaposition. These potential impacts are discussed in greater detail in Section 3 of this report.

This work attempts to bring together studies which focus on identifying and characterizing DSF potentially suitable for storage and their relationship to fresh groundwater resources, at a regional scale. As data availability is very variable, particularly with respect to deep saline formations where little hydrocarbon exploration has been undertaken, regions have been selected to illustrate what can be gleaned and where further work is required. Available data are reviewed globally and then compared in selected regions – focussing on Europe and North America but also looking at China where assessment is less fully developed. In these areas the juxtaposition of deep saline formations to freshwater aquifers are discussed and potential impacts considered. Lastly, a typology of impacts based on geological settings is postulated and tested for selected European countries.

2.1. ASSESSMENTS OF POTENTIAL IN SELECTED REGIONS

Assessment of distribution and extent of DSF potentially suitable for storage of has been carried out at a variety of scales and detail across the globe. Major efforts are being made in the nations with high industrial carbon emissions in the developed and developing world. For countries with a high proportion of fossil fuels in their energy balance such as USA, India, Germany, U.K., Australia, Brazil and South Africa (ranking according to CARMA; .carma.) geological storage of is one promising option to decrease their emissions.

Collating data about distribution and extent of geological formations potentially suitable for storage of is a major task that has been undertaken in some regions, but not in others. Focussing on the big industrial carbon emission nations in the developed and developing world, this study has collected regional data compilations, and where available, GIS representations of the distribution and scale of potential reservoirs in deep saline formations. GIS representations are available at a regional scale for Europe (GEOCAPACITY) and for North America (NATCARB), as well as some areas of China.

At the global scale, the extent and nature of groundwater resources have been illustrated in the “World-wide Hydrogeological Mapping and Assessment Programme (WHYMAP)” launched in 2000 (see .whymap.), and groundwater maps widely exist (BGR and UNESCO, 2008). However, the groundwater resources maps prepared within the WHYMAP project currently do not include information on multi-aquifer systems, i.e. depth information on freshwater bearing formations that would be desirable for juxtaposition with DSF. Depth-related data have been collated at a regional scale in Europe, to evaluate findings from the juxtaposition of WHYMAP and GEOCAPACITY data.

2.1.1. Distribution and scale of deep saline formations potentially suitable for geological storage

A first approach to identify geological reservoirs suitable for storage is to map the distribution and extent of sedimentary basins with a sediment thickness of more than 800 -

1000 m. At this depth, hydrostatic pressure and in situ temperatures exceed the critical parameters so that is stored as a dense supercritical fluid.

Suitable storage reservoirs are structures (e.g. anticlines) within a geological formation that have a sufficiently high storage capacity and that are overlain by impermeable barrier rocks. For a volumetric-based assessment of storage capacities in sedimentary basins information is needed on thickness and lateral extent of potential storage formations, available pore space (porosity) and accessibility/connectivity of pores (permeability).

Price and Oldenburg (2009) argue that the site selection process should be based on injectivity and 'effectiveness of the formation to store/trap the in addition to storage capacity and that the regulatory framework should be based on consequences of failure not the probability of failure as the later is difficult to calculate'.

Knowledge gaps identified by the IPCC Special Report on Carbon Capture and Storage (2005) include comparable storage capacity estimates due to inconsistency in methods of assessment and lack of data in global, regional and local estimates, particularly in Africa, South America and much of Asia (Michael *et al.*, 2009a).

Data availability in different regions of the world

Europe

Identification of sedimentary basins and geological formations potentially suitable for storage (Figure 2.1) and capacity assessments have been carried out in the European Framework Programme, FP6, project GeoCapacity for Europe (.geology.cz/). Contributing countries carried out assessments of potential storage capacity in relation to potential load using a standardized methodology. For more information see Chapter 2.2.1.

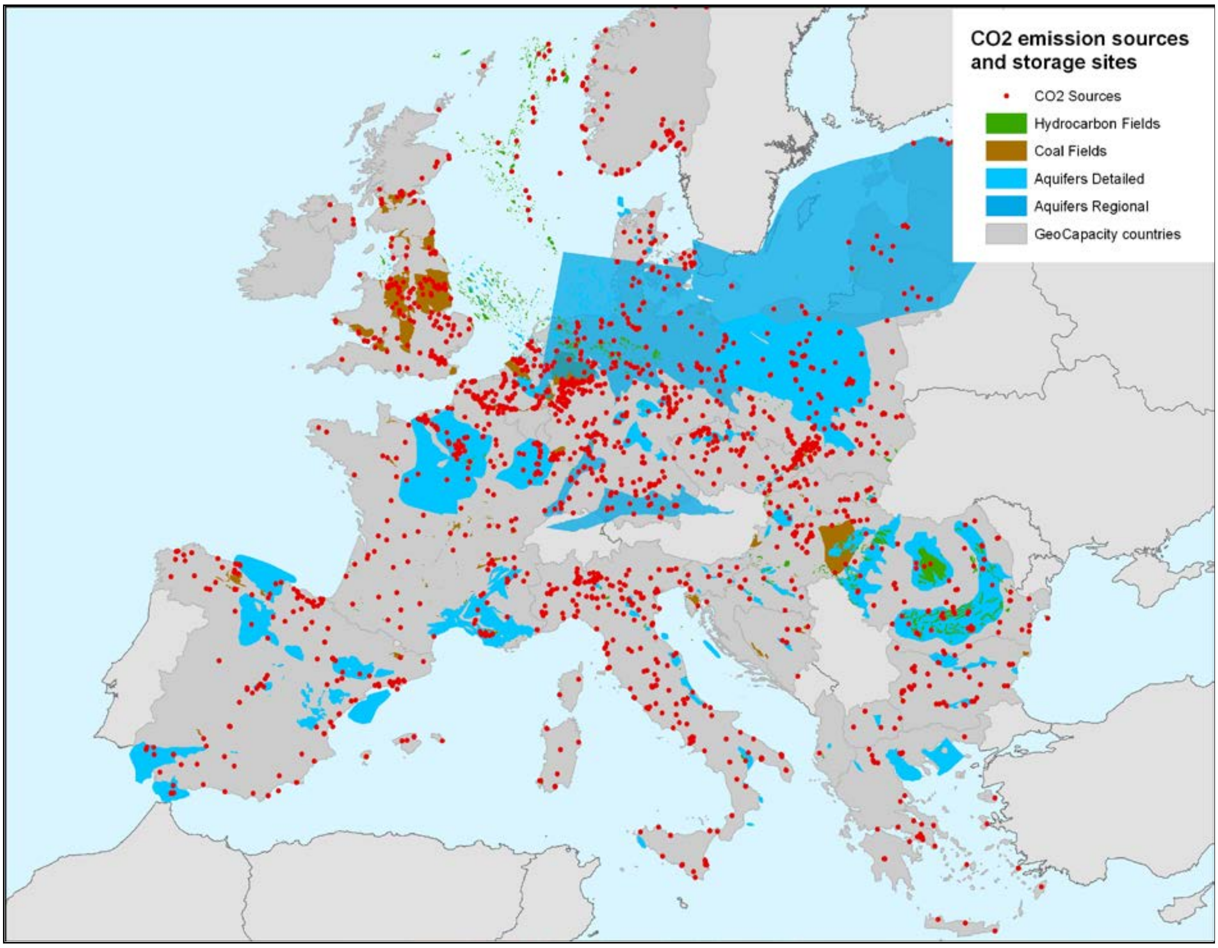


Figure 2.1: Location of emission sources and potential storage options in Europe, as identified by the GeoCapacity project.

North America

In the Carbon Sequestration Atlas of the United States and Canada (DOE NETL, 2010; www.netl.doe.gov) information about potential storage formations has been compiled by the National Energy Technology Laboratory considering the following storage options: saline formations, coal seams, oil and gas reservoirs, shale, and basalt formations. Potential storage formations were identified and assessed by the U.S. Regional Carbon Sequestration Partnerships. Boundaries of saline formations identified as suitable for storage are mapped in the "North Americas Saline formations Map" (Figure 2.2). For more information see Chapter 2.2.1.

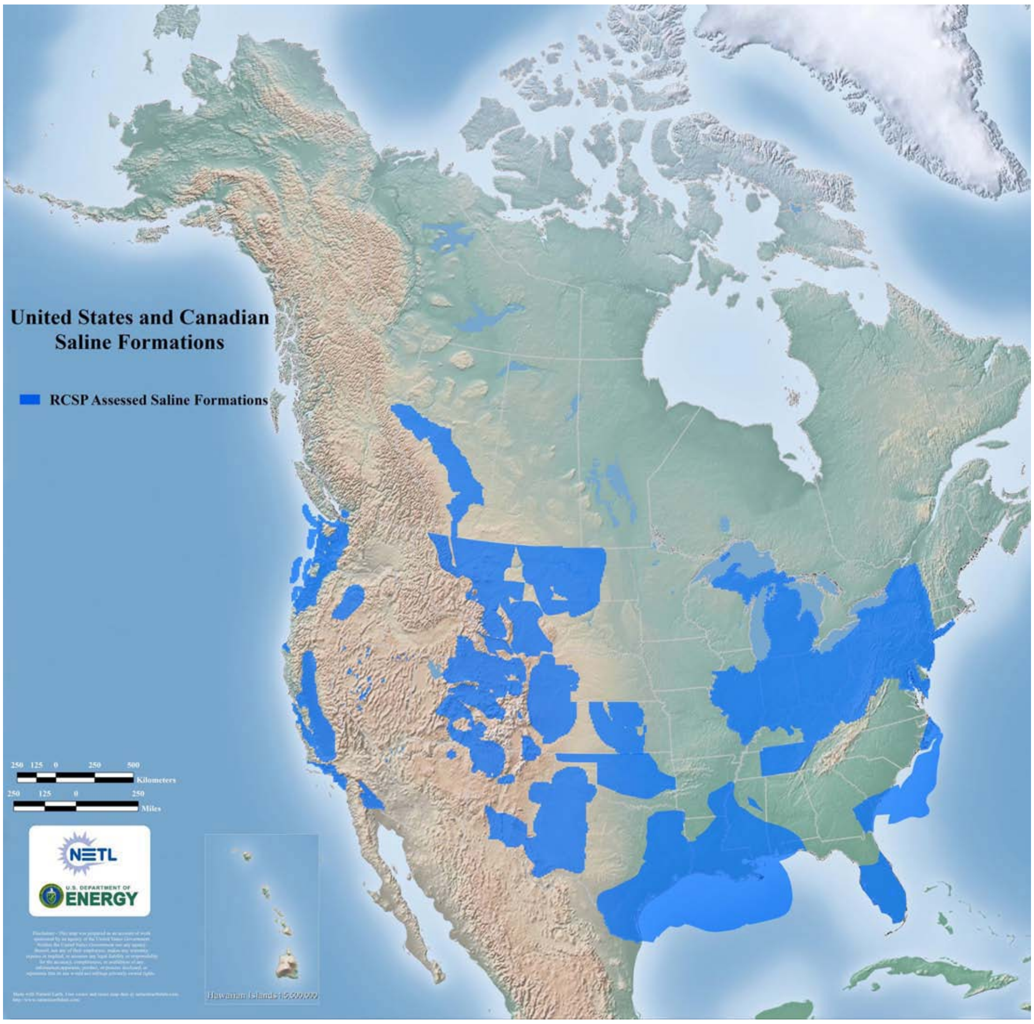


Figure 2.2: Location of assessed deep saline formations in N. America (from DOE NETL, 2010). Note that saline formation data resulting in a straight edge in the map above is indicative of an area lacking sufficient data and is subject to future investigation.

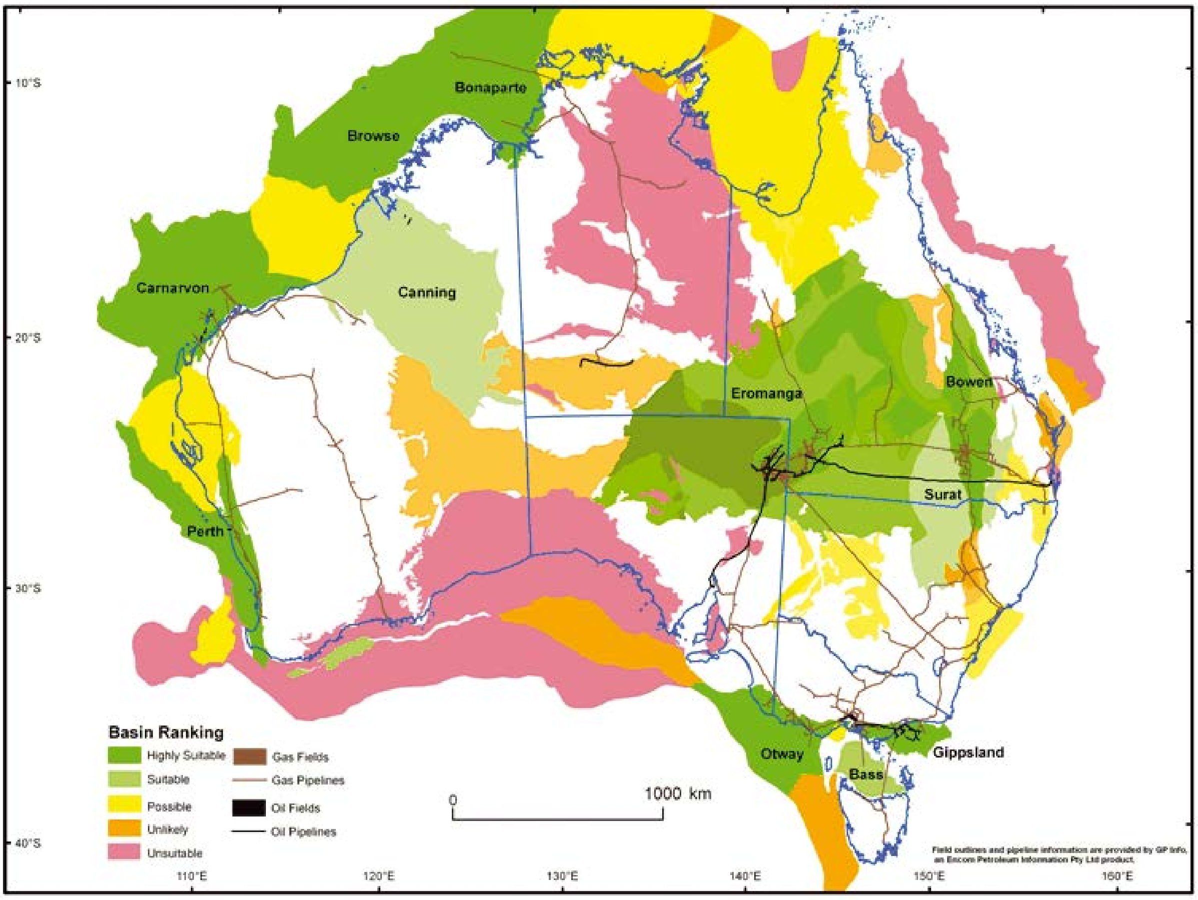
Australia

The Australian CO2CRC have been undertaking research into the geological storage of with particular focus on Queensland being a major producer of electricity (see "Queensland

Carbon Dioxide Geological Storage Atlas and GIS”[3] in which 36 basins have been assessed for their geological storage prospectivity) and Victoria being home to large, industrial sources (CO2CRC, 2006). Capacity estimates for New South Wales are currently underway (://www.co2crc.com.au/). The assessment of Environmentally Sustainable Sites for Injection (ESSCIs) has also been undertaken in Australia with a risk assessment based on storage capacity, injectivity, containment and natural resources (Bradshaw *et al.*, 2003).

The potential storage at a national level has been summarized in the National Carbon Mapping and Infrastructure Plan (Figure 2.3, Carbon Storage Taskforce, 2009), which identifies areas with greatest potential; both onshore and offshore. Major onshore basins identified as being suitable or highly suitable, include the Canning Basin and the majority of the confined Great Artesian Basin (GAB) (Eromanga, Bowen and Surat sub-basins). These areas are also classified as ‘major groundwater basins’ on WHYMAP (BGR and UNESCO, 2008); hence areas of immediate juxtaposition and potential impact on fresh groundwater.

The GAB is a hydrogeological setting (Figure 2.4) where groundwater is the only major source of freshwater on which the economy and livelihoods of people depend. It is therefore imperative that geological storage in adjacent DSFs does not impact the groundwater resources. An assessment of the impacts of storage (Hodgkinson *et al.*, 2009) examined the distribution of groundwater types, the mineralogy of reservoirs and seals and the reactions of injecting into freshwater aquifers. The preliminary conclusions were that storage could operate without significant impact on the aquifers.



Field outlines and pipeline information are provided by GP Info, an Encom Petroleum Information Pty Ltd product.

Figure 2.3: Australia’s basins ranked for storage potential (Carbon Storage Taskforce, 2009).

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[3] at http://www.dme.qld.gov.au/mines/carbonstorage.cfm

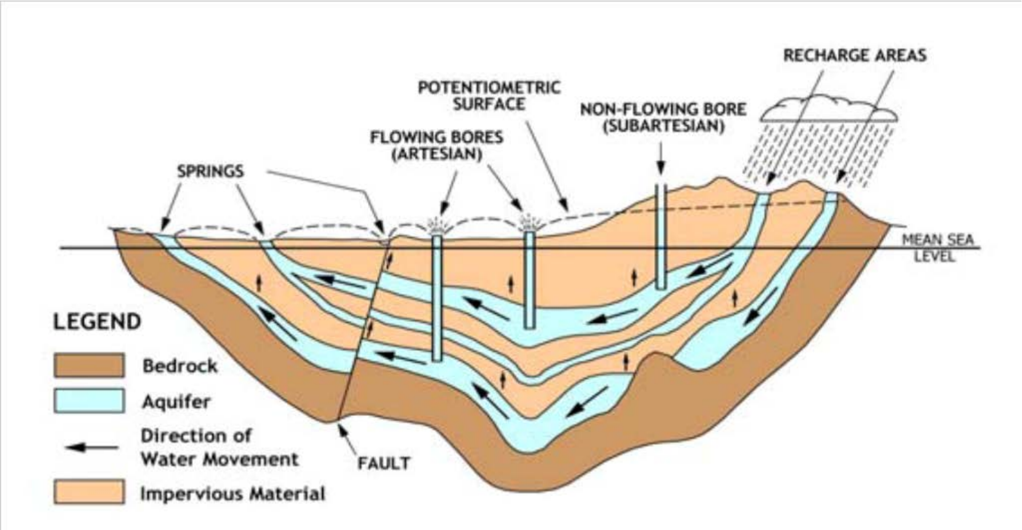


Figure 2.4: Generalized cross-section of the Great Artesian Basin. (Queensland Department of Environment and Resource Management).
The GAB is up to 3000 m deep and the average depth of bores is 500 m, although some are drilled to 2000 m. The oldest groundwater is up to 2 million years old in the extremities of the basin but is of good quality in the main aquifers.

India

The India project (IEAGHG, report 2008/2) was a high level study where deep saline formations were described on a basin-by-basin basis (Figure 2.5). Country- and basin-scale assessments were carried out as described by Bachu *et al.,* 2007. The project also included a review of Pakistan, Bangladesh and Sri Lanka. The basins were ranked using the following criteria (Holloway *et al.,* 2008):

- **Basins with good potential** contain hydrocarbon fields (proving containment of buoyant fluids over geological timescales) and there is expectation of good reservoir and seal quality at depths below 800 m over at least a significant part of the basin.
- **Basins with fair potential** contain one or more potential regional seals, underlying reservoirs at depths greater than 800 m and potential structural closures. However, containment of buoyant fluids over geological timescales is not yet proven by the discovery of hydrocarbon fields.
- **Basins with limited potential**. Porous and permeable reservoir are absent or not sealed in these basins, or the basins lack structural closures, or are in structurally complex fold belts, or they face major potential impacts on other use. Data often limited.

Comparison of the results of this methodology with the WHYMAP distribution of aquifers was not undertaken as the majority of basins with good potential lie offshore.

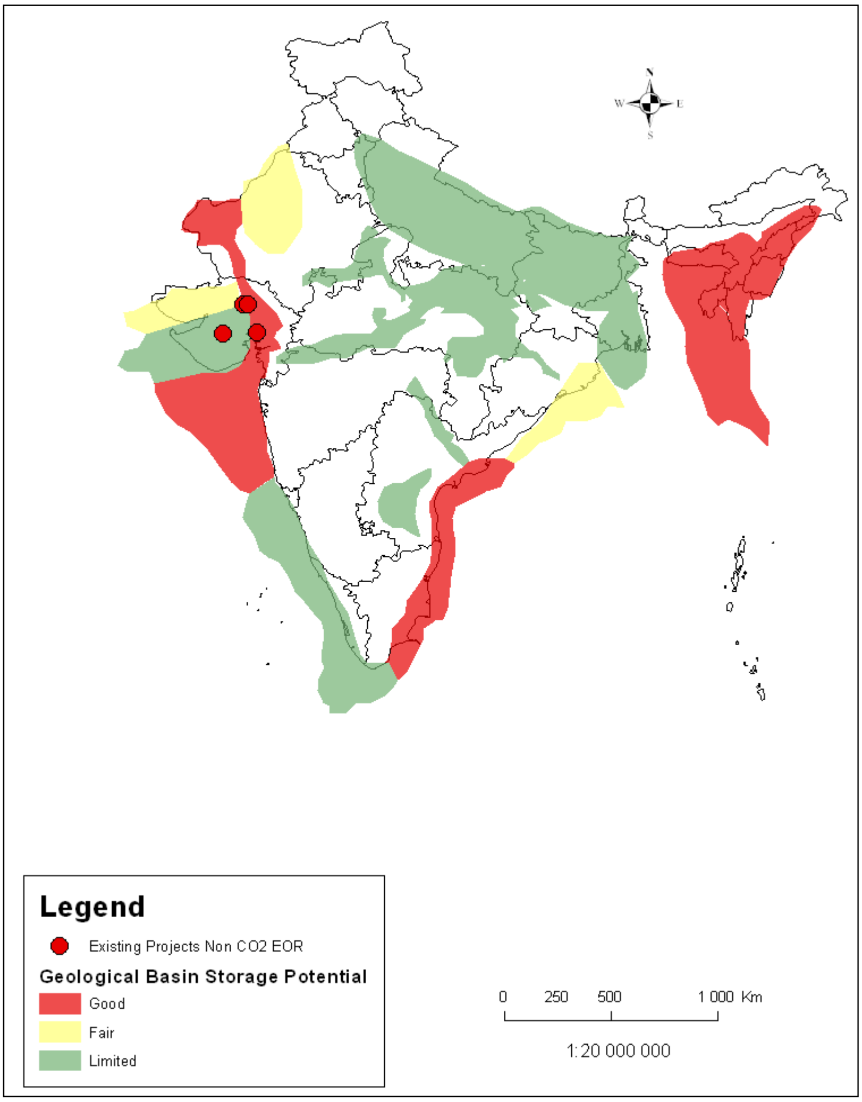


Figure 2.5: Potential for geological storage in Deep Saline Formations in India (IEAGHG, 2008/2).

Latin America, Africa and Asia

Studies undertaken in Latin America, Africa and Asia are less advanced (Michael *et al.*, 2009a) but currently several assessments are in progress or recently completed.

There has been the “Assessment of potential storage sites in the Asia Pacific Economic Cooperation region: China, Indonesia, Republic of Korea, Malaysia, the Philippines, Chinese Taipei and Thailand” by (://www.co2crc.com.au/research/regional_apec.) with more detailed capacity studies carried out in Japan (Ogawa *et al.*, 2010) and China (.geology.cz/). An atlas on geological storage of in South African (://www.sacccs.org.) was published in November 2010 and the PUCRS/CEPAC - Brazilian Carbon Storage Center has produced an atlas for Capture, Transport and Geologic Storage under its CARBMAP research programme (://www.pucrs.br/cepac/).

Global

A potential source of additional data is the USGS Energy Resources Program world petroleum assessment which has identified global hydrocarbon-bearing basins (USGS website, September 2010). This could provide a starting point to carry out a global assessment of where suitable aquifers may exist, but has not been investigated further in this study.

An IEAGHG report has compiled data from existing operations in ‘CO2 Storage in Saline Aquifers II – Experience from Existing Storage Operations’ (Michael *et al.*, 2009b). More than ten saline aquifer injection operations have been conducted worldwide and information on these test sites such as injection depth, injection rate, aquifer permeability and aquifer porosity has been compiled by Michael *et al.* (2010). However, the authors question whether the existing test sites are representative of reservoir/aquifer characteristics that will be targeted for storage in the future since it is likely that considerably larger storage capacity will be required than is demonstrated at existing sites. Highly permeable homogenous aquifers have been considered most suitable but these aquifers may lead to increased migration rates of Therefore, attention has turned to investigation of low-permeability heterogeneous saline formations as potential storage sites.

2.1.2. Global distribution of groundwater

Groundwater is the largest global store of freshwater on the planet that is not frozen. Many estimates have been made, but available fresh groundwater globally is in the range 8.0 to 10.5 million . Estimates of annual recharge to aquifers range from about 0.011 to 0.013 million km3, (Margat, 2008); i.e. about 1/800th of global fresh groundwater storage.

In addition to the global fresh groundwater resources, there is estimated to be between 12.8 and 13.6 million of brackish and saline groundwater down to a depth of 2 km and larger estimates of saline and inaccessible groundwater include that at greater depth and that in low permeability rock types. The majority of this brackish and saline water has been identified at depths of less than 500 m; too shallow for injection of as a supercritical fluid. The proportion of the identified saline groundwater that lies below the threshold depth of 800 m has not been estimated. However, if an arbitrary figure of 20% is taken, this equates to some 2 to 3 million .

Calculations of the global storage capacity for in DSFs vary greatly but can be put into context of the estimates of brackish and saline groundwater, above. In IEAGHG report 2008/12, the global estimates of storage potential are discussed and total an estimate 11 680 Gt (Figure 6 of the report). Taking a relative density of supercritical of 0.7 (relative to freshwater at surface temperature) this equates to a volume of about 8200 ; i.e. about three to four orders of magnitude less than global saline groundwater resources. The relative density of saturated brine, typically found at depth is up to about 1.2.

The areal extent, quality and recharge rates of major fresh groundwater resources on earth have been illustrated by the “World-wide Hydrogeological mapping programme (WHYMAP)”, e.g. in the map “Groundwater Resources of the World”, scale 1:25,000,000; (Figure 2.6) (BGR and UNESCO, 2008). WHYMAP is a joint programme of UNESCO, the Commission for the Geological Map of the World (CGMW), the International Association of Hydrogeologists (IAH), the International Atomic Energy Agency (IAEA) and the German Federal Institute for Geosciences and Natural Resources (BGR) with contributions by numerous international institutes and experts bringing together hydrogeological mapping efforts at regional, national and continental scales. The aim of WHYMAP was to collect, collate and visualize hydrogeological information on freshwater resources on a global scale as a basis for a sustainable management of aquifers world-wide.

WHYMAP maps show the shallowest major freshwater aquifers irrespective of depth. Hence, both resources in major basins in Europe, extending to depths of a few hundred metres, and those in the Great Artesian Basin in Australia which is over 3000 m at its deepest.

The Groundwater Resources Map of the World also indicates areas where heavy groundwater abstraction and overexploitation is already occurring, e.g. in some areas in North Africa and the southern USA (Figure 2.6). This will lead to changes in regional pressure regimes and gradients from adjacent groundwater bodies, including DSFs, and hence impacts on potential migration of CO2 plumes need to be considered. Exploitation in this manner is not sustainable and, in extreme cases where there is effectively no recharge (fresh groundwater was emplaced in pluvial period several thousand years ago) it is referred to as groundwater 'mining'. Examples of this are found in arid and semi-arid regions of the world; e.g. much of North Africa and the Middle East. As groundwater may be the only source of potable water in these areas, it is extremely precious and needs to be exploited with the utmost efficiency and protected from pollution, including leakage of . The research site at Krechba in Algeria is investigation this situation. Areas of overexploitation and groundwater mining are indicated on WHYMAP (Figure 2.6).

The distribution and dimensions of groundwater resources are generally known in greater detail at the regional, national and local scales. For example, in Europe data and GIS representations are available on EU groundwater bodies delineated for the Water Frame Work Directive implementation (://cdr.eionet.europa.eu/) and are mapped e.g. in the International Hydrogeological Map of Europe (IHME1500; scale 1:1,500,000; ://www.bgr.de/app/fishy/ihme1500/download.). Where aquifers cross international boundaries there is scope for conflict over fresh groundwater resources, as there is with allocation of surface flows. These issues are addressed by ISARM (Internationally Shared Aquifer Resources Management) which is a multi-agency initiative led by UNESCO and IAH. Findings of this initiative, which includes descriptions of major groundwater basins where deep saline formations may occur, are summarized in the Atlas of Transboundary Aquifer Systems (.isarm.).

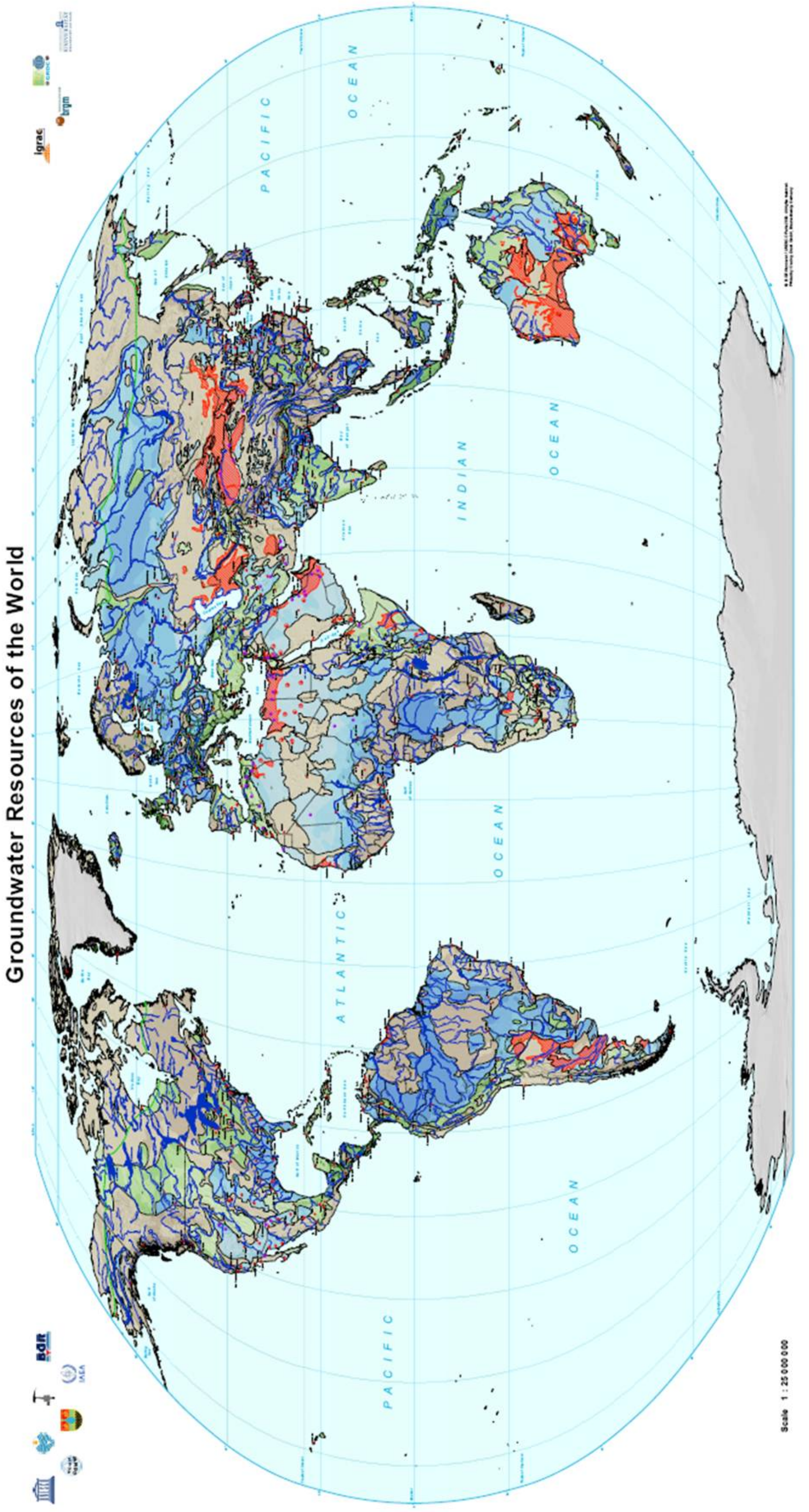


Figure 2.6: Groundwater resources of the World (1:25,000,000; WHYMAP, BGR and UNESCO, 2008).

Distribution of saline groundwater at shallow depth

As indicated in the Groundwater Resources Map of the World, in some regions, e.g. in parts of Australia, South America and Central Asia, areas with already high surface salinity (salinity >5 g/l) occur. These areas relate to shallow groundwater bodies where saline water is found, due to both natural and anthropogenic causes. They do not correspond to deep saline formations.

More information about the occurrence and genesis of saline groundwater may be obtained from the International Groundwater Resources Assessment Centre (IGRAC; .igrac. ., van Weert *et al.*, 2009). This study considers only groundwater to depths less than 500 m and with a minimum Total Dissolved Solids (TDS) concentration of 1000 mg/l (Figure 2.7). These groundwater bodies are therefore not of immediate relevance to storage, as a depth of greater than 800 m is needed. However, the occurrence of already saline groundwater in the vicinity of or overlying deep saline formations needs to be taken into account during the evaluation of the suitability of a potential storage reservoir, in particular for risk assessment and for establishing monitoring concepts.

In areas of over-exploitation of groundwater resources, saline aquifers, if present, may become important sources of potable water after desalination in the future. This needs to be considered for strategic planning of underground uses in particular in regions of the world with low or no groundwater recharge.

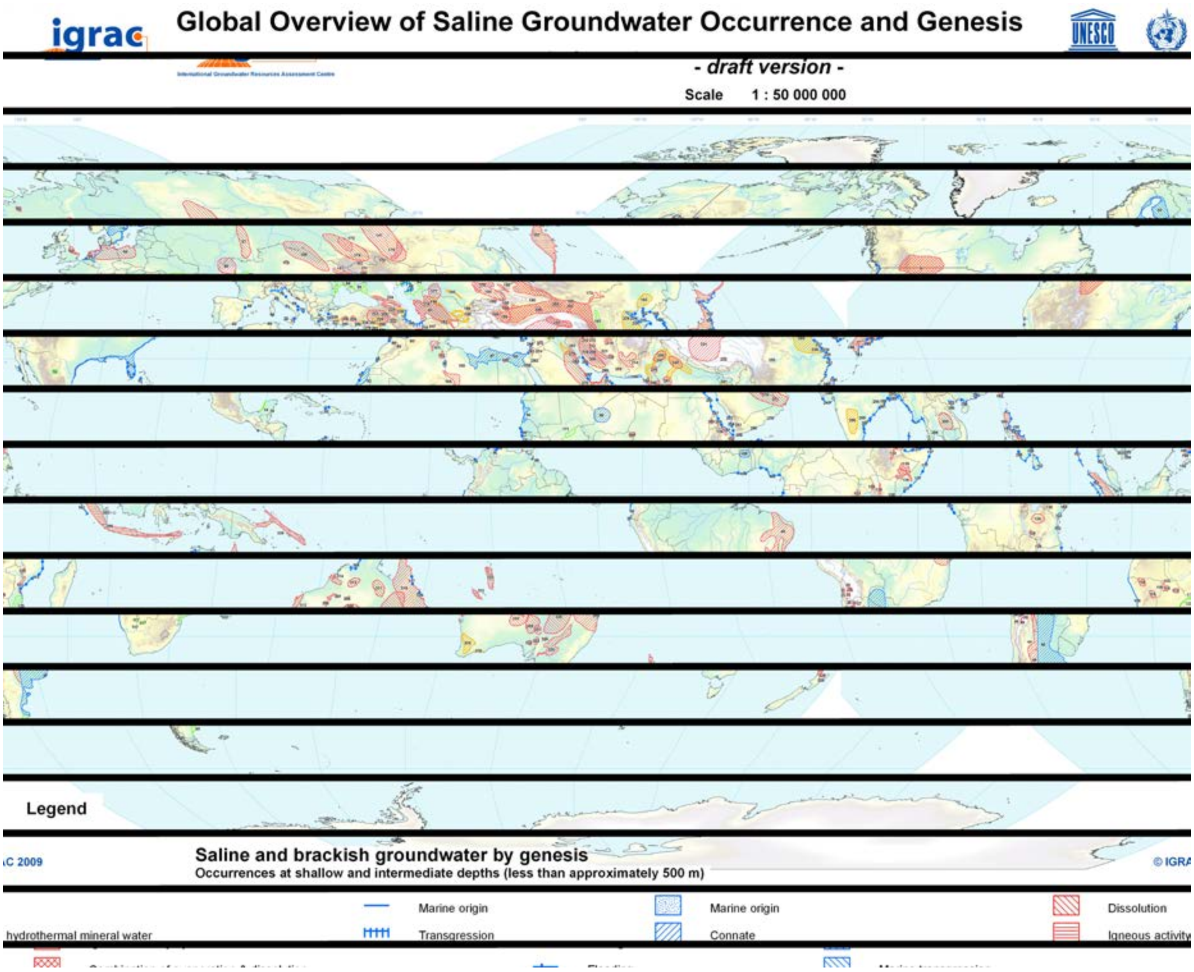


Figure 2.7: Global overview of saline groundwater occurrence and genesis, draft version (from IGRAC, 2009).

2.2. GIS-BASED REPRESENTATION OF JUXTAPOSITION OF POTENTIAL STORAGE RESERVOIRS AND GROUNDWATER RESOURCES

In order to identify potential areas of interaction of storage on freshwater aquifers, a GIS-based methodology of combined representation of groundwater resources/areas with storage potential has been developed. The GIS approach will only be able to visualize on a single map the juxtaposition of groundwater resources and potential storage areas, not considering their depth relationship as these data are either not available or only available locally in most parts of the world. This juxtaposition will however highlight potential areas of impacts of storage on freshwater aquifers.

A typology of geological settings where conflicts could occur has been developed and tested for Europe and North America where groundwater resources and potential storage sites are reasonably well understood. In addition, areas in China and India were assessed where the locations of deep saline formations with potential for geological storage of are less well defined. Selected areas where details of groundwater resources at depth are known are then used to act as test cases.

2.2.1. Description of available GIS representations

Datasets used for GIS-based combined representations of groundwater resources/areas with storage potential include:

- WHYMAP (.whymap.),
- GEOCAPACITY (.geology.cz/)
- Carbon Sequestration Atlas of the United States and Canada by the National Energy Technology Laboratory (.netl.doe.)

In the following, a brief description of the information contained in each dataset is given.

WHYMAP

The “Groundwater Resources of the World” map established by the WHYMAP illustrates the areal extent, quality and recharge rates of major potable groundwater resources on earth on a scale of 1:25,000,000 (.whymap.) As a general principle, aquifers, their hydrogeological characteristics and the contained groundwater are represented in much more detail on this map than strata containing little or no groundwater. Three different colours are used to distinguish between (Figure 2.8):

- Large and rather uniform groundwater basins (aquifers and aquifer systems usually in large sedimentary basins that may offer good conditions for groundwater exploitation);
- Hydrogeological environments of complex structure where productive aquifers (including karst aquifers) may occur in close vicinity to non-aquiferous strata;
- Areas with local and shallow aquifers in which low-porosity bedrock is exposed to the surface. In these areas, groundwater is limited to the alteration zone of the bedrock and overlying shallow layers of weathered bedrock.

This categorization is based on the IHA recommendations for hydrogeological maps (Struckmeier and Margat, 1995).

The intensity of the colour gives information about groundwater recharge: A dark tone indicates high recharge areas, while lighter tones represent groundwater basins receiving less recharge. Areas coloured in the lightest tone are merely suitable for groundwater ‘mining’ as recharge is negligible.

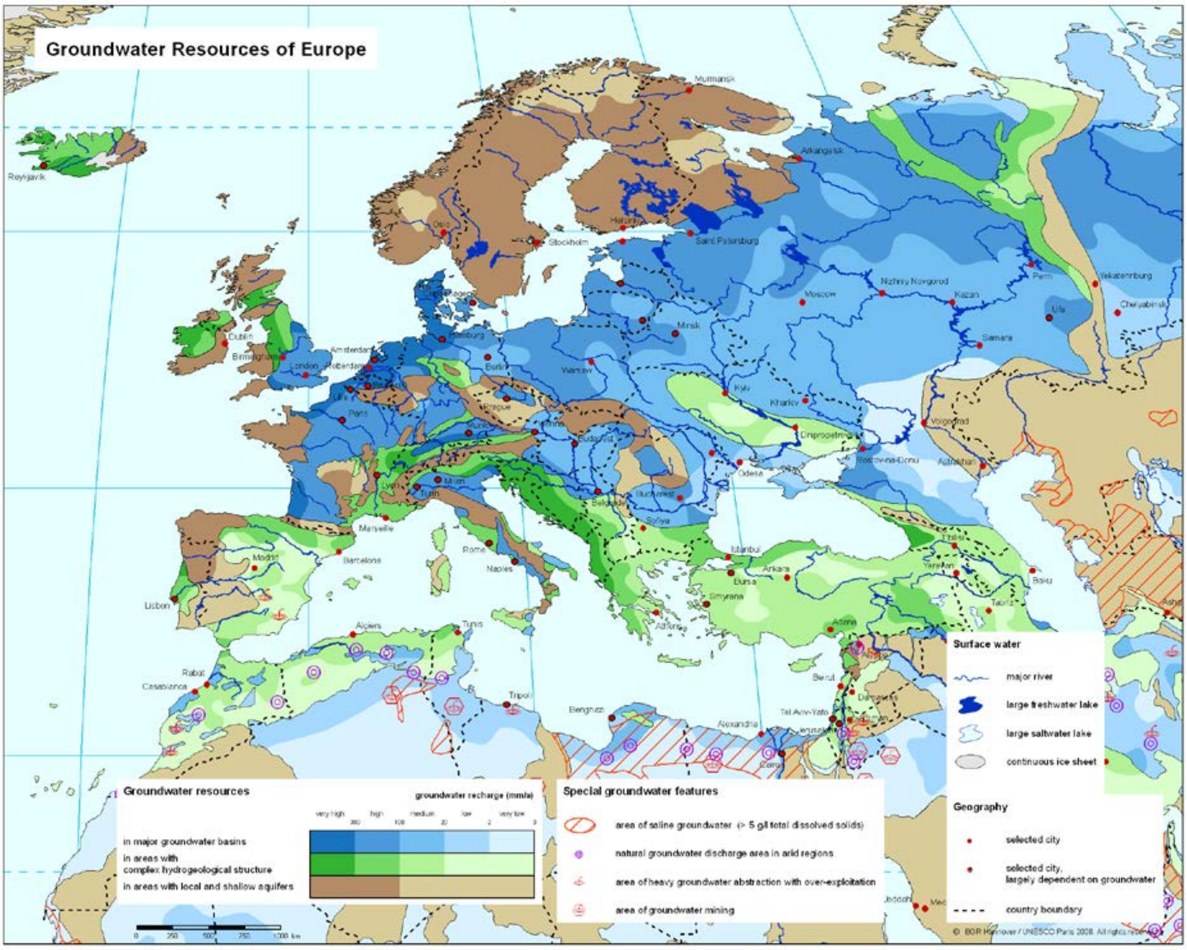


Figure 2.8: Groundwater resources of Europe (WHYMAP, 2008).

GEOCAPACITY PROJECT:

In the GeoCapacity project, a methodology for storage potential and capacity assessment was developed on experience from previous studies including the assessment scale guidelines as described by Bachu *et al.,* 2007.

A country-scale assessment was carried out initially by each of the countries to identify suitable sedimentary basins. An assessment at this scale was used to identify types of storage capacity available (e.g. hydrocarbon fields, deep saline formations and coal fields) and to determine whether there is sufficient storage capacity available to meet potential load.

The next stage was to carry out a basin-scale assessment by evaluating a specific sedimentary basin where storage potential was quantified and the best regions were highlighted. The most prospective areas are usually related to a storage site's proximity to a stationary emissions source. In some cases, where enough data were available, a more detailed assessment was performed. A set of criteria were then applied to the sites to provide standardized methodology using the following geological site selection criteria:

- Sufficient **depth of reservoir** to ensure that will be stored in supercritical fluid phase but not so deep that permeability and porosity are too low. At depths between approximately 600 and 800 m, undergoes a rapid change in its density and becomes a supercritical fluid rather than a gas. With increasing depth, the porosity and permeability of sandstone may start to decrease due to digenetic effects and therefore it was recommended that a depth of >2500 m should not be investigated unless there are available data to verify the reservoir quality.

- **Integrity of seal** to prevent migrating out of the storage site. Typical formations with good sealing properties are rocks with low permeability such as lacustrine and marine mudstones, evaporites and carbonates. Carbonates can form either sealing or reservoir rocks. The integrity of the seal is governed by the permeability and thickness of the sealing formation, the absence of faults crossing the formation as well as the impact of geochemical interactions between and the cap rock.
- Sufficient **storage capacity** to hold the required volumes of from the source e.g. lifetime emissions of a power plant.
- Effective **petrophysic reservoir properties** to ensure injectivity is economically viable. As a guide, the formation permeability must exceed 200 mD for sufficient injectivity (van der Meer, 1993). However, values greater than 300 mD are preferred. As a general rule-of-thumb, porosities should be larger than 20% (Chadwick *et al.,* 2006). Porosities below 10% are poor prospects because, not only is available storage capacity low, but also pore connectivity (permeability) is likely to be reduced; reducing injectivity.

Each country had access to variable levels of data to carry out their assessments. Generally saline aquifers are poorly known especially outside of oil and gas provinces due to their lack of economic interest making it difficult in some areas to assess their carbon dioxide storage potential.

Carbon Sequestration Atlas of the United States and Canada:

In this Atlas (DOE NETL, 2010) potential storage formations identified by the U.S. Regional Carbon Sequestration Partnerships have been compiled. As defined in the Atlas; a “saline formation” must contain water with a content of total dissolved solids greater than 10000 ppm. Further, a “saline formation” can include more than one named geological formation or may be defined as only part of a formation.

The areal extent of potentially suitable storage formations and the capacity estimates are intended to be an initial assessment and do not replace a site-specific characterization and assessment. Due to the national and regional scale of the study, the estimates of geological storage capacities have still a high degree of uncertainty.

The assessed storage formations had to meet the following criteria to be potentially suitable for storage:

- The pressure and temperature conditions in the storage formation had to be appropriate to keep the liquid or supercritical. Therefore, a cut-off value of 800 m depth was selected to ensure conditions that yield high-density .
- The presence of a suitable sealing system to limit vertical flow of the to the surface. A seal should consist of low-permeability rocks like shale, anhydrite or other evaporates. The thickness of these sealing systems was not considered, however.
- A combination of hydrogeological conditions to isolate the within the storage formation.

2.2.2. Hydrogeological settings of potential impacts of geological storage on fresh groundwater resources

EUROPE

Overlaying WHYMAP information on groundwater resources in Europe with GeoCapacity data on deep saline formations reveals major regional differences. To better visualize these differences, the three major thematic layers of the WHYMAP, i.e. large/uniform, complex and local/shallow aquifers, were overlain separately with GeoCapacity data:

Large uniform aquifers

In Central Europe, most deep saline formations suitable for storage onshore coincide with areas of large, uniform freshwater aquifers present in the major sedimentary basins (Figure 2.9). Examples are the North German Basin and the Paris Basin.

In the UK, the south eastern half of England is identified as large uniform aquifers but GeoCapacity data only identify potential storage offshore in the North Sea. This is related to the methodology used and seems to be controlled by the proven seal to structures in the hydrocarbon fields. Although potential storage does occur onshore in the Sherwood Sandstone Group at sufficient depth, the capacity of these deep saline formations, the integrity of the seals or traps and the up-dip links to potable aquifers, are not sufficiently understood to warrant inclusion.

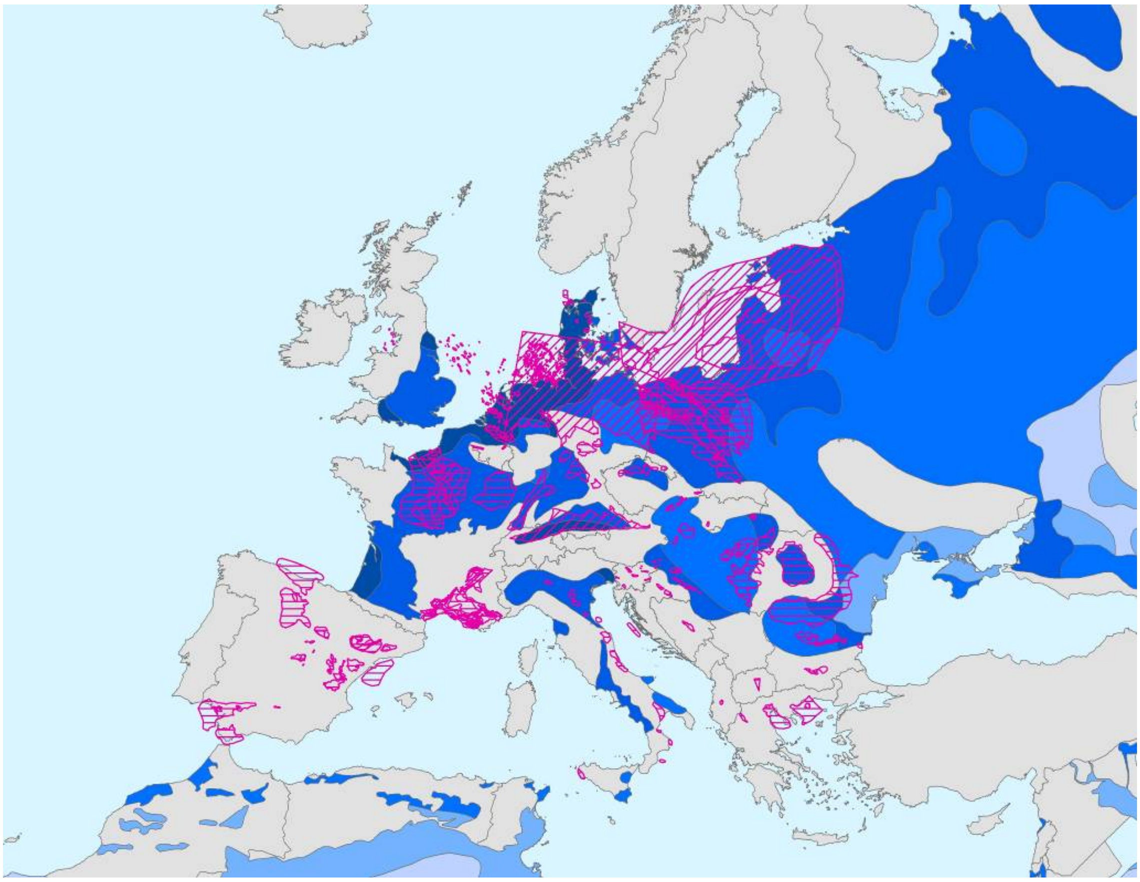


Figure 2.9: Combining GeoCapacity data on potential storage aquifers (both regional and detailed: hatched pink areas) with WHYMAP thematic layers representing large, uniform freshwater aquifers (blue shading).

However, the areas marked in blue (WHYMAP) comprise basins of different characteristics: for example, in the North German Basin, the deep saline aquifers are clearly separated in most parts from the shallow freshwater aquifers by impermeable barrier layers, e.g. the Rupelium clay (Figure 2.10).

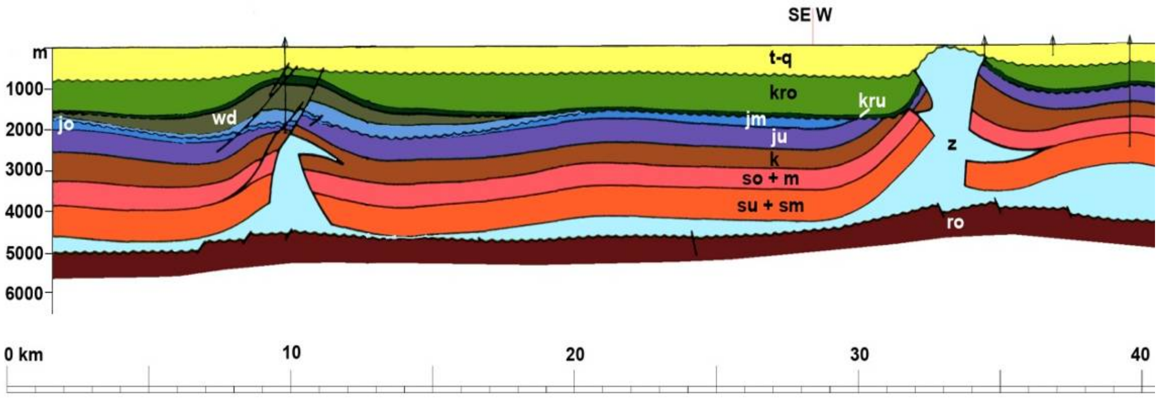


Figure 2.10: Schematic representation of a depth profile typical of the North German Basin.
Note that freshwater is present in the uppermost part of the yellow layer, e.g. above the Rupelium clay, whereas strata below contain saline water. (ro: Rotliegend; z: Zechstein (evaporites); su+sm: Lower and Middle Bunter; so+m: Upper Bunter & Muschelkalk; k: Keuper; ju/jm/jo: Lower/Middle/ Upper Jurassic; Wd: Wealden; kru/kro: Lower/Upper Cretaceous; t-q: Tertiary (including Rupelium) to Quaternary; modified from Baldschun et al., 2001).

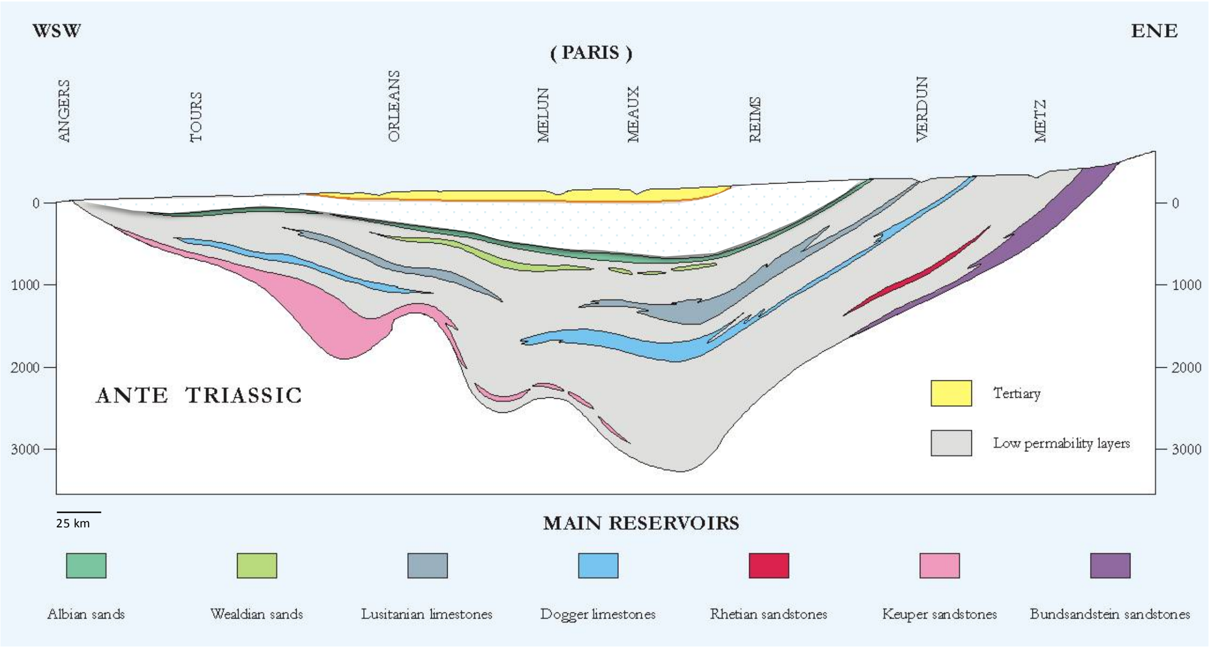


Figure 2.11: Schematic representation of a depth profile typical of the Paris Basin.
Note that freshwaters are present in the uppermost part above the Albian sands, whereas strata below contain saline water. Main reservoirs identified in the Paris Basin as target beds for storage are Dogger, Keuper and Bundsandstein (modified from Bonijoly et al., 2003).

In the Paris Basin (Figure 2.11, France), also deep freshwater resources are present in close vicinity to deep saline formations where storage may be envisaged (Dogger, Trias). Some of these deep freshwater resources may serve as "strategic" potable water resources (Albian sands in the Paris basin), being protected from surface contamination. Information about these deep freshwater aquifers is not contained in the Groundwater Resources Map of the World if there are significant shallower aquifers above them. Therefore regional knowledge of groundwater resources is needed to assess potential impacts by storage in DSF.

The other large sedimentary basin in France, the Aquitaine Basin, comprises complex vertical superposition of groundwater bodies giving rise to up to ten levels. This raises the potential for vertical exchanges and the existence of deep potable aquifers of strategic importance. In both basins, deep saline formation are separated from freshwater by low permeability layers, but given the importance of the freshwater resources, detailed studies will be required to assess the safety of storage.

- **Complex hydrogeological structure**

In Southern Europe, for example in the South of France and in Spain, deep saline formations identified coincide with more complex freshwater aquifer systems (Figure 2.12), including karstic systems.

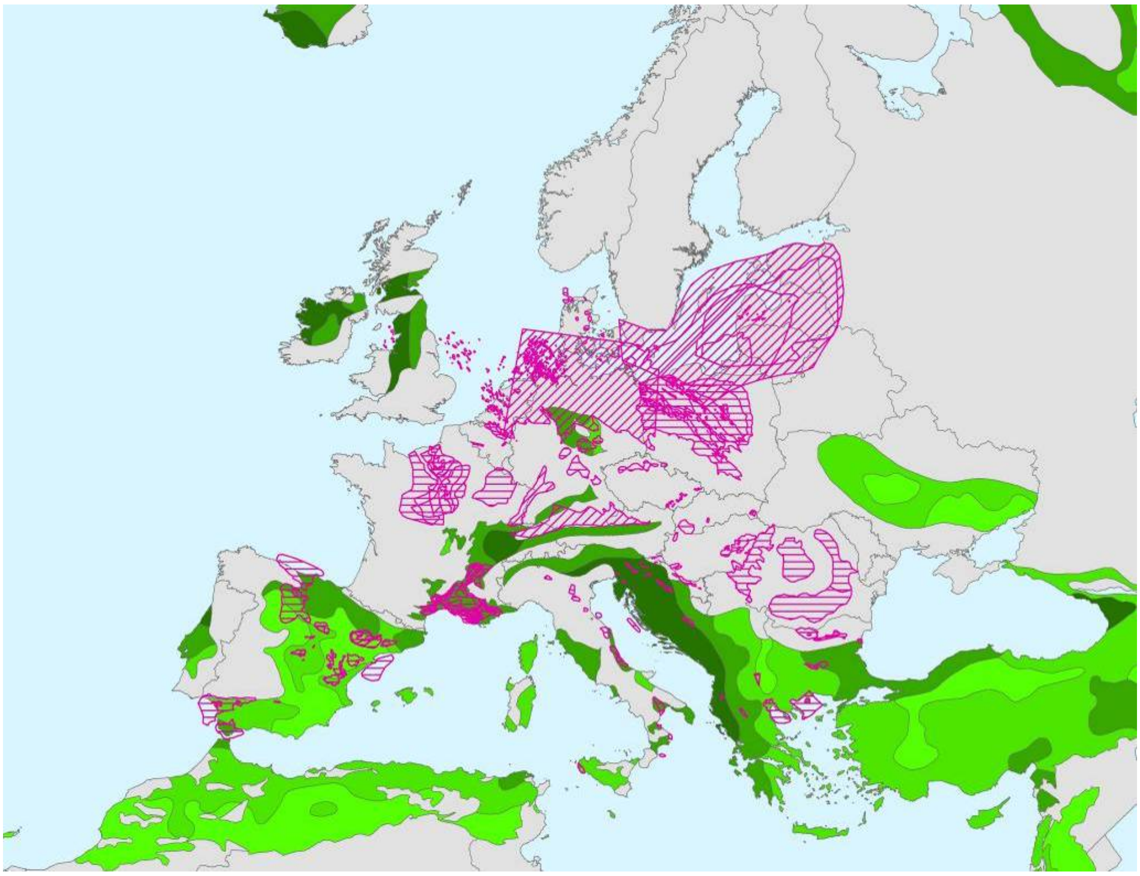


Figure 2.12: Combining GeoCapacity data on potential storage aquifers (both regional and detailed: hatched pink areas) with WHYMAP thematic layers representing areas with complex hydrogeological structure (green shading).

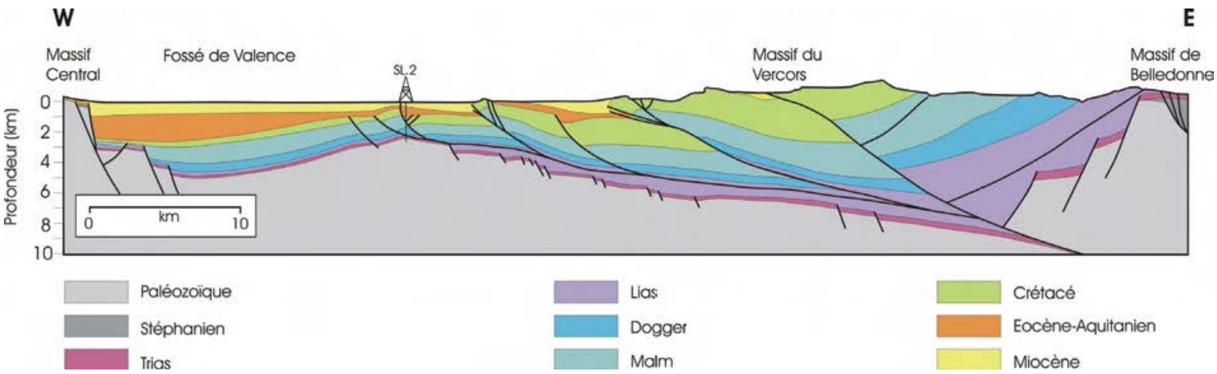


Figure 2.13: Schematic representation of a depth profile typical of Southeast France (Deville, 1994 in Rubert, 2009).

As an example for the complex structure, the Figure 2.13 illustrates the Valence basin (South East France). This basin has been intensely studied as it contains the “natural analogue” site of Montmiral (see section 3.3.3, page 77). This site is a natural reservoir, about 2500 metres below the surface in the Triassic geological layer, near Valence (France). In contrast to large sedimentary basins (e.g. the Paris Basin), this Tertiary basin is oriented along a N-S fault network as a result of successive rifting and collision stages associated with the geological history of the South East Basin (Variscan orogenesis, Tethysian rifting, Pyrenean compression, Alpine compression). Fresh groundwaters are found in the quaternary subsurface aquifers and in Tertiary formations (Miocene aquifer), at depths of about 100 metres below the surface.

- **Local/shallow aquifers**

In the Scandinavian countries, no deep saline formations suitable for storage are present (Figure 2.14). Here, mainly crystalline basement rocks crop out. Similarly, in the WHYMAP only the presence of “local/shallow aquifers” is indicated for Scandinavia, i.e. groundwater is limited to the alteration zone of the bedrock and overlying shallow layers of weathered bedrock.

Similarly across the rest of Europe, where WHYMAP identifies the presence of “local/shallow aquifers”, the GeoCapacity data does not indicate potential for storage. There is particularly good correlation in Eastern Europe towards the Black Sea.

However, some of the smaller storage areas identified by the GeoCapacity assessment coincide with WHYMAP areas indicating the predominance of relatively dense bedrock exposed to the surface, e.g. the Weiden Basin, West of Bohemian Massif, Germany. To test if this difference is caused by the different scales of the two data sets, GeoCapacity data were combined with the International Hydrogeological Map of Europe (IHME1500; ://www.bgr.de/app/fishy/ihme1500/download.) at scale 1:5 000 000. This combination revealed a better agreement indicating that difference in resolution between WHYMAP and GeoCapacity representations was the major factor controlling the observed discrepancy.

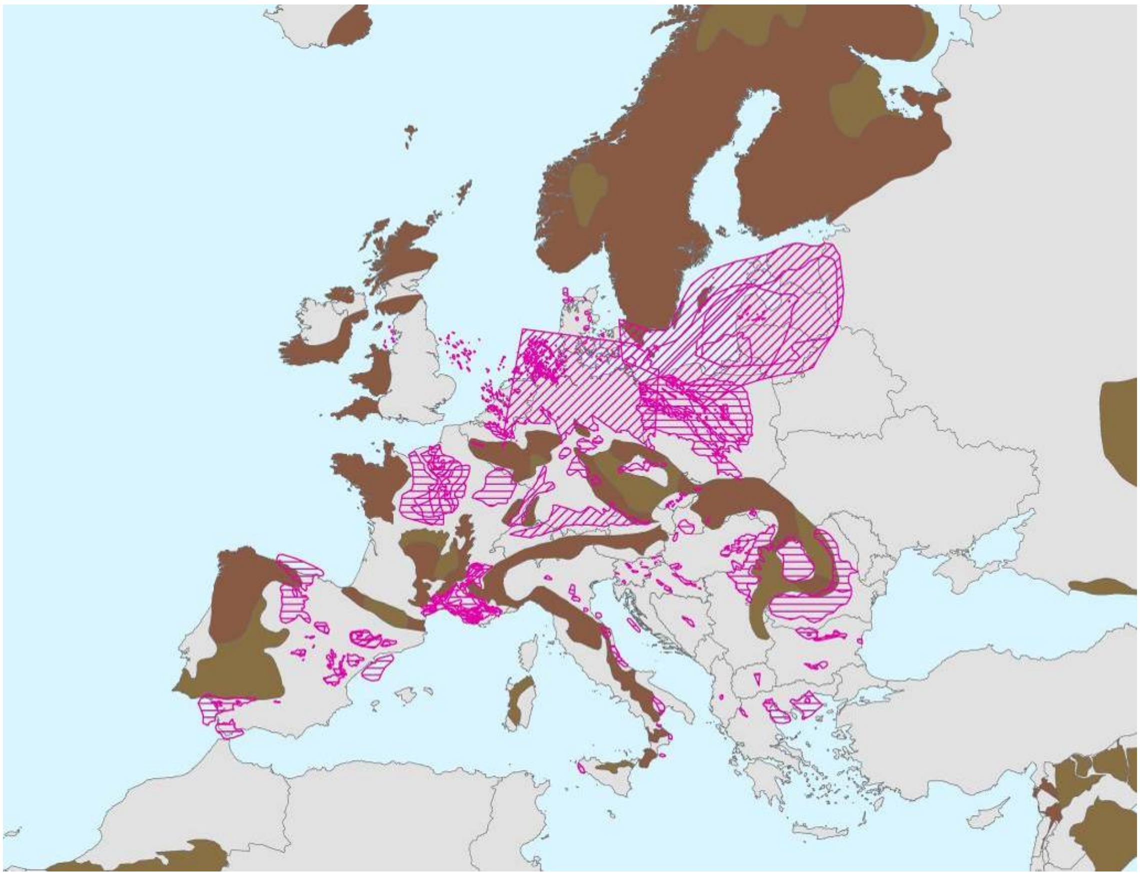


Figure 2.14: Combining GeoCapacity data on potential storage aquifers (both regional and detailed: hatched pink areas) with WHYMAP thematic layers representing local/shallow aquifers (brown shading).

North America

Combining WHYMAP information on groundwater resources in North America with data of the “Carbon Sequestration Atlas of the United States and Canada” reveals a major difference to Europe: Whereas in Europe regions with deep saline aquifers suitable for storage mostly coincide with areas of large, uniform freshwater aquifers, in the U.S. and in Canada deep saline aquifers often coincide with areas with “complex” freshwater aquifer systems (Figure 2.15) e.g. in the central plains of North America. Hydrologically speaking, this region can be divided into bedrock and sediment-dominated terrains with surficial aquifers, particularly buried valley aquifers, and near-surface bedrock aquifers, such as fluvial sandstone, being important. Yield and quality of the latter vary due to interbedded marine mudstone and isolated channel sand deposits (Natural Resources Canada (NRC), 2009). Extensive deep saline formations are present in this region in Paleozoic and Mesozoic formations of Montana and Wyoming’s sedimentary basins. Potential formations for storage are dominated by porous and permeable sandstone, limestone, and dolostone interbedded with evaporates and shales (DOE NETL., 2010).

Few saline aquifers occur in areas indicated by WHYMAP as comprising predominantly local and shallow aquifers (Figure 2.16).

In Alaska, deep saline formations have been screened, but potential storage volumes are not estimated due to insufficient data or pending further evaluations. Therefore, these formations are not included in the Atlas III Map of assessed DSF.

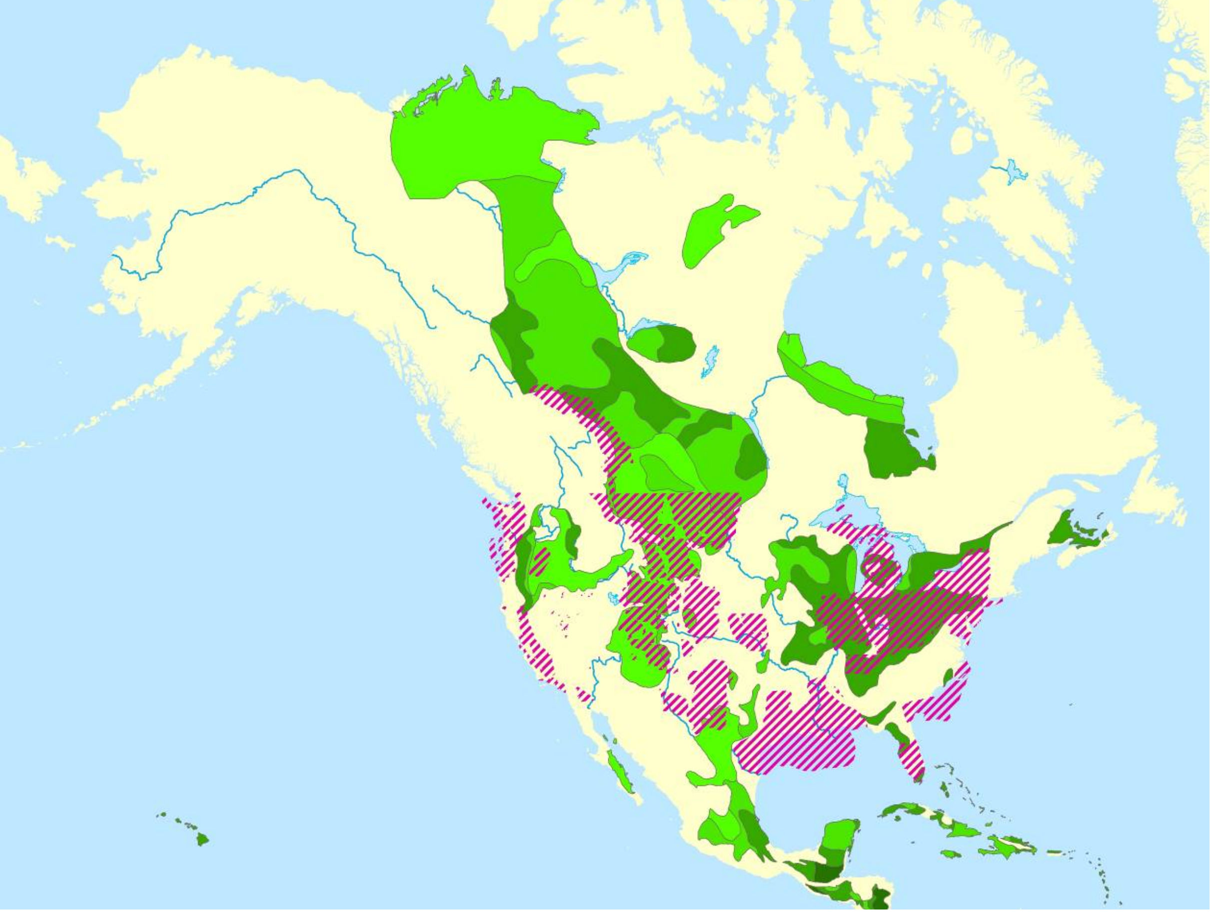


Figure 2.15: Combining data on saline aquifers from the Carbon Sequestration Atlas of the United States and Canada (hatched pink areas) with WHYMAP thematic layers representing areas with complex hydrogeological structures (green shading).

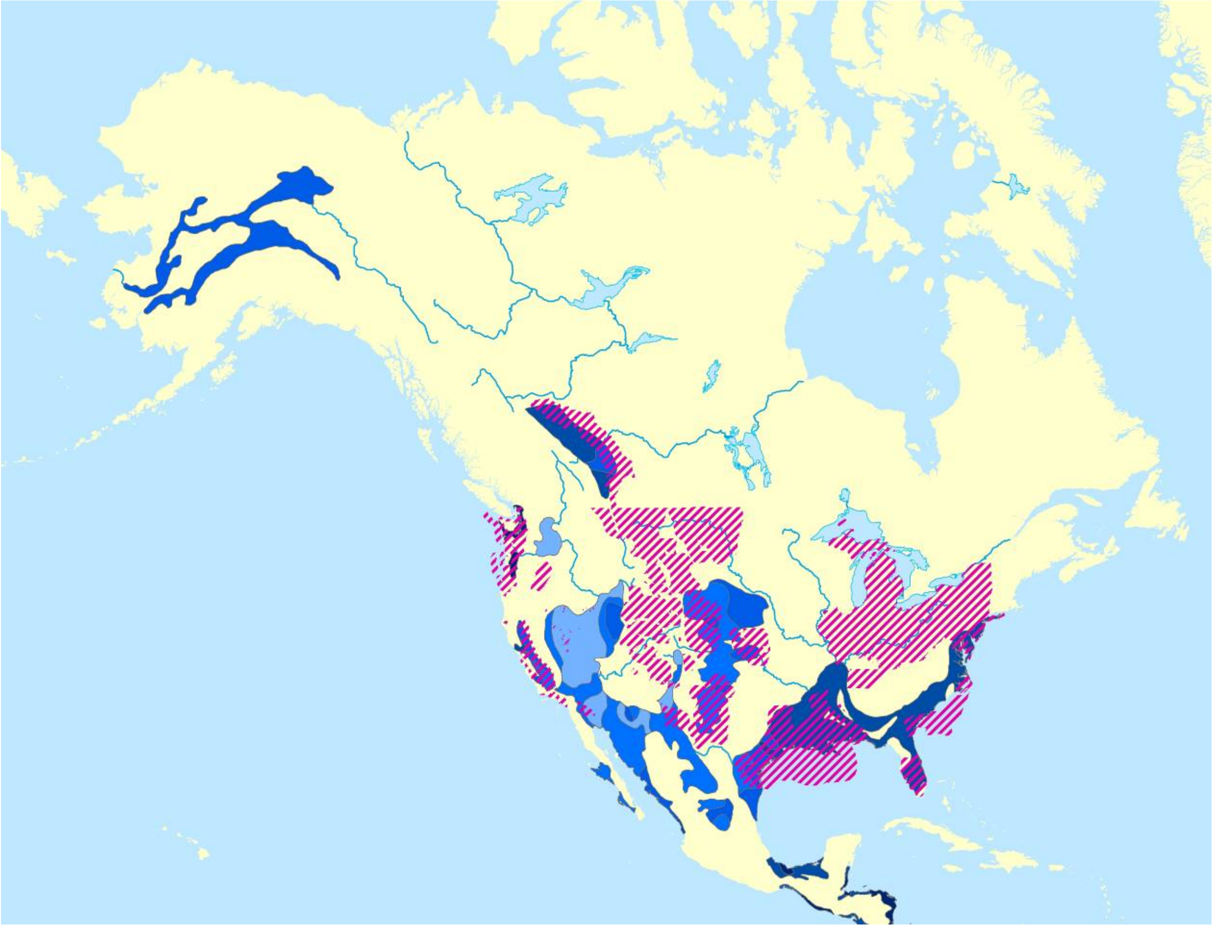


Figure 2.16: Combining data on saline aquifers from the Carbon Sequestration Atlas of the United States and Canada (hatched pink areas) with WHYMAP thematic layers representing large, uniform freshwater aquifers (blue shading).

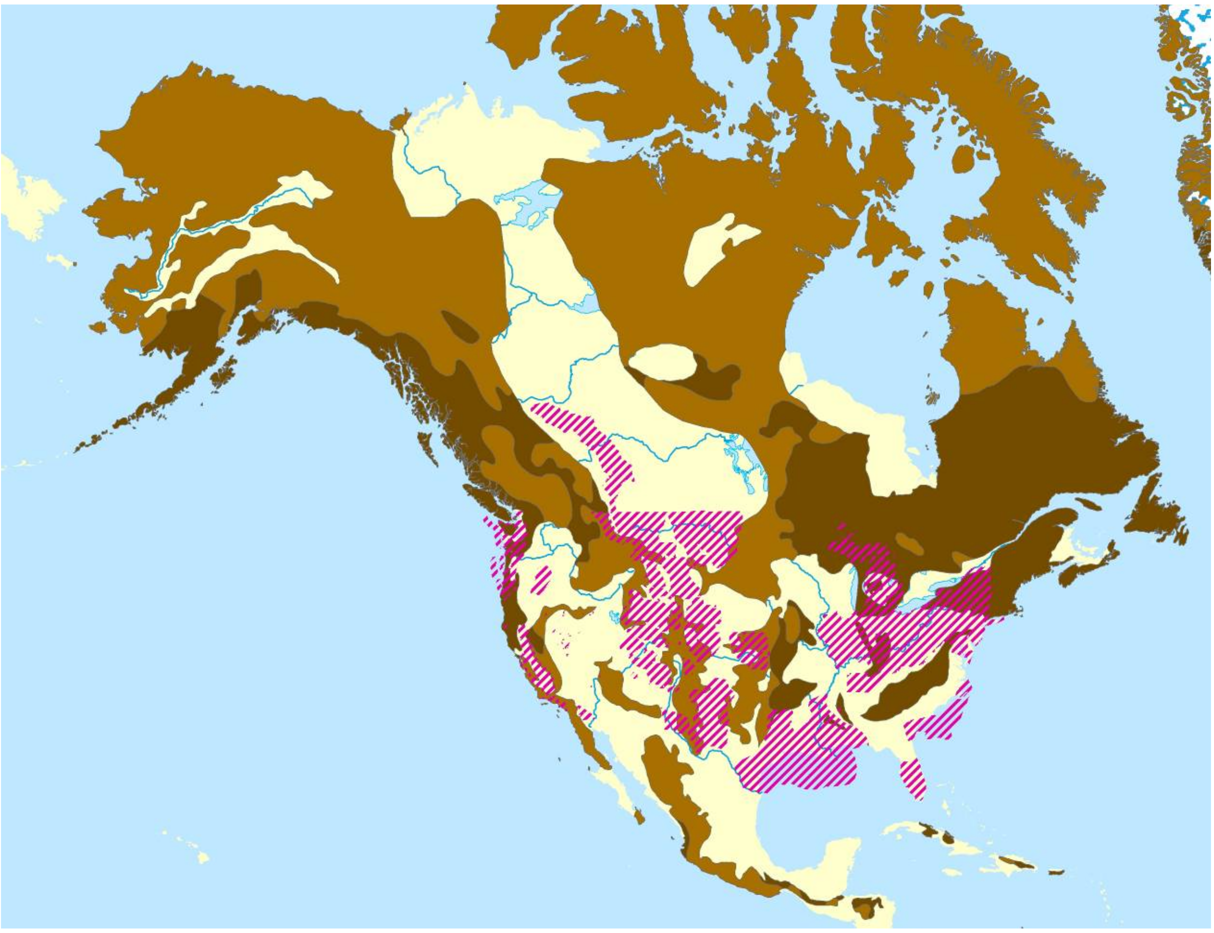


Figure 2.17: Combining data on saline aquifers from the Carbon Sequestration Atlas of the United States and Canada (hatched pink areas) with WHYMAP thematic layers representing areas with local/shallow aquifers (brown shading).

China

WHYMAP information on groundwater resources has been combined with information from the GeoCapacity project (Figure 2.18) in that six principle onshore basins have been identified with potential for storage. Depth data are insufficient to determine the extent to which groundwater containing formations are separated from the deep saline aquifers by lower permeability strata.

The Western Inland Basins (1. Talimu Basin, 2. Zhungeer Basin, 3. Chaitamu Basin and Hexi Corridor) coincide with large uniform groundwater basins. Typically these areas comprise arid land with low precipitation but with large groundwater resources in piedmont plains (Chen and Cai, 2000). Much of these areas are identified by WHYMAP as having high salinity shallow groundwater (>5 g/l TDS).

Also the Huang-Huai-Hai Plain and Songliao (Areas 5) coincide with a large groundwater basin. The Eastern Plains comprise thick unconsolidated sediments with multiple aquifers. 76% of China's groundwater abstraction occurs within the Plains of North China (Chen and Cai, 2000).

The Southwest Karst Hilly Land (Area 6) is identified from WHYMAP as being an area with local, shallow aquifers. The region is dominated by carbonate rocks with karstic flow, 24% of China's groundwater abstraction occurs within the Hilly Land (Chen and Cai, 2000).

The basin (Area 4) identified by GeoCapacity largely covers an area where there are no major groundwater resources. Details of the groundwater basin in the centre of the area are not available and the shallow groundwater in the west is identified as being saline.

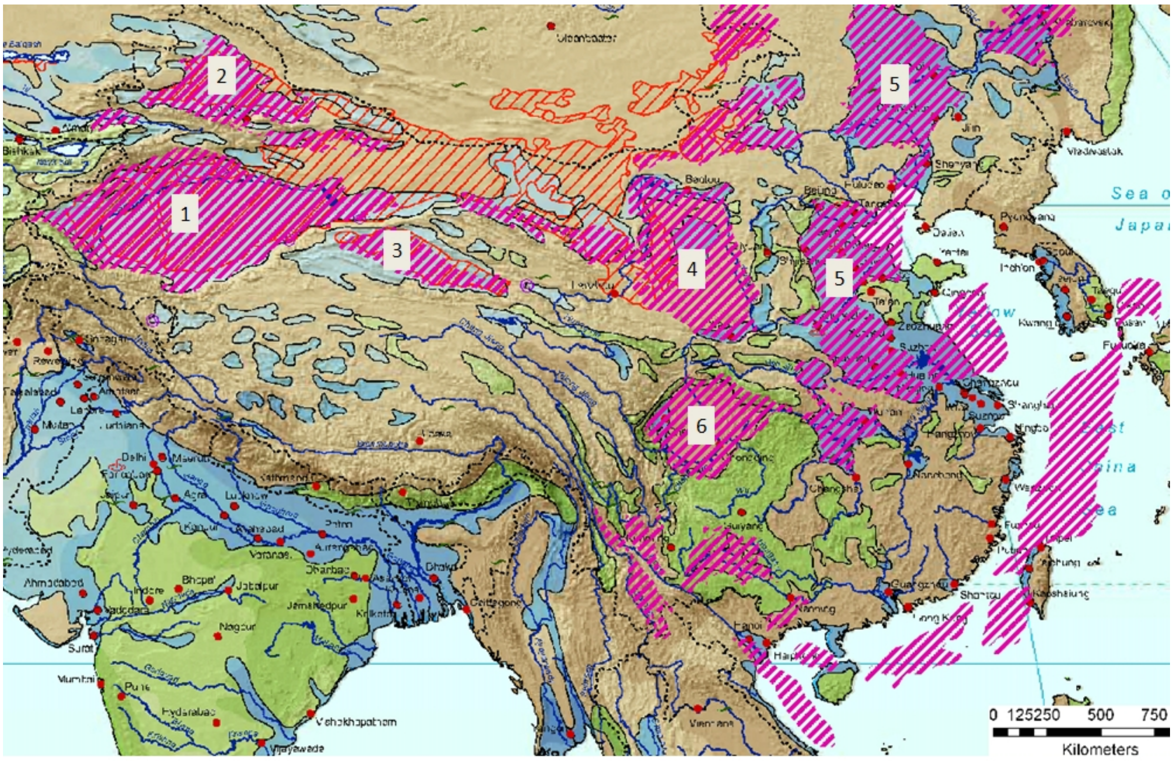


Figure 2.18: WHYMAP and major sedimentary basins combined to show superposition of basins with potential for storage. Numbered basins are described above.

2.3. TYPOLOGY OF HYDROGEOLOGICAL SETTINGS

From the juxtaposition of groundwater resources and potential storage reservoirs for Europe and North America, the following typology of hydrogeological settings where impacts could occur was developed:

a) areas with large and rather uniform freshwater aquifers, both shallow and deep, coinciding with deep saline formations;

b) areas with more complex hydrogeological structures where productive freshwater aquifers (including karst aquifers) may occur in close vicinity to non-aquiferous strata coinciding with deep saline formations;

c) areas with local/shallow aquifers coinciding with deep saline formations;

d) areas with already saline groundwater coinciding with deep saline formations;

e) areas of over-exploitation or mining of groundwater resources coinciding with deep saline formations;

f) areas with no deep saline formations suitable or identified for storage.

In areas without any deep saline formations suitable for storage and in areas without any important freshwater aquifers overlying deep saline aquifers, e.g. in offshore areas, no potential impacts are expected. This is the same case for areas where deep saline formations have not yet been identified due to a lack of data.

This typology may be used on a regional scale as a guideline to assess the types of potential impacts of storage on fresh groundwater resources that may be considered in the selection and evaluation process of suitable storage areas. This has been done for selected European countries in the Table 2.1 to test the usefulness of the typology. The occurrence of the different types in Europe is illustrated in Figure 2.19.

Table 2.1: Application of GEOCAPACITY and WHYMAP mapping to determine potential impacts of storage in Deep Saline Formations on potable groundwater resources.

GeoCapacity mapping	WHYMAP Basin	Geocapacity and WHYMAP identify potential conflict	Hydrogeological typology	Investigation of potential impacts on groundwater resources
United Kingdom				
Only offshore storage sites in oil and gas reservoirs are identified by GeoCapacity mapping. The Sherwood Sandstone Group (SSG) offshore offers the best prospect for storage.	WHYMAP identifies the entire southeast of England as a major aquifer basin. In reality only the Sherwood Sandstone Group and the Chalk are major basins. Only the SSG basins exceed 1000 m in depth over extensive areas to be suitable for CCS.	No, the offshore extension of the SSG was not identified by the GeoCapacity project.	a) Freshwater aquifer (Chalk) overlying deep saline formation in the Sherwood Sandstone Group. Onshore near outcrop this is freshwater but becomes saline where confined and offshore.	The CASSEM project investigated the impact of injection offshore in the Sherwood Sandstone group on shallow onshore groundwater systems. The groundwater model identifies possible impacts on fresh groundwaters.

FRANCE				
Three sedimentary basin (Paris, Aquitaine, Southeast) Geocapacity mapping identified Paris basin offering the best formations capacity for storage	Paris basin and Aquitaine Basin are identified as major groundwater bodies localized in sedimentary basins (clastic and carbonate formations). South east contains complex hydrological structure	The potential conflicts are mainly for the Paris Basin. The Aquitaine Basin has not been mapped because it has not been investigated for this purpose: (low industrial emitters and data on deep formations not available)	a) In the Paris Basin b) In southeast but low storage capacity f) in the Aquitaine Basin	Investigation on potential impacts of storage in Dogger formations on Albian shallow aquifer are conducted. Low permeable layers seems to be sufficient to avoid overpressure and leakage through natural pathways
GERMANY				
Onshore: sedimentary basins with a minimum depth of 1000 m (regional aquifers); offshore: potential storage structures (detailed aquifers)	WHYMAP identifies majority of the sedimentary basins in Germany as “large and rather uniform groundwater basins”	Onshore, regional aquifers potentially suitable for storage largely coincide with areas of large rather uniform freshwater aquifers as indicated in the Groundwater resources of the World Map	a)In the North German Basin, the Franconian Basin, the Upper Rhine Graben and the South German Molasse Basin; b) in the Thuringian Basin and in southern parts of the North German Basin; c) only locally.	BGR is currently mapping distribution, thickness, and properties of the Oligocene Rupelium clay in North Germany, the main barrier between fresh groundwater and DSF.
DENMARK				
On and offshore storage sites in both oil and gas reservoirs and aquifer structures with closure have been identified. Five regional formations offer prospects; the most widespread of which is the Bunter Sandstone Formation	Denmark is classified as large uniform freshwater aquifers and no local shallow aquifers. This is the case for the Pre-Quaternary chalk, limestone, marl, sand succession, but not for the glacial Quaternary aquifers	Offshore conflicts would be due to hydrocarbons in offshore structures, which is unlikely. Onshore there may be a conflict with the interest for the fresh groundwater resource.	Typology only applies to onshore a) In the main part of the country. b) In the Quaternary aquifers in Eastern Jutland. c), d) and e) only occur locally	Potential impacts have been investigated for the Vedsted structure (onshore).

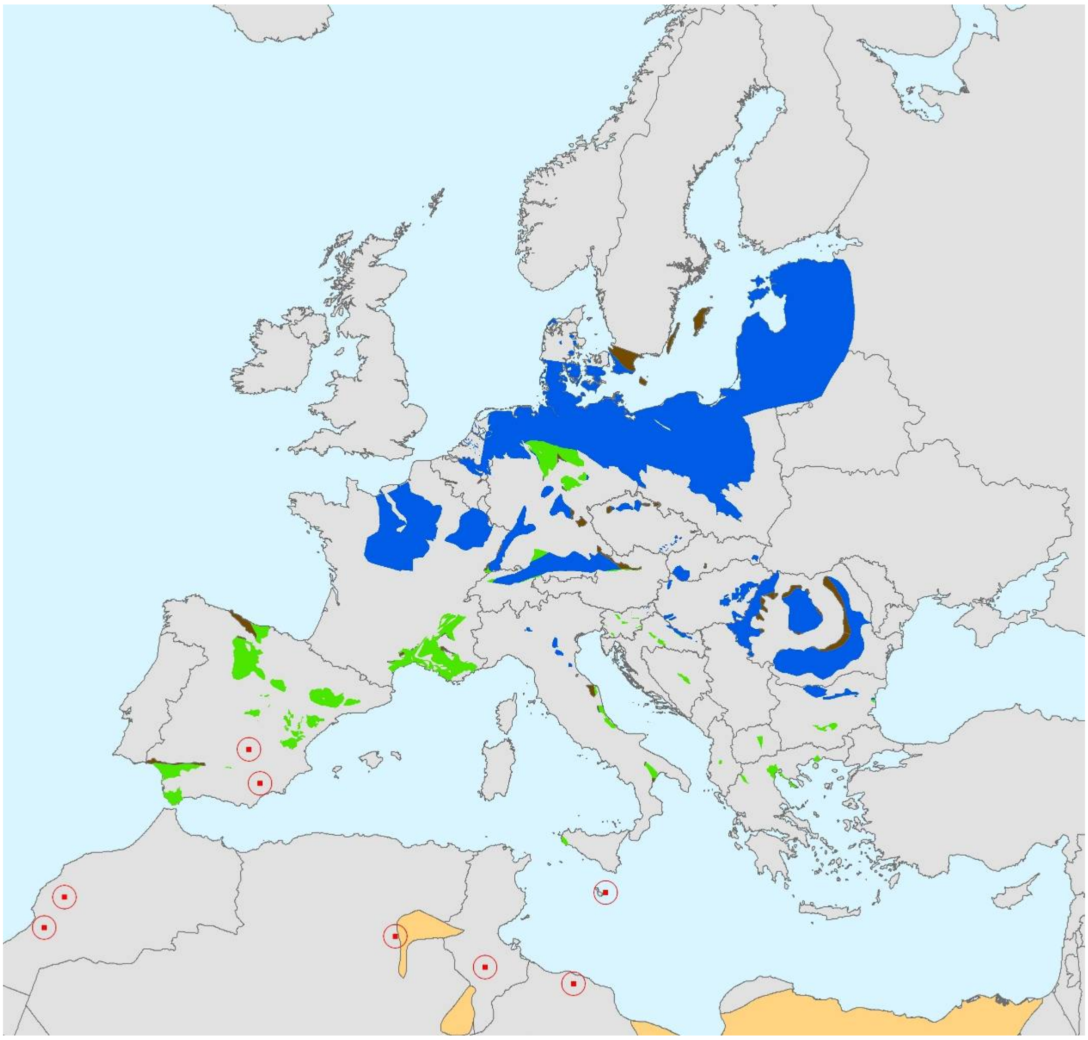


Figure 2.19: Illustration of typology for Europe.
Blue: areas with large and rather uniform freshwater aquifers (Type a). Green: areas with more complex hydrogeological structures coinciding with deep saline formations (Type b). Brown: areas with local/shallow aquifers coinciding with deep saline aquifers (Type c). Grey: areas with no deep saline formations suitable for storage (Type f). Areas with saline surface waters are given in orange. Rred symbols indicate areas of heavy groundwater abstraction with overexploitation.

2.4. CONCLUSIONS

In order to establish a guideline to assess the types of potential impacts of storage on freshwater resources on a regional scale, this study investigated the juxtaposition of deep saline formations (DSF), potentially suitable for geological storage, and shallow potable groundwater resources from the global perspective.

Mapping assessments of potential geological storage, including GIS-based where available, were compared with hydrogeological knowledge at a global and continental scale in order to identify where potential DSFs are in juxtaposition with fresh groundwater resources. Two areas only, Europe (GeoCapacity) and North America (NATCARB) had assessable GIS and these were used for comparison with the global hydrogeological map (WHYMAP).

Information on depth of aquifers and their relationship to underlying DSFs is not available in WHYMAP so local, more detailed information is needed at the country and basin scale. However, as a high level tool, this approach has provided some useful insights. Comparison of groundwater resources information in North America with data of the “Carbon Sequestration Atlas of the United States and Canada” reveals a major difference to Europe.

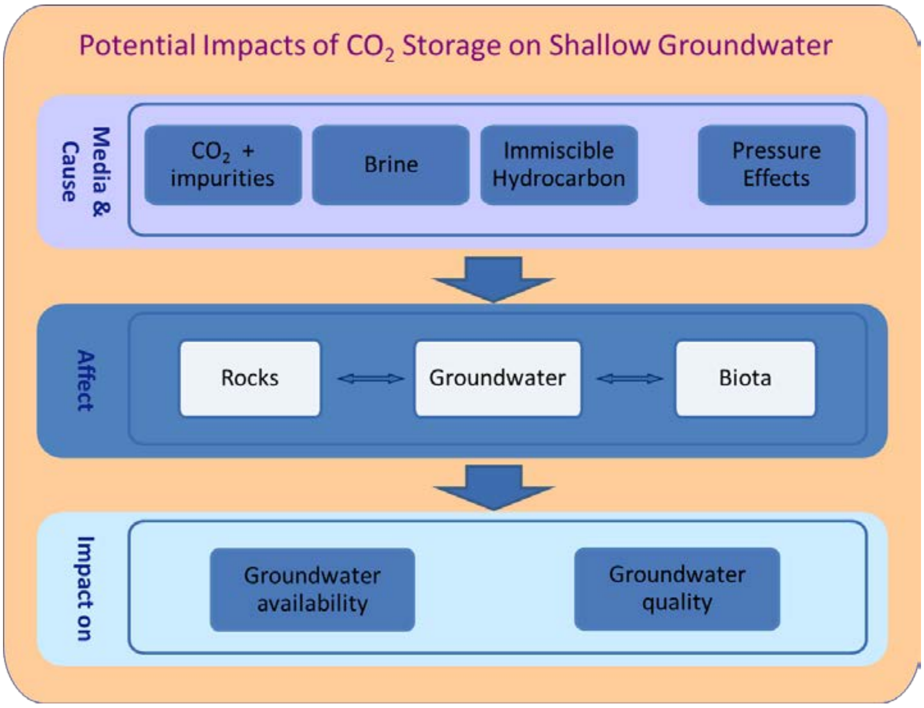
Whereas in Europe regions with deep saline formations suitable for storage mostly coincide with areas of large, uniform freshwater aquifers, in the U.S. and in Canada deep saline aquifers often coincide with areas with “complex” freshwater aquifer systems.

In China where GeoCapacity data are available, the western and north-eastern basins identified as potential areas for storage coincide with large groundwater basins. In other areas, potential storage formations are found in areas with no groundwater resources identified or in areas of complex hydrogeological structure that contain important freshwater resources. In Australia, the major onshore prospects for storage coincide with ‘major groundwater basins’ on WHYMAP, including the Great Artesian Basin. Here fresh groundwater is found at great depth and storage of in fresh groundwater is being investigated. In India, comparison of the results of this methodology with the WHYMAP distribution of aquifers was not undertaken as the majority of basins with good potential lie offshore.

A typology of hydrogeological settings was developed as a general guideline that may be used in the selection and evaluation process of suitable storage areas. It was tested on selected European countries where local detailed knowledge was available and a map of storage prospectivity was produced. This provides a valuable overview but also demonstrated that each site’s geological complexity and the relative positions and depths of deep saline and freshwater aquifers, will determine the degree of potential impacts.

3. Mechanisms of potential impacts on shallow groundwater

In this chapter potential effects of geological storage of in deep saline aquifers and depleted gas fields on shallow aquifers are considered. The study is based on a literature review, to which case studies are added to illustrate actual analogue examples.



Impacts on groundwater can be caused in various ways. The injected , which contains impurities from fuel utilization and capture and transport conditioning, could enter directly into groundwater and affect its quality. Saline reservoir water can be displaced and eventually mix with shallow groundwater. When dissolves in formation waters, it can cause geochemical reactions that release elements from the reservoir and overburden rocks and that may eventually reach shallow groundwater. Natural gas or oil can be mobilized by supercritical or ascend along leakage pathways as a separate phase, together with the -rich phase. This risk is particularly associated with storage in depleted hydrocarbon fields, so is not considered further within this report. Apart from the possible direct effects these media can have on the groundwater composition, the pressure needed for injection into the deep saline formations may cause pressurization or displacement of shallow groundwater.

Alteration of the groundwater composition by media related to storage will also affect interactions between aquifer rocks, fresh groundwater, and organisms living in shallow aquifers. These interactions can cause further alterations of groundwater composition, which are discussed later in this chapter.

Groundwater availability must also be considered for the assessment of potential impacts on fresh groundwater quality. Groundwater quality can be compared to initial background values and to water quality standards. Impacts on groundwater availability have to take into account the relation between groundwater resources and water production, as well as the local use of groundwater, which could be subject to different quality standards.

For the mechanisms of potential impact on shallow groundwater, the concept of the “analogue” is essential. Analogue examples are thought to have some aspects in common with impacts that may result from storage of in deep saline aquifers, although they are not based on real injection case studies. As an example the effects of chemical reactions, when is dissolved in freshwater, on water quality may be unveiled in laboratory or field tests, but the occurrence of the dissolved excess at that location may be just a precondition.

The aim is through the study of analogues within the broad field of physical and chemical effects to illustrate a mosaic of documented or likely tendencies, which may again be combined into potential scenarios.

A problem of timing is common to all foreseeable effects of injection into a deep saline aquifer. The effects studied to date are either short term related to laboratory experiments, or long term related to natural seeps. The effects in between these two extremes is somewhat bridged by flue gas injection and modeling studies, but again only for simplified systems.

Practical experience from injection for EOR purposes into oil fields illustrates for these situations, where nature has proven the sealing capacity to be good, that where seals are appropriate leakage is minimal and unproblematic. Indeed many authors use phrases on the considered potential effects on groundwater aquifers of injection of saying that the effect is very unlikely. Nevertheless the potential exists for to escape from the target reservoir, migration along permeable pathways and discharge in subsurface or surface environments.

Figure 3.1: Periodically erupting well releasing natural -rich groundwater. The “Brubbel”, Germany. Photo courtesy of Franz May (2008).

3.1. INTRODUCTION TO POTENTIAL IMPACTS

Birkholzer *et al.* (2007) presented schematically the large-scale potential subsurface impacts that will be experienced during and after industrial-scale injection of (Figure 3.2). While the plume at depth may be safely trapped under a low-permeability cap rock with anticlinal structure, the footprint area of the plume is smaller than the footprint area of the displaced brine, which in turn is much smaller than the footprint area of elevated pressure. The footprint area of displaced brine illustrates the approximate location of a displaced fluid volume that was originally located within the plume footprint. Of course, brine displacement occurs to some degree wherever a pressure gradient develops in response to injection, which suggests the possibility of water quality changes as brines or brackish water may potentially migrate into freshwater regions. The footprint area of elevated pressure indicates the extremely large subsurface volumes, where such pressure impacts might potentially be expected.

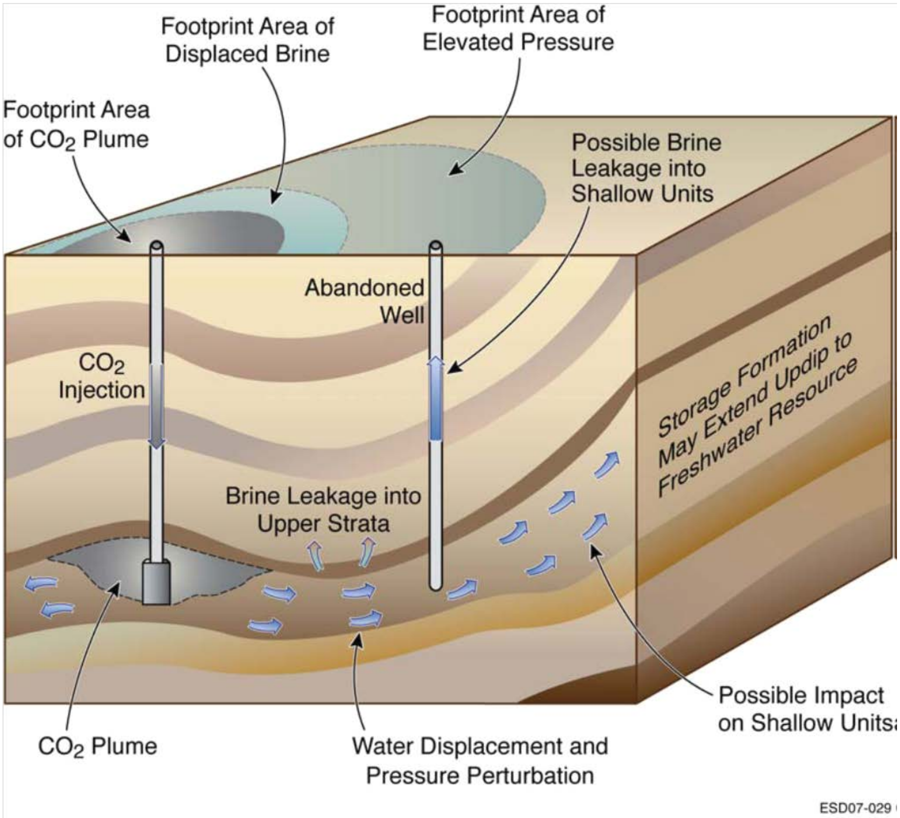


Figure 3.2: Schematic diagram showing different regions of potential influence related to storage (Birkholzer et al., 2007).

The potential upward or lateral leakage of (supercritical, gas, or dissolved) into shallow aquifers may be driven by the pressure of injection. Also, the density of injected supercritical is less than for highly saline formation water. At shallow depth, in particular, and where the geothermal gradient and the surface temperature are high, leakage may therefore be driven by buoyancy effects (Bachu, 2003). The complex behaviour, effects and reactions of stored in the subsurface are given in an overview by Friedman (2007) and in review of modelling approaches by Gaus *et al.* (2008).

It is unlikely that eruptive release of from storage reservoirs may be caused only by the stored mechanical energy in the accumulation of non-condensing gas. Thus, for eruptive release to take place, a substantial contribution from thermal energy is needed (Pruess, 2006a, 2007). Minor, mainly natural eruptions of from wells are well known, but eruption of to land surface of SC- would cause a rapid cooling due to the decompression. Under some conditions flow may be reduced by the subsequent precipitation of hydrates or even ice. Also Joule-Thomson (adiabatic) cooling would occur for the expanding gas (Oldenburg, 2007), although this would be partly compensated by heat transfer from the surroundings.

 injection or the upward migration of a plume from a deep saline formation could potentially lead to several reactions, which could have undesirable effects on shallow aquifers. These potential risks are:

Physical

- A pressure plume may potentially affect shallower aquifers sensitive to pressures changes caused by injection.
- Saline formation water may potentially be pushed into the aquifer
- Fractures may potentially be produced and/or opened

Chemical

- may potentially dissolve into and react with formation water.
- may potentially react by dissolving or clogging the aquifer rock.
- Saline formation water may potentially mix with fresh groundwater.

Biological

- may be used by microorganisms and modify biodiversity
- may mobilize organic compounds from the geological formation

In this chapter these risks caused by storage in deep saline formations, including the changes they may cause, will be addressed. Natural analogues to potential effects on shallow groundwater of storage have been referred to from literature as well as detailed via different case studies, Table 3.1.

Table 3.1: Case studies illustrated in the present report as natural analogues for potential pressure and chemical effects (natural as well as industrial) of storage.

Case studies	Topic	Name	Country
Potential pressure effects	Natural gas storage	Lussagnet and Isaute	France
	Saline water boundary	Ringsted	Denmark
Potential chemical effects	driven springs	Central Germany	Germany
	Natural accumulation	Montmiral	France
	Brine injection	Werra	Germany
	Acidification by acid rain	Grindsted	Denmark
	Sinkhole formation	Central Italy	Italy
	Travertine & tufa	Various location	World

3.2. POTENTIAL PRESSURE IMPACTS IN SHALLOW GROUNDWATER

Pressure changes induced by a plume may potentially impact the groundwater flow magnitude and directions (regional flow), the water table levels and the distribution of discharge areas in shallow aquifers (Nicot *et al.*, 2006; Tsang *et al.*, 2008; EPA, 2008; see also Chapter 4 for details on the numerical modelling of such pressure changes).

This potential impact may influence the water resources available for municipal water supplies causing interference with abstraction wells, springs or seeps (See Lussagnet and Izaute case study, page 60). Any modification of groundwater pressure would change the water table levels and concomitantly change flow rates and the geometry of the water bodies (EPA, 2008).

3.2.1. Hydrodynamic effects

Pressure build-up

Injection of in a deep saline formation requires excess pressure to overcome pore throat entry pressures and displace the pre-existing formation fluid. Hereby, a pressure plume is developed, which spreads in the deep saline formation both laterally and vertically. This pressure plume may potentially affect overlying potable water aquifers.

The potential changes in groundwater table to be expected in an unconfined aquifer can be estimated from the predicted pressure changes, equating the compressibility-related pore space increase in the confined system to the additional pore space occupied by water table rise (Birkholzer *et al.*, 2009).

The storativity of the confined aquifer can be calculated as:

$$Ss = b\ \phi\ \rho w\ g\ (\beta w + \beta p)$$

where b is the aquifer thickness, ϕ is porosity, ρw is water density, g is gravity acceleration, and βw and βp are water and pore compressibility, respectively.

Multiplying storativity with predicted pressure increase and dividing by porosity gives the approximate water table rise in an unconfined aquifer. These potential rises in the groundwater table are negligibly small (e.g. Yamamoto *et al.,* 2009a, 2009b; Birkholzer *et al.,* 2007, 2009; Nicot 2008) - see Section 4.2 for details on the numerical modelling of such water table changes.

The original pressure in the pore space of the deep saline formation may ideally be hydrostatic, only deviating due to salinity variations (or the presence of hydrocarbons). Excess pressure must be exerted when is injected into a deep saline formation resulting in a pressure transient that will disperse and equalize within the deep saline formation at a rate which depends on the flow properties of the formations (deep saline formation and sealing formation). For deep saline formations that are sealed both vertically and laterally, or if transmissivity properties are too low for the selected injection flow rate, the pressure may increase to the point where it overcomes the entry pressure of fractures in the cap rock or imperfections in well completions, or it overcomes lithostatic pressure and causes hydro-fracturing (Rutqvist, 2006). The pressure build-up will be less in deep saline formations that extend without lateral seals as may be caused by faults or facies changes.

Pathways via lateral natural or man-made discontinuity may potentially connect the storage formation to overlying aquifers or aquitards modifying hydro-regional flow and chemistry of the native fluid (see Tsang *et al.*, 2008 and citation therein as well as section 4 of this report dedicated to the case study modelling).

Behaviour of during potential upward migration

Supercritical is less dense than brines, and due to buoyancy effects it tends to move naturally upward from the storage formation. Along the ascent route, as confining pressures decrease, the supercritical will expand as a gas phase (and potentially cause icing due to the required energy consumption), whereas dissolved will degas if the solubility threshold is surpassed (unless it is diluted into percolating fresh groundwater).

The physicochemical process of dissolution and degassing of may potentially occur repeatedly along the flow path of ascending saturated water, depending on pressure, temperature, and the flux ratio of deep fluids to shallow groundwater. At shallow depths the effect of decreasing pressure dominates over the temperature effect on solubility, so that -rich waters in springs often tend to become super-saturated and degas (May, 2002a; Pruess, 2007), causing to migrate as a separate gas phase and carbonate minerals to precipitate.

Due to slow degassing kinetics, the water discharging from wells and springs is usually oversaturated with respect to , so that the water is sparkling or bubbling at the surface. Some wells discharge regularly over-saturated water in vigorous eruptions (“Sprudel-Quellen”, Germany). Figure 3.1 is one example of this common phenomenon, scientifically explained by Henrich (1910). Due to contact with atmospheric oxygen, dissolved iron precipitates, leaving distinct rusty colours in streams or wells. Because of these obvious features, leakage of would probably be detected soon after ascent to the surface in densely populated regions.

Macpherson (2009) states that the amount of that will degas from produced groundwater is not simply the difference between atmospheric and groundwater partial pressures, because of dissolved inorganic carbon (DIC) redistribution with degassing, trapping by carbonate mineral precipitation and because of pH adjustment due to precipitation of other solids. It is, instead, dependent on the major-element chemistry of the water in addition to pH and temperature.

Migration of brine

The term ”brines” refers to several types of fluid. First it is deep saline water as encountered in deep saline formations, secondly it is water trapped in argillaceous seal and cap rocks. These old and deeply situated waters are usually saline because their primary salinity is preserved (connate waters) or because water-rock interactions (e.g. evaporative dissolution) have been relatively extensive.

Migration of brine into overlying and adjacent freshwater aquifers could potentially cause deterioration of water quality as water with high amount of total dissolved solids is not recommended for human consumption. As an example total dissolved solids greater than 500 mg/l is not recommended for human consumption in USA (EPA, 2009a). Moreover, brines most often contain elevated concentrations of trace elements, as exemplified by the Dogger aquifer in the Paris Basin, France, which contains trace elements such as Ba, F, Sr, or Li (Michard and Bastide, 1988; Coudrain-Ribstein and Gouze, 1993). Other contaminants such as radon, organic gases and benzene may also potentially migrate through groundwater (Gal *et al.*, 2011).

3.2.2. Potential analogues for pressure effects

 is naturally occurring in groundwater. partial pressures are typically ~10-100 times higher in groundwater than in the atmosphere (Macpherson, 2009). The higher occurs near aquifer water tables and at depths greater than about 1 km (Figure 3.3). Shallow groundwater, with many data, has the most variable , whereas few data are available from depths greater than about 0.5 km.

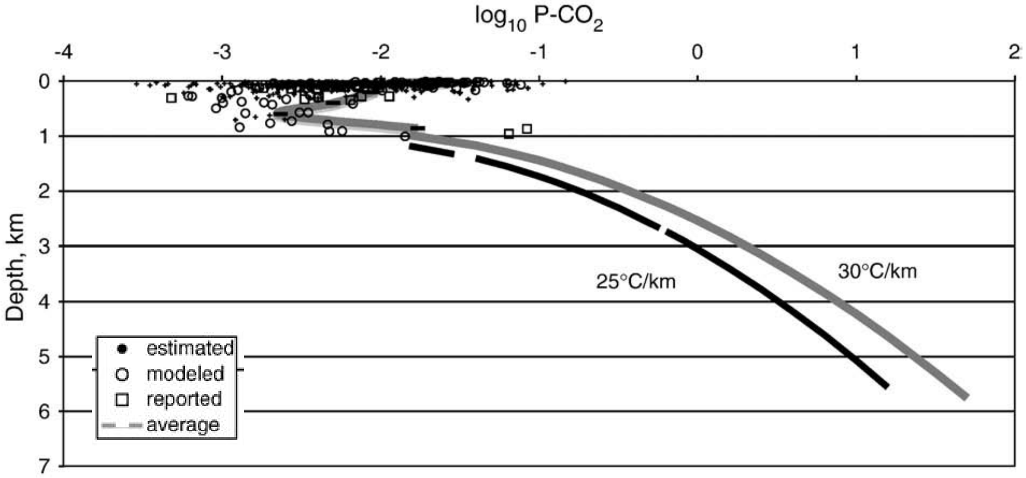


Figure 3.3: The depth- trend, after an average low at about -600m, rises into deeper saline aquifers, as estimated from temperature– relations (Gouze and Coudrain-Ribstein, 2002 cited in Macpherson, 2009) converted to depth using typical geothermal gradients.

Natural accumulations of occur throughout the world both within and outside tectonically active zones (Benson *et al.*, 2002). For Europe the natural accumulations have been described by Pearce *et al.* (2004) who find that some accumulations are well contained, while others are leaking. The leaking may have been going on for thousands of years, often in densely populated areas, and often along narrow vents clustered in zones with a width of a few metres (Holloway *et al.*, 2007).

In contrast to the gradual and long duration pressure effect from natural accumulations, the potential pressure effect of stored is, from a geological point of view, spontaneous. Therefore, the geological storage of natural gas in deep saline formations is potentially a better analogue to the storage of (IPCC, 2005 and IEAGHG report 2009/13).

Natural gas storage projects provide for peak loads and balance seasonal fluctuations in gas supply and demand. The storage of natural gas offers experience relevant to storage (Lippmann and Benson, 2003; Perry, 2005) from almost 100 years of successful operation in many parts of the world. The majority of gas storage projects are in depleted oil and gas reservoirs and saline formations, although caverns in salt have also been used extensively. While underground natural gas storage is generally safe and effective, some projects have leaked, mostly caused by poorly completed or improperly plugged and abandoned wells and by leaky faults (Gurevich *et al.*, 1993; Lippmann and Benson, 2003; Perry, 2005).

Abandoned oil and gas fields are easier to assess as natural gas storage sites than are saline formations, because the geological structure and cap rock are usually well characterized from existing wells. At most natural gas storage sites, monitoring requirements focus on ensuring that the injection well is not leaking.

Examples of pressure effects on water quality are the documented leakage of injected waste water in Florida, (Kieth *et al.*, 2005; see section 3.3.3) and the brine injection from potassium mining described in chapter 3.3.4.

3.2.3. Case studies for pressure effects

Case studies include both industrial pressure analogues related to storage of natural gas and displacement of the boundary between fresh and saline groundwater by intrusion of saline water.

Gas storage, Lussagnet and Izaute, France

One illustrative case of natural gas storage operations is provided by the two French underground storages facilities in Lussagnet and Izaute located in the multi-layered South-West sedimentary basin of “Aquitaine” region.

Geographically close to each other (a few tens of kilometres), Lussagnet and Izaute were commissioned at the end of the 1950's and of the 1980's, respectively, to respond to the increase in gas demand, with maximum stored gas of 3000 million of in October 2008 (David, 2010).

Both reservoirs are situated in the “Infra-Molassic Sands Aquifer” (corresponding to the Eocene sands aquifer) at depths of 500m and 900m, respectively. This aquifer, characterized by a detritus facies, extends over 150 km from East to West and 200 km from South to North. The overburden corresponds to the “Aquitaine molasse”, which consist of plastic clay and carbonate beds with thickness over 500 m in the storage area.

The Eocene sands aquifer is used by a large variety of economic sectors: 81.8% (9028274 /y) for potable water; 7% for thermal water; 6.6% for industrial water catchments such as aquaculture, 3.6 % for geothermal activities, and 1% for irrigation (David, 2010). This competition for groundwater use has led to detailed hydrogeological studies (Labat, 1998; Le Fanic, 2002; Seguin, 2003; André *et al.*, 2005; Le Fanic, 2005; Douez, 2007) based on a monitoring network composed of nearly 60 observation wells reaching the depth level of the Eocene sands aquifer (as depicted in Figure 3.4).

Influence of the storage operations can be investigated through piezometric level monitoring. Figure 3.5.A depicts the temporal evolution of the volume of injected natural gas between 1999 and 2008 (David, 2010). In the near-zone of the injection wells, the piezometric level changes can reach a maximum value of 100 m (Figure 3.5.B). The amplitude of these fluctuations decreases with the lateral distance from the core of the storage zone. For instance a value of ≈50m is reached at the “Uby” observation well located at the Eocene outcrop in the “Barbotan” sector (at a distance of ≈20km towards North, Figure 3.5.C). The time for the pressure perturbation to propagate is almost instantaneous in the zone close to the store. Outside this zone, the propagation may take up to a few months depending on the sector considered. For instance, the pressure perturbation is observed with a delay varying between 3 and 4 months at the “Lespielle” sector located in the Southern part of the storage zone (at a distance of ≈40km). It is worth underlining that, contrary to the rapid propagation of the pressure perturbation, the mass transfer velocity is very much lower as demonstrated by recent coupled hydrodynamical, thermal and geochemical simulations (Douez, 2007). Such conclusions are consistent with the geochemical analysis carried out by André and co-authors (André, 2002; André *et al.*, 2005), who have reported that there were no changes in the chemistry of the sampled waters during the cyclic storage operations.

The impacted area (i.e. the pressure-influenced zone) can be estimated using numerical simulations based on either multiphase flow transport models or on single-phase flow models with adjusted hydraulic properties accounting for the presence of gas (e.g. Le Fanic, 2002; Douez, 2007). Using a threshold of 5m piezometric head, the impacted area reaches 20 km in the Northward direction and between 20 and 40km in the Eastward direction (Labat, 1998).

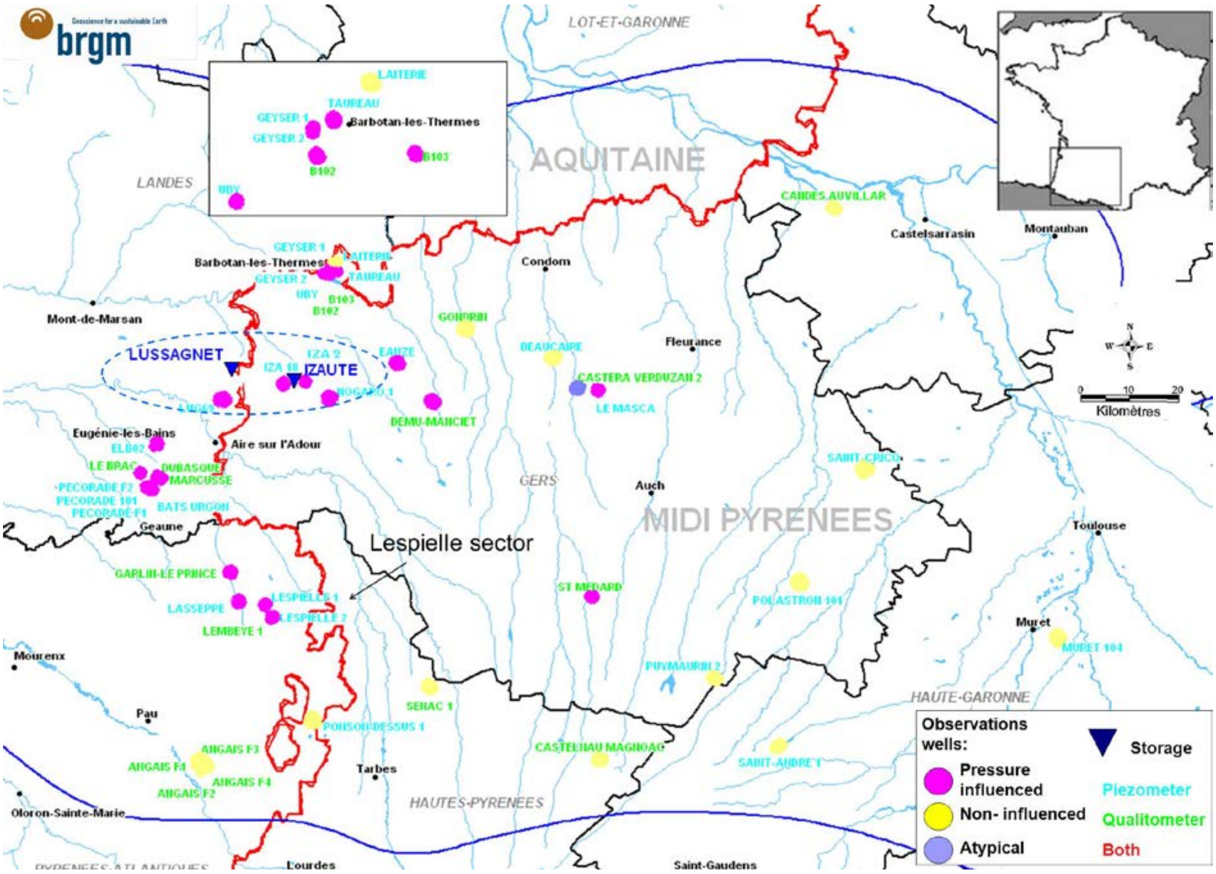
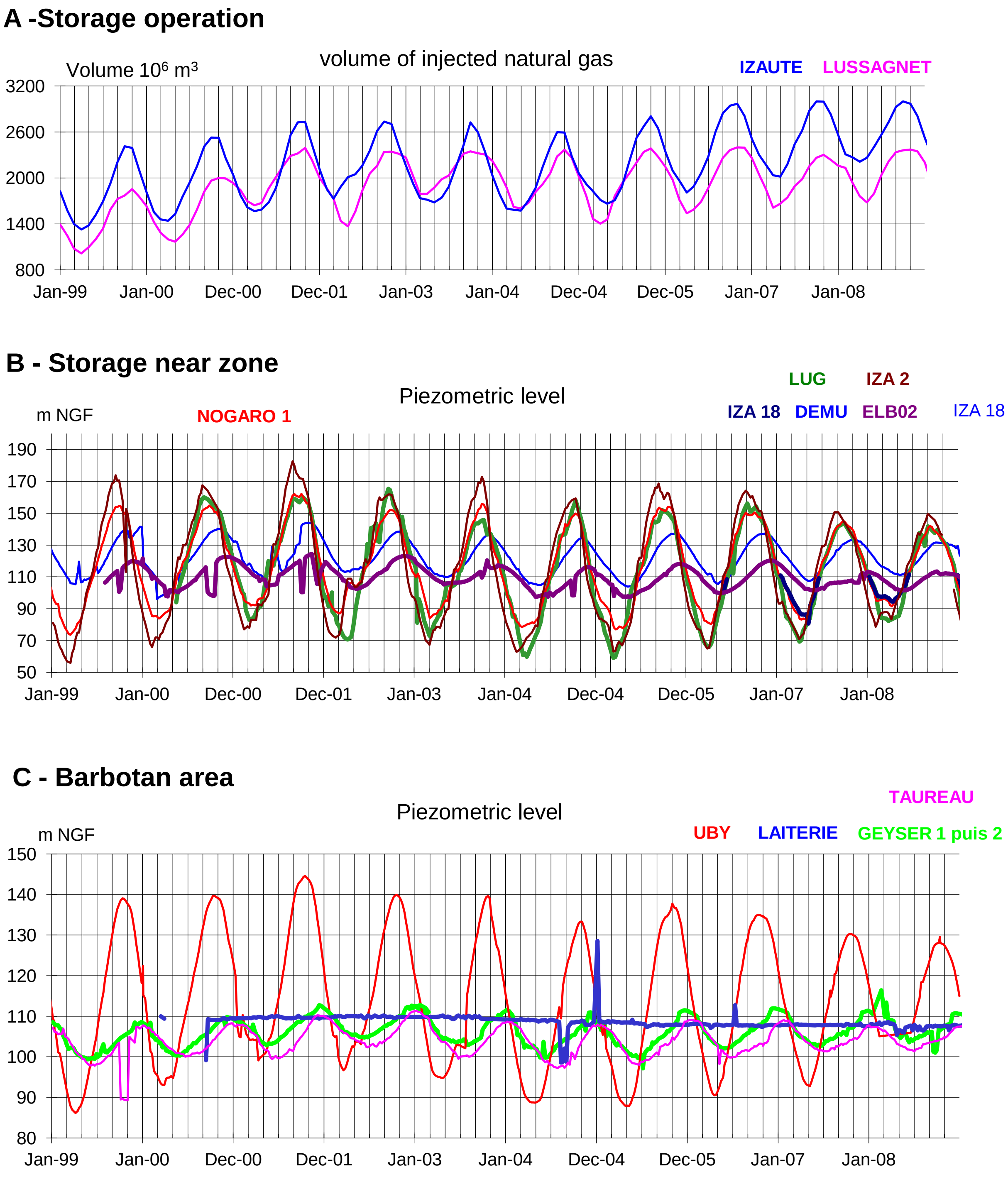


Figure 3.4: Location of the observation wells screening the Eocene aquifer.
The observation wells where the influence of the storage operations has been reported are indicated by magenta dots (modified from David, 2010).

Temporal evolution of the piezometric level at the monitoring wells can also be used to estimate the area to review. Figure 3.4 outlines the observation wells where an influence of the storage operations could have been identified (magenta dots). Cyclic patterns were identified in the temporal evolution profile of the piezometers located at a distance between 50 and 60 km (in the Eastern part of the storage zone), hence suggesting a correlation with the storage operations, but such a conclusion still requires further investigations (David, 2010).

This pressure influence has led to conflicts with thermal water activities located at the western outcrop of the aquifer, corresponding to perturbation in the water extraction operations, but to date no contamination of the thermal water with deep fluid has been reported. No influence of the storage activities have been reported in the overlying aquifers, mainly due to the presence of the thick "Aquitaine" Molasse, but such a conclusion may be biased by the scarcity of observation wells reaching the depth of the Oligocene aquifer (N. Pedron, regional hydrologist, pers. com.).


A -Storage operation

B - Storage near zone

C - Barbotan area

Figure 3.5: Influence of the storage operations on the regional piezometric level (m a.s.l.) A) Temporal evolution of the injected natural gas volume () at Izaute (blue straight line) and at Lussagnet (magenta straight line); B) Temporal evolution of the piezometric level (m) in the near-storage zone; C) Barbotan area at ≈20 km from the injection wells. (modified from David, 2010).

Ringsted case study on pressure effects, Denmark

This case study illustrates the possible effects of a displacement of the boundary between fresh and saline groundwater which may be caused by the pressure build-up in the deep saline storage aquifer. Thus, propagation of the pressure plume from the deep aquifer, where injection has taken place, or pressure propagation from over-pressured accumulations of more shallow gaseous accumulations fed by leaching from a deep saline formation may eventually cause changes in the vertical pressure gradient of the shallow groundwater aquifer.

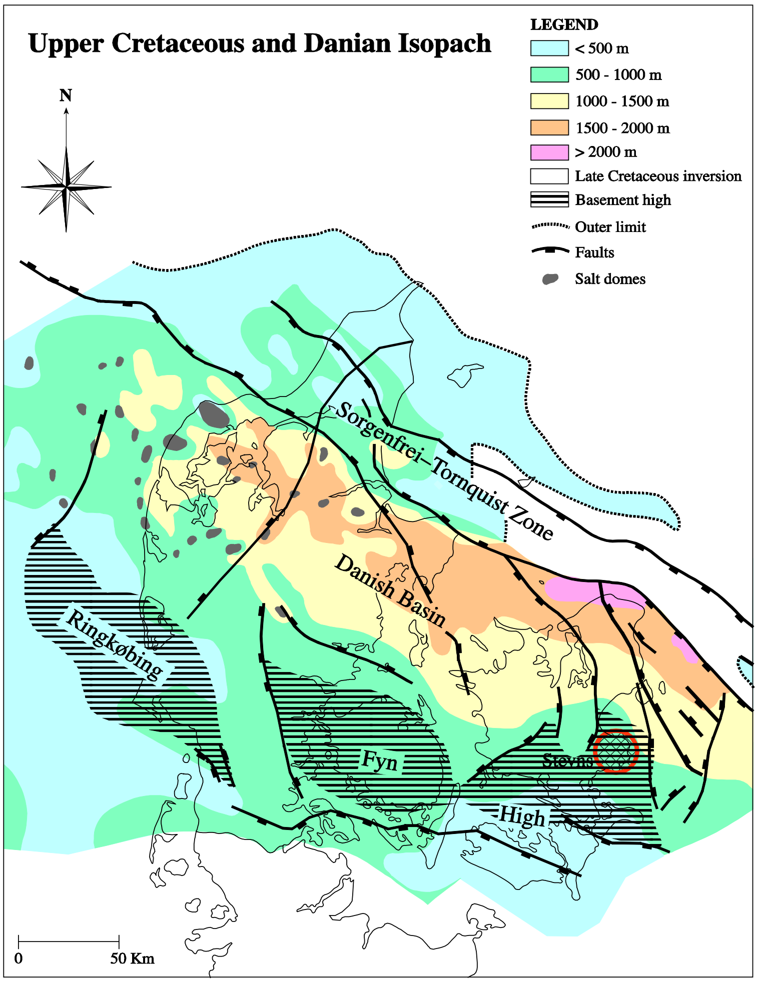


Figure 3.6: Denmark overlies the Sorgenfrei-Thornquist thrust zone and the deep Danish and North German basins, which are separated by the Ringkøbing Fyn High.
The area of concern is located immediately West of the red circle signature, at the flank of the subsurface high. The map shows isopachs of the Upper Cretaceous and Danian.

As previously mentioned, the pressure propagation is expected to reach much further into the shallow aquifer than the actual migration of saline water from the storage reservoir. Assuming that no direct leakage pathways from the storage reservoir are present such as fractures and faults in the cap-rock, there is still a potential risk of migration of saline water into the freshwater aquifer as a result of the storage operation. Thus, potential expulsion of connate formation water from a sealing aquitard (cap-rock) or shallow saline formation to the freshwater aquifer in the scale of 1 to a few bar for a confined aquifer or 1 to a few metres for an unconfined may be expected based on the literature (e.g. Yamamoto *et al.,* 2009a, 2009b; Birkholzer *et al.,* 2007, Birkholzer and Zhou 2009; Nicot 2008).

Throughout much of Denmark, salt from the Permian Zechstein and the Triassic periods render the deeper groundwater in the inland a higher salinity. Moreover the main part of Denmark is situated over basins (Figure 3.6) which are deep and dynamically filled in with deposits during the Permian until present.

In the regime of compaction, which accompanies the infilling, saline mineral water is squeezed into the overlying section. This is one of the main reasons for the formation water in the Danish subsurface to be saline at depths, where it is not diluted by circulating fresh groundwater.

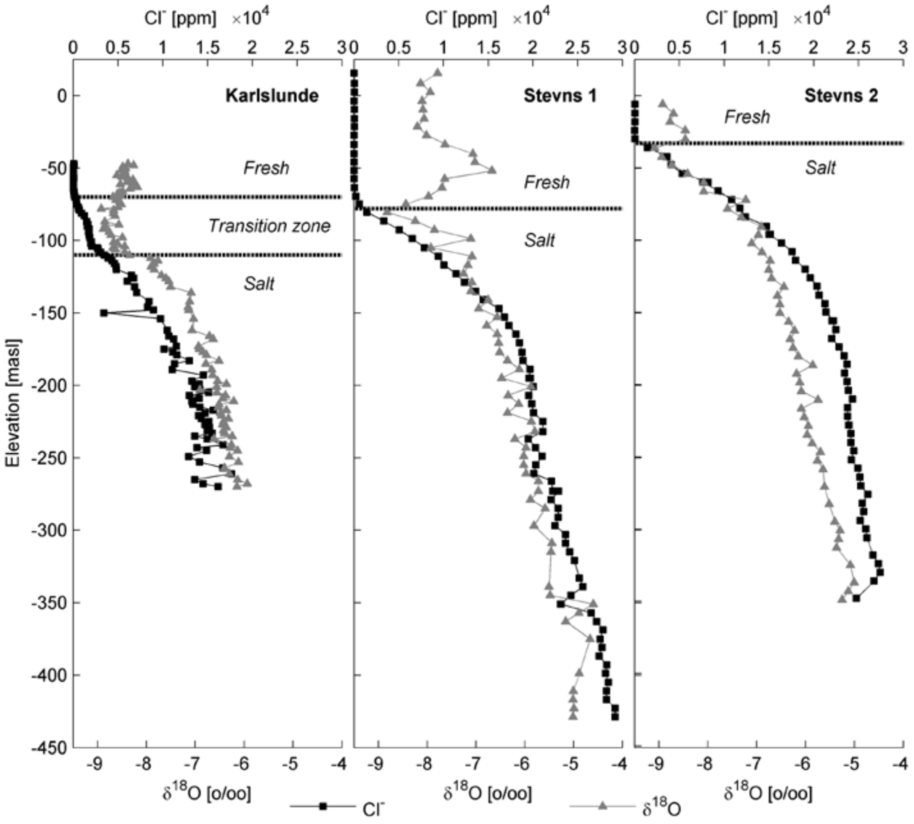


Figure 3.7: Depth profiles of chloride and pore water concentration (Bonnesen et al., 2009). Stable oxygen isotope composition of the porewater shows a freshwater type (δ about -8 to -9 ‰) in the upper part. The less negative values signify that water could be mixed with a seawater component.

The boundary between fresh groundwater with a chloride content of about 100 mg/l and the deep seated saline mineral water, in which the salinity is an order of magnitude higher, would likely be transitional, if it was to be found within a high permeable reservoir rock. Due to the bedded nature of alternating aquifers and aquitards of most of the deposits in the Danish subsurface, the lower boundary of circulation of the fresh groundwater is rather relatively more abrupt, possibly stepwise in the dynamic situation, and following along the top of aquitard units (Andersen, 1993; Bonnesen *et al.*, 2009).

The bottom of the freshwater zone is defined by a balance between diffusion of saline water from below and dilution by the fresh groundwater circulating from above. The imprint of an additional pressure from below may therefore potentially displace the saline/fresh groundwater boundary not only by the cited 1 bar for confined aquifers or 1m for the unconfined aquifers. Due to the dynamic flow system the boundary may rather be displaced beyond the next aquitard bed into the overlying aquifer bed.

Such a displacement could potentially be problematic in areas, where the fresh/saline groundwater boundary is close to the land surface or, where the deeper part of the freshwater resource is abstracted for drinking water purposes (Figure 3.7).

An analogue to the upward displacement of the saline/fresh groundwater boundary caused by a pressure build-up in a deep-seated storage reservoir is here exemplified by a case from the central part of Zealand (Ringsted) where the pressure in the freshwater zone of a shallow aquifer is lowered considerably due to abstraction of groundwater for drinking water purposes (Nygaard, 1993; Figure 3.8). In both situations it is the increase of the vertical pressure gradient that is assumed to be the driver for the displacement of the saline/fresh groundwater boundary.

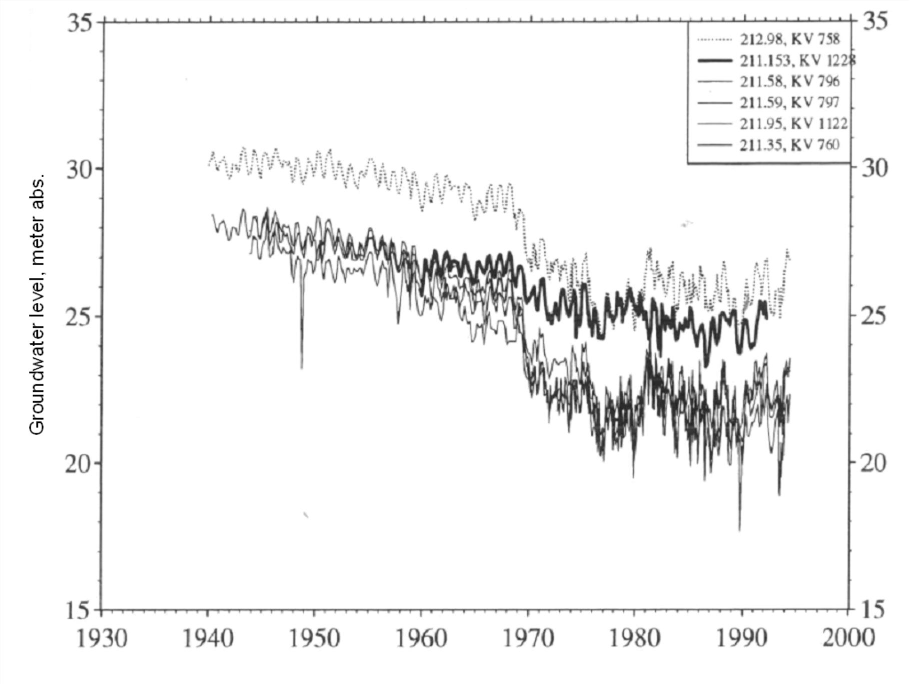


Figure 3.8: Draw down in the area around well no 211.409. The draw down is accelerated in 1969 after the opening of a new water abstraction plant for supply of Copenhagen city, (after Andersen, 1994).

In the natural water cycle at Ringsted, outflow takes place in topographic valleys along the water courses, which are interpreted to be localized in part in reflection of deep-seated tectonic fault zones. Natural outflow into the streams does, however, also have a component of saline water from below. This is illustrated by groundwater fed moors in the area having halofile floras, despite the fact that the water level is well above sea level (levels ~+20m, Ødum, 1960). The principle of the groundwater flow system in the area is illustrated in Figure 3.9.

After water abstraction has been carried out for more than five decades (Figure 3.8), the water table has decreased with up to 8 m, thereby causing an increase in the differential pressure between the deeper parts of the aquifer and the shallow part of the aquifer where abstraction of fresh groundwater takes place. Apparently, the change in the differential pressure causes up-coning of saline water from the deeper marly parts of the aquifer (Figure 3.9) to the abstraction wells in the originally fresh part of the aquifer. This is illustrated by the increased number of observations of saline water in wells with time Figure 3.10). Similar effects resulting in increased salinity of previously fresh parts of shallow aquifers may potentially be expected if the increase in differential pressure is caused by pressure propagation from a deep storage reservoir.

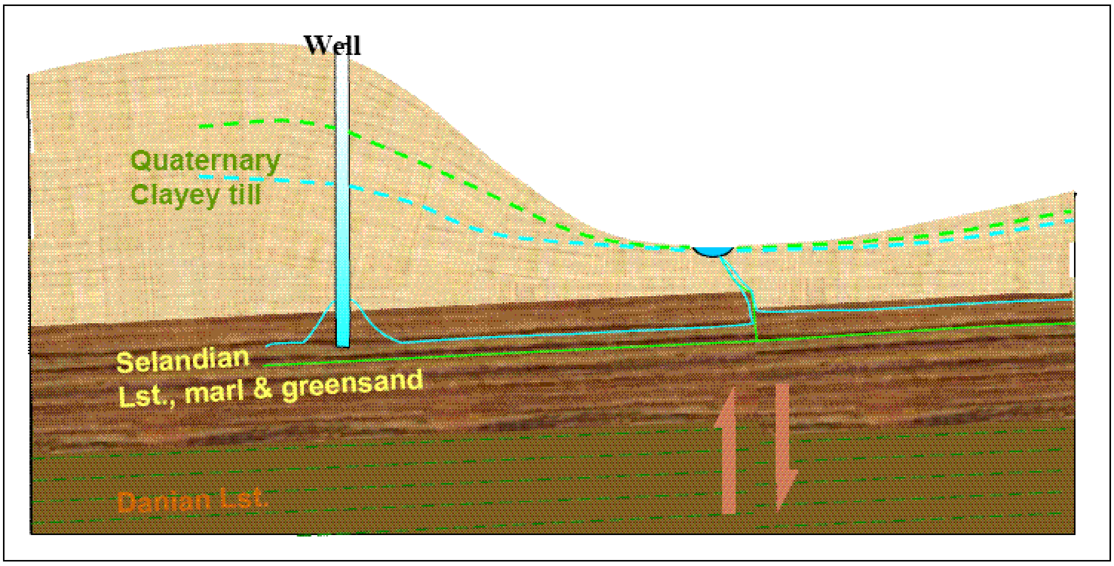


Figure 3.9: Hydrogeological cross section through the central part of Zealand.
The potential effect of a relative increase in pressure in the lower, saline groundwater on the quality of abstracted and discharged water is illustrated by lowering of the groundwater table. Green lines illustrate the initial situation prior to pumping. Solid green is the fresh/salt water boundary, which coincides with a low permeable marl bed, except in disturbed zones where there is some leaching to the stream. Stippled green is the analogue groundwater table. Blue lines similarly show the situation after lowering of the groundwater table (application of relative overpressure in the saline groundwater). In this new situation the saline water mixes into the deeper screened levels. Run off of saline water in the valley areas is not increased due to the rather stable groundwater level (this may be altered by pumping from wells along the stream). See text for further explanation.

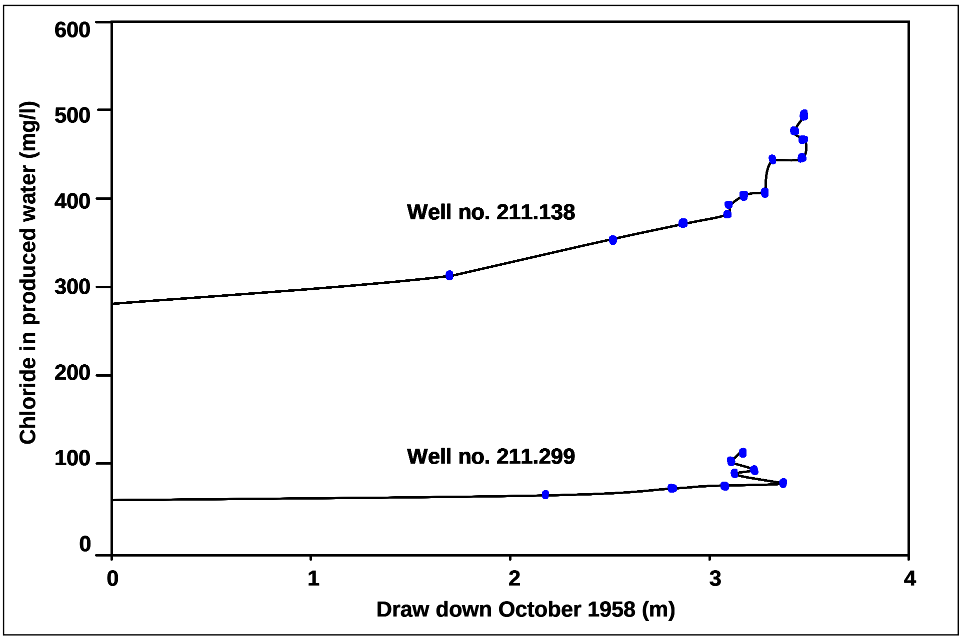


Figure 3.10: Example of increased salinity in production wells within the study area a function of draw down (after Andersen, 1991).

Thus, the example from Ringsted, Denmark, illustrates that indeed, under the present circumstances of this site, if there is a change in the pressure balance between deep saline water and more shallow freshwater, it will potentially express itself in a changed quality of the abstracted water. Chloride is here taken as an example of a component in the deeply sourced water for which the concentration would change. Clearly the concentration of other chemical components in the freshwater would potentially also be affected depending on the actual composition of the saline component of the groundwater.

Clearly, the example illustrated above applies only if there is a risk of mobilizing connate saline water from marine deposits such as marl or mudstone or if the saline/freshwater boundary of the groundwater aquifer affected by the pressure changes is relatively shallow. In other cases, where the saline/freshwater boundary is located at deeper levels, the risk of affecting the potable resources is much smaller.

3.3. POTENTIAL CHEMICAL EFFECTS IN SHALLOW AQUIFERS

No studies monitoring the potential effects of on groundwater quality after an occurrence of seepage from a store in a deep saline formation have been available. Therefore there are virtually no data available in the area of heavy metal mobilization into or acidification of groundwater systems as effects of storage in deep saline formations (IEAGHG, report 2007/3). Potential impacts on groundwater are therefore here apprehended via natural or industrial analogous sites, experiments or modelling.

Chemical reactivity of in reservoirs containing concentrated brines, where there is a large transfer of mass between the aqueous and the solid phase, has been discussed in many papers (Gaus, 2010 and therein). By contrast it is more subtle geochemical reactions (mineral dissolution, ion desorption) that may potentially occur under circumstances, where they affect the quality of the fresh groundwater (dilute water). Therefore because of differences in pressure conditions and due to the industrial injection rate, direct analogies between potential chemical reactivity with the deep saline formation host rock around the injection point (Gaus *et al.*, 2005a; André *et al.*, 2007; Audigane *et al.*, 2007) and potential effects on fresh groundwater is not possible.

3.3.1. Chemical reactions and processes affecting water composition

The chemical composition of natural water is derived from many different sources of solutes, including gases, rock interactions and solution or precipitation reactions.

Pure is not reactive, but in aqueous solution a small portion of the will, depending on temperature and pressure, react with water () to form carbonic acid (). Carbonic acid in turn will dissociate into H^+ and bicarbonate ion $^-$. The bicarbonate ion again dissociates into a proton (H^+) and carbonate ($^-$). All together the activity of in aqueous solution reflects the concentration of H^+ and hence the pH (dimensionless log of H^+ activity). For low pH in the carbonate buffer system bicarbonate will prevail, while for high pH carbonate will prevail. This is described in the chemical reactions below for pure aqueous solution and in the absence of any buffering minerals by Appelo and Postma (2005).

(g) + -> ; = 1.5

-> H^+ + $^-$; = 6.3

$^-$ -> H^+ + $^-$; = 10.3

On rearrangement the reactions provide a general relation between the bicarbonate concentration in the water, the partial pressure, and the pH of the water (Appelo and Postma, 2005):

log[$^-$] – pH – 7.8 = log []

Thus, in groundwater where the partial pressure of increases, pH would be expected to decrease and the bicarbonate concentration to increase. However, in any aquifer, minerals, e.g. calcite, will be present to buffer the pH by dissolution and therefore the resulting pH cannot be calculated by the above equation. Understanding the role that mineral precipitation/dissolution play within the aquifer is important because mineral will tend to buffer pH changes. This potentially reduces risk to human health since trace element mobility, caused by pH reduction, may be prevented. A negative consequence, however, is that detection of leakage via monitoring groundwater pH will be more difficult (Keating *et al.,* 2010).

The potential chemical impacts of on aquifer quality are complex. All the potential chemical reactions are tightly coupled and interdependent, and it is difficult to evaluate the overall effect of the combined potential individual reactions and processes.

Processes potentially leading up to water contamination

In this report we consider , formation water, and elements potentially liberated by -water-rock interaction. Within this limited assessment potential impurities and hydrocarbons in the injected are not further treated.

Several processes are potentially subject to change due to injection or following an accidental release of into aquifers. The most important are:

- Flow modifications that play a role in the transport of elements; the contributions from brines by seepage through matrix or along faults;

- Migration of dissolved organic compounds enriched in , as is an excellent solvent for organic compounds;

- Mineral dissolution may increase the mineralization of the water and release associated elements;

- The co-precipitation and sorption of metals which act as a contaminant trap or source

- The microbiological activity

- The aqueous complexation of metals that can promote the solubility (organic complex, Cl, carbonates)

All these mechanisms are interdependent. The potential impact of these processes on water quality is controlled by the basic factors: pH, redox potential and flow directions. The water rock interactions controlling water composition also depends on the physicochemical conditions of the aquifer. Thus, potential arrival of in a balanced system causes changes in physicochemical conditions modifying water-rock equilibrium.

• Potential mineral dissolution and precipitation

The impacts of a potential intrusion will depend on the water-rock interaction as controlled by the mineralogy of the aquifer. The principle geochemical process associated with is, as stated, dissolution, the formation of carbonic acid (), a drop in **pH** of the brine, and subsequent reactions with the mineral constituents of the surrounding rocks. Therefore, aquifers composed of geological materials with low buffering capacities (sandstone) may be more susceptible to acidification than, for example, limestone. Mineral dissolution dominates at low concentrations of dissolved . At higher concentrations of dissolved the saturation thresholds of progressively more minerals are exceeded, so that secondary minerals are formed. While limestone aquifers will be more buffered, the greater range of cations released during dissolution in sandstone aquifers will result in a greater variety of subsequent secondary mineral precipitates.

At shallow depths the effect of decreasing pressure dominates over the temperature effect on solubility. This implies that -rich waters often tend to become super-saturated and degas (May, 2002a) so that carbonate minerals are precipitated and the exsolved migrates as a separate gas phase.

On the basis of monitored annual variations in and alkalinity Macpherson *et al.* (2008) propose that groundwater is a sink through weathering of limestone: soil-generated is transformed to alkalinity through dissolution of calcite or dolomite.

The **redox potential** is largely controlled by the degree of aeration of the system, degradation reactions of organic matter, and other redox reactions. The redox conditions have a significant influence on the solubility of some minerals including sulfides (pyrite, PbS, ZnS, CuS) and oxy-hydroxides. In addition, some elements such as Fe and Mn are more mobile in reduced form (and). At the opposite, V, U and Cr are more mobile under oxidizing conditions.

The nature of the mineral phases that compose aquifers and their stability in presence of is a major control for water quality. The dissolution of major phases such as carbonates leads to increased mineralization of the solution and could potentially exceed the maximum allowable concentrations for major elements such as calcium, magnesium or iron. The dissolution of major phases also causes the release of associated trace elements. For example, carbonate minerals are able to release co-precipitated elements such as Sr, Mn, F, Zn, Ni, Pb, and sandstone minerals may potentially release elements such as Mn, Ba, F, Cr, Zn, Pb; and elements from clays such as Mn, F, Ba, Sr, Cr, Zn, Pb (Hem, 1985). Lead has affinities with K-feldspar, copper with biotite, zinc with biotite and magnetite, arsenic with pyrite (Wedepohl, 1972; Selinus 2005).

The metals in geological formations may also constitute ore, mainly oxides, sulfides or carbonates. The most common oxides are hematite ( ), tenorite (CuO) for carbonates, cerussite ( ) smithsonite ( ) and sulfides chalcocite ( ), sphalerite (ZnS) and galena (PbS).

The distribution and abundance of carbonate, silicate, oxide, and phyllosilicate minerals are identified as key variables in controlling changes in groundwater geochemistry (Wilkin and Digiulio, 2010).

- **Sorption processes**

The mineral phases present in an aquifer also play a role as carrier phase for the sorption mechanisms. The various processes indicated by the general term “sorption” are absorption and ion exchange. The term adsorption refers to the adherence of chemical to the surface of solid, while absorption suggests that chemical is taken up into the solid, and exchange involves replacement of one chemical for another at the solid surface (Appelo and Postma, 2005). A major difference between precipitation/dissolution reactions and desorption is that sorption depends on the presence of a pre-existing solid surface. The main carrier phases are oxides of iron, manganese, aluminium, organic matter and clays. Also other minerals have surface properties, but their potential is lower.

Sorption is an important topic since these processes regulate the transport of pollutant chemicals in aquifers and soils. Thus numerous papers exist on this topic for each type of solid surface and contaminant (e.g. metal(loids), organic compounds).

This mechanism is potentially significant in controlling metal mobility in aquifers, potentially impacted by leakage. Intrusion of in groundwater could potentially destabilize sorption equilibriums and enhance contaminant releases through: pH or Eh modifications, or counter-ion effect for surface sites.

Elevated levels of dissolved in freshwater aquifers can potentially enhance trace metal mobility as the pH is a determining factor on the mobility of elements. pH is generally controlled in the medium by the buffer system (system of carbonates) and biological activity, or chemical reactions such as oxidation of sulfides that leads to acidification. Generally, the decrease in pH causes an increase in the solubility of metals and carbonates, and dissolution of metal salts, as well as dissolution of the phases of retention with oxy-hydroxides and desorption of cations of surface sites (clays, oxides, organic matter, Apps *et al.*, 2010, Pavlova and Sigg, 1988).

As examples on the interplay between more of the listed relations the dependence of heavy metal sorption on ferrihydrite-surfaces as a function of pH are illustrated in Figure 3.11, and the anion adsorption as a function of pH for different levels of competing anions in Figure 3.12.

Saalfield and Bostick (2010) underline that adsorption of calcium or magnesium with bicarbonate leads to As desorption from ferrihydrite, under flow and when calcite is dissolved and producing dissolved Ca and bicarbonate, adsorption of Ca or Mg leads to As. At the opposite, enhanced retention of arsenic by soil and aluminum and iron hydroxides in the presence of Ca has been reported (Masue *et al.,* 2007).

Mixing with saline water that moves upward changes in water chemistry by a change from Ca- to Na-rich water. This enhances a counter-ion effect which may mobilize other anions and oxyanion-forming elements that are correlated with As (F, V, Se, B, Mo and). Competition among the oxyanions for sorption sites may enhance As mobilization (Scanlon *et al.,* 2009).

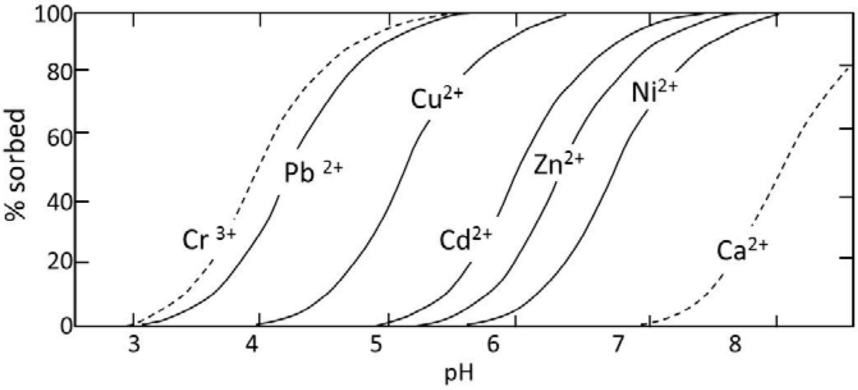


Figure 3.11: Adsorption of heavy metals on the surface of ferrihydrite as a function of pH, redrawn from Appelo and Postma, 2005 (after Stumm, 1992, and Dzombak and Morel, 1990).

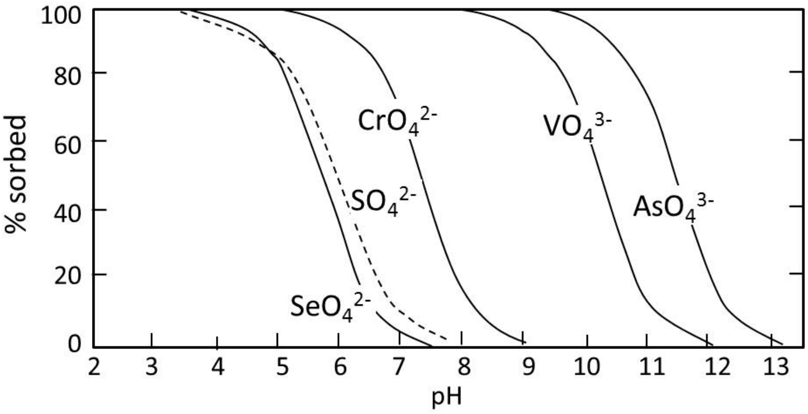


Figure 3.12: Adsorption of ligands on the surface of FeOOH(s) as a function of pH, redrawn from Sigg et al., 2000 (after Sigg and Stumm, 1981 and Dzombak and Morel, 1990).

In addition, redox potential influences the amount of sulfides or oxy-hydroxides present and their adsorption capacity. The dissolution of these phases leads to the release of associated metals into the environment (adsorbed or co-precipitated). The complexity in the chemical interplay is further exemplified by Swedlund *et al.* (2009), who find that at low pH (~4) absorptive removal of toxic oxyanions, such as $^{-}$, from ferric oxy-hydroxides and oxides (iron oxides) may be inhibited by reduction of surface reactive sites due to reactions with silicic acid ( ).

- **Microbial activity**

The behaviour of metals in a natural system is also controlled by living biomass. Microorganisms interact with dissolved species and organic compounds (e.g. exsudats) that can affect the solubility and eventual transport of these compounds. These processes largely determine the biogeochemical speciation of elements and influence their solubility, mobility, bioavailability and toxicity (Adriano, 2001). The major factors controlling the bacterial populations and activity are pH, CEC, redox conditions, temperature, pressure, salinity and other abiotic factors, which could all be potentially influenced by intrusion.

Soil sciences provide large studies which underline that alteration in concentrations and temperature may alter soil respiration, soil carbon dynamics, and microbial community structure (French *et al.*, 2009). Microbial activities can for example increase the dissolved inorganic carbon portion by pH shift or organic matter degradation, assimilate carbon (in biomass or exopolysaccharides), or induce biomineralization of carbonate. In deep aquifers and hydrothermal systems, numerous metabolic reactions are observed such as the reduction of elemental sulfur by , and the oxidation of methane to yield and . Amend and Shock (2001) show that biosphere exists in the deep subsurface. For example, autotrophic methanogens, fermenters and $^{-}$, $^{+}$, $^{+}$, $^{-}$ reducers or $^{+}$ oxidative bacteria. All these metabolisms could modify groundwater quality.

Until now, our knowledge is limited about the potential influence of injection and long-term storage of in saline aquifers on the microbial community. Recent studies show as expected that there is a strong influence of injection on the microbial communities and their functioning (Morozova *et al.*, 2010). The availability of the has an influence on the metabolism of both heterotrophic microorganisms, which are involved in the carbon cycle, as well as lithoautotrophic microorganisms, which are able to use as a sole carbon source and electron acceptor. Therefore any modification of these factors could perturb the biogeochemical equilibrium and modify groundwater quality and trace element availability.

For Emberley *et al.* (2005) seems, over time, to increase the activity of bacterial reducing bacteria. Microbial mediated conversion of to methane may be possible in some environments (Pruess 2007: in citation of Hoth *et al.,* 2005), where it could potentially cause large pressure and volume increases, as the gas compressibility factor for methane is twice as large as for under relevant PT conditions.

It is being recognized that microbial activity is an important catalyser for chemical reactions such as oxidation of Fe (Appelo and Postma, 2005).

- **Organic compounds**

Scherf *et al.* (2011), recently evaluated the effects of supercritical (SC-) on the quantitative and qualitative extraction of organic compounds from reservoir rocks. SC- is known as an excellent solvent of non- to moderately polar organic compounds depending on temperature and pressure. In the context of geological storage activities it is of special interest what types and amounts of organic matter (OM) will be extracted and mobilized from the reservoir rocks in conjunction with the injection of SC- into a saline aquifer, and thus, may be transported by the formation fluids.

Increased concentrations of organic acids and high DOC (dissolved organic carbon) contents have been described in formation waters from the Frio Formation after the injection of carbon dioxide (Kharaka *et al.,* 2006, 2009). “It is difficult to rule out contamination as the source for the very high DOC values, but they likely represent a ‘slug’ of organic matter mobilized by the injected “, as it generally happens during EOR operations (Shiraki and Dunn, 2000).

Laboratory experiments, simulating the geological storage of have only been done until now in the framework of an ECBM study by Kolak and Burruss (2005) on coals. They showed, that the organic matter extracted by SC- equated qualitatively to the organic matter present in the coals. If this conclusion is supported by future studies, then mobilization of organics, including BTEX and other toxic organics from non–oil-bearing saline aquifers, could have major implications for the environmental aspects of storage and containment. The concern here is warranted as high concentrations of toxic DOCs, including benzene, toluene (up to 60 mg/l for BTEX), phenols (20 mg/l), and polyaromatic hydrocarbons (up to 10 mg/l for PAHs), have been reported in oilfield waters (Kharaka and Hanor, 2007).

Kharaka and Hanor (2007) discuss the possible role of organic ligands as complexing agents of metals in basinal waters. Aliphatic acid anions, such as acetate, which are generally the most abundant of the reactive organic species, have received the most attention. There is however an inverse correlation between metal content and organic acid concentrations in basinal waters. Dicarboxylic acid anions form stronger metal-organic complexes, but field data and geochemical modelling indicate that the occurrence of high metal concentrations is not directly related to high concentrations of dissolved organic species. Despite this, some researches highlighted the fundamental role played by colloids and dissolved organic matter (DOM) in the mobilization/immobilization and transport of pollutants (McCarthy and Zachara, 1989; Calace *et al.,* 2001) and the mobilization of metals by organic colloids in soils is recognized as a factor promoting the transfer of trace elements including lead (Denaix *et al.,* 2001).

In addition to the potential toxic and pollutant mobilizing effects, simple organic compounds such as the fatty acids acetate and formate may act as substrates for increased microbial activity in the groundwater. Thus, in anaerobic aquifers increased concentrations of acetate and formate may induce increased iron reduction, sulfate reduction and/or methanogenesis (e.g. McMahon and Chapelle, 1991), thereby affecting the present redox state of the aquifer. As discussed previously, one result of increased iron-reduction could be that trace elements sorbed on the oxides is released to the groundwater.

- **Flow and water table dynamics**

The major processes affecting groundwater composition along the flow path lead to geochemical evolution of groundwater as observed in alluvial settings (Sharif *et al.,* 2008). Near the recharge area, groundwater is oxygenated. Dissolved organic (DOC) concentrations decrease along the flow path, presumably due to consumption by aerobic microbes (and the oxidation of organic matter). Specific types of microbial activity, most notably aerobic respiration and Fe oxide reduction, lead to a net generation of acid and an increased alkalinity, but reaction of groundwater with minerals, especially carbonate minerals, in the aquifer consumes the acid, thereby driving up pH. The rate of microbial respiration and creation of different redox zones favourable for specific microbes is not directly dependent on the relative richness of dissolved organic matter. Instead initial fermentation has been identified as a factor limiting the rate of microbial respiration in different redox environments (e.g. Postma and Jakobsen, 1996). Once DOC is depleted, groundwater enters a zone rich in dissolved $^{+}$, likely supplied by Fe reducing bacteria (by reducing HFO). Next, the groundwater enters a relatively Fe-poor zone in which $^{-}$ reducing bacteria are believed to predominate. The separation in distinct redox zones may not always be observed since the simultaneous reduction of and $^{-}$ may in many cases be thermodynamically possible and often an overlap between the Fe- and $^{-}$-reducing zones is observed in field studies (Postma and Jakobsen, 1996)

The various redox processes described above may also take place in and near the unsaturated zone as a result of seasonal variations in the groundwater table. If pressure propagation from a deep storage reservoir causes an additional rise in the water table as described previously in section 3.2, the zone affected by these processes will be thicker than in the non-affected aquifer.

Ponnamperuma (1972) described thoroughly the various possible chemical effects when a soil is submerged and suggested that the most important chemical change taking place when a soil is saturated, is the reduction of iron and the accompanying increase in its solubility. Similarly, Larsen and Postma (1997) showed that submersion of a previously oxidized zone of an aquifer caused the reduction of Mn-oxides and the concomitant release of both Mn and Ni to the groundwater (Figure 3.13).

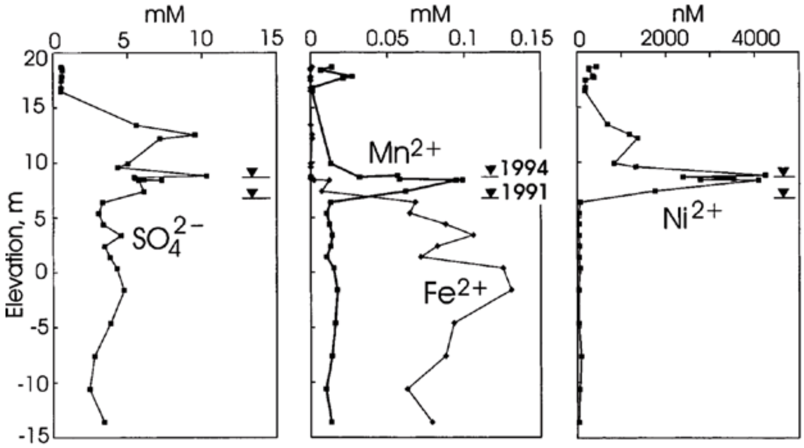


Figure 3.13: Groundwater composition with depth of an aquifer located in Jutland, Denmark. The groundwater level rose during the period 1991-1994 causing increased concentrations of Ni and Mn in the water (Larsen and Postma, 1997).

Conversely, if the water table is lowered, the previously submerged zone will be exposed to atmospheric air, thereby providing the possibility of oxidation of reduced components in the solid phase such as pyrite and other sulfide minerals. The oxidation of sulfides may cause an increase in the concentration of various trace elements such as Ni and As (e.g. Larsen and Postma, 1997; Schreiber *et al.*, 2000). Indeed, the spatial and vertical distribution of redox zones is one of the most important factors controlling the spatial, vertical, and temporal variation of As in groundwater. Sharif *et al.* (2008) demonstrate that hydrogeochemical data and redox environment in the Mississippi River Valley alluvial aquifer suggests reductive dissolution of Fe oxyhydroxide as the dominant As release mechanism.

Also Scheytt (1997) show large temporal variations of physico-chemical parameters and groundwater constituents. In winter and spring, generally a higher redox potential and higher contents of oxygen, K, $^{-}$, and $^{-}$ are observed as compared to the remaining part of the year. Near the water table, the groundwater chemistry is influenced by recharge due to low evapotranspiration.

Another effect of a fluctuating water table may be that , that may have escaped to the unsaturated zone can be redissolved in the groundwater when the water table rises, thereby causing a lowering of the pH and the previously described associated effects (cf. also the Grindsted case study in section 3.4.4). Likewise, infiltrating rainwater may cause the redistribution of to the groundwater if has escaped to the unsaturated zone.

Potential alteration of water quality

It is therefore apparent that slight modifications of the chemical conditions in aquifer rocks that contain natural trace elements (e.g. Se, As, Ni, or F), could destabilize these elements and potentially release them to the groundwater. But it is not possible to predict the impact of potential intrusion into specific aquifers without a site specific study. However general mechanisms can be detailed, see above, referring to potential impacts on groundwater quality.

Potential impacts of or brine on shallow groundwater can only be quantified, if the natural background and its variability are known. Compilations of groundwater background quality references or baselines are available for many regions of the world (Edmunds *et al.*, 2003; Morgantini *et al.*, 2009; Celle-Jeanton *et al.*, 2009). Such statistics of element distributions are useful indicators about potential detections. They indicate regions, where drinking water standards may be exceeded naturally. They should, however, not be used for claiming of general threshold values. Site specific baseline values are required for the differentiation between natural and anthropogenic-induced fractions of solutes in groundwater.

Based on a geochemical groundwater model for the drinking waters of the United States, including relation of mineral assemblages to hazardous elements, the trace elements of greatest concern were evaluated by Apps *et al.* (2010) for the impact of potential leakage. The trace metal concentrations in equilibrium with host minerals as a function of partial pressure influences the composition of the groundwater in the aquifer as illustrated by Figure 3.14 (Apps *et al.,* 2010) and is therefore, albeit this effect may be significantly altered by adsorption or desorption via surface complexion of mineral surfaces and by the mineralogy/chemistry of a specific aquifer, of concern for influence on drinking water quality and the aquatic environment.

Also Birkholzer *et al.* (2008) indicate that the concentrations of some of the studied constituents, for example Ba, Cd, Sb, and Zn, are sensitive to changes in P( ), but that As, and to a lesser extent Pb and Zn, have shown the potential for exceeding their respective MCLs at elevated concentrations. Primary emphasis was placed on the evaluation of the response and transport of As and Pb under intruding . Under some chemical conditions the level of admissible content in drinking water may be exceeded in the groundwater as evaluated by models for As and Pb (Apps *et al.*, 2010; Birkholzer *et al.*, 2008; and Wang et Jaffe, 2004; see modelling section, chapter 4 for further details).

Keating *et al.* (2010) show at the Chimayo´ site that there are a number of factors that could mitigate the impact of leakage on shallow groundwater quality. These include (1) simple mixing and dilution of -impacted groundwater with ambient groundwater, (2) pH buffering reactions such as calcite dissolution and/or silicate mineral weathering, (3) limited trace metal availability in aquifer minerals, and (4) trace metal scavenging by secondary mineral precipitation.

Moreover, Keating *et al.* (2010) conclude that brine that might either leak directly from the reservoir or be entrained into the plume as it passes through rocks above the reservoir could have a much greater impact on shallow groundwater quality than the itself or by mineral reactions in the aquifer driven by elevated . -rich brackish water could locally co-transported As, U and Pb into the aquifer.

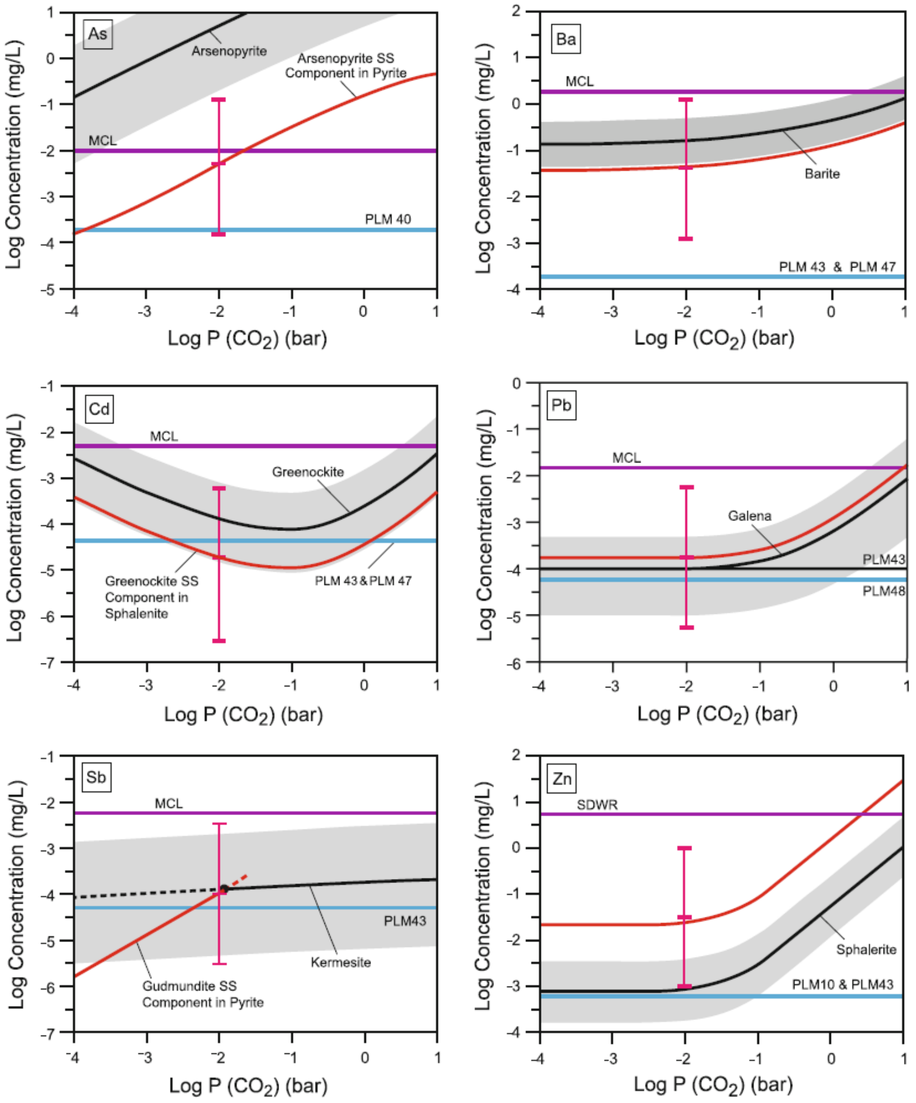


Figure 3.14: Variation of trace metal concentrations in equilibrium with host minerals as a function of partial pressure.
The black line with shaded ±1σ envelope represents model predictions obtained without calibration of solubility products. The red line and associated ±2σ error bar represents the calibrated concentration based on the solubility products calibrated to ensure consistency with the modal concentrations of hazardous elements in NWIS waters. SS refers to solid solution. PLM10, PLM40, PLM43, PLM47, and PLM48 are analytical methods cited in the NWIS database. MCL signifies the maximum contaminant level for each element. SDWR stands for secondary drinking water regulation. (From Apps et al., 2010).

3.3.2. Laboratory experiments and experimental site studies

Laboratory experiments on potential impacts of on freshwaters are appearing progressively in the literature (Smyth *et al.*, 2009, Little and Jackson, 2010; Lu *et al.*, 2010). These authors perform experiments with water rock interaction in batch tests for various mineralogies (aquifer sediment or aquifer rock samples). The results of the laboratory experiments are in agreement with the main assumption: partial pressure increase has an immediate impact on water chemistry by lowering pH and increasing the concentration of total dissolved solids.

In a study concerning the effects on fresh groundwater in the depth interval 30 – 700ft, (9 – 213 m) overlying the SACROC oil field, Texas, where injection had been performed for 35 years, both laboratory experiments and evaluation of geochemical field monitoring have been undertaken (Smyth *et al.*, 2009). The laboratory flow through reactor experiments were conducted on core samples from various aquifers in Texas and throughout the Gulf Coast region. After two weeks of bubbling argon through the samples injection was changed to . After every sampling period the chemical state was measured as well as cation concentrations in the effluents (normalized for pre/post experiment comparison). Results show a significant elevation in many cations. pH value decreases in presence of confirming that the different mineral assemblages have varying buffering capacities and that carbonate minerals have higher pH than others (Smith *et al.*, 2009; Lu *et al.*, 2010).

Lu *et al.* (2010) demonstrate that a found correlation between decreasing pH and release of cations suggests dolomite as the source from which elements Ca, Mg, Mn Ba and Sr are mobilized. Dolomite also contains trace elements of Mn, Sr and Ba, which substitute for Mg and Ca. K-feldspar when present in rocks also dissolves, but to less extent than carbonate minerals, releasing K and Si into the water. As K in solution increases, the Si content in water is reduced due to precipitation of quartz. They noticed that clays (illite, smectite) appear inert in contact with . Lu *et al.* (2010) showed that Al and Fe are controlled by desorption/adsorption, and that release rates of metals are higher, when pH is reduced. The authors suggest also that sorption could control also Mo, Cr, Cs and Cu. Further Little and Jackson (2010) suggest that Co and Ni could be mobilized as a result of desorption from Fe and Mn oxy-hydroxydes.

In addition, the redox state of the freshwater is important for predicting the behaviour of some element such as U. Little and Jackson (2010) demonstrate that uranium can be released under oxidized conditions.

Considering the release of trace elements, Little and Jackson (2010) showed that increased Al, Mn, Fe, Zn, Cd, Se, Ba, Tl and U concentrations approached or exceeded their MCL. Conversely oxyanions (As, Se, Sb, Mo, V and Cr) decreased in experiments, consistent with the behaviour of oxyanions, which are generally immobilized in moderately acidic, oxidizing aqueous systems.

While carbonate mineral dissolution is established in presence of , the behaviour of silicate (quartz, feldspar, clays) minerals is controlled by the whole system (mineralogy, water composition) and not unequivocal. This potentially has direct implications on release of associated trace elements.

It is well known that reaction rates in laboratory experiments tend to be higher by orders of magnitude than those in field conditions (Lu *et al.*, 2010).

The investigations of potential effects of injection have primarily been focussed on the chemical effects in the deep saline formation itself, such as the study at the Frio test site (Kharaka *et al.*, 2006). More recently, attention has also been given to the potential effects on overlying formations and freshwater aquifers, such as the work conducted at the ZERT experimental injection site (Spangler *et al.*, 2010).

At the ZERT site (Bozeman, Montana) gaseous has been released under the groundwater table (at a depth of ~2.5 m, water table at ~1.6 m) to study migration processes and to test techniques to detect and quantify potential leakage from geological storage sites (Lewicki *et al.*, 2007). The dissolution of into groundwater was found to be minimal as virtually all injected was re-found in the unsaturated zone over the injector. This implies that potential chemical effects in fresh groundwater will primarily be related to seeping of dissolved . Here the effect of injection of 300kg /day during one month is investigated. Kharaka *et al.* (2010) observed that lowered pH values (7 to 5.6) caused dissolution of carbonate minerals with increases in concentrations of solutes ($^-$, Ca, Mg) and desorption-ion exchange causing increases in the concentrations of solutes. injection is potentially responsible for detection of BTEX (e.g. benzene, 0 to 0.8 ppb) and mobilization of metals (Fe, Mn), in concentrations significantly below the maximum contaminant levels (MCL's) (Kharaka *et al.*, 2010). The significant increase of Fe and Mn suggest that these constituents may potentially constitute a tool to identify the effect of leaching. In the injection experiment changes in pH occur fast upon start and stop of injection. With injection into the fresh groundwater alkalinity was found to increase due to dissolution of limestone. Both Ca and Mg concentrations were found to increase as a result of this dissolution, as well as due to, perhaps, ionic exchange with Fe on clay surfaces.

Assayag *et al.* (2009) published results on push–pull test experiments performed at the Lamont–Doherty Earth Observatory (New York, USA). Chemical reactions following aqueous phase injection at a depth of 250m were investigated. Dissolution of carbonate minerals was the dominant neutralization process, followed by cation exchange and/or dissolution of silicate minerals. The results confirm the rapid dissolution kinetics of carbonate minerals compared to those of basic silicate minerals, despite natural variability not being accounted for.

3.3.3. Natural analogues for potential chemical effects

Globally, natural is in many places contained in geological accumulations either as pure or as an associated constituent, which may present relevant natural analogues examples for storage of . Natural sources of occur, as gaseous accumulations of , mixed with natural gas and dissolved in formation water. Natural accumulations of have been studied mainly in the United States, Australia and Europe (Annunziatellis *et al.,* 2008; Pearce *et al.*, 2004; Gaus *et al.,* 2005b; Stevens *et al.*, 2001; Stenhouse, 2009; Beaubien *et al.*, 2008; Keating *et al.*, 2010) as potential analogues for, in part, well contained storage of , as well as in part for potential leakage from engineered storage sites.

Production of for EOR and other uses potentially provides operational experience relevant to capture and storage. Natural accumulations of differ from engineered storage sites by being accumulated over very long periods and at "random" sites, many of which are made up as naturally 'leaky'. Natural accumulations of relatively pure are found all over the world, particularly in sedimentary basins, intra-plate volcanic regions and in faulted areas or in quiescent volcanic structures. Most relevant are the natural accumulations in sedimentary rocks, principally limestone, dolomites and sandstones and with a variety of seals (mudstone, shale, salt and anhydrite) and a range of trap types, reservoir depths and -bearing phases.

Keating *et al.* (2010) describe two major categories of natural analogues: (1) locations where diffuse is rising and flowing through an aquifer and (2) locations where is rising along a fault or other conduit and expressed itself at a point at the ground surface (spring or geyser). These second type are far more common studied due in part to the ease of sampling springs and geysers rather than wells.

The study of natural analogues presents several advantages, as stated by among others Auqué *et al.* (2009) and Keating *et al.* (2010):

- Processes have been occurring over long time periods, which facilitate an approach towards geochemical equilibria;
- Long flow paths facilitate propagating reaction fronts, reactive element transport, phase separation, and a wide range of fluid/rock ratios (“open” and “closed” systems).
- The transition from reducing to oxidizing conditions, which causes redox reactions within shallow aquifers.
- Natural minerals with impurities or lattice defects which differ from pure substances e.g. used in laboratory experiments;
- Surface constrained reactions, microbiological processes and a wide range of potential ligands, that may limit heavy metal concentrations in natural systems;
- Chemically complex systems that contain weakly fixed heavy metals that can potentially be released through leaching, acidification or mixing processes.

According to Auqué *et al.* (2009), hydrothermal systems with low pressure are probably the main natural analogues for studying the water-rock interactions in the long term. Only natural analogues provide the spatial and time scales and the complexity of heterogeneous subsurface conditions for -water-rock interactions, that cannot be mimicked adequately by laboratory experiments and numerical models.

At the opposite, natural analogues studies raise some difficulties. Natural analogue sites where is actively upwelling through shallow aquifers are usually located in volcanic or geothermal settings (Keating *et al.*, 2010). These sites are known to be highly fractured and cannot be considered as analogue for geological sequestration. One can, however, consider these sites as potential analogues for leaking into shallow groundwater. But the principal processes (acid alteration, mixing with brines, dilution and degassing) may occur repeatedly and in various combinations and sequences along a potential leakage pathway. As water analyses potentially reflect the integral product of such processes, the definition of the exact geochemical reactions in the subsurface is sometimes not possible. The lack of quality data on “pre flux” water inhibits comparison of pre and post conditions to evaluate the impact on water quality (Keating *et al.*, 2010). Moreover, natural upwelling can be accompanied by deep thermal fluids. These fluids are usually saline and might contain contaminants such as F, As, Sb as observed in -rich spring waters (Criaud and Fouillac, 1986).

However, despite nature’s variability, statistical analyses of extensive geochemical data sets can allow the distinction of various water types and the identification of the principal reactions controlling the overall water chemistry (Birkholzer *et al.*, 2008). Chemical reaction rates (i.e. kinetics) have a significant influence on final water chemistry. Fast reactions may potentially have geotechnical consequences during the injection period, typically in the deep saline aquifer, where injection is performed, whereas slow reactions may potentially cause on going alteration processes in the long term (May, 2004). Slow reactions may, for example, potentially disintegrate cap rocks or well bore cements, or the gradual accumulation of heavy metals in slow moving solutions may potentially impose risks of groundwater contamination, even after abandonment and plugging of the injection wells. The impact of uncertainty in kinetic rate on predicting metal mobility is a major constraint in geochemical modelling works as discussed in Chapter 4 (Gaus *et al.*, 2008; Wang and Jaffe, 2004).

3.3.4. Industrial analogues for potential chemical effects

Acid gas injection operations represent potential commercial analogues for some aspects of geological storage. Acid gas is a mixture of and , with minor amounts of hydrocarbon gases that result from petroleum production or processing. Although the purpose of the acid gas injection operations is the need to dispose of , significant quantities of are injected at the same time because it is uneconomic to separate the two gases. Both Western Canada (Bachu and Gunter, 2005) and US holds many examples of acid gas injection, as operators are increasingly turning to acid gas disposal by injection into deep geological formations (Benson *et al.*, 2002). Since new regulations have been implemented (1988) no incidents of drinking-water contamination have been reported.

Carbon dioxide often is the largest component of the injected acid gas stream. A total of 2.5 Mt and 2 had been injected in Western Canada by the end of 2003, with an aggregate annual injection rate in 2003 of 0.45 Mt yr^{-1} and 0.55 yr^{-1} (Bachu and Gunter, 2005).

Potential chemical effects (in the fresh groundwater) due to leaching of the component dissolved in injected liquid waste are, as well, comparable to the effects of leaching stored for its own good. The overall potential effects are, however, smaller, reflecting the generally relatively smaller volume of liquid waste injected, as compared to the assumed need for injection itself (Tsang *et al.*, 2008).

In Florida more than 3 billion /y of secondary treated sewerage is injected for storage via 62 facilities (93% of which are deeper than 900m) into a heavily fractured and dissolution affected dolomitic formation (Keith *et al.*, 2005). Due to a very high permeability the injectivity is enormous and the pressure build-up very low. Despite these circumstances, because of the fractures, sewerage affected fluid has migrated into the drinking water aquifer at more instances (indicated by freshening of the host formation water, enhanced ammonia content and fecal coliforms). The reasons for the leakage may be low sealing quality and defects in well strings or cementing.

As the potential chemical effects of the component itself of injected industrial waste, when leaching into freshwater aquifers, is the same as for injected for its own purpose of disposal, the main concern is for the documentation of the leaching process itself.

3.4. CASE STUDIES FOR POTENTIAL CHEMICAL EFFECTS

Natural -rich and bicarbonate rich waters are frequent in many countries of the world (e.g. Carlé, 1975; Zötl and Goldbrunner, 1993; Michard, 1987; Sanjuan *et al.*, 1988). They discharge together with fresh groundwaters that could be used for drinking water purposes. Because of the reaction of carbonic acid with wall rocks, the -rich waters are often enriched in chemical species. The mineral water compositions reflect the mineralogy of the aquifer rocks. The concentration levels of some of these natural chemical components exceed drinking water standards. Potential mixing of fresh and mineralized water depends on the geometry of the flow systems and the type of the shallow aquifers (e.g. locally restricted in fractured reservoirs or extensive mixing in alluvial sediments).

3.4.1. -rich springs, Central Germany

-rich springs and wells are frequent in central Germany (Figure 3.15). Carbon isotopes, noble gas ratios and noble gas isotopes indicate that the origin of the -phases in the springs and wells is within the Earth’s mantle. The examples described below are not influenced by recent volcanic or high-enthalpy geothermal systems. Apart from low amounts of mantle derived noble gases or atmospheric gases taken up from shallow ground waters, the gas phase only contains .

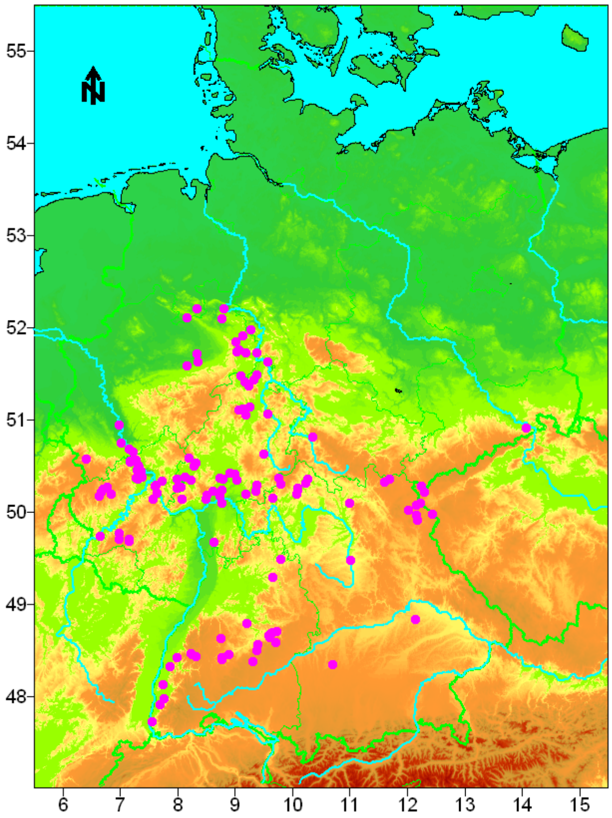


Figure 3.15: Natural sources of -rich water in Germany.

Locally, the gas phase vents directly to the surface. Generally, it discharges together with deep, saline or shallow fresh groundwater. The ratio of dissolved carbon species to free gas is highly variable. It depends on the gas/water flow ratios in the aquifer systems. In hilly terrain, groundwater flow is gravity-driven and generally follows the trend of topographical gradients. Ascending will dissolve in groundwater passing shallow aquifers and may not reach the surface, if water flow rates are sufficiently high to take up all the and carrying it away downstream towards springs or surface water bodies.

Along its way the chemistry of -bearing groundwater is altered due to water-rock interactions (Figure 3.16). The degree of alteration can be described by reaction progress models. Deep, extensive flow systems provide long residence times and larger surface areas for the passing fluids to react with the rock matrix. entering into shallow flow systems with small catchment areas is less consumed in water rock reactions, than in deep systems. Hence, waters with higher concentrations of free and lower amounts of dissolved elements result from shallow flow systems. The systematic variation of mineral water composition within a single topography-driven flow system indicates progressive wallrock alteration () and mixing with saline basement brines (Na) along the flow path.

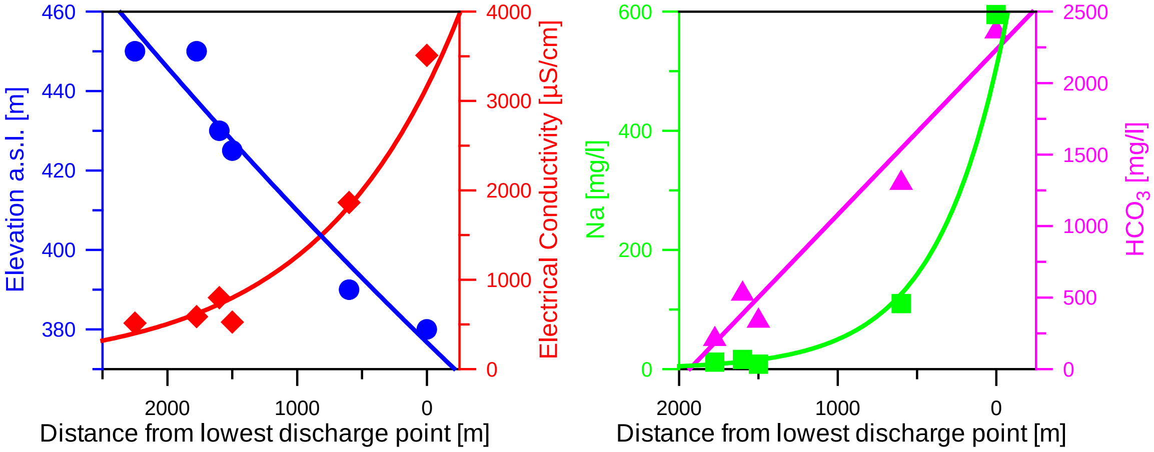


Figure 3.16: Variation of chemical parameters in spring waters discharging in a Westeifel valley near Niederstadtfeld (May, 2002a).

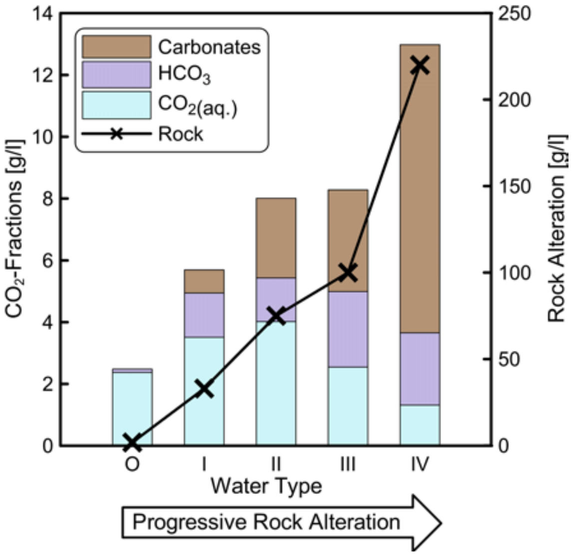


Figure 3.17: Examples of the carbon species distribution in -rich mineral waters from the Westeifel and mass of rock altered per litre of water (after May 2005).

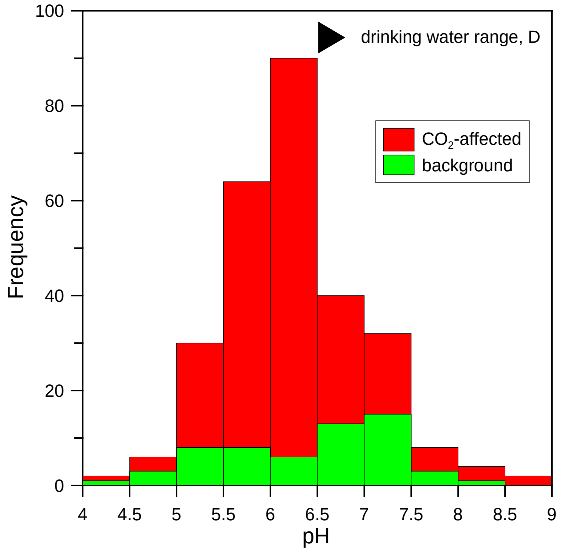


Figure 3.18: Histogram of pH values of -affected groundwater and background values in the Westeifel (Germany). Data source listed in May (2002b).

According to the degree of wall-rock alteration or “neutralization of carbonic acid”, and the water to gas ratios, the carbon species are distributed between “free” (gas phase), dissolved , and bicarbonate (and associated complex species). Considerable portions of the ascending have been left in the subsurface by mineral trapping, mainly in siderite and ankerite (Figure 3.17). Precipitation of these carbonates could potentially help self-sealing fractures.

For many of the waters that are naturally affected by hydrochemical parameters exceed drinking water thresholds: pH, electrical conductivity, Na, Mn, Fe, Ni, Al, Cl, . The pH-values are often lower than in unaffected groundwater (Figure 3.18). pH is, however, not an unambiguous indicator. Sulfur and nitrogen oxides were emitted at large quantities, primarily from power plants, prior to the installation of flue gas desulfurization units. The buffer capacity of soils for the nitrous and sulfuric acids is locally exhausted, so that acid precipitation contributes to groundwater recharge. The bimodal distribution of background values reflects this tendency towards anthropogenic groundwater acidification. On the other hand, carbonic acid has been neutralized by mineral alteration in “mature” carbonated waters with neutral pH values that result from advanced reaction progress. Sodium is released from feldspar alteration in -rich waters. It often slightly exceeds drinking water limits. Mixing of fresh groundwater with saline fluids from deeper parts of the fractured bedrock has resulted in waters with elevated sodium and chlorine concentrations.

These basement brines discharge together with e.g. in the springs from Bad Kreuznach at the southern margin of the Rhenish Massif, containing up to 18 g/l of total dissolved solutes. The concentrations of , Na, Ba, Fe and Cl exceed the drinking water limits in all the wells at Bad Kreuznach (Hemfler and Büchel, 1995). The mineral waters from Wiesbaden discharge on the southern boundary fault of the Rhenish Massive as well, passing, however, through different aquifer rocks. They are bearing thermal waters that contain about 8.5 g/l of total dissolved solutes. Arsenic, iron and ammonium have been leached from the gneisses in the subsurface. Their concentrations exceed drinking water limits by about a factor of 10, despite of the precipitation of barite, FeS and silica (Kirnbauer 1997, Schwenzer *et al.*, 2001). Because of these elevated element concentrations, the springs have been used since Roman times for spas and for therapeutic purposes.

Iron and manganese exceed drinking water values in both, naturally affected and in regional groundwaters (Figure 3.19). However, high iron concentrations above of 10 mg/l are restricted to affected waters. During progressive rock alteration, is converted to bicarbonate ions, so that the saturation of siderite is soon exceeded and iron starts to precipitate from solution. Thus, mature carbonic waters of higher TDS and pH generally contain less iron (and other metals) than waters that have not much reacted with aquifer rocks.

If the minerals waters do not discharge from fractures to the surface, but into alluvial sand and gravel aquifers, they get in contact with atmospheric oxygen or mix with oxygen-rich groundwater. In any case, the redox conditions change drastically and metal-oxides can precipitate at the redox-boundary. The redox-boundary can be subject to temporal changes of groundwater table levels, which can cause repeated precipitation and dissolution of iron and manganese oxy-hydrates (co-precipitating other heavy metals). Because of aging and water-loss of these minerals and also by the reduction of permeability often redox-fronts manifest themselves by the formation of stable iron-rich metal oxide bands within the aquifers. This way, -rich mineral water discharging near Rhens has formed an iron oxide-cemented conglomerate in the alluvial sediments of the Rhine River (Figure 3.20).

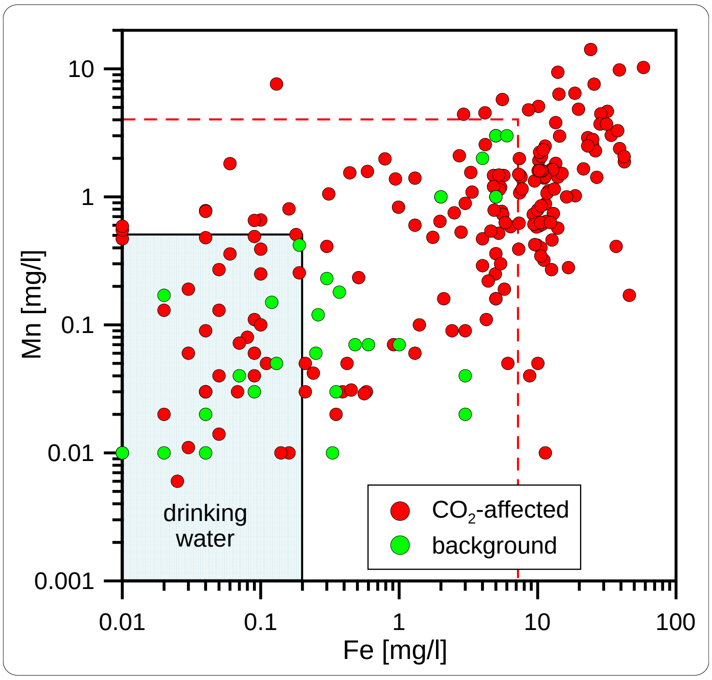


Figure 3.19: Iron and manganese concentrations in a Westeifell well and spring waters. Drinking water limits are shown by the solid black line and limits of the background values by the red hatched line. Data source listed in May (2002b).

Figure 3.20: Holocene sediment of the Rhine river, cemented by iron oxi-hydrate near the mineral springs of Rhens.

As iron and manganese can be easily removed from groundwater by aeration, they are not seen as a major problem for the utilization of the -bearing waters for drinking water, provided the other dissolved species are within acceptable limits. Natural -bearing waters are bottled at several locations in the Eifel. High Mg concentrations (280 mg/l) are found in the mineral water from Dreis in the Westeifel. The water discharges from a maar crater, surrounded by Mg-rich volcanic rocks (melilith (and nepheline) bearing foidite). Elevated aluminium concentrations have been observed in several wells, up to 2 mg/l. Though Al is eco-toxic, no adverse effects are known from springs discharging their waters into streams or rivers.

In carbonate aquifers, ascending natural promotes carbonate dissolution. Examples are the mineral waters produced from the middle Devonian strata below Gerolstein, western Germany. These waters have higher Ca to Na ratios, compared to adjacent waters from siliclastic aquifers, where alteration reactions can liberate Ca from feldspar alteration only (May 2002b). Elevated concentrations are found in the springs from Rosport in Luxembourg. These waters pass through gypsum bearing beds of the upper Triassic. Even higher concentrations are found in the mineral springs from Bad Cannstadt, near Stuttgart, which pass through limestone, dolomite and gypsum bearing rocks of the middle and upper Triassic (Uffrecht and Einsele, 1998).

Areas where natural -rich fluids or deep formation waters discharge at the surface are rather confined, on the order of several tens of meters. They are generally surrounded by a zone of mixing with the local shallow groundwaters, on the order of several hundred meters. Vertical and lateral concentration gradients mark these mixing zones and the superposition of deep and shallow flow systems (e.g. in Gerolstein (Köppen, 1987)).

In extensive sand and gravel aquifers, ascending fluids can potentially be transported and diluted downstream in the groundwater flow. Then the affected areas can extend for several kilometres, e.g. in the Rhine valley near Bonn (Fricke, 1960).

Potential impacts of or reservoir fluids on shallow groundwater can only be quantified, if the natural background and its variability are known. Distributions of concentrations and maximum values for ubiquitous background values have been derived from extensive data sets for various lithologies (Table 3.2). For Fe, Mn and Al drinking water standards should not be used for risk assessments for the shallow sand and gravel aquifers in North Germany, as the background values of these elements locally exceed drinking water standards. Element concentrations in shallow Bunter sandstone aquifers do not exceed drinking water standards. Deep Bunter formations considered for storage do, however, frequently contain brines in excess of 100 g/l of dissolved solids.

Table 3.2. Examples of maximum values (mg/l) allowed in drinking water standards in Germany and ranges for ubiquitous groundwater in different aquifers (data from Kunkel et al., 2004).

Chemical Species	Maximum concentration at tap in Germany (mg/l)	Quarternary sand and gravel 0-10 m depth	Bunter aquifers
B	1	0.233	0.022
F	1.5	0.3	0.18
Hg	0.001	0.0003	0.00008
Se	0.01	0.0003	0.00087
Sb	0.005	0.0001	0.0004
As	0.01	0.0044	0.0031
Pb	0.01	0.0043	0.00075
Cd	0.005	0.0003	0.00041
Cu	2	0.01	0.0026
Ni	0.02	0.013	0.0044
Al	0.2	**0.283**	0.039
	0.5	0.1	0.01
Cl	250	87	17
Fe	0.2	**8**	0.09
Mn	0.5	**1.4**	0.07
Na	200	38	16
	240	189	58
pH	From 6.5 to 9.5	6.8 – 8.2	6.7 – 7.6
Electrical cond. [µS/cm]	2500	993	692

3.4.2. accumulation, Montmiral, France

The peri-Alpine province exhibits a variety of geological environments and illustrates different contexts of generation, migration, accumulation and leakage linked to the regional geological history. Several natural accumulations (from 66 to 99% in gas phase) were discovered during gas and oil exploration in the 1960's. They show that can remain trapped underground for millions of years at various sites characterized by specific geological contexts. Conversely, many springs and boreholes currently being exploited for their carbo-gaseous water (Perrier, Vichy, etc.) prove that can potentially migrate from the mantle towards the overlying formations and even up to the surface leading to natural leakage without major risk (Czernichowski-Lauriol *et al.*, 2003).

The gas reservoir of Montmiral (97 to 99% in gas phase) is natural accumulation located in this Valence province (South East, France). This -rich brine accumulation is located between 2300 to 2500 m depth in a compound reservoir consisting of Triassic wedge reservoir (sandstone) overlain by Rhetian and Liassic carbonate. The reservoir is sealed by Lias-Dogger (Domerian to Callovian) marl and clay (around 500 m thick), (Figure 3.21).

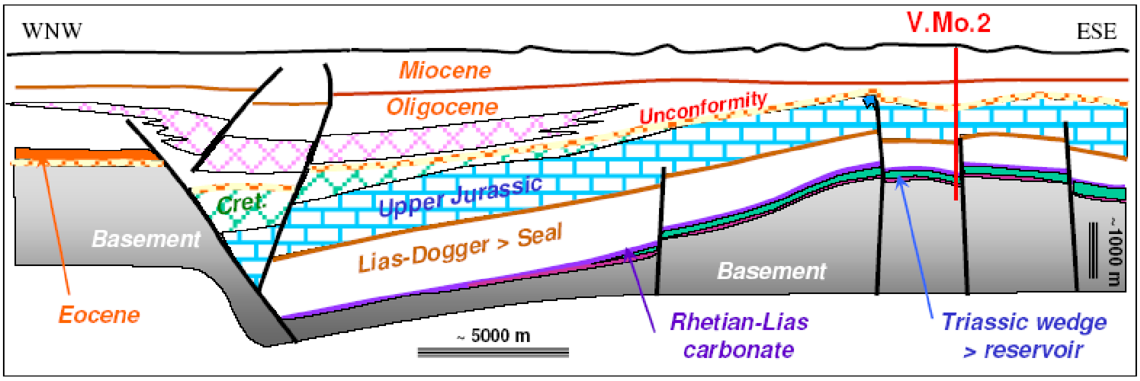


Figure 3.21: Montmiral cross section (Le Nindre, 2006).

In the subsurface, there are two aquifers: one is superficial (alluvial), the other is a regional aquifer (molasses Miocene) with older groundwater. In these aquifers the measurements of the dissolved and the isotopic did not show any influence of the deep .

Lafortune *et al.* (2009) postulates leakage through a deep well, based on the evolution of the ratio He/Ne in the deeper aquifer but the evolution of the carbon signature is not clear and groundwater quality is not affected (Pauwels *et al.*, 2007).

3.4.3. Brine injection, Werra, Germany

Saline waste water from the potassium salt processing for fertilizer production has been injected into the subsurface since 1925 in the Werra potassium mining area. This particular example is considered by the German alliance of public water works (AÖW) as an industrial analogue from what they fear from storage in saline aquifers. However under the current CCS legislations impacts such as described below should not happen, because of the regulatory requirements on site exploration, permitting, monitoring, safety concepts and remediation requirements. The example is still illustrative in the light of the current discussion about “pressure relief” wells or “aquifer management” ideas, where large quantities of brine could be produced from injection formations and injected in other underground formations.

The formation for brine injection is a saline carbonate aquifer, the Upper Permian Plattendolomit. Shale and claystone layers separate the deep saline aquifer from the Lower Triassic Bunter Sandstone aquifer that is widely used for drinking water extraction (Figure 3.22).

Based on a compilation of monitoring data Skowronek *et al.* (1999) conclude that an area of 480 km² contains mixtures of initial formation water and injected brines, at various ratios. About 60 wells have been used to inject about one billion m³ of brine up to now. The waste waters were Na, Mg>K-Cl> brines with 280 to 300 g/l of dissolved salt. The initial formation water chemistry is quite variable ranging from freshwater in recharge areas to brines of more than 100 g/l in areas affected by subrosion of the Zechstein salt.

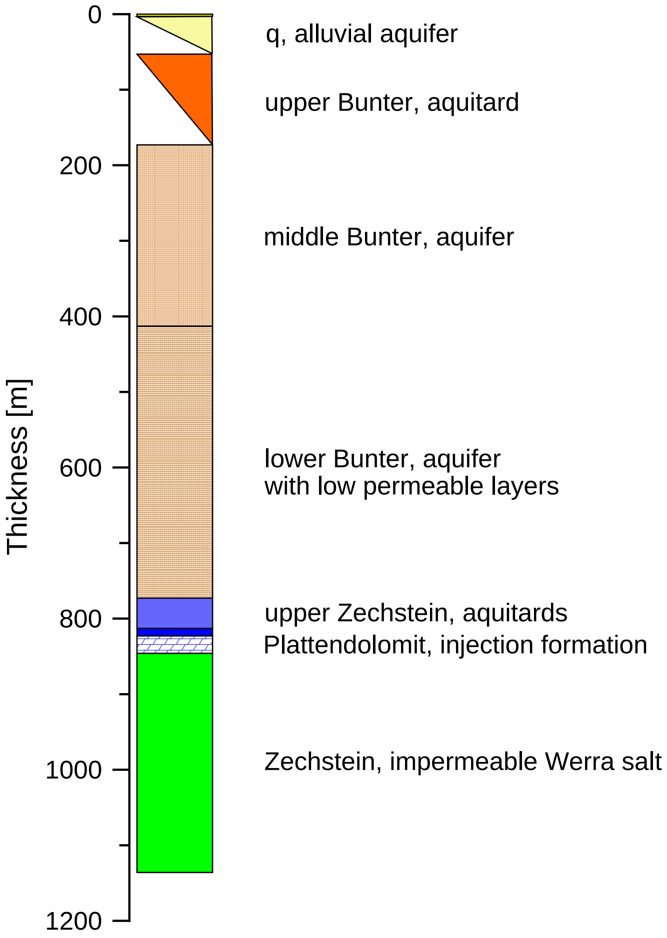


Figure 3.22: Hydrostratigraphic column of the Werra potassium mining area (after Skowronek et al., 1999).

In most of the area the clay stone and shale layers form an effective barrier between the injection formation and the freshwater aquifers in the overburden. To the north of the injection area, the Zechstein crops out at the surface. There the Zechstein salt underneath the Plattendolomit has been removed by subrosion. As a consequence of the subrosion of the salt, the overburden has collapsed and has been fractured in the salt slope area (“Salzhang”). Locally intensive fracturing of the overburden at the inner edge of the subrosion slope of the Zechstein salt (“Salzhang”) created connections that facilitate the ascent of brines from the injection formation to the Bunter aquifers. According to the Hessian environmental ministry only 43 % of the injected brines remained within the “Plattendolomit” reservoir, 37 % (up to 300 million m³) have made their way into the overburden Bunter and 20% diffusively discharged along the Werra river (Mayer, 2008).

Salt water discharges in the Werra valley, in the area of the “Salzhang”. In the discharge area, the alluvial sediments lie above the lower Bunter, as the younger parts of the Bunter sandstone have been eroded. The mixed water or displaced formation water discharge diffusively directly or via the alluvial gravel deposits into the Werra River. The temporal variation of dissolved element concentrations in groundwater observation wells has been used to distinguish between the natural discharge of salt water from subrosion and injection-induced salt water impacts. Skowronek *et al.* (1999) estimate that about 15 to 25 % of the injected chloride discharges along the Werra. The discharge area stretches over about 5 km, in a distance of 5 to 10 km from the injection areas. The travel time from the injection area to the discharge area along the Werra River is in the order of 15 years. The waters discharging in this area contain a waste water fraction of up to 20 % in the formation water. Because of the high salt concentrations these waters are an environmental problem in fresh ground- and surface water.

The brines do not reach areas where the salt has been leached away completely. The clay rich subrosion breccia forms an impermeable barrier to the hydraulically possible further lateral movement of brines within the Plattendolomit. In the areas of intact Zechstein salt the Bunter and Quaternary freshwater aquifers are locally affected by saline water. The induced pressure increase within the Plattendolomit promotes the ascent of injected and displaced brines into the Bunter aquifer. Local public water works are afraid, that further groundwater production wells have to be closed down (Frank and Reitinger, 2010).

This example illustrates two potential risks for the industrial scale storage of in saline aquifers:

- potential lateral displacement of brines and diffuse discharge to shallow aquifers and surface water bodies
- potential local vertical ascent of brines from pressurized aquifers along faults, that could be supported by the extraction of freshwater from shallow aquifers.

3.4.4. Acidification in a siliciclastic aquifer, Grindsted, Denmark

Half of the Danish freshwater aquifers consist of arenaceous glacial deposits inter-bedded with till. During the last (Weichselian) glaciation fans of siliciclastic sand from melt water were accumulated in, among others, the Grindsted area (Jutland, Western Denmark), which now holds an important source of potable water. The aquifer is non-calcareous and consists of 15-25 m of well sorted coarse grained Quaternary sand underlain by up to 60 m of limnic sand of Miocene age. A continuous layer of marine clay, which is also of Miocene age, comprises the hydraulic bottom of the aquifer.

The effects of acidification of a freshwater aquifer due to precipitation of acid rain are here taken as analogues to the potential effects of seepage addition of dissolved from deep saline formations to the aquifer and the concomitant decrease in pH. The relation between acidification of groundwater and the mobilization of nickel and other trace metals in a shallow sandy aquifer in Grindsted has been studied by Kjøller (2001) and Kjøller *et al.* (2004).

The pH in the uppermost saturated part of the sandy aquifer is rather low (4.4-4.6), whereas the values are between 5.2 and 6.5 in the deeper parts. (Kjøller, 2001; Kjøller *et al.*, 2004). The depth where the pH-values change abruptly from low to higher (Figure 3.23) constitutes an acidification front. The change in pH with depth is reflected in a corresponding change in the concentration of aluminium across the acidification front. Thus, in the upper acidified part of the aquifer, the aluminium concentration is high (about 0.2-0.3 mM), while the aluminium concentration is negligible below the acidification front.

The high concentration of aluminium in the acidified zone is a result of the dissolution of gibbsite ($Al(OH)_3$) in response to the infiltration of acid rain. Thus buffering of the acid rain takes place according to the bulk reaction:

$Al(OH)_3 + 3H^+ \rightarrow {}^{+} +$

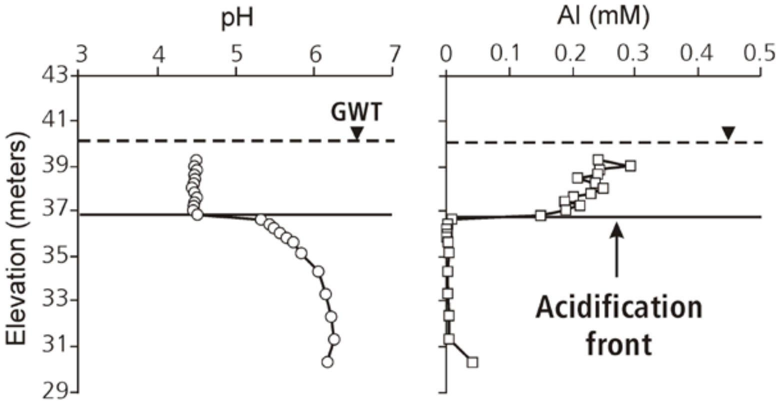


Figure 3.23: pH and aluminium concentration in the groundwater of a shallow sandy aquifer affected by acidification. GWT denotes the groundwater table (Kjøller et al., 2004).

Since the position of the acidification front is due to a reactive process it will, in the one-dimensional case, be displaced downwards through time dissolving Al in the acid zone and reprecipitating it at the acidification front. Kjøller (2001) and Kjøller *et al.* (2004) found that the vertical velocity of the acidification front is controlled by the vertical flow component and retardation caused by pH buffering and ion exchange of aluminium ions for base cations ($^+$, $^+$, Na$^+$, K$^+$).The pH buffering and exchange of aluminium ions for base cations is the signature of the acidification front, in which the H$^+$ stems from the introduction, via the precipitation, of and into the aquifer.

Also, in response to acidification of the aquifer, relatively higher concentrations of trace metals are observed in the acidified zone (Figure 3.24). Contrary to the depth distribution of the aluminium the concentration of dissolved trace metals does, however, reach a high peak level at the acidification front (Figure 3.24). Kjøller *et al.* (2004) modelled the trace element transport using surface complexation theory (e.g. Appelo and Postma, 2005) and illustrated that accumulation of dissolved trace metals would take place at the acidification front as it progresses further downward in the aquifer (Figure 3.25). For groundwater percolating further down beyond the acidification front (where pH is higher), the dissolved trace metals are immediately adsorbed to the sediment. When, eventually, the acidification front migrates further down in the aquifer, the adsorbed trace metals are remobilized in the regime of low pH in the acid zone. Thereby a “trap” for dissolved trace metals is formed, which is the reason for the peak in (dominantly adsorbed) trace metals at the acidification front. Based on a detailed solid speciation analysis Kjøller (2001) and Kjøller *et al.* (2004) suggested that trace metal adsorption mainly takes place on the surface of Fe- and Mn-oxides.

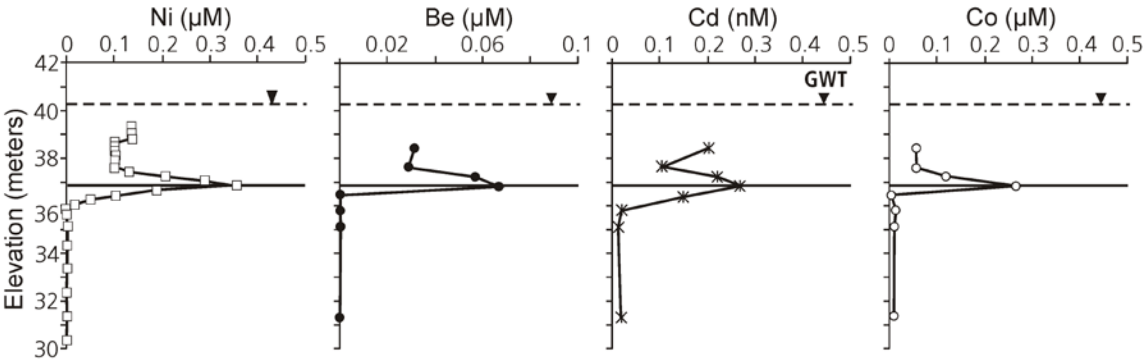


Figure 3.24: Accumulation of trace metals at the acidification front (trace metal “trap”) in a shallow sandy aquifer. If the acidification front is displaced downward, the peak in (dominantly sorbed) trace metal concentrations is also displaced (Kjøller et al., 2004).

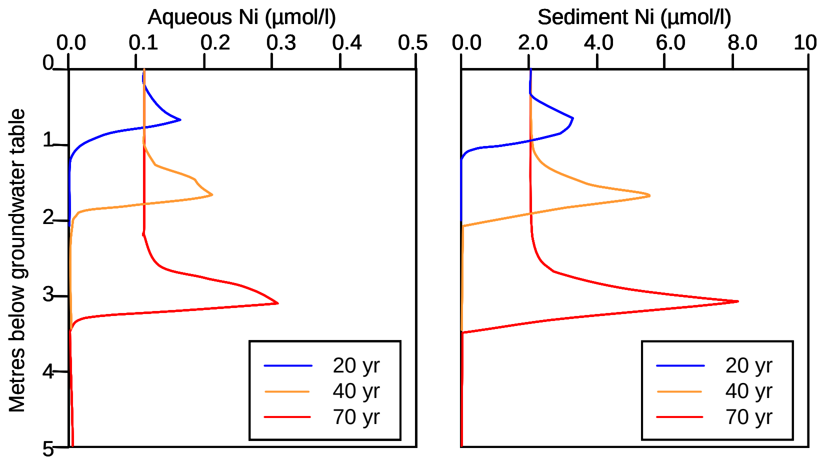


Figure 3.25: Modelling of the accumulation of trace metals in the trace metal trap as the acidification front migrates downward in an aquifer.
The modelling is carried out using PHREEQC with an implementation of the Dzombak and Morel (1990) surface complexation model. From Kjøller (2001).

The concentrations of trace metal ions are also slightly higher in the acid zone than below the acidification front, but the most conspicuous peak in the concentration profile is at the acidification front. For a given depth, this peak concentration is temporary and restricted to the period of passage of the acidification front. For dissolved aluminium there is no peak in concentration at the acidification front (Figure 3.23). The relatively high concentration of dissolved aluminium in the acidified zone stays at this level until the supply of aluminium is exhausted, which in this case equals the point where all gibbsite is dissolved. At this point pH buffering will presumably take place by dissolution of other minerals, e.g. primary silicates. The reason for the difference in behaviour between aluminium and trace metals is that pH-dependent adsorption of trace metals takes place on reactive surface hydroxyl sites, while aluminium adsorption is related to structural charge sites, where adsorption is not pH-dependent (Kjøller, 2001; Kjøller *et al.*, 2004).

In applying this case story of an acidified aquifer to a case where a potential leak of into a shallow aquifer has caused a decrease in pH in a zone of the aquifer, some degree of trace metal mobilization caused by the intrusion could be expected. Further, elevated aluminium concentrations might potentially be expected in aquifers buffered by gibbsite equilibrium. The exact level of trace metal and aluminium concentrations would depend on the specific aquifer and the pH – and thereby on the partial pressure in the aquifer.

Anticipating that , which has potentially leaked to the aquifer, is present as some kind of plume with elevated partial pressure and lowered pH values, an accumulation of trace metals may potentially be anticipated to occur at the rim of the plume. Trace metal concentrations seemingly increase as the plume migrates in the aquifer, and the acidification front sweeps the aquifer. Further, directly transferring the results of the acidification study, it might be expected that the potentially leaked leaves behind a footprint in the aquifer with decreased pH values, elevated aluminium concentrations in the water and slightly elevated concentrations of trace metals, albeit lower than peak levels.

3.4.5. Acidification in siliciclastic aquifers, examples from Germany and Denmark

The Bunter sandstone aquifer is an example of the most extensive DSF proposed for storage in the EU. The DSF is both, laterally connected to, and widely used as an important drinking water resource, where it is located at shallow depth. This example demonstrates the vulnerability of this aquifer and the soils derived from the Bunter rocks, because of their low buffer capacity, which, when exceeded, has a lasting negative effect on groundwater-pH. The acidification caused by acid rain could only partly be compensated by the liming of the forest soil in the German example. This limited effect is also a warning of the limited buffering potential the aquifer may have for the remediation of extensive or continuous leaks into shallow groundwater.

Figure 3.26 displays the temporal evolution of pH and discharge rates from a small creek, fed from groundwater discharging in an area of acidified groundwater (Landesamt für Umwelt, Wasserwirtschaft und Gewerbeaufsicht, 2005). The buffer capacity of the soils formed on quartz rich Bunter sandstone, was exceeded in the 1980's. Little buffering capacity is left, indicated by the annual changes. Groundwater recharge occurs in Nov-March, when the discharge of the shallow, fast flow system is also highest. (No distinction is made between surface run-off, inter-flow and true GW recharge in this diagram). 3 t/ha of ground limestone were added in 1996. The remediation effect is obvious, but the pH-fluctuations are higher than before. This probably reflects different reaction rates between the former, probably silicate buffer and the new carbonate buffer, which is still too slow to buffer all of the acid input during the hydrological winter season.

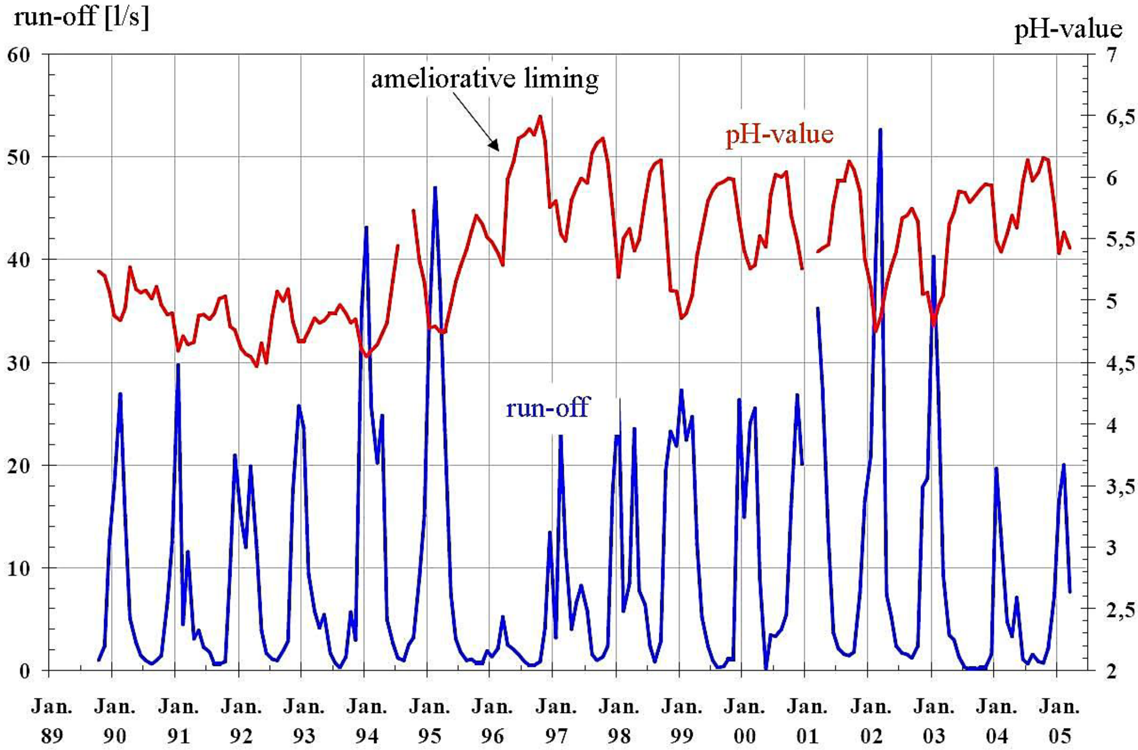


Figure 3.26: Seasonal variations of pH caused by groundwater recharge in the Bunter sandstone catchment area in Western Germany, where the buffer capacity of the soils is exhausted (Landesamt für Umwelt, Wasserwirtschaft und Gewerbeaufsicht, 2005). Some buffering of the acid deposition from air pollutants has been re-established by amelioration liming (3t/ha).

3.4.6. Sinkhole formation, central Italy

As in central Germany there are a large number of sites throughout Italy, where natural, deep-origin migrates towards surface and is released to the atmosphere. This gas has different origins depending on the local geology; however the principle sources are thermo-metamorphic reactions altering carbonate rocks as well as magma and mantle degassing. In addition to the impact that this natural has had on local ecosystems and groundwater chemistry, it has also been responsible for sinkhole (dissolution reactions) formation. Although the mechanisms and processes that create sinkholes are numerous, most can be grouped into three large categories: karstic, anthropogenic, and deep piping sinkholes. The first type can be considered the “classic” definition, whereby these features form in recharge areas via the dissolution of atmospheric and vadose zone into rainwater and its subsequent acid reactions with shallow, fractured carbonate units. The second type is linked to underground excavations, often forgotten, related to shallow mines or tunnels that cave in due to a loss of roof rock cohesion. The third type is rarer, given its occurrence only under certain specific geological conditions, however considering that it has certain traits in common with what might occur at a -leaking CCS it shall be discussed here.

According to Nisio *et al.* (2007), deep piping sinkholes are typically associated with faults or fracture systems that provide the original conduit (“pipe”) for the upward migration of natural deep origin and groundwater towards the surface. The migrating dissolves into the water making it acidic and chemically aggressive against carbonate minerals, while the flowing groundwater transports away the dissolved minerals and maintains mineral solubilities below saturation (i.e. stagnant groundwater would quickly become over-saturated and dissolution slowed or stopped). Once structural stability has been compromised by sufficient under-mining of the roof rock, collapse occurs and a sinkhole is formed. Often these sinkholes fill with water and are associated with active gas bubbling and a flowing mineral-water spring. Nisio *et al.* (2007) created a database of 555 sinkholes throughout central and southern Italy, of which about 70% are believed to have formed by the deep piping mechanisms. These features tend to be clustered in sinkhole-prone areas, and often aligned along faults along the Tyrrhenian margin-near carbonate ridges.

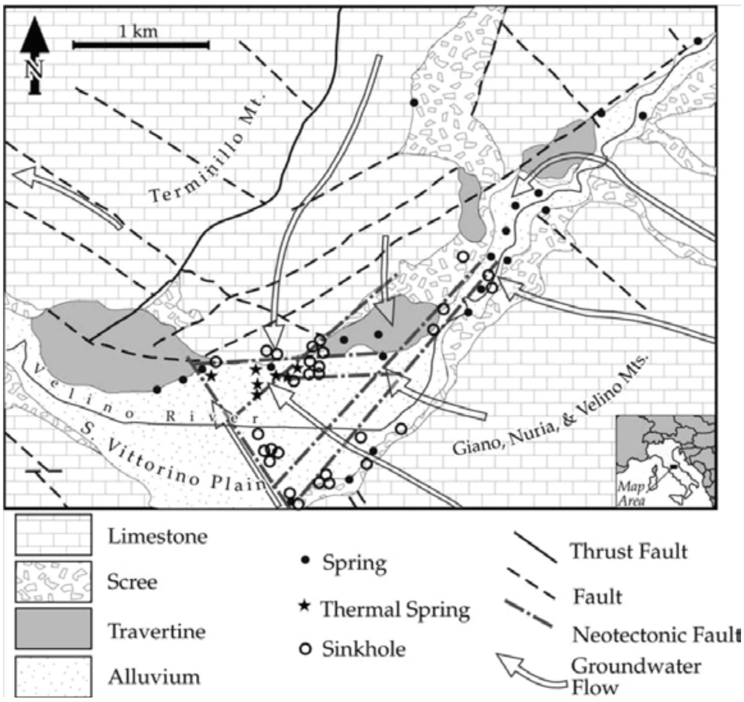


Figure 3.27: Map of the San Vittorino Valley showing geology, groundwater flow, and sinkhole locations. (After Salvati and Sasowsky, 2002).

One such example is the San Vittorino Valley in central Italy (Figure 3.27), a triangular-shaped intramontane basin occurring at between 400 and 420 m above sea level. The surrounding peaks reach elevations of 1850m asl and are formed primarily of carbonate and flysch units, with groundwater flow towards the valley floor from the surrounding mountains (Petitta, 2009). The basin is filled with Pleistocene to Upper Holocene fluvial-lacustrine sediments, including silts (60%), clays (20%) and sands (10%), as well as local lenses of gravel and travertine deposits. More than 30 sinkholes (5-100m diameter) can be found in the central and eastern sectors of the plain, with the formation of some being described in historical documents dating back hundreds of years. Many of the sinkholes are water-filled, some at the level of shallow groundwater table, whereas others have a spring indicating groundwater under confined, artesian conditions. Salvati and Sasowsky (2002) showed the association between the sinkholes and the flowing springs, bubbling gas, low pH values and elevated and TDS levels, and concluded that these features are likely formed by the leaking (±). In an extensive water sampling of the sinkholes and springs of the valley, Annunziatellis *et al.* (2004) defined three different water types (Figure 3.28).

Groups 1 and 3 both have concentration levels typical of carbonate aquifers, although they are clearly distinguished by their differing Ca/ ratios (Figure 3.28a). These two water groups were found primarily along the northern (group 1) and southern (group 3) boundaries of the valley, with samples originating from both from normal springs and from “stable” sinkholes with no gas bubbling or water flow. In contrast the group 2 water type, with its elevated TDS values and low pH, is associated with sinkholes and springs with active gas bubbling and often flowing water, indicating that dissolution is still active. Whereas some of the data indicates that the anomalous groundwater chemistry may be due to only direct dissolution of carbonate rocks along the flow-path, other results imply an additional component in the form of mixing with deep saline water that might be co-migrating with the gas (Figure 3.28b). Despite the significant change in water chemistry, the waters of the anomalous group mentioned did not exceed potable water standards (likely due to the local lithological chemistry) but did exceed nuisance levels for some components (e.g. sulfate).

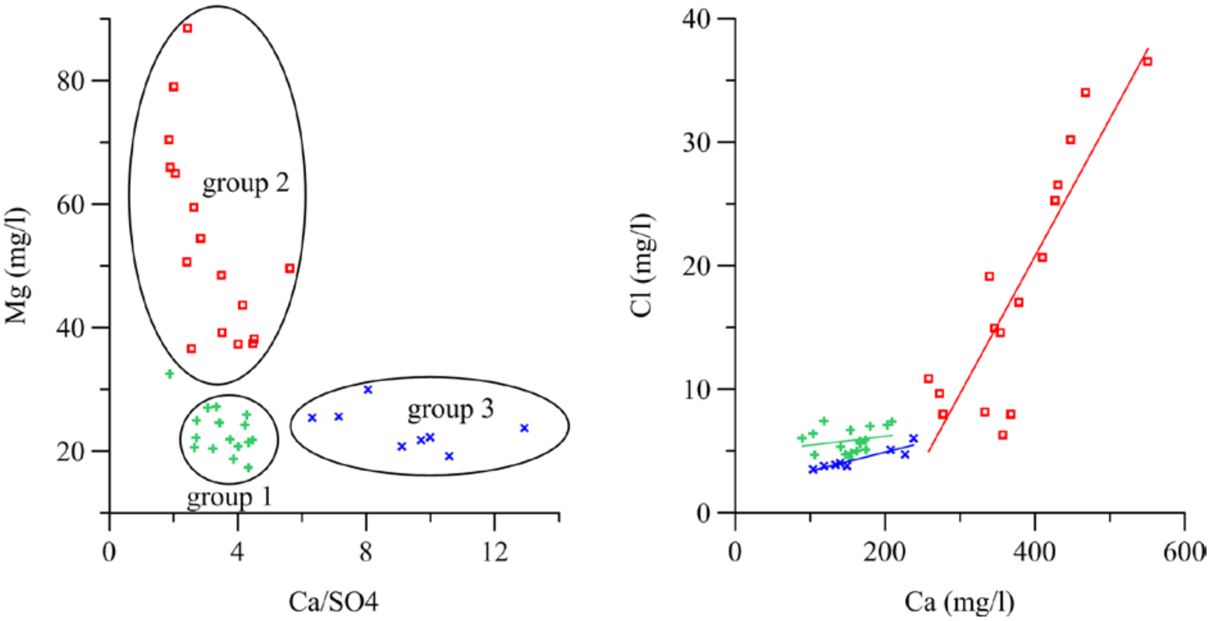


Figure 3.28: Major ion chemistry plots of data from springs, wells and sinkholes in the San Vittorino Valley. (After Annunziatellis et al., 2004).

In summary it can be stated that although sinkholes could potentially be formed via leakage from a CCS reservoir, the unique conditions associated with the natural sites located in Italy imply that this risk is likely relatively small. In particular, high groundwater flow rates are needed (together with the) over long time periods to remove dissolved ions and thus maintain mineral saturation levels low enough to promote dissolution. According to the theory of how these sinkholes formed (Nisio *et al.*, 2007) a specific geological and hydrogeological setting is also necessary, which includes an over-pressurized aquifer within a soluble rock type (e.g. carbonates) confined by a rigid low-permeability layer, all of which is cross-cut by a gas and water permeable fault. Although a potentially small risk, the possibility of sinkhole formation should be taken into account during initial geological – structural site assessment and characterization.

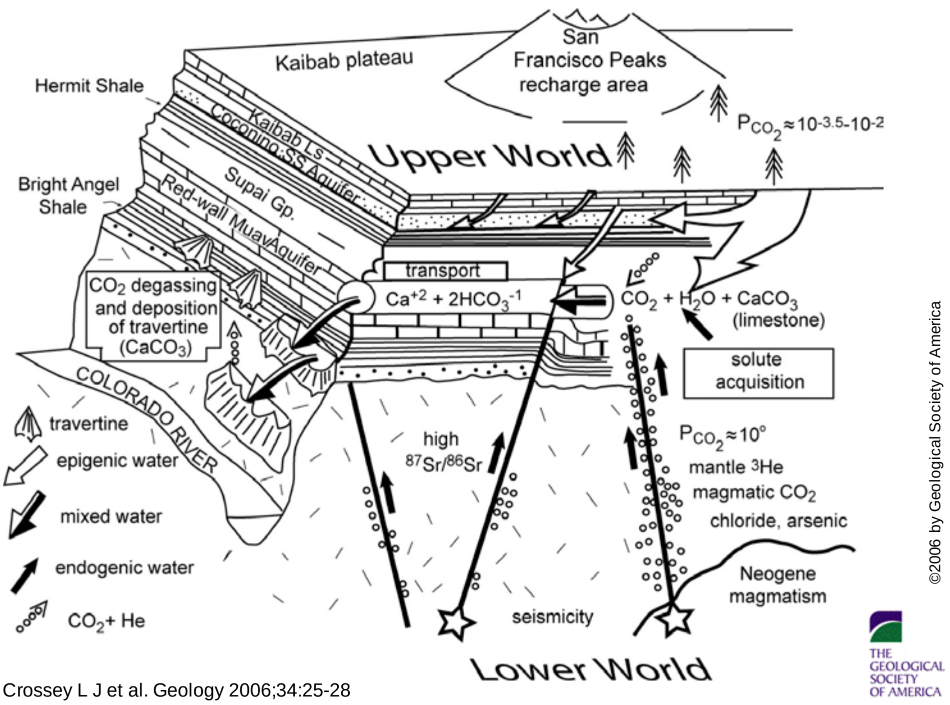
3.4.7. Travertine and calcareous tufa formation (various locations)

Whereas sinkholes involve dissolution reactions that undermine rock integrity, precipitation reactions are also possible in the surface or near-surface environment when migrating groundwater becomes over-saturated in calcium carbonate due to changing environmental conditions that cause degassing. The two main reasons for degassing is the pressure decrease along the flow path of ascending water and the temperature increase of cool groundwater discharging at springs. Turbulent flow of springs further fosters the degassing of spring waters may still be super-saturated with dissolved . Calcium carbonate precipitation due to degassing is illustrated in the following equation:

$^{+}{}_{(aq)} + {}^{-}{}_{(aq)} \rightarrow (g) + \; +$

Although the nomenclature is not totally standard in the literature, there are two general terms (based on their source waters) that are used to differentiate the resultant chemical precipitate rocks that are formed (Ford and Pedley, 1996). Travertine is typically used to describe rocks derived from precipitation from hot water sources (where degassing occurs due to cooling and/or pressure drops), while calcareous tufa refers to rocks from cold water sources (where degassing is often caused by pressure changes or changing surrounding chemistry). Both pathways are tightly linked to processes regulated by different microbial populations (Golubić *et al.*, 2008), with consumption of dissolved by plants growing along or in cold springs also contributing to carbonate precipitation. Although these two end members exist, it should also be remembered that there is also a range of environments between these two extremes. This is particularly true when a hot water source flows on surface and progressively cools as it moves further away from the source. For the case of natural analogues of potential effects of (± brine) potentially leaking from a storage reservoir, the low temperature end-members would be more representative.

The size and shape of such deposits can vary widely, from local ridge structures that form along the fault or fracture system, which provides the upward conduit for the migrating super-saturated thermal waters (Rapolano, Italy, Brogi and Capezzuoli, 2008; Grand Canyon, Crossey *et al.*, 2006; Nyalam, Tibet, Zentmyer *et al.,* 2008) (Figure 3.29), to immense tabular deposits like that at Tivoli, Italy, which covers 20 with an average thickness of 60 m (Faccenna *et al.*, 2008). Research has shown how the deposition of both travertine and tufa can be regulated by environmental factors, such as groundwater fluctuations (Faccenna *et al.*, 2008) or seasonal temperature effects (Matsuoka *et al.*, 2001).



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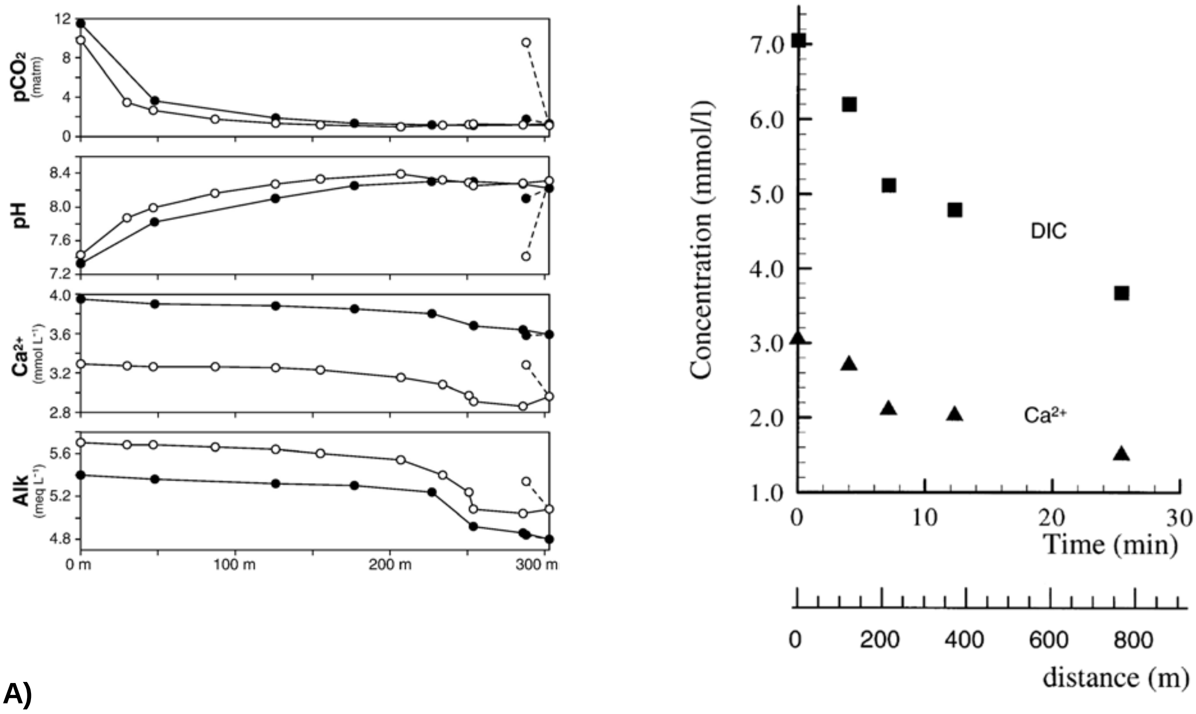
Crossey L J et al. Geology 2006;34:25-28

Figure 3.29: Model of the Grand Canyon hydrologic system showing interaction of epigenic and endogenic water components during acquisition, transport, and deposition phases of travertine genesis.
Depicted are major aquifer units and schematic flow lines indicating surface recharge and chemical evolution of epigenic waters (white arrows) and input of endogenic waters along faults (black arrows). Small circles depict upward transport of mantle-derived He and its carrier gas, . (Crossey et al., 2006).

As outlined in Pentecost (2005), the precipitation of travertine and tufa consists not only of pure but also various other mineral phases and incorporated trace and minor elements, which will clearly affect the chemistry of the remaining waters. The two main forms of calcium carbonate, calcite and aragonite, typically consist of between 93 and 99% of the mineral content of these deposits. Their precipitation results in a down-gradient decrease in the concentrations of calcium, bicarbonate, alkalinity and DIC and an increase in pH (Figure 3.30). Various elements that have been found to be incorporated within the calcium carbonate minerals as impurities can include significant amounts of Fe, Mg, Sr, and Mn as well as variable quantities of Al, Ba, Cl, K, Si, and S (Pentecost, 2005). Significant secondary minerals can include gypsum, barites, manganese and iron oxides and hydroxides, amorphous silica like opal and chalcedony, and sulfur. The formation of oxides and hydroxides, caused by addition of oxygen in the surface environment and the subsequent increase of Eh, can also be important for decreasing the concentration of numerous trace elements due to the process of adsorption.



A)

B)

Figure 3.30: Plots showing the change in aqueous chemistry as -charged water moves away from its spring, resulting in degassing, an increase in pH, and a decrease in Ca and alkalinity. (A - after Shiraishi et al., 2008; B – after Lu et al., 2000).

3.5. CONCLUSIONS

Potential leakage of, or pressure perturbation from, injected into deep saline formations influencing shallow aquifers with fresh groundwater to any significant extent is generally considered very unlikely. This presumption seems to hold for the practical examples studied, where is injected into oil or gas fields, or other strata, where the ability to contain liquids or gas at high relative overpressure is already proven.

To study the processes and likely results stemming from any such potential leakage or pressure perturbation, injection experiments (physical or by simulation) must be conducted for situations where the containment capability is less proven or obvious, as could potentially be the case for relatively deep saline aquifers. For such situations there seems to be little direct documentation of the fate of the shallow freshwater upon actually injected into the saline aquifer within the time frame of geological storage. Rather possible effects are based on the study of natural analogues, which have continued over relatively long time, processes that are in isolation or simulation with simplified presumptions.

Although reaction conditions are better controlled in laboratory experiments, natural analogues and field experiments offer many advantages that may facilitate more reliable geochemical predictions for the potential assessments of long term impacts as compared to extrapolations based on simple experiments and thermodynamic computer simulations.

Arrival of in a balanced system potentially causes changes in these physicochemical conditions thereby modifying the water-rock equilibrium. These impacts are widely investigated in studies on chemical reactivity of in reservoirs. In contrast geochemical reactions affecting fresh groundwater (dilute water) occurs under circumstances, where the minor chemical reactions (mineral dissolution, ion desorption) may potentially affect the water quality. Analogies between potential chemical reactivity with the deep saline formation host rock around the injection point and potential effects on fresh groundwater is not possible because of differences in pressure conditions and the industrial injection rate.

Following an accidental release of into aquifers, the most important changes would potentially be:

- Modifications in the pressure regime which could result in a change in the flow, which plays a role in the transport of solutes, and contamination from brines seeping through leaking wells, the matrix or along faults;
- Migration of dissolved organic compounds, as SC- is an excellent solvent for organic compounds;
- Mineral dissolution increasing the mineralization of the water and the release of associated trace elements;
- Precipitation of carbonates and other secondary minerals resulting in alteration of rock and aquifer characteristics
- Co-precipitation and sorption of metals, which may act as either a contaminant trap or source
- Changes in microbiological activity
- Aqueous complexation of cations that can promote the solubility (organic, chloride, bicarbonate complexes…)

All these mechanisms are interdependent, each affecting the others. The processes depend on the physicochemical conditions of the aquifer (mineralogy, temperature, pH, Eh, etc.), and transport of mobilized elements which may potentially alter water quality. In some natural analogues, despite relatively high levels of , pH depression and consequent trace element mobility are relatively minor effects due to the buffering capacity of the aquifer (Keating *et al.*, 2010).

Whereas the themes in this “bank” of related phenomena that could in some combination turn out to occur in a real injection case are relevant and broad, the weight with which the different processes will potentially interplay will be case dependent. There is therefore a need for specific case studies over the most realistic time scale possible to exemplify the combined effects that would occur.

4. Modelling case studies

This chapter is dedicated to the description of numerical modelling case studies of hydrodynamic and geochemical impacts of storage on groundwater displacement and chemical quality. A literature review has been performed using available published literature providing numerical modelling results on chemical reactions and groundwater flow changes occurring within geological formations neighbouring a injection site (either hypothetical or from real case studies).

The interest in predicting reactive front evolution in space and time remains crucial for the assessment of the potential impacts on adjacent formations. Batch (no flow) geochemical modelling offers the possibility of understanding the complex reactive chains controlling the changes of elements' concentrations in the aqueous phase due to dissolution and/or precipitation of the solid phase representing the rock, or the sorption and/or desorption of trace elements existing in the rock, or the redox potential modification, etc. In addition, being able to estimate the fluid displacement and the flow rate due to the reservoir pressure increase induced by the injection of the allows for the analysis of water table changes and brine displacement potentially occurring within the basin sediment layers. The coupling of the two processes (chemical and hydrodynamic) is still a numerical challenge in terms of computational capacity of actual simulators. Still, the integration of fluid displacement (due to either the regional flow or the injection) is needed for a better tracking of the impacted area and the recommendations to be provided regarding monitoring and detection techniques.

The chapter is split into three sections. The first section summaries modelling performed on chemical reactivity and reactive transport process dedicated to groundwater chemistry changes induced by dissolution and associated fluid-rock interactions with specific attention on trace elements mobilization. The second section focuses on hydrodynamic modification in the aquifer due to the overpressure occurring during the injection of the , as well as the pressure decline after injection. Simulations can be either based on field case examples or using synthetic data. Finally the limitations of modelling techniques and simulated scenarios are analysed and discussed.

4.1. GROUNDWATER CHEMISTRY MODELLING

While a lot of studies focus on geochemical fluid-rock interactions occurrences in reservoir and cap rock formations, little attention is paid to shallow groundwater. Indeed, many years of research studies have been carried out to evaluate the feasibility of storage without paying attention to surrounding geological formations. Only recently has the interest been brought onto impacts assessments of storage and particularly on shallow groundwater impacts with specific attentions to potable water resources.

Studies carried out on chemical reactivity evolving in the reservoir porous rock are largely developed in terms of laboratory experiments, field monitoring and/or modelling. They cover a large range of lithology, pressure and temperature conditions (e.g. Weyburn, Canada, in a carbonate oil reservoir, Ketzin, Germany, in sandstone highly saline aquifer, Sleipner, North Sea, in an unconsolidated sandy formation, Hontomin, Spain, in a carbonate aquifer). These studies generally focus on (i) the evaluation of the impact of the reactivity in the porous media on the injectivity efficiency by considering the modifications of porosity & permeability of the reservoir rock, integrity of the near-well zone and trapping mechanisms. This is in order to evaluate the feasibility and the efficiency of storage technology.

As storage is envisaged in either deep saline formations or oil and gas reservoirs the injection is performed in media containing non potable water (high salinity) and therefore impact on water quality is never measured as it is not supposed to change. Moreover large modification of the chemical composition of reservoir waters will not significantly affect the composition of the brine (Gaus *et al.*, 2010). However, small changes in chemical composition of fresh groundwater could significantly alter its potable character which is the case for the intrusion of or brine into potable water aquifer.

Thus studies on reservoir reactivity only cannot help to assess chemical impacts on groundwaters. However, as dissolution of implies water acidification, analogy with mechanisms occurring in shallow groundwater subjected to leakage is possible. Acidification triggers metal mobilization (see studies on the behaviour of trace element in soils and groundwater) and the main mechanisms involved are well identified and characterized (dissolution-precipitation, adsorption-desorption, oxidation-reduction). The current objective is to quantify the mobilization of trace elements potentially induced by a intrusion using experimental studies (Smyth *et al.*, 2009, Ardelan and Steinnes, 2009), field pilot measurements (ZERT - Kharaka *et al.*, 2010; Frio - Nance *et al.*, 2010) and geochemical modelling. The objective of this section is to report on modelling studies performed on the chemical impacts on shallow groundwaters due to storage activity. To date few studies can be found in the scientific literature and the main papers identified are listed in Table 4.1.

4.1.1. Chemical processes

Geochemical model set up is based on the specification of initial conditions such as initial abundance and distribution of hazardous trace elements, aquifer mineralogy, initial water chemistry and oxidation state. These parameters are generally defined by data on water chemistry and aquifer mineral composition. However, a lack of data is not uncommon and parameterization often relies on literature review.

Mineralogy (mineral hosts for hazardous trace element, aquifer minerals)

Identification of minerals which are most likely to determine the water composition and the buffering capacities are the major constraints on the reaction paths calculated by chemical models.

In order to identify which minerals are most likely to act as the primary thermodynamic controls in determining the concentration of HTE (hazardous trace element) in groundwaters, Birkholzer *et al.* (2008) analyses more than 38,000 groundwater analyses from US-drinking water. The authors concluded that galena is likely to control lead in reducing waters while cerussite () is the primary control under oxidizing conditions. Arsenian pyrite is probably the dominant host for arsenic under reducing conditions. When adsorption is the predominant process in controlling arsenic, the proportion of adsorption sites on clays and ferric oxyhydroxydes must be considered (Zheng *et al.*, 2009a).

The mineralogy of the host rock of the aquifer, as shown for the reservoir (Gaus *et al.*, 2008) or shallow groundwater (Wilkin and Digiulio, 2010), can have a significant influence on the water quality and impact its composition in case of ingress of (buffer effect, aqueous solute release). gas dissolution into groundwater and subsequent reactions with aquifer minerals will control the evolution of pH-bicarbonate plumes. These parameters provide geochemical context for predicting how contaminants associated with aquifer minerals will react. Wang and Jaffe (2004) show the influence of metal release in solution by using two cases with simplified aquifer mineralogy: carbonate and siliceous.

Wilkin and Digiulio (2010) stress that site-specific risk assessments may require characterization of aquifer geology, mineralogy and groundwater chemistry prior to injection.

Expanded Thermodynamic database

Geochemical reactions (precipitation-dissolution; desorption-adsorption) can be considered according to equilibrium thermodynamics or kinetics. The success of the thermodynamic modelling depends on the quality of the database (all the reactions must be mentioned and the values controlled) while kinetic models depend also on using kinetic law and on parameters, which are complex and largely not well-known.

Reaction paths calculated by geochemical models must be interpreted carefully, keeping in mind that only the minerals defined in the database are likely to precipitate. In the field, the expected controlling phases, which are more soluble and precipitate easily, are usually amorphous phases. To partly solve this problem, some authors expand the thermodynamic database (Birkholzer *et al.*, 2008, Apps *et al.*, 2010). Some authors revised thermodynamic properties of some minerals and aqueous species as uncertainties are related (Xu *et al.*, 2010). This is mainly true for mineral such as dolomite, magnesite, siderite and ankerite which are carbonated minerals with a great variety of natural compositions (solid-solution).

Zheng *et al.* (2009b) undertook sensitivity analyses on solubility products of trace-element-bearing minerals. They show that the thermodynamic values are the most critical parameters for dissolution-related increases in aqueous concentration of lead (galena) and arsenic (arsenopyrite). The variability could impact the interpretation of the results while comparing aqueous concentrations with MCL, but Zheng *et al.* (2009a) showed that the variability on product solubility do not modify their conclusion.

The study of complex systems can be approached with thermodynamic models considering the equilibrium state. The thermodynamic model is easier to outline and it highlights the potential main reactions occurring in complex systems. To highlight the evolution of the system with time and to describe the reaction pathways, it is necessary to take into account precipitation and dissolution kinetic rates.

Kinetic rate & law

The kinetic rates for dissolution-precipitation reactions vary across a large range; some are instantaneous and others are extremely slow i.e. comparable to the geological scale. To model the evolution in time of the geochemical system, one needs to know all factors controlling reactions and their rates. Data on these processes are very rare for complex systems but are problematic only according to the time scale of the model. In other systems, the reaction time is not controlled by the kinetic rate of the reaction but by flow rate or arrival time of the fluid. From a modelling point of view it is possible to consider this fast reaction as instantaneous. Some reactions do not occur in the absence of catalysts, therefore they are so slow that they did not occur at the model scale and could be ignored.

Many kinetic laws are described in the literature (Plummer *et al.*, 1978; Pokrovsky *et al.*, 2005; Lasaga *et al.*, 1994). Some of them can be written only for a specific mineral or consider multiple aqueous species. A general form of the rate law for mineral surface reaction is proposed by Lasaga *et al.* (1994):

$$r_m = \pm A_m k_m e^{-Ea/RT} \prod_i a_i^{n_i} f\left(\Delta G_r\right)$$

Where is the reactive surface area of the mineral, Ea is the activation energy, R is the gas constant and T is the absolute temperature (K). The terms involving the activities of others species in solution incorporate the possible catalytic or inhibition effects on the overall rate. f(Δ) accounts for the variation of the rate with the deviation from the equilibrium. This law contains two factors playing a major role in the overall kinetic rate of dissolution/precipitation the pH via activities of ions H+ and the temperature via Arrhenius equation.

The kinetic law most usually used in geochemical modelling applied to the storage of is a simplified law from Lasaga *et al.* (1994) considering that for many minerals, the kinetic rate constant *k* can be summed from three mechanisms: neutral, acidic and basic.

Therefore, even if a general law is used, nousually values and assumptions are applied. The sum of the three mechanisms is rarely applied in geochemical modelling of storage (Xu *et al.*, 2010; Zheng *et al.*, 2009a) and the basic mechanism is frequently neglected in kinetic modelling. In fact, the effect of is considered to be controlled through H^+ as is a weak acid. Moreover, the basic term would not be important in disposal as the high pressure of would force the formation water to remain on the acid side of neutrality. Some authors consider only the neutral mechanism (Wilkin and Digiulio, 2010) or the acidic mechanism while some others consider both neutral and acidic mechanisms (Gaus *et al.*, 2008).

Dissolution rate data are often available from a variety of sources giving different rate values and a choice must be made as to which is the best data, thus authors refer to various kinetic rates and parameters for the same mineral (Gaus *et al.*, 2008). The sensitivity of the model to the dissolution rate is clearly illustrated by Apps *et al.* (2010), Wang and Jaffe (2004). However Palandri and Kharaka (2004) proposed a compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modelling based on a compilation of experimental dissolution rates.

The last variable parameter between authors of kinetic models is the reactive surface area. The dissolution of minerals depends on the available surface area in contact with the aqueous solution. The BET method is most used but it overestimated the mineral surface area in contact with water. Conversely, the calculated geometry of the surface area method underestimated the surface areas involved in the reaction (particles surface are rough, disrupted and porous) but the surface area is included in the kinetic constant which compensates for the overestimate. Therefore is important to correctly apply a kinetic constant with the associated surface area. Interaction with the minerals is generally expected to occur only at selective sites at the surface and the difference between total surface area and reactive surface area can be between 1 and 3 orders of magnitude (White and Peterson, 1990). Other assumptions must be considered such as coatings and surface areas are arbitrarily reduced by one to three orders of magnitude (Xu *et al.*, 2005; Gaus *et al.*, 2005a). Consequently, the geometric surface area, underestimated, is usually more applied in the models rather than BET surface areas. Nevertheless the variability of the surface areas between the authors is set between 1 and 3 orders of magnitude as this is the range of uncertainty within the measurement of the reactive surface area.

Until now, the absence of precipitation rate data has required application of the principle of validity of Transition State Theory as for dissolution equations to rate laws of overall reactions. However experimental data have demonstrated that the precipitation rates of some minerals, such as alteration minerals, can be slow: minerals do not immediately crystallize out of supersaturated solution even in the presence of nucleation seeds (Lasaga *et al.*, 1994).

Surface complexation

Surface complexation and ion exchange are usually considered in reactive transport models based on chemical models such as CRUNCH (Steefel, 2001), PHREEQC/PHAST (Parkhurst and Appelo, 1999) or Chess/HYTEC (van der Lee, 1998). Moreover, the parameterization of this process requires literature review or data information to describe the relevant surface complexation reactions: e.g. the principal adsorbents phases and their thermodynamic constants for these cations. Specific surface area and site density are two other important parameters affecting adsorption. Thus modelling these processes is not easy.

For storage, these processes are considered only recently. Thus surface complexation and ion exchange were generally not included until recently (Wang and Jaffe, 2004; Vong *et al.,* 2010). Increasingly, studies emphasize the importance of these processes in relation to hazardous trace elements (e.g. metals, As) fate and transport. To correctly evaluate the impacts of storage, authors modified the code ToughReact to account for surface complexation (Zengh *et al.,* 2010, Xu *et al.*, 2011).

4.1.2. Chemical Impacts

Acidification

In an arenaceous aquifer, Zheng *et al.* (2009a) calculate in a shallow aquifer (50-100 m deep) a pH decrease from 7.6 to 5.6 within the two-phase zone (from 5 to 10 bar) and about 5.9 outside in the dissolved plume in the presence of calcite. Calcite acts as a pH buffer, but for a non-buffered system a minimum pH around 4.5 could be expected. Carroll *et al.* (2009) conducted reactive transport simulations to evaluate the impact of intrusion into a sedimentary aquifer (High Plains Aquifer, USA). The purpose of their study was to understand only the resulting changes and to evaluate the ability of detecting the resulting acidic plume. They demonstrated that the acid plume is controlled by groundwater flow and buoyancy and leaks produce measurable change in pH that is still within range of natural waters.

Humez *et al.* (2011) simulated the upward migration of CO_2 at a rate of 1.1 kg/s in freshwater aquifer. The zone impacted by dissolved CO_2 covers a 0.3 km radial extent, whereas gaseous CO_2 occurs only directly above the intrusion point and acidification of water ranges from pH 7.3 to 4.9. As the pH is controlled by partial pressure, the intrusion rate influences the simulated results (Zheng *et al.*, 2009b).

Solutes releases (metals & arsenic)

Chemical model results permit evaluation of hazardous trace element mobilization and controlling mechanisms (dissolution-precipitation; sorption). Associated with sensitivity studies under various geochemical and hydrological conditions, one can understand the complex conditions and processes affecting shallow groundwater quality in the case of intrusion.

Wang and Jaffe (2004) conducted reactive-transport simulation to assess the impact of intrusion into an aquifer containing galena. Their results suggest strongly increased lead concentration levels because of galena dissolution, in poorly buffered aquifer (quartz) to levels higher than the maximum contaminant level (MCL) for lead. Their simulations do not necessarily represent realistic conditions as their geochemical system is greatly simplified. Thus it is not clear how severe and widespread the problem would be in reality.

Zheng *et al.* (2009b) conducted reactive-transport simulations to assess the impact of ingress into a shallow aquifer representative of Underground Source of Drinking Water (USDW). They concluded that significant mobilization of lead and arsenic contaminating the groundwater can occur near the intrusion. For these results, the MCL for arsenic in groundwater is exceeded in a minority of cases whereas the MCL for lead is never exceeded. The fate of As and Pb is mainly controlled by desorption/adsorption process occurring at the surface of clay minerals (illite, smectite).

Vong *et al.* (2010) conducted reactive transport modelling based on the mineralogical and geochemical composition of an existing glauconitic-sandstone aquifer, to which trace element bearing minerals are added in average proportions found in similar mineralogies. Dissolution of decreases the pH to 5.0 and leads to dissolution of trace element bearing minerals, enriching trace elements concentrations including Cd, Pb, Zn. Their concentrations may locally exceed quality parameters. The total amounts of mobilized health-significant-elements (HSE) increase with increasing intrusion rates. A strong limitation of the model is currently that sorption processes on clay minerals as well as on oxy-hydroxydes have not been taken into account. This certainly means that computations are conservative, as these mechanisms could strongly and quickly inhibit the mobilization of trace elements that would follow acidification and dissolution processes.

Apps *et al.* (2010) conducted a thermodynamic study on the stability of heavy metal bearing minerals. They evaluated the solubility of hazardous elements as a function of the partial pressure of . The most serious problem resulting from intrusion may be the enhanced dissolution of pyrite with consequent release of As with MCL exceeded; Ba, Pb and Zn may approach or exceed the MCLs. Bruno *et al.* (2002) evaluated the applicability and limitations of thermodynamic geochemical models to simulate trace element behavior in natural water. Their study aims to understand key phenomena and processes in natural systems related to those expected to occur in radioactive waste repositories. They review and discuss the results from blind predictive modelling carried out within six natural analogue studies. The results obtained from the calculated aqueous speciation, as well as by comparing solubility calculations with the actually observed concentrations, permit differentiation into two categories of elemental behavior: those elements like U under reducing conditions that can be fairly well described by assuming solubility control exerted by pure solid phases as their oxyhydroxides; and the elements such as Sr, Zn and U under oxidizing conditions for which the association to major geochemical components of the system must be considered in order to explain their concentrations in groundwaters.

Table 4.1: Overview of published models that refer to chemical impacts of storage on shallow groundwater: main characteristics and findings

References	Background	Model	Process	Water quality
Zheng *et al.,* 2009b	Evolution of Pb & As after the intrusion of into a shallow confined GW.	Reactive transport simulations: 2D & 3D simulations (ToughReact).	Sensitivity analyses on hydrological and geochemical conditions adsorption/desorption	As & Pb mobilized but in quantity below maximum contaminant levels (MCLs).
Zheng *et al.,* 2009a	Mobilization of lead & As after the intrusion of into an arenaceous aquifer.	Reactive transport simulations: 2D (ToughReact) Augmentation of required thermodynamic data (EQ3)	kinetic, surface complexation Sensitivity study (adsorption/ desorption, surface site, log K)	As exceeds MCL in few case, Pb not (sorption > release from PbS).
Carroll *et al.,* 2009	Transport & detection of carbon dioxide in High plains aquifer (sedimentary)	reactive flow and transport calculation using a parallel version of NUFT code (3D)	Sensitivity analyses on groundwater flow and flux rate	Changes in pH still within range of natural waters.
Apps *et al.,* 2010	systematic evaluation of the possible water quality changes in response to CO2 intrusion into aquifers currently used as sources of potable water in the United States .	EQ3 geochemical code and SUPCRT with revised database	kinetic, surface complexation Identification of thermodynamic controls defining the concentrations of hazardous element	Dissolution of pyrite with consequent release of As with MCL exceeded. Baand Zn are slightly affected and may approach or exceed the MCLs. Significant increase of As and Pb but concentration values remain below or close to specified MCLs. Adsorption/desorption from mineral surfaces may strongly impact the mobilization of As and Pb.
Wang et Jaffe, 2004	Dissolution of a mineral phase in potable aquifer due to release.	Numerical simulation using MinteqA2 + transport module.	Initial assumption oversimplified	Pb mobilization sensitive to pH, buffering capacity of the system (calcite vs. quartz).

Moore *et al.,* 2005	Mineralogical and geochemical consequences of the long term presence of Springerville St Johns field, Arizona.	Reaction path using Geochemists Workbench with LLNL thermodynamic database.	Water-rock interaction and reaction path	Dissolution of carbonates cements and detritical feldspar & precipitation of dawsonite (at 20 bars) and kaolinite (lower). Precipitation of travertine in surface.
Auqué *et al.,* 2009	Evolution of a Spanish thermal system in carbonate rocks. (1000 m confined by a low permeability cap rocks).	Reaction-path calculation, using PHREEQC code and WATEQ4F thermodynamic database.		Existence of dedolomitization relevant for hydraulic properties of carbonates aquifers because of their effects on porosity and permeability.
Bruno *et al.,* 2002	The applicability and limitations of thermodynamic geochemical models to simulate trace element behavior in natural water.	PHREEQE, EQ3NR, MINEQL, MINTEQ, PHREEQC, Chess, KINDIS.	Blind predictive modelling exercises	Study related to understand key phenomena and processes in natural systems related to those expected to occur in radioactive waste repositories. The elements selected are: Sr, Ni, Zn, Ree, Th, U.
Wilkin and Digiulio, 2010	leakage of gas into aquifers with variable formation mineralogy.	Geochemist's workbench with LLNL thermodynamic database.	Reaction path and kinetics models	leak induce increase of (aq) rather than alkalinity due to low pHs. promote dissolution of Fe hydroxides.
Xu *et al.,* 2010	Reactive transport modelling at the Frio-I Brine Pilot (high permeability sandstone)	Reactive transport simulations: 1D radial (ToughReact) .	Kinetic model of Fe release	Heavy metals, adsorption sites, kinetics and thermodynamics are not well understand in natural system.

4.2. HYDRODYNAMIC MODELLING

Large scale injection of carbon dioxide into deep geological formations with moderate permeability will induce, for most cases, an increase of the pore pressure of the geological system. This pressure build-up may impact the injectivity efficiency of the storage process but it may also induce some fluid displacements, both inside the storage formation and through overlying geological formations impacting freshwater resources in a “domino” effect. A number of studies on the magnitude of the induced pore pressure increase and the extent of the impacted region have been investigated using numerical and analytical approach (see details below for associated references).

Experiences of pressure evolution during injection within a deep saline aquifer formation can be observed at several demonstration sites behaving differently. The largest and the longest-running megatonnes-per-year storage is conducted at the Sleipner site (North Sea). Modelling indicates that pressure increase should be negligible, which is in agreement with the wellhead pressures observed (few bar) since injection started in 1996 (Chadwick *et al.*, 2009; Ringrose, 2010). At In Salah (Algeria), the injected has generated a higher level of pressure increase (several tens of bar) with a displacement of the land surface of several centimetres. In Snovith (North Sea), the high pressure increase has limited the injection rate.

Though the Sleipner Utsira storage formation is providing a successful industrial “real-case” implementation, special attention should be paid not to generalize too quickly as warned by van der Meer and van Wees (2006). Indeed, the “Sleipner case” presents very good characteristics, being extremely (i) large, extending from the Norwegian coast far into the UK sector, (ii) thick, and finally (iii) very permeable and porous. Furthermore, the injection rate is of about 1 million tonnes of per year with a total amount of stored of 12 Mt. This is far lower than the tens of gigatonnes envisaged as numerically estimated for instance by Lindeberg *et al.* (2009) within the same formation (at a value of 7% of the pore volume corresponding 40 Gtonne (Gt)).

Given that no such gigatonne industrial scale injection of has been performed yet and that no proper observation data are available on the impact of the injection to surrounding aquifers, numerical (and analytical) approaches remain the only solution to provide some prediction on impact of storage on a regional scale of the hydrological system. Though some analogy may be found with waste water injection or natural gas storage (see Section 3.2.3 of this report), the impact on pressure and native brine displacements cannot be considered totally identical as the time scales of interest (of the order of hundreds of years for the geological storage) and volume of injected fluid involved are not of the same order. Besides, these underground injection technologies are generally associated with some fluid withdrawal compensating pore space invasion. Brine production might be considered as an alternative to compensate pressure increase and to limit hydrodynamic impact as proposed for instance in the Gorgon project, Western Australia.

In the following, descriptions of several studies performed with numerical modelling tools only are provided in order to analyse the capacity of numerical modelling (associated for some cases with mathematical analytical solutions) to predict the impacts of storage on groundwater resources. Three subsections are provided. One is dedicated to warnings on reservoir pressure increase regarding both the capacity of storage and associated impacts on neighbouring geological formations (4.2.1). The next subsection (4.2.2) is dedicated to the modelling of pressurization of the storage formation and surrounding geological formations. And finally, the last subsection (4.2.3) summarizes and compares all presented simulations results relevant to the impacts on groundwater resources with a specific focus on water table changes and fluid displacement as illustrated in the following diagram (Figure 4.1).

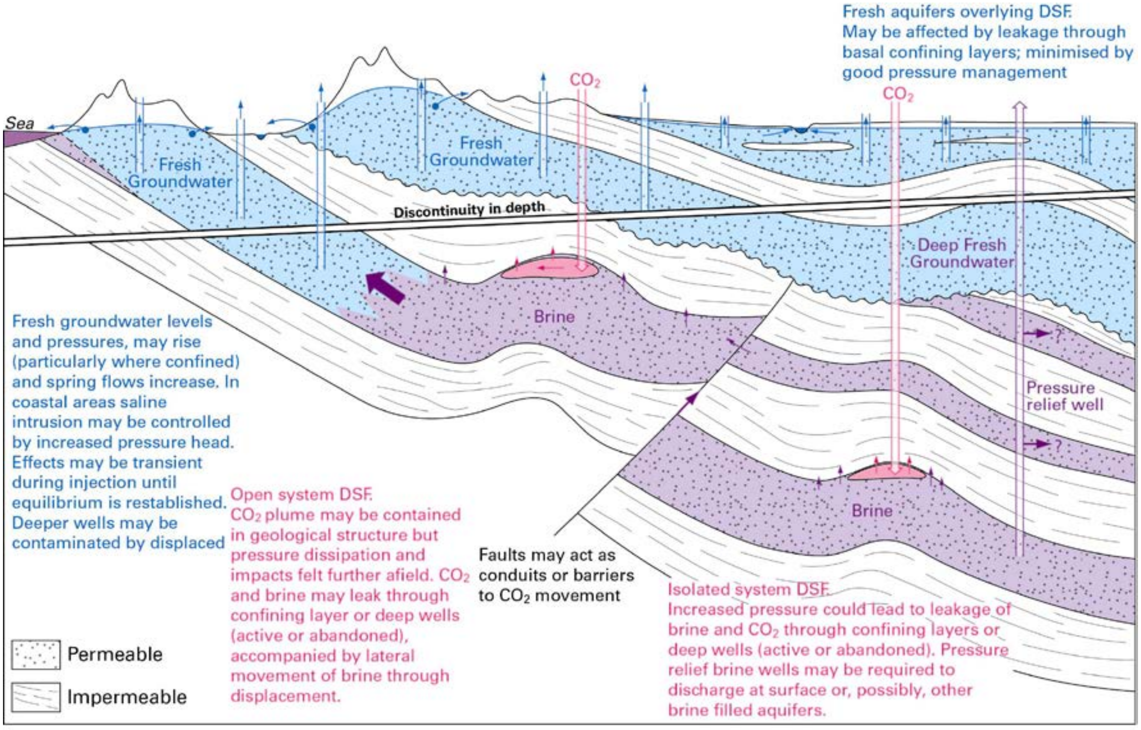


Figure 4.1: Schematic representation of potential leakage mechanisms and impacts of storage on fresh groundwater (not to scale).

4.2.1. Warnings on reservoir pore pressure increase and associated impacts

Concerns about the capacity of injecting into porous rock due to compressibility and geo-mechanical integrity limitations have been noted some decades ago by several authors. Pore pressure uncertainties may correlate to impact on groundwater resources regarding water table level and native fluid displacement. Van der Meer (1992a, 1992b) warned that limitations of injecting is controlled by induced over pressure itself depending on storage formation properties with a high concern on low permeable or compartmentalized reservoirs. As recalled by Nicot (2008), Bergman and Winter (1995) have also mentioned concerns about the impacts on native fluid velocity, discharge changes and the risks of mixing brines with drinking water aquifers. They suggested that ‘‘acceptance of large-scale disposal of by underground injection will require much more intensive research to minimize the technical uncertainties and risks’’. More recently, Nicot (2008) noted that “over the last decade little if any ‘‘intensive research’’ has been done to address Bergman and Winter’s concerns”. Birkholzer and Zhou (2009) assessed more intensively the issue of pore pressure increase and impacted area during injection of carbon dioxide to discuss the implications at a regulatory level. They mentioned that “estimates of storage capacity, if solely based on the effective pore volume available for safe trapping of , may have to be revised based on assessments of pressure perturbations and their potential impacts on cap rock integrity and groundwater resources”.

4.2.2. Modelling approach for pressurization estimates

Only recently researchers have paid more attention to evaluating the large-scale pressure responses expected for future industrial-scale carbon sequestration. These predictive simulations have been conducted for idealized geological systems as well as for “more realistic” systems representing large sedimentary basins.

Analytical approaches

Analytical solutions for pressure build-up inside the storage formation during injection exist (Burton *et al.*, 2008; Mathias *et al.*, 2009a) considering an idealized radially symmetric geometry of a mono-layer homogeneous aquifer formation. In particular, Mathias *et al.*, 2009a have developed approximate solutions for pressure build-up during injection in laterally “open” (infinite) brine aquifers accounting for two-phase Forchheimer flow (of supercritical and brine) and compressibility of the rock formation and both fluid phases. Such solutions are useful for understanding pressure changes and fluid migration within the reservoir formation in a screening and selection phase of the storage project, hence providing an order of magnitude of the area affected by pressurization (Mathias *et al.*, 2009b; Oruganti *et al.*, 2011). Nevertheless, such models cannot account on the fraction of displacement fluid that migrates into and through sealing units because the overlying and underlying seals are assumed perfectly impervious so that native brine can be only laterally displaced by injected . The importance of the sealing properties (permeability and pore compressibility) of the over- and underlying formations have been analytically calculated by Zhou *et al.* (2008) providing the brine displacement contributions in response to the estimated average pressure build-up in the “closed”, “semi-closed” (i.e. with low permeable sealing units) and open system. More recently a review on the role of shale unit on the pressure increase using analytical (and numerical) calculation has been published revealing the importance of the boundary conditions to control pressure pulse in the storage formation (IEAGHG, report 2010/15).

These models relying on idealized geometry can be used as broad approximations because they do not account for the variation in porosity, permeability within the aquifer formation (spatially distributed porosity), asymmetry of the reservoir, and dip of the beds etc. In addition, these simple models are not capable of predicting the interference between different injection sites within the same reservoir as outlined, for instance, by (Leetaru *et al.*, 2009).

Numerical approaches

More complex situations have been numerically modelled either based on an idealized, laterally open groundwater system, comprising a sequence of laterally extensive aquifers and aquitards (Birkholzer *et al.*, 2009) or based on real groundwater systems representative of extensive “open” sedimentary basins (Nicot, 2008; Birkholzer and Zhou, 2009; Yamamoto *et al.*, 2009; Person *et al.*, 2010; Zhou *et al.*, 2010; Smith *et al.*, 2011) or of partially compartmentalized basin with numerous fault zones (Birkholzer *et al.*, 2010). Three main numerical approaches can be identified in the literature.

Nicot (2008) employed a “traditional” 3D single-phase flow model using MODFLOW96 simulator (Harbaugh et McDonald, 1996) to investigate the regional-scale brine flow processes in the Carrizo-Wilcox system within the upper Gulf plains of Central Texas in response to a hypothetical storage injected over 50 years through 50 wells at an annual rate of 1 Mt (case 1) or 5 Mt (case 2). The injected volume of water is equivalent to the cumulative volume of injected (assuming a density of 700 kg/). The model was built on the basis of calibrated regional-scale groundwater flow and the original properties were modified locally to take into account the presence of so that the original porosity was modified to integrate the impact of residual water saturation and the permeability was modified to account for the density and viscosity of . Though the single phase approach do not capture the two-phase - brine regime, neither the variable density effects nor the compressibility effects within the near zone of the injection wells, it yields satisfactory results compared to “sophisticated” multi-phase flow transport simulator (as compared to the commercially released reservoir simulator CMG-GEM, Nicot *et al.*, 2009b). One additional attractive feature is the ability to account for complex hydrological processes such as stream-baseflow and groundwater evapotranspiration.

In a similar manner, investigations have been conducted in the UK on the Sherwood Sandstone Group (SSG) which is classified as a principle aquifer unit of strategic importance for water supply and significant contributor to river baseflow. The potential conflict between offshore storage in DSFs and onshore groundwater use was investigated as part of the CASSEM[4] project using a hypothetical storage site in the SSG just off the Lincolnshire coastline (Smith *et al*., 2011). The Sherwood Sandstone Group is overlain and confined by the Mercia Mudstone Group (MMG) which acts as the cap rock. The dynamic effects caused by injection into the SSG were approximated using the ZOOMQ3D numerical groundwater model developed by the BGS.

The capability of single-phase flow transport model to address far field flow processes has also been recently demonstrated by Pearson *et al.* (2010) considering a homogenous, isotropic aquifer overlain by a leaky confining unit following the approach of Hantush and Jacob (1955) and considering a total injection of 80 million metric tons of per year over a period of 100 years into the “Mt Simon” sandstone aquifer overlaid by the “Eau Claire” shale sealing unit (in the context of the Illinois basin (USA), see hereafter).

The second approach relies on multiphase-flow transport modelling both accounting for two-phase behaviour in the near field of the injection zones and single-flow processes in the far field.

The role of sealing units in the lateral and vertical volumes affected by pressure build-up was numerically investigated by Birkholzer *et al.* (2009) using the TOUGH2/ECO2n simulator (Pruess *et al.*, 1999; Pruess, 2005). The study was limited to industrial scale storage at a unique project site using an idealized two dimensional radially symmetric, laterally open groundwater system, comprising a sequence of laterally extensive aquifers and aquitards (sealing units) that extend from the deep saline storage formation to the uppermost freshwater aquifers. To account for “more realistic” basin-scale applications (hence requiring multi-million gridblock models), the massively parallel version of multiphase flow transport codes have recently been developed.

Yamamoto *et al.* (2009b) employed a model of more than 10 million gridblocks (requiring 1 to 2 days of computer time with 1024 processors) using the TOUGH2-MP/ECO2n simulator (Zhang *et al.*, 2008) to evaluate both local –brine flow processes and large-scale groundwater patterns in response to a storage scenario of 10 Mt CO2 per year at 10 injection sites (each of them spaced by 5 km) in the Tokyo bay, Japan.

Such a simulator has also been used to consider the storage scenario of 50 Mt per year at 20 injection sites (each of them spaced by 30 km) in the Illinois basin, USA (Birkholzer and Zhou, 2009; Zhou *et al.*, 2010) accounting for the spatially heterogeneous distribution of the “Mt Simon” sandstone reservoir properties. Another application has recently been carried out in the Southern San Joaquin Basin in California, USA for an injection scenario of 5 Mt per year at one injection site accounting for the compartmentalization induced by the presence of fault zones (Birkholzer *et al.*, 2010).

A third numerical approach for pressurization estimates at basin scale has been proposed relying on multi-phase sharp-interface finite-element models of injection, extending the

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[4] CASSEM is a project funded by the EPSRC which brings together industrial and academic partners from across the CCS development chain, to develop methodologies, workflows and insights, essential for the successful identification and evaluation of safe and effective CO2 storage in saline aquifers

approach of Nordbotten *et al.* (2004) and based on the methodology of Ledoux *et al.* (1990) with theoretical details described in Gasda (2008). The application is the Illinois basin, USA and the results of this approach were compared to the results of Birkholzer and Zhou, 2009 (who used a multiphase flow transport simulator). It appears that the calculated maximum pressure anomaly was 6 times higher (18 MPa) than the one calculated using the two-phase simulation results, which may mostly due to the differences in selection of petrophysical parameters according to Pearson and co-authors (Pearson *et al.*, 2010), hence outlining the importance of the characterization of the hydraulic properties at basin scale.

4.2.3. Impact on groundwater resources

In this section, we focus on the results provided by “real-case” applications (Nicot, 2008; Birkholzer *et al.*, 2009; Birkholzer and Zhou, 2009; Yamamoto *et al.*, 2009a, 2009b; Pearson *et al.*, 2010; Zhou *et al.*, 2010; Birkholzer *et al.*, 2010; Smith *et al.* 2011) in terms of potential impact of deep injection on shallow groundwater resources. The main characteristics and findings of each these studies is summarized in Table 4.2.

Far reaching pressure perturbation induced by the injection

In the case of the Illinois basin over pressure extends up to 150 – 200km reaching the limit of the basin-scale model. Defining the “area of review” for a pressure threshold between 0.05 to 0.5 MPa provides an area encompassing the entire region of the centre basin (Birkholzer and Zhou, 2009). Figure 4.2 depicts the evolution of the pressure field (in MPa) at the top of the reservoir aquifer of Mount Simon Sandstone (i) at 10 and 50 years (after start of injection) (ii) during the 50-year injection period, and (iii) 100 and 200 years during the post-injection period.

Such a conclusion appears in agreement with the value calculated by Pearson *et al.* (2010) for pressure envelop on the order of 250km using the single-phase analytical model.

In the case of Texas Gulf Coast basin, an average water-table rise of ≈1 m (0.01 MPa) was estimated at the outcrop by Nicot (2008), with minor increase in stream baseflow and larger increase in groundwater evapotranspiration (≈50 % for the 1 Mt/y injection scenario).

Birkholzer *et al.* (2009) found relatively small water table rise (about 0.5 mm) for overlying aquifers separated by shale caprock (with relatively high permeability of 10^{-16} m²) from the storage formation.

In the case of Tokyo Bay, Yamamoto *et al.* (2009a, 2009b) concluded that the build-up of groundwater pressure in shallow confined aquifers on the order of few bars (0.1 MPa) could occur over extensive regions, including urban inlands.

In the Sherwood Sandstone Formation case study, for an injection rate of 15 Mt/yr, spread over eight injection wells, groundwater heads within the injection zone were increased by as much as 200 m (Figure 4.3). After 20 years, groundwater head increase of 10 m may be expected at distances of 50 km up-dip, while groundwater levels increases at outcrop, some 80 km from the injection zone, were found to be in the region of 0.1 m. An increase in river baseflow of approximately 1.7% was also predicted.

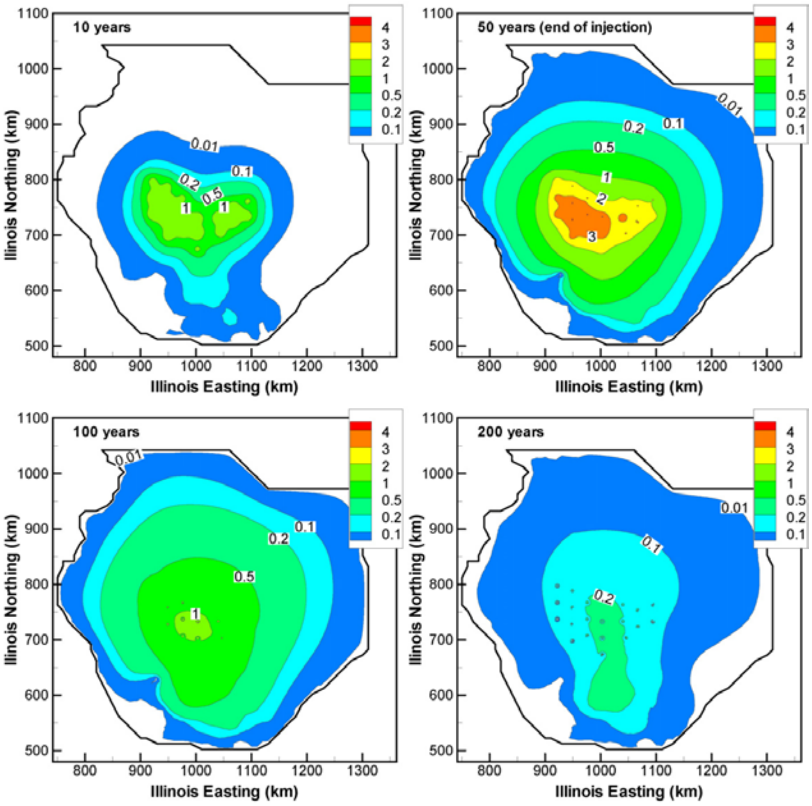


Figure 4.2: Pressure build-up (in MPa) at the top of the Mount Simon Sandstone at 10 and 50 years (after start of injection) during the 50-year injection period, and 100 and 200 years during the post-injection period (adapted from Birkholzer and Zhou, 2009).

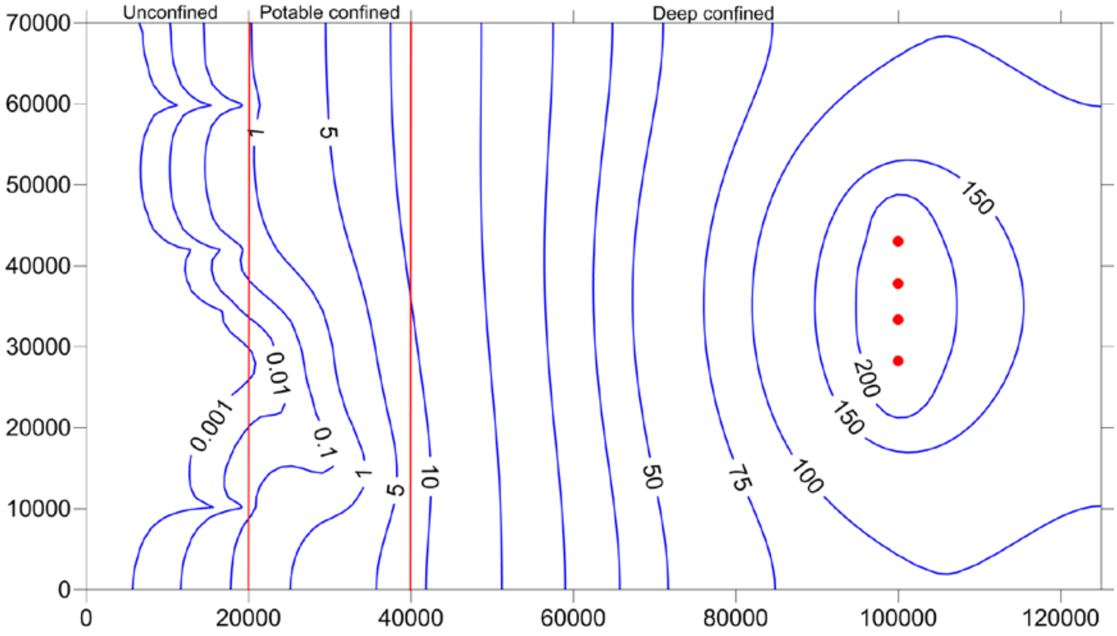


Figure 4.3: Difference in groundwater head (m) between the baseline and injection model runs. The injection wells are indicated by red dots. Divisions of the unconfined, shallow confined and deep saline aquifer are indicated by red lines (Smith et al.*, 2011).*

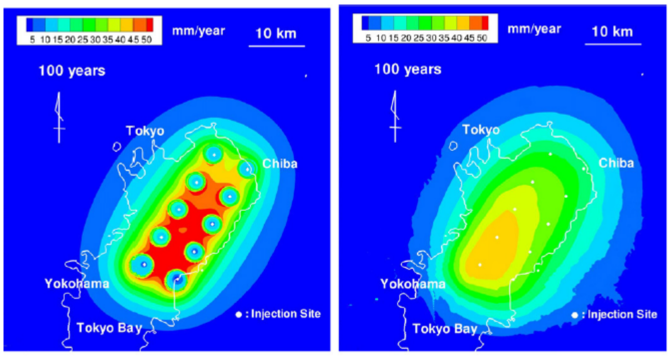
Low injection-induced flow velocities

In the Illinois basin case, Birkholzer and Zhou (2009) and Zhou *et al.* (2010) showed that after 50 years of 5 Mt/year injection period (through 20 wells), the Darcy velocity (averaged over the model domain), does not exceed 1 mm/y at the top domain (above the Eau Claire sealing unit) and that the average Darcy velocity reaches 200 mm/year (maximum velocity of 1.2 m/year) across the lateral boundaries. Considering the volume of displaced fluid, the volumetric balance showed that the majority of the displaced brine (nearly 90 %) was stored in the system through the additional pore space made available by brine and pore compressibility induced by pressure build-up during the injection period (Zhou *et al.*, 2010). At 200 years (150 years after the injection ceased), the volume of out-flowing brine (through the lateral boundaries) and of leaked brine (through the sealing units) respectively accounted for 18% and 62% of the total volume of displaced brine. Though the volumes involved were very large, the velocities were small (hence the travel distance of fluid particles was small for the time scale of interest of the order of hundreds of years) so that salinity changes were negligible (of the order of 0.2 % relative to the initial conditions) in the single-phase zone just outside the CO2 plumes (Zhou *et al.*, 2010). It was concluded that the migration distances of saline water associated with these boundary flows were small and did not constitute a concern for the groundwater resources in overlying aquifers or neighbouring basins.

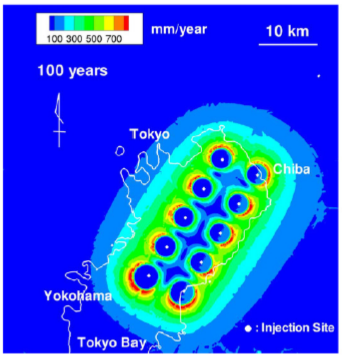
Such findings are consistent with the conclusion of Pearson *et al.* (2010) indicating in the same context that the “long-range (>5 km) lateral movement of brines was insignificant due to increasing radial distance from injection well and leakage across the Eau Claire confining unit”.

In the case of Texas Gulf Coast basin, the injected at a rate of 1 Mt/y during 50 years through 50 wells displaced fluid particles set on the current ≈3000 ppm TDS boundary by about 3–5 km up-dip, as opposed to a fraction of one kilometre in the reverse direction (down-dip) in natural conditions (Nicot, 2008).

In the case of Tokyo Bay (Yamamoto *et al.*, 2009a, 2009b), the maximum vertical pore velocities of about 50 mm/year were found along the bottom of the primary seal (Figure 4.4a, left), hence suggesting that it would take more than 1000 years to penetrate the 75 m thick secondary seal. In addition, the discharge mainly occurred under the seabed so that Yamamoto *et al.* (2009b) concluded that “the impact on shallow groundwater quality from saline water migration into shallow aquifers should be very small, and even negligible” (provided that no fast flow conduits such as conductive faults present). The horizontal pore velocity was found to reach a maximum value of 700 mm/y near the gas/ water front (Figure 4.4b), but rapidly decreasing with the lateral distance from the injection zone (≤100 mm/year at a lateral distance ranging from 10 – 15 km).



(a) Increase of vertical groundwater velocity at bottom of primary (left) and secondary (right) seal.



(b) Increase of horizontal groundwater velocity in the storage aquifer

Figure 4.4: Change in pore velocity of groundwater after 100 years of injection. Injection at a rate of 10 Mt/year through 10 wells: (a) increase of vertical groundwater velocity at bottom of primary (left) and secondary (right) seal; (b) increase of horizontal groundwater velocity in the storage aquifer (Yamamoto et al., 2009b).

The common finding of such “real-case” modelling studies is that the pressure build-up in the storage formation may be considerable with an “area of review” (pressure threshold of 0.01 MPa) more than 100 km away from the injection zone, depending on the aquitard (i.e. sealing unit) conductivity, whereas the lateral and vertical distance migration distances of saline water should rather be small, hence not constituting a concern for the groundwater resources in overlying aquifers or neighbouring basins.

Nevertheless, these “real-world” applications put into perspective these findings regarding two main key-aspects that are forth being further explored.

Role of the sealing unit

As outlined by Yamamoto *et al.* (2009b), the latter findings are strongly linked to the proper characterization of the whole column of lithofacies up to the surface. Nicot (2008) and Nicot *et al.* (2009a) also underlined the importance of mudstones in attenuating the impact of the pressure pulse, especially regarding their compressibility values.

The importance of sealing units in the lateral and vertical volumes affected by pressure build-up was analytically investigated by Zhou *et al.* (2008) and further studied by Birkholzer *et al.* (2009) through intensive sensitivity analysis of numerical simulations. The latter study showed that in the vertical direction, the pressure perturbation from storage could reach shallow groundwater resources only if the deep storage formation communicates with these aquifers through sealing units of relatively high permeability (higher than 10^{-2}) as shown in Figure 4.5. The vertical brine migration through a sequence of layers into shallow groundwater bodies was extremely unlikely, as the vertical pore velocity reached 0.006 m/year within the first aquitard above the storage formation considering the 10^{-16} m^2 seal permeability case.

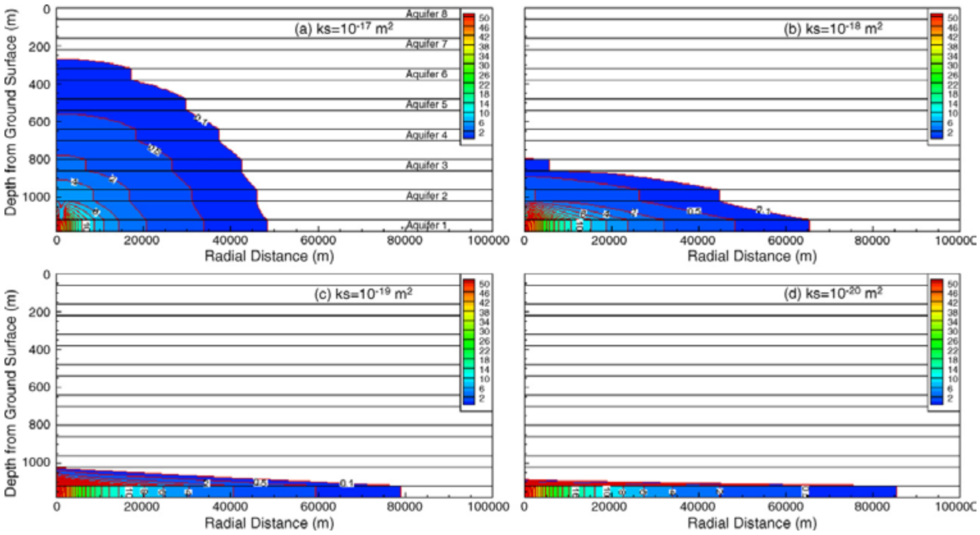


Figure 4.5: Pressure build-up (in bars) at 30 years of injection, for different values of seal permeability (adapted from Birkholzer et al., 2009).

More recently, a complete review of the impact of geological storage in DSF on pressurisation and brine displacement has been published in IEAGHG report 2010/15, discussing the role of sealing unit and the size of the storage compartment. It highlights that threshold pressures are insensitive to caprock thickness and that an ideal case would be a relatively thin shale caprock with microdarcy permeability allowing brine dissipation to maintain injectivity while maintaining in the storage formation.

Existence of fast flow conduits or flow barriers

Yamamoto *et al.* (2009b) concluded that “the impact on shallow groundwater quality from saline water migration into shallow aquifers should be very small, and even negligible”, but indicating that their conclusion was valid provided that “no fast flow conduits such as conductive faults are present”. Similarly, Nicot *et al.* (2009) concluded that “the freshwater zone was not significantly impacted on average but the effect could be locally focused, in particular by the presence of flow barriers (such as the Mexia-Talco Fault zone just down-dip of the outcrop)”.

Recently, Birkholzer *et al.* (2010) presented a local sensitivity procedure based on iTOUGH2 software (Finsterle, 2010) to assess the importance of 27 input parameters and the role of assumed sealing or conductive faults within the complex compartmentalized system Southern San Joaquin Valley in California. The results showed that the partial compartmentalization could cause additional pressure build-up not only near the injection location compared to the case with no fault as depicted in Figure 4.6 (top: no fault scenario; bottom: partial compartmentalization), but also beyond the bounding fault, which in turn can increase sensitivity to the flow parameters in this region. Birkholzer and co-authors (Birkholzer *et al.*, 2010) pointed out that further studies were required to explore the compartmentalized effect of fault zones.

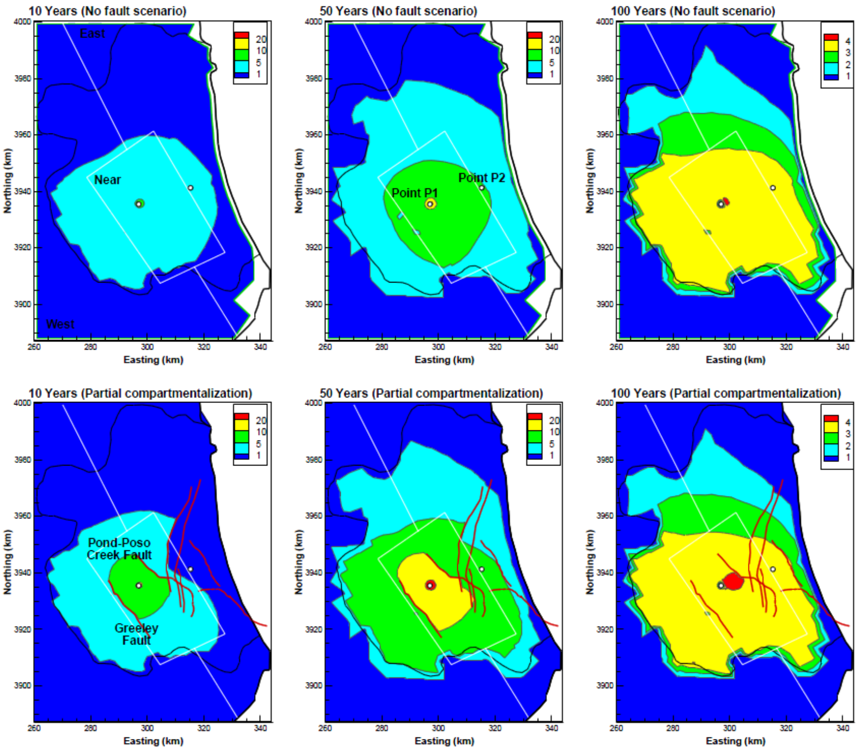


Figure 4.6: Pressure build-up (in bars) in the Vedder Sand (sandstone basin in the Southern San Joaquin Valley, California) for both fault scenarios, at 10, 50, and 100 years of 5 Mt/year injection (Birkholzer et al., 2010).

Considering the presence of man-made pathways such as unplugged wells, Nicot *et al.* (2009b) investigated the possibility that brine could be displaced upward into potable water through wellbores with a “continuous” open pathway between the injection formation and the potable groundwater formation based on approach considering the density differences due to temperature and salinity subsurface variations. Nicot *et al.* (2009b) showed that a pressure increase of a fraction of a bar up to several bars (0.1 MPa) could be sustained without flow, but such conclusions highly depend on the modelling of the initial pressure profile, which was assumed to be hydrostatic and on the design of the borehole, which may present cement plugs and mud-filled sections.

A sensitivity analysis of leakage coefficient used to represent potential movement of groundwater out of the Sherwood Sandstone Group into the Mercia Mudstone Group was undertaken (Smith *et al*., 2011). This exercise was especially important since there are two other principle aquifer units (Lincolnshire Limestone Formation and the Chalk Group) which occur at shallower depths above the SSG storage formation. Varying the leakage coefficient had the effect of reducing groundwater heads in the injection zone from 300m (no leakage) to 55m (maximum leakage 0.1). Groundwater levels at outcrop were largely unaffected by the variation in leakage coefficient. Particle tracking was used establish the extent to which saline water might be displaced up-dip as a result of the injection. At the interface between the deep saline aquifer and shallow confined potable aquifer, the particle tracking showed a small movement up-dip (up to 6.6 m) of water over the 20 years of analysis. This was more influenced by ongoing abstraction from the aquifer than by injection however. Large movements of the saline interface laterally are unlikely to be a major problem within the SSG, assuming groundwater flow is inter-granular.

Table 4.2: Overview of published models that refer to basin-scale hydrogeological impacts of storage: main characteristics and findings

Reference	Basin setting	Domain size	Injection Scenario	Modelling approach	Pressurization disturbance	Fluid displacement
Nicot, 2008 and Nicot *et al.*, 2009a	Carrizo-Wilcox system within the upper Gulf Coast plains of Central Texas	100×800= 80 000 km²	Through 50 wells injecting at a yearly rate of 1 Mt (case 1) or 5 Mt of (case 2) over 50 years followed by a 500 years post-injection period.	3D single-phase flow code with equivalent injected volume of water and modified properties.	Pressure build-up at the outcrop of ≈1m (0.01 MPa).	Fluid particles set on the current 3000ppm TDS boundary displaced by about 3-5 km updip.
Birkholzer *et al.*, 2009	Generic multi-layered laterally open system composed of 8 aquifer and aquitard formations.	π×200×200 ≈ 125 000 km²	Through one single injection zone at a yearly rate of 1.52 Mt over 30 years followed by a 70 years post-injection period.	2D Radially symmetric multiphase flow transport model	Pressures extend more than 100 km away from the injection zone and possible pressure perturbation in shallow aquifers for high seal permeability (higher than $1.e^{-}$).	The vertical pore velocity reaches 0.006 m/year within the first aquitard above the storage formation considering the $1.e^{-16}$ m² seal permeability case.
Leetaru *et al.*, 2009; Birkholzer and Zhou, 2009; Zhou *et al.*, 2010	"Mt Simon" sandstone aquifer in the Illinois basin overlaid by the Eau Claire shale	570×550 = 241 000 km²	Through 20 wells (each of them spaced by 30 km) at a yearly rate of 5 Mt over 50 years followed by a 150 years post-injection period.	3D one-million gridblock model using massively parallel version of multiphase flow transport simulator	Pressures extend very far to 150 – 200km reaching the limit of the model to 1-2 MPa.	Darcy velocity (averaged over the model domain) < 1 mm/y at the top domain (above the Eau Claire sealing unit) and the average Darcy velocity ≈200 mm/year across the lateral boundaries.

Reference	Basin setting	Domain size	Injection Scenario	Modelling approach	Pressurization disturbance	Fluid displacement
Yamamoto *et al.*, 2009b	Tokyo bay composed of the selected storage formation, the Umegase (sandy) and Higashi-Higasa Formation (gravely)	60×70 =4200 km²	Through 10 wells (each of them spaced by 5 km) at a yearly rate of 10 Mt over 10years followed by a 900 years post-injection period.	3D multi-million gridblock model using massively parallel version of multiphase flow transport simulator.	The build-up of groundwater pressure in shallow confined aquifers on the order of few bars can occur over extensive regions, including urban inlands.	Maximum vertical pore velocities of about 50 mm/year along the bottom of the primary seal. The horizontal pore velocity ≤100 mm/year at a lateral distance ranging from 10 – 15 km
Person *et al.*, 2010	Illinois basin composed of the “Mt Simon” sandstone aquifer overlaid by the Eau Claire shale cap rock layer.	620×375 = 232 500 km²	Through 726 injection wells (located near 42 power plants) Total yearly rate of 80 Mt; Over 100years followed by a 100 years post-injection period.	Single-phase model considering a homogenous, isotropic aquifer overlain by a leaky confining unit. Multi-phase (sharp-interface) models of CO2 injection	The pressure disturbance (>0.03 MPa) propagated 10–25km away from the injection wells resulting in significant well–well pressure interference.	Long-range (>5 km) lateral movement of brines was insignificant due to increasing radial distance from injection well and leakage across the Eau Claire confining unit.
Birkholzer *et al.*, 2010	Complex compartmentalized system of sandstone basin in the Southern San Joaquin Valley in California.	84×112 = 9 408 km²	Through one injection well Total yearly rate of 5 Mt; Over 100years followed by a 900 years post-injection period.	3D model using massively parallel version of multiphase flow transport simulator combined with local sensitivity procedure	Partial compartmentalization may cause additional pressure build-up near the injection location, and beyond the bounding fault	

Reference	Basin setting	Domain size	Injection Scenario	Modelling approach	Pressurization disturbance	Fluid displacement
Smith *et al.*, 2011	The Sherwood Sandstone Group in the UK (CASSEM project)	100 x 100 = 10 000 km²	15 Mt/yr, spread over 8 injection wells	Single phase approach Model built up from a simplified single layer model, to a three layer	Groundwater heads increase within the injection zone by as much as 200 m, and 10 m at distances of 20 km up-dip, while negligible increases at outcrop, some 80 km from the injection zone, River baseflow increased by about 0.5%.	Groundwater levels at outcrop were largely unaffected by the variation in leakage coefficient
IEAGHG,2010 Report 2010/15	Generic sandstone formation model based on the SPE comparative solution data set n°2 (Christie and Blunt, 2001) with open edges boundaries	17 x 27 km², 20 m thick	Base scenario: 2 injection wells, with a 10 m injection interval with a bottom hole pressure of 10 MPa	Single phase approach	Average reservoir pressure increase of 5MPa, insensitive to heterogeneity, the pressure increase impact the whole reservoir domain	Brine flux directions controlled by heterogeneity. The average brine flux rate within the boundary shales is low at around 1 mm/year with a higher value at about 2 mm/year just above the injection well. Brine flux rate inside the storage formation reaches up to 10 m/year near the injection well and decrease down to 1 m/year within a few kilometres and are as low as 0.01 to 0.001 m/year in poor permeable zone

4.3. CONCLUSIONS

Assessing the impact of injection on the storage formation and potentially on the overlying aquifers requires the understanding of complex hydrogeological and hydrogeochemical systems. Basin scale modelling requires the gathering of a large amount of data, often limited for a precise characterization and therefore involving modelling assessment through sensitivity analysis and multiple-run scenarios. One of the main difficulties for modelling impacts of storage on shallow groundwater is to handle both the changes of the hydrodynamics of the geological formations and the associated fluid-rock interactions. And one can notice in the literature that often the two disciplines (hydrodynamics and geochemistry) are assessed separately for providing modelling estimates. Thus, the modelling of reactive transport for multiphase flow systems is still under active research and development.

The limited number of geochemical simulations assessing water quality alteration due to leakage, confirm that acidification will lead to trace element release (metals and As) from dissolution of metal-bearing sulfides. This release may potentially breach water quality standards according to the leakage assumptions (rate, pressure) and the geochemical parameters (mineralogy, water composition).

To simulate chemical fluid-rock interactions, batch (no flow) models allow for a characterization of the potential magnitude of minerals dissolution and precipitation along with the modification of elemental concentrations present in the aqueous phase (water or brine). Incorporation of kinetic rates helps to describe long-term evolution of the system. Complex mineralogy characterization of different geological formations can be calibrated from core analyses, and fluid sampling allows the description of the elements concentration in the aqueous phase. Acidification induced by dissolution will trigger mineral dissolution and associated elements release. The magnitude of trace element mobilization can be assessed to evaluate the impact on water quality. Lead and arsenic are the key elements for which specific attention has been paid to evaluate the potential of mobilization due to desorption processes and comparison with the maximum contaminant levels (MCLs) according to state legislations. Identified mineral hosts are sulfides and carbonates but sorption on clays and oxides may also affect trace element mobility. Processes of sorption are not systematically implemented in all codes. Still, when taking into account these sorption processes it can significantly reduce metal mobility. Given the complexity of these processes, the availability of data from field observations and experiments are crucial for model calibration.

The potential hydrodynamic impacts of storage may be assessed with different modelling approaches. In a single phase modelling approach, injected water will provide an approximation of injection for an analogue pressure pulse. This allows for the use of numerical codes originally dedicated to hydrogeological issues and able to properly incorporate corresponding data. Alternatively, a reservoir flow simulator may account for the gas phase in the over-pressured injection zone. Although a reservoir flow simulator is preferable for prediction of the gas propagation and mixing, such codes are often not suited for complete incorporation of hydrogeological features mentioned above. Alternatively, analytical modelling using a simplified geometry of the hydrogeological system may allow a quick estimate of overpressure and the associated fluid movement.

Predictions of pressure increases and associated fluid displacements related to injection of demonstrate that the pressure footprint will rapidly attain a large areal extent (up to 100 or 200 km) within the storage formation, but with a sharp decline in pressure away from the injection point. This pressure footprint is largely controlled by the total amount of injected and the permeability of the sealing rock. The pressure in the vicinity of the injection well can reach values of several tens of bars, while the impact on the head pressure in surface outcrops is in general predicted to not be of a particular concern. It differs according to the size and the boundary limits of the storage formation. Water table changes do not exceed few millimeters for fresh aquifers overlying DSF and are of the same order of magnitude as seasonal and inter-annual variations for lateral fresh groundwater in open system DSF. In some specific conditions to be more fully explored numerical estimates can reach up to few meters. Strongly controlled by the cap rock permeability, predictions of brine fluxes through shale are of the order of millimeters per year while the reservoir fluxes are meters per year.

5. Regulatory constraints

This chapter first reviews current CCS regulations in order to consider the existing constraints on injection and storage activities that are directly related to the protection of groundwater. Three regulations are reviewed: i) the European Union Directive on the geological storage of (CCSD), ii) the Underground Injection Control (UIC) program for geological sequestration wells of the United States of America - Environmental Protection Agency (US EPA), and iii) the Greenhouse Gas Geological Sequestration Act 2008 of the State of Victoria in Australia. The relevant articles from these regulations are reported in a table (see Appendix 1) according to various types of constraint:

- Storage target
- Risk assessment
- Monitoring
- Remediation
- Geographical
- Construction requirements
- Other

The second part of this chapter reviews existing water and environmental laws. The goal is to assess potential constraints on CCS activities arising from these regulations.

The third part of this chapter is the conclusion of both reviews with some recommendations.

5.1. –STORAGE-SPECIFIC REGULATIONS IN THE MAIN CCS COUNTRIES

The relevant articles from the regulations reviewed are compiled in a table in Appendix 1.

Groundwater protection is not explicitly taken into account in the European Union (EU) Directive on storage (CCSD), but it is indirectly covered by the global philosophy of the text summarized in Article 1.2: “prevent and, where this is not possible, eliminate as far as possible negative effects and any risks to the environment and human health”. The main actions that appear in the text relative to groundwater protection are data collection and monitoring. The EU CCSD will be translated into national law by each Member State. This means that the final regulation in Europe will differ from the content of this CCSD, which only indicates the minimum of what each regulation should do. Some Member States will hence have more prescriptive rules than those laid out in this Directive.

The US Environmental Protection Agency (US EPA) rule is issued under the Safe Drinking Water Act that aims to protect water in the US. In this regard, every aspect of the rule can be considered as a constraint for the protection of groundwater. The main security requirements are summarized in the table in Appendix 1, but they are not necessarily specific to the protection of groundwater. As for the other legislations studied in this chapter, the global constraint is to avoid any leakage of and to maintain containment. Only data collection and monitoring are specific means of protection for underground sources of drinking water (USDW). The proposition for siting a storage site only below the lowermost USDW is also very specific. However, the operator can be granted a waiver in order to inject above the lowermost USDW. But the operator seeking a waiver must submit specific information, meaning that specific studies must be carried out in relation to the protection of groundwater.

In addition to their rule, US EPA (EPA, 2008) has issued a Vulnerability Evaluation Framework (VEF), that suggests the following approach for groundwater protection (Figure 5.1):

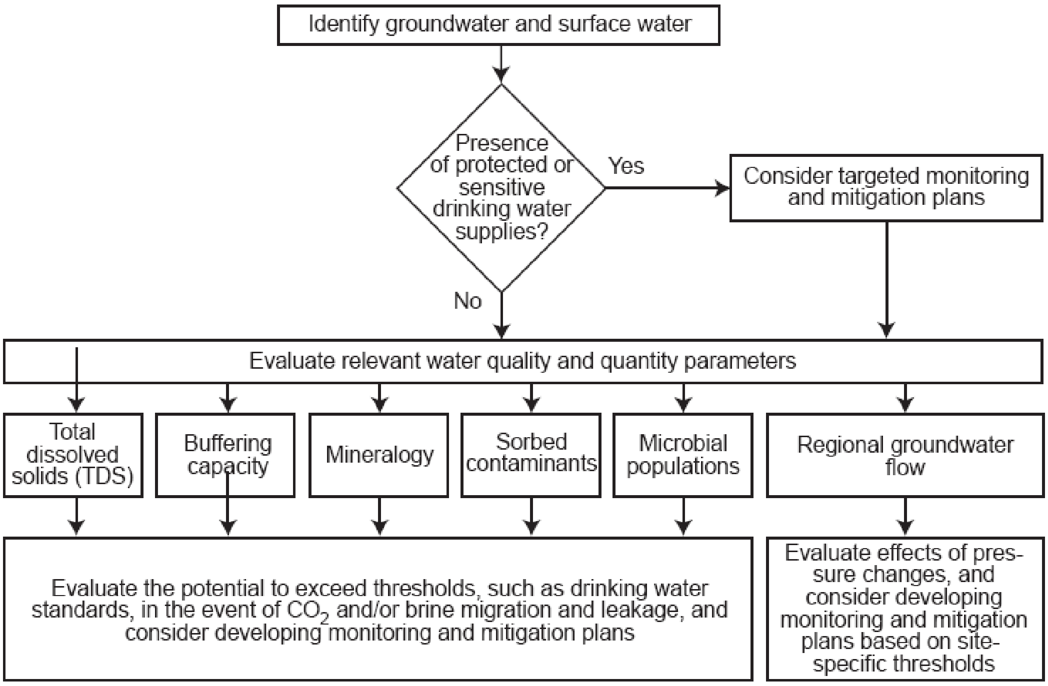


Figure 5.1: Groundwater and surface water evaluation in the Vulnerability Evaluation Framework (VEF) (EPA, 2008).

The method identifies key parameters for water evaluation, and then the concept is to build monitoring and mitigation plans based on these parameters. Note that the VEF is an accompanying document and will not be binding for the operators.

The Australian Victorian regulation is even less prescriptive than the former two regulations. The main constraint concerning the protection of groundwater is that the regulatory authority for the use of water will review the plans submitted by the storage operator and can make binding comments. The Environment Protection Authority may require the holder of an injection and monitoring licence to vary the monitoring and verification plan prepared as part of the injection and monitoring plan. All plans (injection testing, special access well, etc.) submitted are accepted if, and only if, the plan does not present a risk to public health or the environment.

Lastly, the table in Appendix 1 shows that construction requirements only exist for US regulations. This is an important aspect of groundwater protection, which does not seem to be taken into account in either the EU or in Victoria, Australia. It should not be a gap as other activities, such as geothermal activities, are facing similar issues. It will nonetheless be an important factor to consider when implementing injection operations and hence should be explicitly taken into account in the regulatory regime.

5.2. WATER PROTECTION AND ENVIRONMENTAL IMPACT ASSESSMENT REGULATIONS

5.2.1. United States of America: Safe Drinking Water Act

As mentioned above, the US EPA proposes regulation of injection according to the Underground Injection Control (UIC) Program. This program is placed under the authority of the Safe Drinking Water Act (SDWA) that is designed to protect the quality of drinking water sources in the US. Therefore, the core principle of the regulation for injection and storage is the protection of water and, by extension, groundwater resources. Consequently, all possible constraints stemming from the protection of groundwater is included in the CCS regulation.

The general principle is to avoid any movement of fluids (, brine) into the so-called Underground Source of Drinking Water (USDW). The definition of USDW is:

> *"An aquifer or portion of an aquifer that supplies any public water system or that contains a sufficient quantity of groundwater to supply a public water system, and currently supplies drinking water for human consumption, or that contains fewer than 10,000 mg/l total dissolved solids and is not an exempted aquifer."*

The threshold of 10,000 mg/l of total dissolved solids is hence a regulatory constraint for potential storage aquifers. This also raises the issue of potential brine migration due to injection into zones of the same aquifer with lower salinity or into adjacent, hydraulically connected, fresh aquifers. In certain cases, waters that were considered "drinking water" could be contaminated by brine and have total dissolved solids over 10,000 mg/l.

5.2.2. European Union: Directives

Water Framework Directive (WFD)

The purpose of the WFD is to establish a framework for bodies of water, including groundwater, in Europe.

This Directive, through Article 4 in particular, defines the general objectives of achieving good ecological status for groundwater, which is obtained by attaining both good chemical status and good quantitative status. Injection and storage of could have a potential impact on both. For instance:

- Unwanted leakage of or induced movement of brines could impact the chemical status of fresh groundwater:
- Pressure build-up in aquifers, e.g. those situated above the pressurized reservoir could impact the good quantitative status.

In this Directive, the most obvious constraint on injection in deep saline aquifer is Article 11(7)(j) that prohibits the "*direct discharges of pollutants into groundwater*".

However, Article 32 of the Directive on the geological storage of (CCSD) is an amendment to this article; it authorizes injection of in aquifers "*permanently unsuitable for other purposes*", "*provided such discharges do not compromise the achievement of the environmental objectives established for that body of groundwater*".

There are several points worth mentioning regarding this article. Firstly, the authorization for injection is always bound to the Member States. This is in line with Article 4(1) of the CCSD:

> *[…] This includes the right of Member States not to allow for any storage in parts or in the whole of their territory.*

This means that if a Member State puts priority on achieving the environmental objectives for groundwater quality, one possible decision could be to prohibit injection and storage in its territory.

Secondly, the possible formations for injection and storage are 'geological formations which for natural reasons are permanently unsuitable for other purposes'. This definition is vague and could cause debate about whether a formation is permanently unsuitable or not, i.e. technological advances will be able to render non-potable waters drinkable. It will be interesting to see how each Member State will transpose this disposition into national law. Moreover, the geological formation is defined as "a lithostratigraphical subdivision within which distinct rock layers can be found and mapped". This raises the issue, for example, of a geological formation that is dipping from the surface to depths suitable for storage (see Figure 4.1, page 108). On one side, the formation contains fresh and drinkable groundwater; on the other side, the formation contains only highly saline waters creating favourable conditions for storage. If the Directives are strictly followed, then this formation should not be selected for injection and storage.

Thirdly, Article 4(1) stipulates that the storage of carbon dioxide should not compromise the environmental objectives established for *that* body of water. According to this sentence, only the targeted aquifer is concerned by the definition of 'body of groundwater': "a distinct volume of groundwater within an aquifer or aquifers". The groundwater bodies are not strictly speaking identical to physical aquifers because their delimitation is influenced by the location of boundaries, pollution and human pressure on the contained water resources, as well as the nature of the superficial cover, if any. Again, the issue here is more concerned with aquifers where part could serve as a potential reservoir and other parts could serve for other uses. The Directive does not seem to take into consideration the case where the injection of could compromise the environmental objective of a groundwater body situated in another overlying aquifer. All these considerations are strongly dependant on the way each Member State defines its own groundwater bodies, which is the management unit in the WFD. It will be interesting to see if and how storage site complexes will be defined in relation to groundwater bodies. This task will be up to each Member State and, as with the definition of groundwater bodies, some discrepancies are expected.

Another important article of the WFD is Article 7 that provides the broad objective of reducing the level of treatment required for drinking water, and asks Member States to "*establish safeguard zones*".

Two important constraints can arise from this article:

1. Even if injection and storage of is tolerated, the operation should not induce more treatment for drinking water.
2. The way each Member State defines the "safeguard zones" could be crucial for siting of injection operations. These definitions could be revised in order to allow an optimal cohabitation of storage activities and abstraction of drinking water.

On the other hand, Article 4(7) of the Directive stipulates that "*Member States will not be in breach of this Directive if failure to achieve good groundwater status*" is the result of a new modifications that is due to activities of "*overriding interests*".

In the case of storage, this can be in contradiction with Article 11(7)(j): CCS, as a climate change mitigation option, could be tolerated, even with impacts on the status nearby groundwater aquifers because the fight against climate change can be interpreted as 'overriding interest'.

Both the CCSD and the WFD require that Member States identify a Competent Authority for the application of the rules of the Directives (for the WFD, the River basin districts are the Competent Authority). The way that these authorities interact and communicate with each other will be very important. In particular, the WFD explicitly mentions the good groundwater quantitative status as an objective (in addition to the good chemical status). As defined in Annex V of the Directive, the parameter for the classification of quantitative status is the groundwater level regime. As described in Chapter 4, certain research results (e.g. Birkholzer *et al.,* 2009 and therein) have demonstrated that the large pressure modification that will result from the injection of large quantities of could result in alteration of the groundwater level in aquifers situated above the storage reservoir, even those situated close to the surface. The study does not state that the impacts will necessarily be negative, but if the Member States follow strictly the WFD, this may prevent the development of storage as widely as intended. This is important because the impacts here are related to a normal behaviour of the storage complex and not an altered behaviour (such as leakage).

Groundwater Directive (GWD)

The Groundwater Directive (Directive 2006/118/EC) is a "daughter' directive of the WFD and builds on its earlier provisions in relation to groundwater assessment and protection measures.

The University College London Carbon Capture Legal Program (CCLP) did an analysis of the text on its website[5]:

- **Key legal issues concerning CCS**
    - While CCS activities would not seem to be primarily affected by provisions in the Groundwater Directive, which are more directly concerned with nitrates and pesticides, injection of streams could potentially be regulated under Article 6(1)(b), were Member States to decide that fell within the definition of 'hazardous substance'. However, Article 6(3)(a) of the Directive ensures that the exemptions given to particular activities in Article 11(3) (j) of the WFD also apply to the daughter provisions. This would include the amendment exempting CCS activities made to the WFD by the Directive on the geological storage of carbon dioxide (Directive 2009/31/EC) (CCS Directive)"

This exemption should not be in contradiction with the objective of "good groundwater status" laid down in the WFD.

Environmental Liability Directive

The purpose of the Environmental Liability Directive is to establish a framework of environmental liability based on the 'polluter-pays' principle, to prevent and remedy environmental damage.

CCS has been included in the list of activities concerned by this Directive. Moreover, in 'environmental damage', the term "*water damage"* is explicitly included.

With the definition of environmental damage, this Directive is fully coherent with the WFD and the quantitative status is explicitly mentioned. This means that not only the risk of leakage will have to be taken into consideration, but also the risk of pressure changes in other geological layers. As stated in the previous paragraph, these pressure changes could be related to the normal behaviour of the storage complex, meaning that under specific conditions, even normal behaviour could cause 'environmental damage' from this Directive's point of view.

The constraints arising from the inclusion of CCS in this Directive mainly consist of preventive (Article 5) and remedial (Article 6) actions against possible environmental damage. The operator must take preventive measures in case of an imminent threat of environmental damage, while he must take remedial measures if damage has occurred.

The "preventive measures" could be seen as overlapping with the "corrective measures" that the operator of the storage site must take in case of "significant irregularity". The CCSD mentions that corrective measures should "*prevent or stop the release of ".* This means that the notion of "preventing" the damage from occurring is indeed present in both definitions. The preventive actions hence only create a small constraint on the operator because the constraint is already created by the CCSD. However, a more stringent constraint could arise from the remedial actions that, as stated above, are the actions needed when the environmental damage has occurred.

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[5] http://www.ucl.ac.uk/cclp/index.php

Annex II of the same Directive gives guidance for the choice of remedial action. The objective of the actions is the restoration of the environment to its baseline condition. Annex II lists 3 types of remediation:

a) “*Primary*”

b) “*Complementary*”

c) “*Compensatory*” (compensation for the interim losses of the ecological functions of the damaged resources)

If primary remediation is not effective, then complementary and compensatory remediation must be undertaken.

The principle of this Directive is that the operator shall bear the costs for all actions taken. Details of potential remediation measures are given in Chapter 6 of this report, and it seems that there are no easy remediation measures for potential impacts of storage activities. Considering this, this constraint appears to be one of the most stringent for all operators, but again, it will depend on the actual transposition into the national laws by each Member State.

- **Potential transboundary issues**

Within Article 15 (Cooperation between Member States), the principle of the Directive is reinforced: the polluter pays. Therefore, when environmental damage affects several Member States, the costs of remediation should be covered by the “polluting” Member State. Consequently, the main difficulty will be to prove that a certain environmental damage suffered in a given Member State is created by a storage site implemented in another Member State. When the relationship between cause and effect is proved, then the Directive can be applied.

As for the other European Directives, the articles cited here should be interpreted more as a framework or a global concept that is implemented. The actual laws will be those transposed into each national regulation.

5.2.3. South Africa: National Water Act

As stated in Beck *et al.* (2010), CCS could be a crucial technology for a country like South Africa that relies heavily on coal for its electricity production. A presentation by Andrew Gilder during a meeting of the International Energy Agency CCS Regulators Network (Gilder, 2010) listed the existing relevant legislation that a potential regulatory development for a CCS framework will have to take into account:

- National Environmental Management Act
- National Water Act
- Mineral & Petroleum Resources Development Act
- National Environmental Management: Air Quality Act
- Gas Act
- National Environmental Management: Waste Act
- Road Transport Act

- Pipelines Act …

The present short review focuses on the National Water Act. Due to time constraints, it was not possible to review other potentially interesting texts, such as the environmental legislation. However, the presentation also gives some insight.

The environmental legal concept of South Africa relies on:

- National Environmental Management Principles
- Polluter pays, Precautionary, Sustainable Development (international)
- Public Trust, Cradle-to-Grave Responsibility.

This list tends to show that the general principles are more or less the same as in Europe, meaning that similar constraints should apply on CCS activities: the operator will be responsible for any environmental damage the injection or storage may cause and shall pay for remedial actions.

The National Water Act is an important regulation that dates from 1998 and which served as an example for other regulations in the water field. One of the stated purposes of this act is the reduction and the prevention of pollution of water resources.

The act is a “high-level” law that avoids any prescription but rather provides the tool for the appropriate management of water resources in South Africa.

Potential constraints for CCS activities that could result from this act stem from Part 4 of Chapter 3, which deals with pollution prevention. In case of pollution resulting from onshore activities, then the owner is responsible and must take any measure to prevent pollution.

This is similar to the EU Environmental Liability Directive, although specific to the protection of water resources: this article is the realization of the “polluter pays” principle adapted to the protection of water. For potential small effects on water resources arising from CCS activities, it will be up to the catchment management agency to judge whether or not intervention is required. This could have a major impact on the potential capacities in relation to potential overpressure created, for example, by the injection of .

Part 1 of Chapter 4 (Use of water) defines and lists the different “*water use*”, including “*waste discharges and disposals*”. It is said that a water use needs a license or a form of authorization by the responsible authority. The injection of into a deep aquifer is thus included in the term “water use” and hence the operator would need to obtain a license.

Part 5 of the same chapter defines the “*controlled activities*” and mentions “*aquifer recharge using waste*”. CCS could thus be included in the “controlled activities” if is considered as waste. If so, a public consultation would be required in order to obtain the authorization to inject into a deep aquifer.

In conclusion, no real barrier exists in the National Water Act that could prevent development of CCS in South Africa, although some form of negotiation and licensing will have to take place between the operator, the authority regulating CCS in South Africa and the authority regulating the water use, such as the catchment management agencies. The acknowledgement that we made for the European Union case is also valid here: a good communication and an optimal sharing of data will be needed between the different state representatives that will be relevant to the implementation of CCS in South Africa.

5.2.4. China: results from STRACO2 (2009)

The aim of the STRACO2 project, a FP7-funded project that finished in 2009, was to make a complete state-of-the-art of several issues of CCS in order to give recommendations that could help to accelerate its development. There was an international aspect to this project. Applicability to the context of China was systematically sought, both for the findings and the issues studied. Here, we cover some findings concerning the protection of groundwater based on the final report of the project.

Extract from paragraph 1.8.4.3 Storage:

“(8) Law of the People’s Republic of China on Prevention and Control of Water Pollution

Chapter V under the law is the regulation on underground water pollution prevention and control. The pollution and leakage prevention measures are required for underground activities, e.g. mining, exploration and construction. […] The protection of underground drinking water and the monitoring of groundwater should therefore become an important component of the future CCS regulation. And the CCS regulation should not conflict with the existing water law.”

Chapter 2.8 of the same report also presents interesting findings concerning the potentially relevant institutions:

“In the case of storage in saline aquifers, the Ministry of Water Resources (MWR) would have to be involved in the permitting process as the ministry is tasked with overview of the aquifers and permitting their use.”

“The Ministry of Environmental Protection could fulfil a similar monitoring body function as it does in nuclear issues and the Ministry of Land and Resources and Ministry of Water Resources already have control over the monitoring of groundwater and geological hazards. The standards relating to location would have to be amended according to the requirements of CCS, like the allowance of storage in saline aquifers.”

From the results of the STRACO2 project, it appears that, as for South Africa, the implementation of CCS will have to deal with the existing institutions that manage the protection of water. There will be a trade-off to find a compromise between large capacities of storage and the absence of any impact on fresh groundwater. This trade-off will not necessarily materialize in the regulations itself, but will be present in practise.

5.3. CONCLUSIONS

In conclusion of this regulatory review, two approaches exist to avoid impacts of storage on groundwater quality.

The first approach is to select and operate the site with great care. The main issue is the permanent containment of within the reservoir. Following the first developments of CCS regulations, the general rule is “zero-leakage” assumption. The containment is assured by the quality of the cap rock and the absence of any (man-made or natural) pathways from the reservoir. In addition, different risk assessment methods are needed in order to monitor, during the whole life-cycle of the storage site, any adverse effect on groundwater due to storage. During the operations, risk management relies mainly on appropriate monitoring, including monitoring of the water quality of potential “receptors” and on corrective actions. All these actions will be decided between an operator and a “CCS authority”.

The second approach is the best practice in the management of the water resource. The various regulations stipulate that any damage on the status of an aquifer should be detected as soon as possible and remediated, and that the cost shall be recovered from the responsible authority. Here, the responsibility of such actions mainly lies with the “water authorities”. Their main difficulty will be to prove that an observed damage to water is caused by a storage site, which could be extremely problematic in certain cases.

A recurrent conclusion of this review is that there will be different “authorities” that will have different priorities. An optimal and early communication between the concerned authorities will be essential for environmentally safe storage. Participation of the water authorities throughout the whole process of site qualification for storage should be required in order to have an independent review from a player with different priorities to those of the operator or the CCS authority, namely the protection of water.

However, pressure alterations far from the storage site could be important in case of a large storage project with high injection rates and large capacities. In this case, the assessment should allow some flexibility on the quantitative status of groundwater if it is proven that there is no danger for human health or the environment. Otherwise, initial estimations of storage capacities will be greatly reduced.

In the US, the situation will be slightly different since for some states, the water authority and the CCS authority will be directed under the same agency: the US EPA. However, the states that are most likely to start CCS operations in the near future are also the states where operations will be controlled by oil and gas agencies (e.g. Texas and North Dakota). Here, the active participation of Water authorities in the licencing process would be highly beneficial.

6. Prevention, mitigation and remediation

The geological sink and the integrity of the containment of injected in the underground strata must be ascertained through the application of various monitoring options in order to fully understand the migration paths, leakage possibilities and the interactions of with the formation itself. The fate of long-term storage will be jeopardized if a pathway exists between the storage formation and the open environment or other geological formations including groundwater resources. The main possible leakage pathway in storage is through or along geological features, such as fractures and faults caused by tectonic activity, or improperly abandoned wells.

Leakage would reduce the effectiveness of CCS and possibly lead to health, safety and environmental issues with identified impacts to the ecology and water quality of near-surface aquifers used for drinking water. leakage to groundwater reduces the pH, increases mineral dissolution and can release metals that contaminate the potable groundwater resources. Concerns have been raised by the public and regulatory bodies with respect to the possibility of leakage from deep saline aquifers used for storage to groundwater, although the likelihood of leakage is extremely low (IPCC, 2005) if storage sites are selected appropriately (exclusive of post-injection tectonic activity).

To forestall public concerns about a potential leakage of stored anthropogenic back to the environment and to establish the viability of long-term geological storage of as a means of reducing emission to combat global climatic change, mitigation and remediation strategies must be put in place, as undue reliance on the low probability of leakage is not a proactive approach. Mitigation refers to techniques that can alleviate or reduce the adverse impacts of a leak, whereas remediation techniques aim at stopping the leakage and any associated adverse effects.

In this Chapter we present an extensive review of the current state-of-the-art in leakage mitigation and remediation. We have also performed a series of numerical simulations to perform a case study by applying some of the proposed mitigation strategies to a particular case. The detailed results of this case study are presented in Appendix 2 of this report.

6.1. INTRODUCTION TO MITIGATION AND REMEDIATION

6.1.1. Possible mitigation options

Injected for the purpose of storage in underground geological strata, such as saline aquifers, should be conducted in a safe manner that minimizes risks for its migration and/or leakage out of the injection target, which would potentially contaminate potable groundwater resources, energy and mineral resources, and endanger life and property.

An evaluation process that can be used to examine the confining system (storage formation) is proposed by the EPA (2008) and is shown in Figure 6.1.

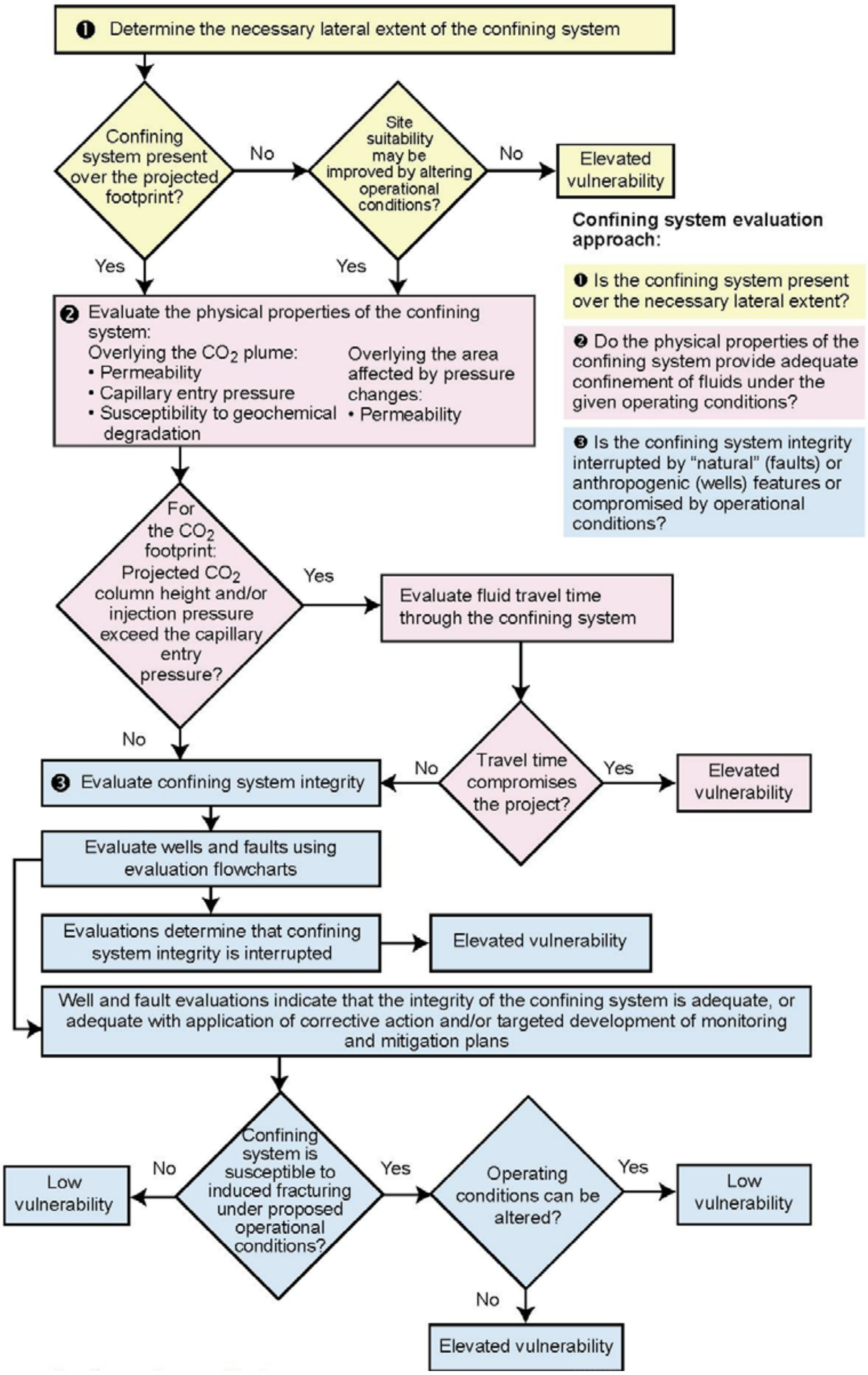

Figure 6.1: Evaluation process of a potential confining system (EPA, 2008).

In this process, elevated vulnerability characterizes a confining system that is inadequate for storage and may also increase the potential for adverse impacts. On the other hand, low vulnerability describes a storage formation that is anticipated to be adequate for the injection of for storage proposes.

6.1.2. Possible leakage mechanisms

 migration (leakage) outside of the limits of the storage formation can occur either in the vertical or lateral directions. In the first case, moves vertically upward through either the overlying geological strata or a well (abandoned, monitoring, active). The second case relates to the lateral confinement of the storage structure and refers to the migration of the injected from the injection site/well through the formation either to the surface or until it reaches a confining structure.

Figure 6.2 provides an illustrative summary of possible leakage paths for the stored from the storage formation and associated remediation measures as proposed by IPCC (2005).

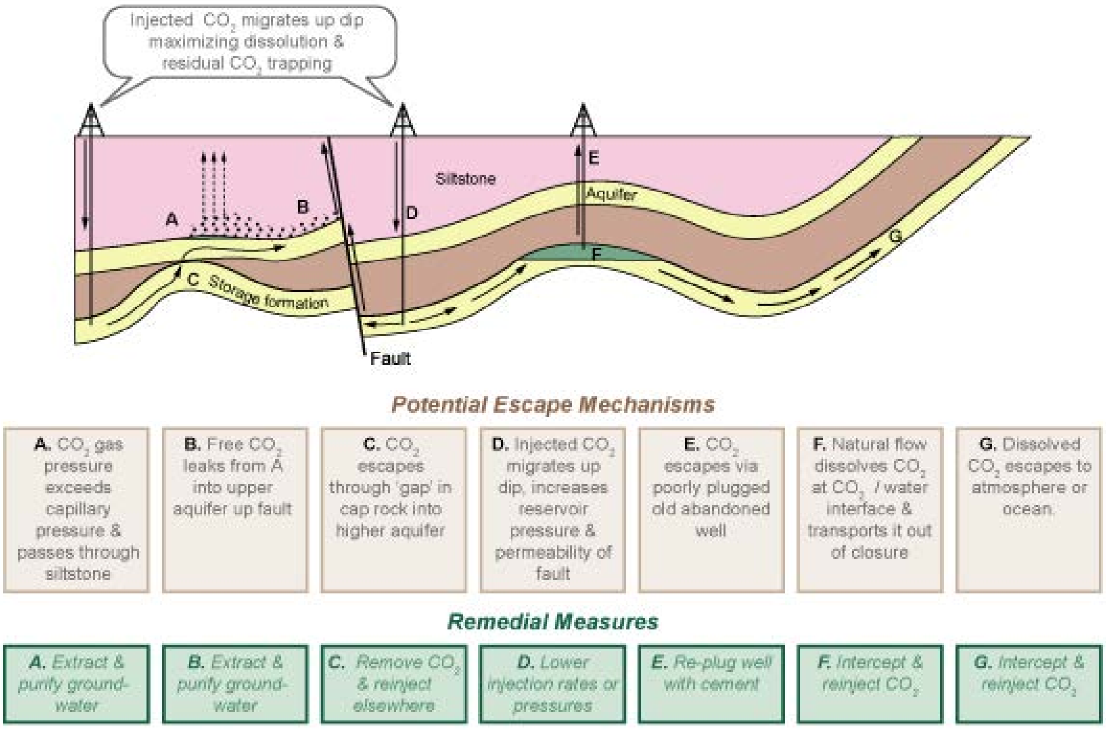

Figure 6.2: Schematic diagram illustrating possible leakage paths (from IPCC, 2005).

- Stored escapes from the top of the stored formation (saline aquifer) into overlying freshwater aquifer strata via natural fractures existing due to tectonic folding of the trapping cap rock formation (Case C). If escapes from the storage formation (saline aquifer) or if brine is displaced as a result of pressure changes into an overlying aquifer, a pronounced impact on groundwater may occur, including increased salinity and acidity (reduced pH), as well as mobilization of metals and other impurities (Jaffe and Wang, 2003; Wang and Jaffe, 2008; Tsang *et al.*, 2008; and Zheng *et al.*, 2009a, 2009b).

- Once in the overlying aquifer, injected will either become trapped in existing geological structures (e.g. anticlines) or escape into the overburden, the surface or the ocean via existing leakage paths from the newly formed accumulation (Case A) or from an existing fault (Case B).
- recently accumulated in a freshwater aquifer escapes into the overburden geological strata due to pressure build-up that exceeds the capillary threshold pressure and causes to pass through the siltstone cap rock (Case A).
- migrated into a freshwater aquifer escapes to the overburden strata and/or surface/ocean through an existing fault or natural fractures (Case B).
- Injected migrates up dip via an existing geological fault (Case D). Reactivation of existing faults could be possible either through tectonic forces acting in the region, pressure increase due to storage or chemical reactions between stored and fault minerals.
- Accumulated escapes to the surface/ocean or overburden via a poorly plugged abandoned well (Case E).
- Due to natural water flow into the stored formation, saline water dissolves at the water/ interface and transports it outside the storage formation limits (Case F).
- Dissolved or free is transported to the surface or ocean passing through the spill point of the storage geological formation, a process exacerbated by the presence of lateral formation heterogeneities (Case G).

6.2. PREVENTION, MITIGATION AND REMEDIATION MEASURES

IEAGHG report 2007/11 provided a detailed review of seepage remediation from storage formations by classifying the various migration/seepage events, providing remedial procedures for seepage and subsurface impacts, listing a five-part strategy for seepage prevention and remediation and, finally, concluding with the cost related to seepage prevention and remediation. Relevant key issues and a brief summary of the IEAGHG report are included in this report.

1. Classification of a migration or seepage event

Three main migration and seepage mechanisms are identified:

- seepage due to seal failure.
- Migration out of the confining structure.
- Seepage due to lack of well integrity.

2. seepage and remediation procedures

The proposed remediation procedures are related to:

- The mechanical integrity of wells and monitoring systems.
- Identification of leakage location through monitoring methods.

- Remedial actions related to loss of injection well integrity. It should be added that observation wells should be also included in addition to the injection wells.
- Remediation of leakage in an abandoned well.
- Required remediation modifications accounting for the actual amount of leaked .

3. Five-part strategy for seepage prevention and remediation

The strategy for prevention and remediation of seepage outlined in the IEAGHG report 2007/11 is summarized below. Additions and modifications are also included where appropriate.

- Select favourable storage sites with a low risk of leakage.
- Place emphasis on the well integrity.
- Conduct a phased series of formation simulation-based modelling to track and predict the location and movement of the plume. In addition, it should be pointed out that a thorough, phased review, evaluation, modelling and simulation of the storage formation to ascertain formation storage capacity, identify injectivity issues and predict migration of is also required.
- Install and maintain a comprehensive monitoring program for storage. However, prior to this step, a careful review of the existing monitoring systems should be carried out with emphasis on selecting, customizing and timely deployment of the most appropriate monitoring systems.
- Establish a “ready-to-use” contingency plan/strategy for remediation of seepage.

4. Cost of seepage prevention and remediation

The prevention and remediation costs listed in the IEAGHG report 2007/11 are related to:

- seepage prevention costs related to:
  - Rigorous site selection and project design.
  - Project monitoring and seepage detection.
  - Wellbore integrity monitoring.
- seepage remediation costs related to:
  - Location of the source of seepage.
  - Well plugging.
  - Well remediation.
  - Remediation of seepage through the cap rock.

Finally the IEAGHG report 2007/11 includes remedial options for leakage from geological storage projects proposed by Benson and Hepple (2005). More specifically, these remedial options are related to:

- leakage through the formation’s cap rock.
- leakage out of the confining structure.
- leakage due to lack of wellbore integrity.
- leakage due to well blowout.

- leakage and accumulation in groundwater.
- leakage into the vadose zone and accumulation in soil gas.
- Large releases in near-surface atmosphere.
- Accumulation of in indoor environments.

In the remaining part of this section, additional details and information are provided related to and supplementing those reported by IEAGHG report 2007/11, and Benson and Hepple (2005).

Migration and leakage of through faults, wellbores and cap rock have been studied through simulation studies by several authors (see for example Celia *et al.*, 2005; Nordbotten *et al.*, 2005; Pruess, 2006b; Pruess, 2008; Yamamoto *et al.*, 2009a; Birkhollzer *et al.*, 2009)

Mitigation and remedial measures of these potential migration/leakage scenarios are mainly associated with operational activities, some of which could be implanted immediately, whereas others require more time.

More specifically, the temporary cease or reduction of injection is the most immediate remedial action that can be implemented once a leakage of is detected. Indeed, reducing the amount of injected will lower the rate of pressure increase that could be the factor causing the detected leak. Other remedial measures include: (a) the extraction and purification of -contaminated groundwater (considering different well configurations as simulated by Esposito and Benson, 2010a, b), which will also provide an additional positive impact of releasing some of the pressure build-up that could have occurred in the fresh-water aquifer, thus reducing the risks or avoiding potential release of into overburden geological strata and/ surface/ocean (Cases A and B) and (b) the injection of water to enhance the immobilization of the plume, through dissolution and residual trapping either within the impacted aquifer (Esposito and Benson, 2010a,b) or directly within the storage reservoir; this could be achieved as either a preventive approach for the enhancement of dissolution (Leonenko and Keith, 2008) or for the enhancement of residual trapping (Qi *et al.*, 2009) or a corrective approach (Manceau *et al.*, 2010).

Benson and Hepple (2005) categorize groundwater remediation methods that may be useful for leakage as passive, active, and other contamination due to the dissolution of minerals secondary to influx. Passive methods utilize natural attenuation of the by dissolution in groundwater, dilution and mineralization. Monitoring is required to confirm that the hazard is being remedied at an acceptable rate. Active methods involved injection or extractions of fluids to accelerate removal or stabilization of .

The most commonly employed method in the case of groundwater contamination is the 'pump and treat' system where contaminated groundwater is extracted from the ground, treated at the surface to remove any unwanted impurities, and discharged into surface waters or re-injected into the ground. For , this could include both gas phase pumping and groundwater extraction. In addition, flow-through treatment, barriers or additives for removal of trace elements mobilized could be applied (Benson and Hepple, 2005). The use of hydraulic barriers to contain the plume of contaminated waters is another possible remediation method.

Pressure build-up due to injection could lead to leakage associated with Cases C and D. Abnormal flow and leakage through faults, fractures and other subterranean pathways call for remediation options such as ceasing , lowering the injection pressure or rate, and removing from the storage formation and reinjecting it into other suitable formation(s) with the same or adjacent wells. Finally, creating a hydraulic barrier (as numerically investigated by Réveillère and Rohmer, 2010), by injecting water upstream, or a chemical sealant barrier to block leaks is also recommended (Sweatman *et al.*, 2010).

The migration of via an abandoned or active well (Case E), in addition to some of the remedial options listed above, calls for repair of the wellbore leaks using cement plugs or relevant chemical sealants in the casing or liner pipe; repairing tubing or packer leaks followed by well recompletion techniques (Marca, 1990); sealing of external leaks using cement or chemical sealants; replacement of pipe weakened by corrosion and repairs such as casing patches (Merritt *et al.*, 2002); or finally plugging and abandonment of wells that cannot be repaired (Lynch *et al.*, 1985; Sweatman *et al.*, 2010).

For lateral migration of , such as Cases F and G, remedial options include the use of hydraulic barriers by injecting water upstream or removing some of the stored and reinjecting it into another zone. In the case of an abnormal flow of and leakage into the vadose zone, Benson and Hepple (2005) and Sweatman *et al.* (2010) list, in addition to the remedial actions listed above, the extraction of from the vadose zone and soil; pumping away from low-lying areas and reinjecting it into another subsurface zone; or passive remediation (diffusion and barometric pumping) to deplete slowly a release into the vadose zone. For an intervention strategy and remediation measures related to leakage of in the vadose zone, Rohmer *et al.* (2010) provide additional details. Finally, Benson and Hepple (2005) and Sweatman *et al.* (2010) provide a list of additional remediation options against other leakage risk scenarios, such as chronic low-level leakage into indoor environments, accumulation of into surface lakes, and large releases of into the atmosphere.

Hydraulic barrier implementation is not appropriate to achieve restoration in many portions of sites due to hydrogeological limitations. The implementation of such technology requires the evaluation of a range of site-specific conditions including: (a) lithological profile of the system, with respect to infiltration and permeability characteristics; (b) confinement status of the aquifer (unconfined, semi-confined, confined); (c) hydrogeological characteristics of the entire system; (d) source-water quality which may also influence the injection rate as well as dictate the likely requirements for pre-treatment to avoid well plugging. This of course may add a significant cost and have an impact on the feasibility of the various mitigation/remediation methods. The implementation of a hydraulic barrier is more appropriate in low-permeable or confined aquifers. Inadequate design and implementation may also severely impact the performance of a ‘pump and treat’ system. Examples of design inadequacies can include the existence of too few recovery wells, insufficient pumping rates, non-optimal well locations or completion intervals (EPA, 2007). Table 6.1 provides a summary of mitigation options for lateral migration.

Table 6.1: Examples of mitigation options for shallow groundwater potentially affected by geological storage projects (non-exhaustive list)

	Options	Methods / Requirements
intrusion	Stop the injection of	Immediate implementation
	Extract -rich water from shallow GW and purify	Extractions wells, degassing, Injection wells
	Inject water in shallow GW to enhance the dissolution of and residual trapping	Injection wells
	Treat the contaminants dissolved in GW	‘Pump and treat’ methods (fluid extraction); flow-through system (reactive barrier); additives-based
	Place a hydraulic barrier to immobilize the contaminated plume	Injection wells
	Place a hydraulic barrier to stop the leak by increasing the pressure upstream	Injection wells
	Place a chemical barrier to stop the leak	Create a chemical sealant barrier upstream of the leak
	Consume by the biomass	Passive method: Natural biogeochemical process
	Extract (gas or dissolved) from shallow GW or directly the reservoir	Extraction wells - require drilling wells that intersect the plume
Pressure increase	Extract water from shallow GW	Extraction wells
Wellbore leak	Repair of wellbore leaks (active, monitoring, or abandoned well)	Immediate implementation
	Plug the leaking well	Cement plugs or chemical sealants
	Implement well intervention/recompletion techniques	Partial isolation and/or side-tracking of an existing well
	Place an external sealing	Cement plugs or chemical sealants
Lateral migration	Stop the injection of	Immediate implementation
	Remove stored	Extraction wells
	Place hydraulic barriers by water injection upstream	Extraction wells

Bouc *et al.* (2010) developed a generic approach, which incorporates a series of simple tools for identifying risk scenarios, modelling risk events and exposure, to provide references for safety assessment of storage. The authors acknowledge the fact that this is not a complete risk assessment workflow, but since no risk assessment workflow or safety standards for storage have been commonly accepted, the proposed approach may provide the means of determining safety references.

6.2.1. Remediation techniques for pressure increase in the storage formation

Saline -storage formations can be classified as open, semi-open or closed depending on the extent of the lateral communication that exists in the system. This distinction is important when it comes to the rate and extent of pressure build-up in the formation during an industrial-scale injection. More specifically, whereas open storage saline aquifers permit the lateral displacement of the formation's brine by the injected , thus displaying a progressive formation pressure increase and avoiding the build-up of high pressures, both semi-closed and closed systems behave differently. The presence of lateral structural or stratigraphic geological characteristics (e.g. low-permeability zones, impermeable faults, salt domes, compartmentalized reservoirs, pinchout stratigraphy) provide limited or no lateral movement of a saline aquifer's brine movement that, depending on the total amount and rate of injection, may lead to a formation pressure build-up that limits the storage capacity of the aquifer and increases the risk of leakage through the formation's cap rock and/or existing abandoned and/or observation wells.

Regardless of the classification of the storage formation, injecting into geological formations will result in increases of pressure (see also section 4.2 for details on the numerical modelling of pressure changes) that could lead to the unanticipated migration of either through existing pathways (cap rock seal, abandoned wells, faults and natural fractures) or induced well fracturing. In addition, increases of formation pressure may also cause fault reactivation.

Zhou *et al.* (2008) presented a single analytical model for a quick assessment of the storage capacity in closed and semi-closed systems. The method is based on the fact that the injected displaces the native brine that can only occupy additional pore volume either within the aquifer formation itself or its surrounding seal(s). The magnitude of the injected that can be accommodated within a given saline aquifer depends on the formation and brine compressibility and the pressure that could be built up based on the guidelines drawn for a safe storage of the injected industrial . The presence of a non-ideal, weak cap rock formation and pressure build-up exceeding the safety limit could force the aquifer's brine or injected into the surrounding formations.

Le Guénan and Rohmer (2010) employ a 2-D layered model to examine four corrective measures aimed at controlling overpressure induced by injection operations, namely (a) ceasing injection and relying on natural pressure recovery, (b) extracting at the injection well, (c) extracting brine from a distant well while stopping injection, and (d) (c) extracting brine from a distant well without stopping injection. The authors used a cost-benefit approach to carry out a comparative study among these four corrective measures for the deep carbonate aquifer of the Dogger geological unit in the Paris basin.

The effects of formation pressure increase associated with the injection of can be determined by both geological attributes of the aquifer system as well as operational issues. The adverse effects could be reduced or avoided through an understanding of the relevant geological attributes, appropriate site characterization, careful application of operational activities according to already established (or forthcoming) laws and regulations, as well as establishment of appropriate monitoring and reporting processes (for more details please refer to EPA, 2008).

Finally, the possibility of using dedicated water production wells to remove saline water from the storage formation in order to reduce excessive pressure increase in the storage reservoir, and thus mitigate adverse pressure build-up impacts on injectivity and existing or induced leakage pathways, should always be examined thoroughly (Hatzignatiou *et al.*, 2011). The management (logistics, costs, handing, disposal, etc.) of the removed saline water from the storage, deep saline formation, is another issue that needs to be addressed in an effective and environmentally friendly manner according to the nature of a given storage site.

6.2.2. lateral leakage

lateral leakage is associated with the closure of the storage site, the presence of abandoned wells and/or faults that the expanding-over-time plume may reach. Cases D, F and G are related to some of the leakage risks associated with the lateral movement of the injected-for-storage . Proper characterization of the saline formation where is to be injected for storage could reveal some of the potential risks associated with this type of leakage. Mitigation and remediation options for this type of leakage are listed above (Table 6.1 provides a summary of mitigation options for lateral migration).

6.2.3. vertical leakage

Possible vertical leakage of is by far the most frequent and possible type of leakage one may anticipate from a storage project. The main mechanisms for vertical leakage relate to failure of (a) wellbore completion/plugging (casing, cement, or abandonment practices), (b) existing geological faults or (c) cap rock (often referred to as seal) to contain the injected .

Leakage through existing wells

Many promising provinces for storage also contain oil-bearing formations and have been extensively drilled (some several-thousand wells). One example is the Texas Gulf Coast in the USA, which has been drilled for more than 100 years and contains over 125,000 wells across an area of approximately 50,000 (Nicot, 2009c). The presence of these wells, which run across perfectly sound seals, increases the possibilities of leakage through either active or older abandoned boreholes.

Wells (injection, monitoring, abandoned) have been identified as one of the most probable conduits for the escape of and other fluids from a target injection zone (Gasda *et al.*, 2004; Carey *et al.*, 2007a and 2007b; Nicot, 2009c). Leakage and well-integrity failure of liquid-waste injection wells have been reported by several authors (see for example Hsieh and Bredehoeft, 1981; and Lehr, 1986). The experience gained from the oil and gas industry is highly valuable when it comes to designing, executing and maintaining wellbore integrity.

Table 6.2 summarizes the five classes of injection well, their use and existing inventory (please note that this well classification is valid only in the USA). This type of well classification is based on the type of injected fluid, activity, construction, injection depth, design, and operating techniques of a given well. This ensures that wells with common design and operating techniques meet all appropriate safety criteria for protecting underground sources of drinking water (USDW) (US EPA Underground Injection Control (EPA-UIC), 2010). Note that the UIC Program does not regulate production wells.

Class II wells are referred to as oil and gas injection wells, most of which are used to inject brine or other fluids for enhanced oil and gas production. There are three types of Class II injection well (a) Enhanced Oil Recovery (EOR) wells injecting brine, water, steam, polymers, or into oil-bearing formations to mainly recover residual oil; (b) disposal wells injecting brines and other fluids associated with the production of oil and natural gas or natural gas storage operations; and (c) hydrocarbon storage wells injecting liquid hydrocarbons into underground formations where they are stored. According to US EPA, approximately 144,000 Class II wells are currently in operation in the United States injecting over 2 billion gallons of brine/fluids every day.

In Alberta, Canada, the injection wells are classified as (a) Class Ia for oilfield, industrial waste, (b) Class Ib for produced water and specified wastes, (c) Class II for produced water and brine equivalent, (d) Class III for hydrocarbon/inert/sour gases, and (e) Class IV for steam/potable water.

Table 6.2: Injection well classification, use and inventory (EPA-UIC, 2010)

Classes	**Use**	**Inventory Well #**
Class I	Inject hazardous wastes, industrial non-hazardous liquids, or municipal wastewater beneath the lowermost USDW	**549**
Class II	Inject brines and other fluids associated with oil and gas production, and hydrocarbons for storage. They inject beneath the lowermost USDW.	**143,951**
Class III	Inject fluids associated with solution mining of minerals beneath the lowermost USDW.	**18,505**
Class IV	Inject hazardous or radioactive wastes into or above USDWs. These wells are banned unless authorized under a federal or state groundwater remediation project.	**32 sites**
Class V	All injection wells not included in Classes I-IV. In general, Class V wells inject non-hazardous fluids into or above USDWs and are typically shallow, on-site disposal systems. However, there are some deep Class V wells that inject below USDWs.	**400,000 to 650,000**

Existing Federal and State regulatory attention focuses on protecting underground sources of drinking water and address issues of fluid injection into subsurface strata such as (a) wellbore integrity, (b) a formation’s suitability to ensure confinement, (c) suitability of the injected stream (nature of fluids and well, formation integrity) (d) reporting, and (e) early detection and mitigation of potential problems.

According to Bachu (2007), the requirements for Class III injection wells in Alberta are the (a) hydraulic isolation of the host zone, (b) cementing across protected groundwater, (c) logging for cement top, hydraulic isolation and casing inspection, (d) initial annulus pressure test, (e) annual packer isolation test, (f) wellhead pressure limitation at <90% of rock fracturing threshold, (g) area of review based on reservoir modelling, and (h) hydraulic isolation of offset wells that penetrate the same zone within the area of review.

Industrial analogues provide examples of unanticipated gas leakage through poorly completed or improperly plugged and abandoned wells (Gurevich *et al.*, 1993; Perry, 2005). Wells not properly sealed and plugged could potentially provide open conduits that can follow from the storage formation to the surface. Even properly sealed wells may also provide pathways along the outside of the well casing, where the presence of well cement, drilling mud, and damaged rock zones could also create opportunities for leakage to the surface or into the overburden strata (Gasda *et al.*, 2004). Note that carbonic acid generated when is brought into contact with water may degrade the well construction materials, thus creating possible pathways for leakage. Celia *et al.* (2005) list leakage paths that include a well plug-well casing interface as: well casing-cement fill interface, cement fill-formation rock interface, flow lines through cement itself, and flow lines through cracks in the well cement and cement fill.

The density of abandoned wells is high in some regions, especially onshore. These wells are more likely to leak due to (a) application of improper abandonment practices, (b) abandonment procedures not properly followed, or (c) well abandonment not designed for long-term protection (e.g. well seal failure) (Friedmann, 2007; Nicot, 2009c) and thus they pose a great leakage risk since there is a good chance that the spreading plume would intersect such a well, thus possibly creating a pathway for vertical leakage of either to the surface/ocean or the overlying fresh-water aquifers.

 leakage through a wellbore could be much more pronounced and faster than leakage through the overburden. The possibility of such occurrence raises questions regarding the viability of long-term wellbore integrity (including wellbore isolation and durability of hydrated cement). Barlet-Gouedard *et al.* (2006) present results of a comprehensive study on cement degradation by simulating the interaction of set cement with supercritical under downhole conditions. The evolution of the cement chemistry and porosity as a function of time was evaluated with SEM analyses, back-scattered electron images, and mercury-porosimeter measurements.

According to Loizzo and Duguid (2007) the interaction between Portland cement and is a three-step process; (a) carbonic acid diffusion, (b) dissolution/carbonation (Portlandite ($Ca(OH)_2$) and CSH gel; precipitation of , and (c) leaching. According to the authors, leakage though wellbores in not limited to storage; it is reported that 15%-20% of wells may show some type of hydraulic communication to the surface. Finally, Loizzo and Duguid (2007) stated that risk factors and scales are casing corrosion and leakage to shallower formations or to the surface. Multiple risk-mitigation measures may be required, especially when repair is difficult, (a) cement system selection and optimization, (b) minimization or elimination of cement sheath defects, (c) minimization or elimination of cement degradation.

Carey *et al.* (2007b) summarized the reconciliation aspects among laboratory results, field observations and modelling studies. Laboratory results vary from extensive reactivity (Duguid *et al.*, 2005) to limited reactivity (Kutchko *et al.*, 2007) and depend on imposed conditions (temperature, pressure, fluid, etc.). Field observations from a 30-year old flooding operation at the SACROC unit in West Texas (Carey *et al.*, 2007b) show -induced alteration similar in character to some laboratory experiments but without significant apparent leakage. Modelling studies may have the potential to reconcile laboratory and field observations and provide a mechanism to predict long-term performance. Carey *et al.* (2009), based on theoretical justifications as well as the field study results of Carey *et al.* (2007b) and experimental studies of Kutchko *et al.* (2007), state that the most likely leakage mechanism is related to flow along a cement-casing microannulus, cement-cement fractures and cement-cap rock interface.

Recently, Deremble *et al.* (2010) developed a simulator that couples fluid flow, elasticity and chemical reactions to investigate the -rich fluid leakage rate through a pathway along a cemented annulus. The simulation results reveal different mechanisms of flow rate variation with time. In particular, flow along cement defect and chemical reaction between cement and may cause mineral deposition in the defect space, thus plugging off the existing leakage pathway.

Leakage through existing geological faults and fractures

Faults are breaks in the earth's crust that can occur when the crustal rock is either compressed or pulled apart due mainly to tectonic geological activity. Fractures are commonly caused by stress exceeding the rock strength. Faults may serve as either barriers or conduits to fluid flow (see for example Omre *et al.*, 1994; Wilkens and Naruk, 2007). However, a potential leakage through faults could only be assessed by analogue studies and the reported rates should be only considered as guidance (minimum) since there is no knowledge of the escaped that is "lost" into underground geological formations. For example, at Latera in Italy, the total flux per day occurring from eight different locations inside a 10x8 caldera is reported to be approximately 7,700 tonnes per year (Lombardi, 2011).

There are several parameters that may be used to evaluate faults and/or fracture zones, including fault/fracture density, stratigraphic position, connectivity, sealing/transmissivity properties, fault stability and fault reactivation pressure, etc. (Bretan *et al.*, 2011). Hermanrud *et al.* (2005) have stated that the analysis of fault conductivity is not addressed effectively in seal evaluation. Chang *et al.* (2008) developed a simplified quasi-1D analytical model and investigated the migration of through faults into overburden geological formations. They conclude that the location of the permeable layer(s) into which the migrates plays an important role; the deeper layers yield much more attenuation than the shallower ones, and therefore, smaller amounts of escaped would reach the surface/ocean in this case.

Shipton *et al.* (2004) examine evidence of migration along two normal faults from a reservoir in Utah. These fine-grained, clay-rich gouge faults were generally considered as fluid-flow barriers. However, geological and geochemical data analyses revealed that these faults could be conduits for to the surface and conclude that injection into faulted geological reservoirs that contain faults with clay gouge should be designed and monitored carefully to avoid either a slow seepage or a fast rupture of .

In a pilot EOR-carbon storage study, Chiaramonte *et al.* (2008) develop a geomechanical model of the Tensleep Formation at the Teapot Dome oil field, Wyoming, USA, to evaluate the potential for injection inducing slip on a bounding fault, thus threatening seal integrity. Monte Carlo simulation is used to incorporate uncertainties in the stress tensor and fault geometry. The authors find that excessive pressure build-up (corresponding to column heights significantly higher than ones permitted by the structural closure of the formation in the pilot injection area) is required to cause fault reactivation and provide a potential leakage pathway, and conclude that injection is not likely to compromise fault stability.

Streit and Hillis (2004), through a geomechanical modelling study, conclude that the modelling of fault stability requires knowledge of the current in situ stresses and formation fluid pressure distributed throughout the potential storage area. The authors estimate fault slip tendency, based on the effective stresses acting on them, and calculate sustainable increases in fluid pressure that will not induce fault slip or new fractures, for various fault orientations and rock strengths.

Pruess (2008) investigated the migration of through a fault zone followed by its accumulation in a shallower formation and eventually its discharge at the surface via another fault. The author reports that parameters such as condensation of gaseous , three phase flow, and cooling due to Joule-Thomson expansion and boiling of liquid are important in the behaviour of the leakage system. The author states that in general, security of storage increases as depth of the storage aquifer increases, but at the same time the overpressures in excess of hydrostatic potentially generated by will also increase with increasing formation depth. The relative importance of one versus the other of these two opposing effects will most likely be site dependent.

Leakage through the aquifer’s cap rock and overlying geological strata

A high degree of uncertainty exists concerning cap rock properties, both hydraulic and mechanical, since cores and analysis results are commonly lacking or very limited.

Associated risks for leakage are related to the ability of the cap rock to confine buoyant for geological time scales related to storage. The mechanisms related to the migration of through a cap rock are related to its properties, namely absolute and relative permeability, threshold capillary pressure, existence of micro- or macro-fractures, existence of faults intercepting an aquifer’s seal, as well as properties such as diffusion rate, state of free in the formation (i.e., viscosity, density). Some of these properties are self-enhancing or self-limiting. The first category includes for example (a) cap rock permeability increase due to chemical reaction between the formed carbonic acid and seal minerals, (b) micro-fracture permeability enhancement due to pressure build-up in the storing formation during the injection of , or (c) fault reactivation causing an increase of the fault’s permeability due to either, or both, chemical and geo-mechanical mechanisms. In the self-limiting category, one could include the decrease of cap rock permeability due to precipitation of inorganic non-soluble salts during the chemical interaction between (carbonic acid) and the seal.

Birkholzer *et al.* (2009) conducted a numerical simulation study to evaluate possible implications for shallow groundwater resources focusing on interlayer communication through low-permeability seals. The simulation results indicate a (a) considerable pressure build-up in the storage formation at distances more than 100 km away from the injection site with a small later migration of brine and (b) pressure perturbation that may reach shallow groundwater resources only if the deep storage unit communicates shallower aquifers sealing units or relative high permeabilities. The authors conclude that vertical brine migration through a sequence of layers into shallower groundwater is extremely unlikely.

Numerical simulation of mitigation strategies

In the present study, we have also performed a series of numerical simulations using ECLIPSE 300 Reservoir Simulator to perform a case study by applying some of the proposed mitigation strategies to a particular case. The case studied in the numerical simulation exercise consists of two aquifers; one representing a deep saline aquifer and the other representing a groundwater aquifer. Various scenarios of leakage and leakage mitigation strategies are simulated and discussed. The leakage pathway was considered as an improperly abandoned well far from the injection well. The results of this case study are presented in Appendix 2.

The following conclusions can be drawn from this exercise.

- Cessation or reduction of the injection rate is the most immediate remedial action that can be implemented once leakage is detected. Indeed, reducing the amount of injected will lower the rate of pressure increase that could be the factor causing the detected leak.
- Increasing groundwater aquifer pressure results in the reduction of the leakage rate. In our case study, the maximum percentage leakage rate drops from 8.1 % to 0.93%. Also the flow of water from the groundwater through the leakage pathway to the saline aquifer (due to the rise in pressure) increases solubility and hence storage security.
- Reducing deep saline formation pressure can decrease the leakage rate. However, it needs careful well placement and completion in order to avoid coning around the well, which would lead to the production of stored and also -saturated brine.
- Based on our simulation results, combining the strategy of reducing deep saline formation pressure and increasing groundwater pressure would be the most effect leakage remediation method. However, as it would involve both production of water from deep aquifers and injection of brine in the surface aquifer, cost would be significant.

Care should be exercised when interpreting the results available in the literature on the effectiveness of the proposed leakage mitigation and remediation strategies. Most of the proposed methods have been investigated mainly through mathematical modelling including numerical simulations, semi-analytical and analytical modelling techniques. Despite the fact that a relatively good agreement is observed between the results of these different modelling approaches, some serious shortcomings exist. One main shortcoming, associated with most existing commercial reservoir simulators, is that the phase distribution calculations are based on equilibrium conditions. This will result in calculation of excessive initial transfer of to the fluid without any content, i.e. in reality it is water rather than . A need therefore exists to develop simulators capable of accounting for non-equilibrium transient conditions involved in the diffusion of into the brine phase.

6.2.4. Well monitoring, remediation and abandonment techniques

Well drilling and completion technologies, for geological storage of injection wells, have been developed extensively in the oil and gas industry. These existing well design technologies would require some modifications when implemented in injection to account for injection rates/pressures (e.g. upgraded downhole components) in addition to well cementing and completion corrosion-resistant materials - exposure of well cement, casing and completion equipment to an acidic environment.

The traditional injection well completion practice for well control is the use of two valves, one for regular use and the other reserved for safety shutoff. injection wells would normally include a downhole tubing safety valve for automatic well shut-down to prevent backflow in the case where the surface equipment fails (Metz *et al.*, 2005). In addition, an automatic shutoff valve is recommended (Jarrell *et al.*, 2002) to (a) ensure that no is released and (b) prevent from inadvertently flowing back into the injection system.

Monitoring the injection wells could help prevent leakage and lead to rapid implementation of remedial actions if any suspicion of leakage arises. Table 6.1 provides a summary of mitigation options for wellbore leakage. The following actions are therefore recommended in injection wells (Metz *et al.*, 2005):

- Design and implement adequate plans for dealing with excess should the injection well need to be shutoff; options may include a backup injection well or perhaps methods to vent safely into the atmosphere.
- Conduct proper well maintenance to avoid well failure and potential leakage.
- Evaluate periodically the mechanical integrity of the well (mechanical integrity test – MIT), especially in older wells, both with respect to the downhole equipment and quality of the cement via appropriate logging programmes.
- Implement practical procedures and measures (such as improved blow-out prevention, BOP, maintenance; installation of additional BOP; improved crew awareness; contingency planning and emergency response training - Skinner, 2003) to reduce/eliminate possibilities of a blow-out and mitigate the adverse effects if such an unwanted event occurs.
- Monitor the annular well pressure to detect potential leakage in the well's packers and/or tubing, which is important for taking rapid corrective action.
- Stop injection as soon as a leak is detected to prevent dangerous build-up of high pressure on the surface equipment and avoid release into the atmosphere. Note that all injection wells must be equipped with a packer to 'direct' pressure only into the injection formation interval.

Well abandonment procedures are designed to isolate the formation under consideration and protect drinking water aquifers from contamination and should follow existing regulations. The existing procedures usually require (a) the placement of cement or mechanical plugs in all or part of the well, and (b) extra care to seal the well sections adjacent to drinking water aquifers. Whereas the abandonment procedures for wells could generally follow those used in the oil and gas industry and for acid-gas disposal wells, special care should be taken to (a) use sealing plugs and cement that are resistant to degradation from and (b) possibly removing the casing (by pulling or milling it out) and the liner penetrating the cap rock to avoid steel corrosion, which may create channels for leakage. In the case where the well casing is removed, a cement plug should be placed into the open borehole. Since the placed cement plug should act as a barrier to future migration, its sealing and bonding quality with the formation cap rock, penetrated by the abandoned well, is of a vital importance. Potentially existing or newly-developed micro-channels/micro-fractures during casing milling operations should be sealed properly. In addition, fluids could be also used to displace the injected away from the wellbore region and help improve the cementing quality and bonding against the sealing cap rock. Finally, it is recommended that the sealing effectiveness of an abandoned well be monitored periodically after storage operations are completed (Metz *et al*., 2005).

6.3. CONCLUSIONS

Assessing the risk of leakage associated with the geological storage of is vital for the long-term fate of the stored as well as for the public acceptance of this concept as a means of reducing greenhouse gas emissions. Although storage sites will be selected carefully in order to minimize the risk of leakage, due to the nature of geological reservoirs and the scale (both time and space) involved in geological storage of , proper mitigation and remediation strategies must be identified and put in place as an essential part of any CCS project.

In this chapter, a comprehensive review of the current state-of-the-art in leakage mitigation and remediation strategies is presented including:

- Reduction of the pressure in the storage reservoir.
- Interception and extraction of the plume from the reservoir before it leaks out of the storage structure.
- Increase of the pressure in the formation into which leakage is occurring.
- Isolation (shut-off) of leaks in identified and accessible locations, for example within wells using existing technologies (cement, polymer gels, mechanical means, etc.) or newly emerging technologies.

For lateral migration of or brines, some remedial options include the use of hydraulic barriers by injecting water upstream or removing some of the stored and reinjecting it into another zone.

In the case of contamination of groundwater resources, “pump and treat’ methods could be employed. For , this could include both gas phase pumping and groundwater extraction. Other possible methods are additive-based, flow-through treatment barriers for removal of trace elements mobilized by groundwater acidification and hydraulic barriers to contain the plume of contaminated water.

The storage project should be carefully designed to minimize any need for remediation and mitigation options, as these depend on a range of site-specific conditions that are difficult to obtain and, at certain sites, it may not be possible to restore these due to hydrogeological limitations.

From the four leakage mitigation scenarios examined here, the results indicate that the combination of saline aquifer pressure reduction and groundwater pressure increase is the best mitigation strategy against leakage. In addition, having more than one well for controlling leakage can help continue to prevent/reduce leakage in the event that one of the well fails, although this approach has a cost implication.

Pressurizing groundwater to reduce/stop leakage and flow from the deep saline aquifer has the advantage of increasing the pressure and the supply of potable water, but the question remains as to the availability, treatment and compatibility of the injected water with the water in situ to avoid altering the water quality. If these conditions are met, then this strategy would be preferable compared to reducing the saline aquifer pressure, as production of brine from the deep saline aquifer is associated with production of either dissolved or free (plume). Reducing the injection rate will prolong the injection phase of the project; this may necessitate the use of multiple wells distributed within the field and further simulation in order to understand dynamics and leakage in this situation.

Investigations are currently ongoing on various aspects of leakage, including possible leakage paths, impacts of leakage on the surrounding environment and possible mitigation and remediation methods. Numerical simulations as well as semi-analytical and analytical modelling techniques have been used to predict or estimate cross-formational leakage rates of and to model various leakage and remediation scenarios. Although a relatively good agreement is observed between these modelling approaches, they all suffer from insufficient description of the effects of diffusion of in fluids resident in the geological formations.

7. General conclusions

Leakage of from onshore or near-shore deep saline aquifers or of the associated brines is frequently cited as a risk for the overlying or neighbouring shallower potable groundwater resources. To date, the impact of storage has mainly been studied at near-well and reservoir scale, whereas risks in the larger context of regional multi-layered groundwater systems have not yet been widely assessed.

During the selection and characterization process of sites suitable for geological storage, the juxtaposition of groundwater resources and any potential impacts or conflicts must be considered on a regional scale. In the present study, a classification scheme has been developed for the various geological settings in which impacts could occur. The geological complexity and relative positions of saline and freshwater aquifers will determine the likelihood and degree of impacts and time scales at which they occur, which will vary on a case by case basis. This scheme includes deep saline formations underlying freshwater aquifers but separated by low permeability layers, both in regional basins and more complex hydrogeological structures, as well as scenarios where deep saline formations extend laterally into freshwater aquifers. In these scenarios it is necessary to assess the potential for migration of injected , both vertically through confining layers/overburden as well as laterally into freshwater aquifers, together with any associated potential impacts.

The injection of into geological formations can increase reservoir pressure, which in turn can lead to the migration of , either through existing pathways (cap rock seal, active or abandoned wells, faults and natural fractures) or by inducing fracturing or fault reactivation. Such pressure changes can potentially have an impact on groundwater flow in terms of magnitude and direction (regional flow), the water table level, and the distribution of discharge areas in shallow aquifers (springs, wetlands). These impacts can be predicted using large scale regional flow models. Studies to date show that although the pressure pulse rapidly attains a large areal extent (up to 100 or 200 km) within the storage formation, pressure declines sharply away from the injection point. This pulse is largely determined by the total amount of injected and the permeability of the confining rock. The pressure in the vicinity of the injection well can reach values of several tens of bars, while the impact on the head pressure at the surface is in general predicted to not be of a particular concern. It differs according to the size and the boundary limits of the storage formation. Water table changes do not exceed few millimeters for confined aquifer and are of the same order of magnitude as seasonal and inter-annual variations for open system. In some circumstances to be more fully explored numerical estimates can reach up to few meters. Vertical brine displacements are usually predicted to be small and strongly controlled by the cap rock permeability.

In a scenario where does escape from the storage formation (saline aquifer) or if brine is displaced, this can potentially have an impact on groundwater with, for example, a respective increase in acidity (reduced pH) or salinity, or the mobilization of metals and other impurities. Changes resulting from intrusion have been investigated through experimental laboratory and field studies, investigations of natural sources of -bearing groundwater and numerical modelling. The processes behind these potential impacts must be fully understood to correctly assess the potential impact on potable groundwater resources due to storage in DSFs. Current understanding should be refined and the potential impacts better defined.

Dedicated storage regulations have recently been drawn up and adopted, for example, in the European Union, the United States of America, and Australia. In addition to the more general measures, such as the prevention of potential leakage, other measures relate specifically to groundwater protection. The most recurrent of these are dedicated to the characterization and monitoring of the surrounding fresh groundwater. The authorities responsible for water protection should be involved in all stages of the qualification process of a storage project, thus providing additional expertise to that of the authorities regulating the storage of .

 storage projects should be carefully designed so as to minimize the need to call upon remediation and mitigation options. These depend upon a range of site-specific conditions that are often difficult to obtain and, at certain sites, it may not be possible to use some mitigation options due to the given hydrogeological limitations.

From this review, the mechanisms associated with the potential impacts of geological storage on adjacent groundwater resources are clearly identified. These mechanisms and processes are well-known as groundwater quality and availability are topics that have been subject to much of research in various different fields (agriculture, industrial pollution…). This knowledge needs to be applied to DSFs and groundwater resources to assess the potential impacts on groundwater in a storage context (impacts of pressure head variations; impact of acidification of groundwater, impact of brine intrusion in freshwater aquifers etc.). However, currently the levels/ranges of potential impacts associated with storage and leakage are not well defined for the following main reasons:

- *Limited data availability.* Although the understanding of potential mechanisms and processes is well-advanced, the impacts are very much case dependant: hydrodynamic impacts will depend on the regional hydrogeology of the basin intended for storage and of the heterogeneity of the saline formation (pressure effects and brine displacement); chemical impacts will depend on the migration/leakage of and brines; the potential alteration of the water quality will be dependent on the aquifer mineralogy and geochemical interaction with the groundwater and the microorganisms in the aquifers. Comprehensive data needed for a detailed assessment of potential impacts associated with a specific storage site are generally not all available.

- *Limited experience of storage.* There are a small number of studies that determine range of impacts. It is only recently that researchers have focussed on the potential impacts of a leak on potable groundwater resources. In some cases, these studies describe any significant water quality changes (natural analogues, pilot site) while in other cases trace element levels could exceed drinking water standards (modelling). It is therefore difficult to give a typology of the risk related to groundwater alteration in cases of intrusion.

- *Limited integrated modelling*. Numerical modelling techniques offer new insights into the potential impacts of storage on groundwater, both in terms of fluid displacement and geochemical interaction issues. However this field of study remains very challenging, as all published studies still suffer from unavoidable simplifications which influence their findings. Basin hydrodynamics impacted by storage requires the combination of hydrogeology features with multiphase flow reservoir modelling. Chemical groundwater quality modelling is also affected by the simplification of the considered mechanisms. Currently available thermodynamic and kinetic data bases do not represent real-complex minerals (e.g. clay minerals) and thermodynamics under pressure/ temperature conditions and salinities typical for DSF do not allow for reliable long-term predictions. The possible mobilization of trace metals often suggested by modelling predictions requires the integration of a detailed mineralogy and water chemical composition specific for the studied area, which is often not available (see above) and, therefore, limits our ability to make general conclusions.

This review does not focus on monitoring tools for groundwater surveys but rather on developing a better understanding of the potential impacts of geological storage on groundwater, i.e. information that is required to correctly establish a Monitoring, Mitigation and Validation (MMV) program for storage sites. A number of approaches have been suggested for mitigating leakage from reservoirs. A prerequisite for any form of remedial work is information on the type, extent and location of a potential leak. A relatively large delay can occur between the onset of leakage, its detection, and the implementation of an appropriate mitigation or remediation programme.

For better assessments of the relevance of the potential mechanisms of quantitative and qualitative impacts of storage on overlying aquifers more research studies are required. These may include:

- *Large scale basin studies* are required to better assess the hydrodynamic impacts for specific sites (e.g. to characterize the connection between deep saline formations and overlying fresh groundwater, to determine the depth of freshwater aquifers and their proximity to storage facility).
- *Investigations of natural groundwater impacted by and/or brine* under in situ conditions will give valuable information on processes occurring on realistic long timescales.
- *Laboratory and pilot scale experiments* in several geological and chemical settings are required to evaluate the potential impacts on groundwater quality. Experimental results should be used to evaluate and improve the data base for geochemical simulations.
- *Development of numerical simulators to improve both the estimates of fluid-flow displacement and the fluid-rock interactions induced by injection.* Existing fluid flow simulators need to be adapted to basin-scale single-phase (water) hydrogeology and deep reservoir multi-phase (and brine) flow. In addition, a constant effort is required to improve existing simulators to 3D heterogeneous systems, including all chemical features needed for a better understanding of the complex induced chemical reactions affecting the mineralogy and the water composition. Comparing pertinent scenarios with real field data will allow for a calibration of the modelling which remains a crucial need to ensure continued progress in modelling prediction.

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Appendix 1: Texts analysed in Chapter 5 ‘Regulatory Constraints’

A.1 COMPARISON OF CCS-SPECIFIC REGULATIONS

	European Union: Directive on the geological storage of (CCSD)	**US: Environmental Protection Agency rule (USEPA)**	**Australia: Greenhouse Gas Geological Sequestration Act (Victoria)**
Storage target constraints	- Article 4.3: The suitability of a geological formation for use as a storage site shall be determined through a characterisation and assessment of the potential storage complex and surrounding area pursuant to the criteria specified in Annex I. - Annex I: Step 1: Data Collection (b) hydrogeology (in particular existence of groundwater intended for consumption); (j) proximity to valuable natural resources (including in particular […] potable groundwater […]) (k) activities around the storage complex and possible interactions with these activities ([…] use of underground water reserves); - Article 4.4: A geological formation shall only be selected as a storage site, if under the proposed conditions of use there is no significant risk of leakage, and if no significant environmental or health risks exist.	§ 146.5 Classification of injection wells. (f) Class VI. Wells that are not experimental in nature that are used for geologic sequestration of carbon dioxide beneath the lowermost formation containing a USDW *(Underground Source of Drinking Water)*; or, wells used for geologic sequestration of carbon dioxide that have been granted a waiver of the injection depth requirements pursuant to requirements at § 146.95; […]. § 146.95 Class VI injection depth waiver requirement [..] (a) In seeking a waiver of the requirement to inject below the lowermost USDW, the owner or operator must submit a supplemental report concurrent with permit application. The supplemental report must include the following, (1) A demonstration that the injection zone(s) is/are laterally continuous, is not a USDW, and is not hydraulically connected to USDWs; does not outcrop; […]	21. Key objects of work program (1) In addition to the requirements set out in section 148, the key objects of the work program applying to the holder of an exploration permit are— […] (d) to ensure that greenhouse gas sequestration exploration is carried out in a manner that— […] (ii) protects public health and the environment from the impact of greenhouse gas sequestration exploration. 94. Content of injection and monitoring plan An injection and monitoring plan must include— […] (b) details of physical, hydrological, geological, chemical and biological conditions of the land in the licence area for the purposes of developing a baseline for managing and monitoring any change to those

		(2)[…] The report shall further characterize the regional fracture properties and contain a demonstration that such fractures will not interfere with injection, serve as conduits, or endanger USDWs. (b) To inform the Regional Administrator's decision on whether to grant a waiver of the injection depth requirements […] the Director must submit […] documentation of the following: (1) An evaluation of the following information as it relates to siting, construction, and operation of a geologic sequestration project with a waiver: […] (vi) Planned needs, potential and/or future use of USDWs and non-USDWs in the area; § 146.82 Required Class VI permit information. […] (a)(5) Maps and stratigraphic cross sections indicating the general vertical and lateral limits of all USDWs, water wells and springs within the area of review, their positions relative to the injection zone(s) and the direction of water movement, where known;	conditions; […] (h) an assessment of the effect any leakage a greenhouse gas substance might have on public health, the environment and other resources; 96. Approval of injection and monitoring plan (1) The Minister must not approve an injection and monitoring plan unless he or she is satisfied that— […] (b) the use of the underground geological storage formation for the injection and permanent storage of greenhouse gas substances will not present a significant risk of contaminating or sterilizing other resources within the license area; […] (d) subject to section 97, the injection and permanent storage of the greenhouse gas substance will not present a risk to public health or the environment 97. Risk to the environment (1) For the purposes of determining whether the injection and permanent storage of a greenhouse gas substance will present a risk to the

		(6) Baseline geochemical data on subsurface formations, including all USDWs in the area of review; […] (19) Proposed emergency and remedial response plan required by § 146.94(a);	environment, the Minister must, within 21 days of receiving an injection and monitoring plan for approval, provide a copy of the proposed plan to— (a) the Minister administering the Environment Protection Act 1970; (b) the Minister administering the Water Act 1989; (c) the Environment Protection Authority. (2) A person or body referred to in subsection (1) may make a recommendation that the injection and monitoring plan not be approved or be approved subject to conditions if the person or body is of the opinion that— (a) the work that is proposed to be carried out under the plan will present a risk to the environment; or (b) the applicant's proposed risk management plan in relation to the environment is inadequate; or (c) the applicant's proposed monitoring and verification plan, including the estimated cost of carrying out monitoring and verification activities after surrendering the greenhouse gas injection and monitoring license, is inadequate.

Risk assessment constraints	Annex I Step 3.3: Risk assessment The risk assessment shall comprise, inter alia, the following: 3.3.1. Hazard characterization 3.3.2. Exposure assessment 3.3.3. Effects assessment 3.3.4. Risk characterization Comment: Nothing specific to Groundwater protection is laid out in the guidelines for risk assessment. The general idea of the methodology is to prevent leakages and any significant irregularity (Article 1&2). The protection of groundwater is not explicit but is included in the definition of significant irregularities: "Any irregularity in the injection or storage operations or in the condition of the storage complex itself, which implies the risk of a leakage or risk to the environment or human health"	Comment: No risk assessment per se required by the proposal. The requirement is more a demonstration that no fluids will penetrate into a USDW. There seems to be no tolerance for a risk.	209. Operation plan to be prepared Before carrying out any greenhouse gas sequestration operation, the holder of the authority under which the operation is to be carried out must give the Minister an operation plan— (a) that identifies the risks of injury or damage that the operation may pose to the environment, to any community, person, land user, land or property in the vicinity of the operation; and (b) that specifies what the holder of the authority will do to eliminate or minimize those risks; and (c) that specifies what the holder of the authority will do to rehabilitate the land that will be affected by the operation;
Monitoring constraints	Article 13 1. Purpose of monitoring (b) detecting significant irregularities (source-transfer) (c) detecting migration of CO2 (transfer)	§ 146.89 Mechanical integrity. (a) A Class VI well has mechanical integrity if: (1) There is no significant leak in the casing, tubing or packer; and (2) There is no significant fluid	

	(d) detecting leakage of CO2 (transfer) (e) detecting significant adverse effects for the surrounding environment, including in particular on drinking water, for human populations, or for users of the surrounding biosphere (target)	movement into a USDW through channels adjacent to the injection well bore. (c) At least once per year, the owner or operator must use one of the following methods to determine the absence of significant fluid movement under paragraph (a)(2) of this section: (1) A tracer survey such as oxygen-activation logging; (2) A temperature or noise log; or § 146.90 Testing and monitoring requirements. The owner or operator of a Class VI well must prepare, maintain, and comply with a testing and monitoring plan to verify that the geologic sequestration project is operating as permitted and is not endangering USDWs. […] Testing and monitoring associated with geologic sequestration projects must, at a minimum, include: […] (d) Periodic monitoring of the groundwater quality and geochemical changes above the confining zone(s) that may be a result of carbon dioxide movement	

		through the confining zone or additional identified zones: § 146.93 Post-injection site care and site closure. (b) The owner or operator shall monitor the site following the cessation of injection to show the position of the carbon dioxide plume and pressure front and demonstrate that USDWs are not being endangered. (b)(1) Following the cessation of injection, the owner or operator shall continue to conduct monitoring as specified in the Director-approved post-injection site care and site closure plan for at least 50 years or for the duration of the alternative timeframe approved by the Director […]. The monitoring must continue until the geologic sequestration project no longer poses an endangerment to USDWs […]. (b)(3) Prior to authorization for site closure, the owner or operator must submit to the Director a demonstration, based on monitoring and other site-specific data, that no additional monitoring is needed to assure that the geologic sequestration project does not pose an endangerment to USDWs. (e) After the Director has authorized	

		site closure, the owner or operator must plug all monitoring wells in a manner which will not allow movement of injection or formation fluids that endangers a USDW.	
Remediation constraints	Article 16 1. Member States shall ensure that in the event of leakages or significant irregularities, the operator immediately notifies the competent authority, and takes the necessary corrective measures, including measures related to the protection of human health. 3. The competent authority may at any time require the operator to take the necessary corrective measures, as well as measures related to the protection of human health. These may be additional to or different from those laid out in the corrective measures plan. The competent authority may also at any time take corrective measures itself.	*Corrective action* means the use of Director approved methods to ensure that wells within the area of review do not serve as conduits for the movement of fluids into underground sources of drinking water (USDW). § 146.84 Area of review and corrective action. (b) The owner or operator of a Class VI well must prepare, maintain, and comply with a plan to delineate the area of review for a proposed geologic sequestration project, periodically reevaluate the delineation, and perform corrective action that meets the requirements of this section and is acceptable to the Director. § 146.94 Emergency and remedial response. (a) As part of the permit application, the owner or operator must provide the Director with an emergency and remedial response plan that describes actions the owner or operator must take to address movement of the injection or	

		formation fluids that may cause an endangerment to USDW during construction, operation, and post-injection site care periods.[…] (b) If the owner or operator obtains evidence that the injected carbon dioxide stream and associated pressure front may cause an endangerment to a USDW, the owner or operator must: (1) Immediately cease injection; (2) Take all steps reasonably necessary to identify and characterize any release; (3) Notify the Director within 24 hours; and (4) Implement the emergency and remedial response plan approved by the Director. (c) The Director may allow the operator to resume injection prior to remediation if the owner or operator demonstrates that the injection operation will not endanger USDWs.	
Geographical constraints	Article 4.1: Member States shall retain the right to determine the areas from which storage sites may be selected pursuant to the requirements of this Directive. This includes the right of Member States not to allow for any storage in parts or in the whole of		195 Greenhouse gas sequestration operations on water authority land (1) In this section, water authority means— (a) a person who holds a water

	their territory.		licence or a water and sewerage licence under the Water Industry Act 1994; or (b) an Authority that has a water district or a sewerage district under the Water Act 1989. (2) A person must not carry out any greenhouse gas sequestration operation on any land that is owned, vested in or managed or controlled by a water authority without the written consent of the water authority. Penalty: 240 penalty units. (3) A person must not carry out any greenhouse gas sequestration operation that involves work at a depth of more than 0·75 metres below any land that is within 100 metres of— (a) a waterway that is owned by, vested in or managed or controlled by a water authority; or (b) any main drains, sewers, aqueducts, channels or pipelines of a water authority— without the written consent of the water authority. Penalty: 240 penalty units.
Construction requirements	Nothing prescriptive in the directive.	§ 146.86 Injection well construction requirements.	

		(a) General. The owner or operator must ensure that all Class VI wells are constructed and completed to: (1) Prevent the movement of fluids into or between USDWs or into any unauthorized zones; […] (b) Casing and Cementing of Class VI Wells. […] (2) Surface casing must extend through the base of the lowermost USDW and be cemented to the surface through the use of a single or multiple strings of casing and cement.	
Other constraints	Source: Requirements that the CO2 stream should not pose a significant risk to the environment or human health « Any such injection is subject to the provisions of Community legislation on the protection of groundwater, and must be in accordance with Article 4(1)(b) of Directive 2000/60/EC and with Directive 2006/118/EC of the European Parliament on of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. Amendment of Directive 85/337/EEC	§ 146.88 Injection well operating requirements. (a) Except during stimulation, the owner or operator must ensure that injection pressure does not exceed 90 percent of the fracture pressure of the injection zone so as to assure that the injection does not initiate new fractures or propagate existing fractures in the injection zone(s). In no case may injection pressure initiate fractures in the confining zone(s) or cause the movement of injection or formation fluids that endangers a USDW. […]	9 Relationship to certain other Acts If this Act makes provision in relation to a matter and provision is also made in relation to that matter by, or under, the Dangerous Goods Act 1985, the Environment Protection Act 1970, the Occupational Health and Safety Act 2004 or the Water Act 1989, the provision made by this Act— (a) if not inconsistent with that other provision, must be observed in addition to that other provision; and (b) if inconsistent with that other

	(environmental impact assessment) the following points shall be added: Storage sites pursuant to Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009 on the geological storage of carbon dioxide In particular: The environmental impact assessment will identify, describe and assess in an appropriate manner, in the light of each individual case and in accordance with the Articles 4 to 11, the direct and indirect effects of a project on the following factors: - soil, water, air, climate and the landscape, 2. The information to be provided by the developer in accordance with paragraph 1 shall include at least: - a description of the project comprising information on the site, design and size of the project, - a description of the measures envisaged in order to avoid, reduce and, if possible, remedy significant adverse effects, - the data required to identify and assess the main effects which the project is likely to have on the environment	(b) Injection between the outermost casing protecting USDWs and the well bore is prohibited.	provision, is, to the extent of the inconsistency, of no force or effect and that other provision prevails. 304 Transitional provision—Water Act 1989 Nothing in this Act affects the operation of a licence, permit or other authority issued under the Water Act 1989 that was in force immediately before the commencement of section 16 of this Act.

A.2 OTHER TEXTS CITED IN CHAPTER 5

Water Framework Directive

Article 1

Purpose

The purpose of this Directive is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater which:

[…]

aims at enhanced protection and improvement of the aquatic environment, inter alia, through specific measures for the progressive reduction of discharges, emissions and losses of priority substances and the cessation or phasing-out of discharges, emissions and losses of the priority hazardous substances;

'Basic measures' are the minimum requirements to be complied with and shall consist of:

[…]

(j) a prohibition of direct discharges of pollutants into groundwater […].

[Member States] may also authorize, specifying the conditions for:

[…]

Injection of carbon dioxide streams for storage purposes into geological formations which for natural reasons are permanently unsuitable for other purposes, provided that such injection is made in accordance with Directive 2009/31/EC […].

Provided such discharges do not compromise the achievement of the environmental objectives established for that body of groundwater.

Article 7

Waters used for the abstraction of drinking water

[…]

3. Member States shall ensure the necessary protection for the bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water. Member States may establish safeguard zones for those bodies of water.

7. Member States will not be in breach of this Directive when:

- *failure to achieve good groundwater status, good ecological status or, where relevant, good ecological potential or to prevent deterioration in the status of a body of surface water or groundwater is the result of new modifications to the physical characteristics of a surface water body or alterations to the level of bodies of groundwater, or*

- *failure to prevent deterioration from high status to good status of a body of surface water is the result of new sustainable human development activities*

and all the following conditions are met:

a) *all practicable steps are taken to mitigate the adverse impacts on the status of the body of water;*

b) *the reasons for those modifications or alterations are specifically set out and explained in the river basin management plan required under Article 13 and the objectives are reviewed every six years;*

c) *the reasons for those modifications or alterations are of overriding interest and/or the benefits to the environment and to society of achieving the objectives set out in paragraph 1 are outweighed by the benefits of the new modifications or alterations to human health, to the maintenance of human safety or to sustainable development, and*

d) *the beneficial objectives served by those modifications or alterations of the water body cannot for reasons of technical feasibility or disproportionate cost be achieved by other means, which are a significantly better environmental option.*

Environmental Liability Directive

> *"water damage, which is any damage that significantly affects the ecological, chemical and/or quantitative status and/or ecological potential, as defined in Directive 2000/60/EC, of the waters concerned, with the exception of adverse effects where Article 4(7) of that Directive applies".*

> *Article 5*
>
> *Preventive actions*
>
> *Where environmental damage has not yet occurred but there is an imminent threat of such damage occurring, the operator shall, without delay, take the necessary preventive measures.*
>
> *[...]*

Where 'preventive measures' means:

> *“any measures taken in response to an event, act or omission that has created an imminent threat of environmental damage, with a view to preventing or minimising that damage”.*
>
> *Article 6*
>
> *Remedial action*
>
> *Where environmental damage has occurred the operator shall, without delay, inform the competent authority of all relevant aspects of the situation and take:*
>
> *all practicable steps to immediately control, contain, remove or otherwise manage the relevant contaminants and/or any other damage factors in order to limit or to prevent further environmental damage and adverse effects on human health or further impairment of services and*
>
> *the necessary remedial measures, in accordance with Article 7.*
>
> *[…]*

Where 'remedial measures' means:

> *“any action, or combination of actions, including mitigating or interim measures to restore, rehabilitate or replace damaged natural resources and/or impaired services, or to provide an equivalent alternative to those resources or services as foreseen in Annex II.”*
>
> *ANNEX II*
>
> *REMEDYING OF ENVIRONMENTAL DAMAGE*
>
> 1. *Remediation of damage to water or protected species or natural habitats*
>
> *Remedying of environmental damage, in relation to water or protected species or natural habitats, is achieved through the restoration of the environment to its baseline condition by way of primary, complementary and compensatory remediation, where:*
>
> a) *'Primary' remediation is any remedial measure which returns the damaged natural resources and/or impaired services to, or towards, baseline condition;*
>
> b) *'Complementary' remediation is any remedial measure taken in relation to natural resources and/or services to compensate for the fact that primary remediation does not result in fully restoring the damaged natural resources and/or services;*
>
> c) *'Compensatory' remediation is any action taken to compensate for interim losses of natural resources and/or services that occur from the date of damage occurring until primary remediation has achieved its full effect;*

d) 'interim losses' means losses which result from the fact that the damaged resources and/or services are not able to perform their ecological functions or provide services to other natural resources or to the public until the primary or complementary measures have taken effect. It does not consist of financial compensation to members of the public.

Where primary remediation does not result in the restoration of the environment to its baseline condition, then complementary remediation will be undertaken. In addition, compensatory remediation will be undertaken to compensate for the interim losses.

South-Africa National Water Act

Purpose of Act

The purpose of this act is to ensure that the nation water resources are protected, used, developed, conserved, managed and controlled in ways which take into account amongst other factors

[…]

(h) reducing and preventing pollution and degradation of water resources

CHAPTER 3

PROTECTION OF WATER RESOURCES

[…]

Part 4: Pollution prevention

Part 4 deals with pollution prevention and in particular the situation where pollution of water resources occurs or might occur as a result of activities on land. The person who owns, controls, occupies or uses the land in question is responsible for taking measures to prevent pollution of water resources. If these measures are not taken, the catchment management agency concerted may itself do whatever is necessary to prevent the pollution or to remedy its effects, and to recover all reasonable costs from the persons responsible for the pollution

Prevention and remedying effects of pollution

[…]

(2) The measures […] may include measures to

(a) cease, modify or control any act or process causing the pollution;

(b) comply with any prescribed waste standard or management practice;

(c) contain or prevent the movement of pollutants;

(d) eliminate any source of the pollution;

(e) remedy the effects of the pollution; and

(f) remedy the effects of any disturbance to the bed and banks of a watercourse.

[…]

CHAPTER 4

USE OF WATER

[…]

Part 1: General Principles

This Part sets out principles for regulating water use. Water use is defined broadly, and includes taking and storing water, activities which reduce stream flow, waste discharges and disposals, controlled activities (activities which impact detrimentally on a water resource), altering a watercourse, removing water found underground for certain purposes, and recreation. In general a water use must be licensed unless it is listed in Schedule I, is an existing lawful use, is permissible under a general authorization, or if a responsible authority waives the need for a licence. The Minister may limit the amount of water which a responsible authority may allocate. In making regulations the Minister may differentiate between different water resources, classes of water resources and geographical areas.

Part 5: Controlled activities

This Part allows the Minister to regulate activities having a detrimental impact on water resources by declaring them to be controlled activities. Four such activities – irrigation using waste or water containing waster from certain sources, modification of atmospheric precipitation, altering the flow regime of a water resource as a result of power generation, and aquifer recharge using waste or water containing waste – are identified in the Act as controlled activities. Provision is made for the Minister to declare other controlled activities as the need arises, but in these cases public consultation is required. Following the identification or declaration of a controlled activity an authorization for that particular category of activity is required under this Act.

Appendix 2: Numerical simulation of leakage and mitigation strategies

In recent years, a significant amount of work has been devoted for improved simulation of interaction with and resident in reservoir rock and fluids. In particular, major commercial reservoir simulators have included options for simulating storage in saline aquifers. For instance, the commercial reservoir simulator ECLIPSE now includes the CO2Store option specifically developed to account for mutual solubility and fluid properties of and .

In addition to the more robust formulation for calculating fluid properties of water as a function of concentration, the CO2Store option also allows i) water to be defined as a component facilitating compositional simulation of this process, ii) diffusion of within water resulting in a more realistic distribution in the water phase, and iii) chemical reaction of water/ system with reservoir rock. However, one of the main shortcomings of all commercial reservoir simulators is that the phase distribution calculations are based on equilibrium conditions. This will result in excessive transfer of to the fluid initially without any content, i.e. water in this case. This lack of ability of such simulators to account for the non-equilibrium transient conditions requires a significant effort to be resolved and is beyond the scope of the current study. Finally, this effect would be more serious when the interaction of three phases of oil, water and are to be studied

A.1 MODEL DESCRIPTION

In this study the ECLIPSE 300 compositional reservoir simulator with CO2Store option is used to simulate leakage from a deep saline aquifer to a shallow groundwater aquifer. The model, with overall dimensions of 2000 m x 1 m x 1100 m, consists of three geological layers with two aquifers: one deep aquifer section at 1100 m, a shallow aquifer at 100 m with a thickness of 100 m for the groundwater section and a homogenous rock layer (aquitard), located between the two aquifers, with a leakage path through it. Figure A.1 shows a schematic diagram of this simplified 2D model. Based on the injection strategies investigated here, different vertical wells were completed through the whole formations and their positions were fixed for all. The leakage pathway was considered as an improperly abandoned well 433.34 m away from the injection well and modelled as a porous medium with a much higher permeability compared to the aquifer permeability.

The initial deep saline aquifer pressure and temperature, at 1100 m depth, were 117 bar and 45ºC, respectively. The two aquifers were isotropic with permeability values equal to 50 mD. The leakage path (well) permeability was 500 mD in all directions and that of the aquitard region was 0 mD, Figure A.1. The porosity for all formation was the same and equal to 0.2. A constant pressure boundary was imposed on the system by setting up four numerical aquifers.

The aquifer brine was considered with a moderate salt concentration of 0.033 mole fraction. The salt was assumed to stay in the liquid phase (no precipitation). The gas density was obtained from the Peng-Robinson cubic equation of state tuned to give an accurate SC- density. The brine density was first approximated by pure water density in line with Kell and Whalley (1975) and then corrected for salt and effects using Ezrokhi's method (Zaytsev and Aseyev, 1992). Phase viscosity values were obtained using either the Lorentz-Bray-Clark or the Pedersen et al. method based on Stokes-Einstein equation at aquifer's initial temperature and pressure conditions, the - brine diffusion coefficient was estimated as 6.2.10^{-}/s.

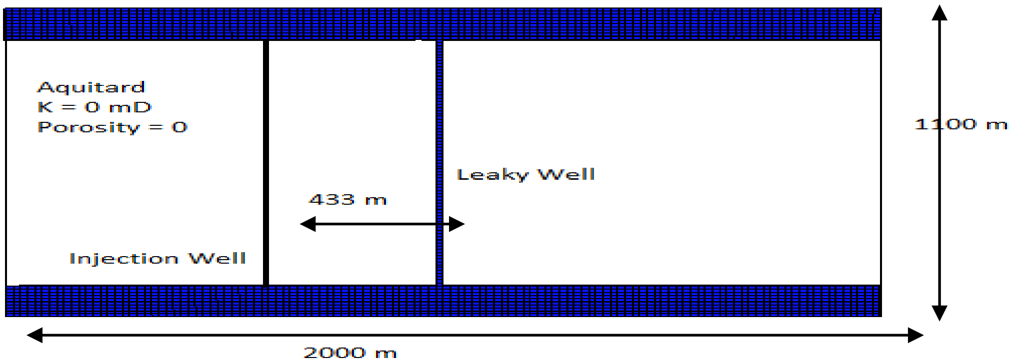

Figure A.1: A schematic diagram of the 2D model considered in this study.

A.2 SENSITIVITY ANALYSIS

A 40 year (supercritical) injection phase (with leakage consideration) followed by a 100 year post-injection period was modelled as the base case for a total simulation time of 140 years.

After developing a base case model, sensitivities were carried out by altering the aquifer pressures to observe the impact on the rate of leakage. Four different mitigation strategies were adopted: (i) brine production from the deep saline aquifer; (ii) creation of a hydraulic barrier through water injection in the overlying aquifer; (iii) combination of the first two strategies mentioned, and finally (iv) reduction of injection rate.

Sensitivity analysis on the groundwater permeability relative to the saline aquifer was also carried out by doubling the groundwater aquifer permeability (i.e., from 50 mD to 100 mD). The result gave a 0.25 % increase in leakage rate at the early time period compared to the base case. Other aquifer properties and simulation input parameters such as salinity, / , dip angle, gas-water relative permeability curves, hysteresis, temperature, groundwater aquifer size relative to the deep saline aquifer were not varied in order to focus on the main objective of the case study, although in practice, they can also contribute to the error involved in the simulation result.

Deep Saline Aquifer Pressure Reduction

Vertical well(s) were included in the base case model in order to produce brine from the deep saline aquifer using the aquifer bottom-hole pressure as the control limit. Three scenarios were considered by varying the water production period for one or two water production wells.

Increasing Groundwater Pressure

Freshwater was injected into the groundwater aquifer with a constant total surface flow rate of 20,000 /day. The scenarios considered included cases in which the number and the bottom-hole pressure control limits of the water production wells were varied (one or two wells).

Reducing Saline Aquifer Pressure and Increasing Groundwater Pressure

A combination of the two strategies explained above was carried out by injecting freshwater into the groundwater horizon and simultaneously producing brine in the saline aquifer.

Reducing Injection Rate

In this leakage mitigation strategy, the injection rate in the base case was gradually reduced from 15000 /day to 8000 /day.

A.3 SIMULATION RESULTS AND DISCUSSION

Base Case

In the base case, was observed to leak from the saline aquifer to the aquitard after 10 years of injection and was noticed on the surface 8 years after the start of leak (this helped to determine the time for the implementation of the mitigation strategy) with a maximum surface leakage rate of 1214.5 /day which represents 8.1% of the injection rate. The red curve in Figure A.2 shows the rate of leakage in the groundwater aquifer. The leakage rate at the surface dropped initially as a result of dissolution into groundwater and thereafter started to increase gradually as the diffusion increases.

The pressure of the groundwater aquifer increased sharply during injection period due to compression and then very gradually decreased with time (when injection was halted) as a result of leakage and slow diffusion into the underlying aquifer as shown by the green curve in Figure A.2. The pressure reduction will become more significant in a longer time scale.

Effects of Reducing Deep Saline Aquifer Pressure

In this leakage mitigation strategy, the pressure of the saline aquifer was reduced by allowing water production from the saline aquifer. Figure A.3 shows the surface gas leakage rate in standard cubic meter per day (/day) on the left y-axis and the pressure in bars on the right y-axis for the case with one producing well being opened after 13 years of injection and continued its production for the whole 100 years of simulation considered after 40-years of injection period. The maximum leakage rate of was drastically reduced from 8.1% in the base case to 2.3% at the early time period when the aquifer pressure was reduced. In this scenario, the leakage rate was then further reduced to almost zero, as evidenced by the red curve in Figure A.3. migration towards the producer increased rapidly thereby reducing the amount of that escaped through the leakage pathway. The water producer(s) must be carefully positioned and completed to avoid or delay free coning. The trade-off in this strategy was between leakage into groundwater and the amount that would be reproduced back to the surface through the producer.

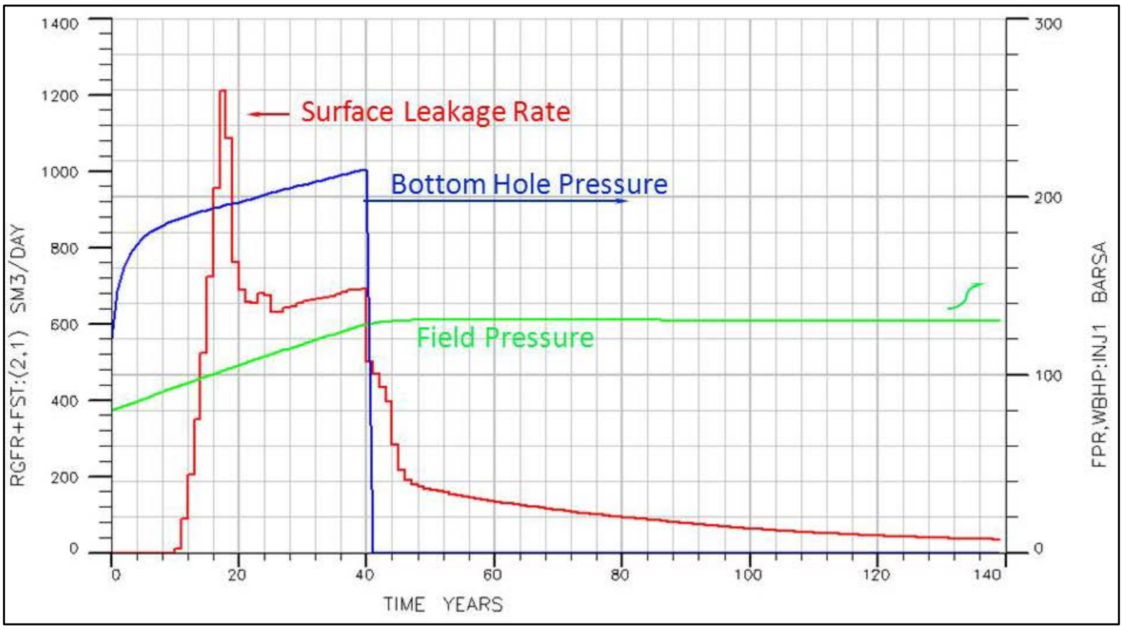

Figure A.2: Surface leakage flow rate (/day) and pressure (bar) profiles versus time, Base case model.

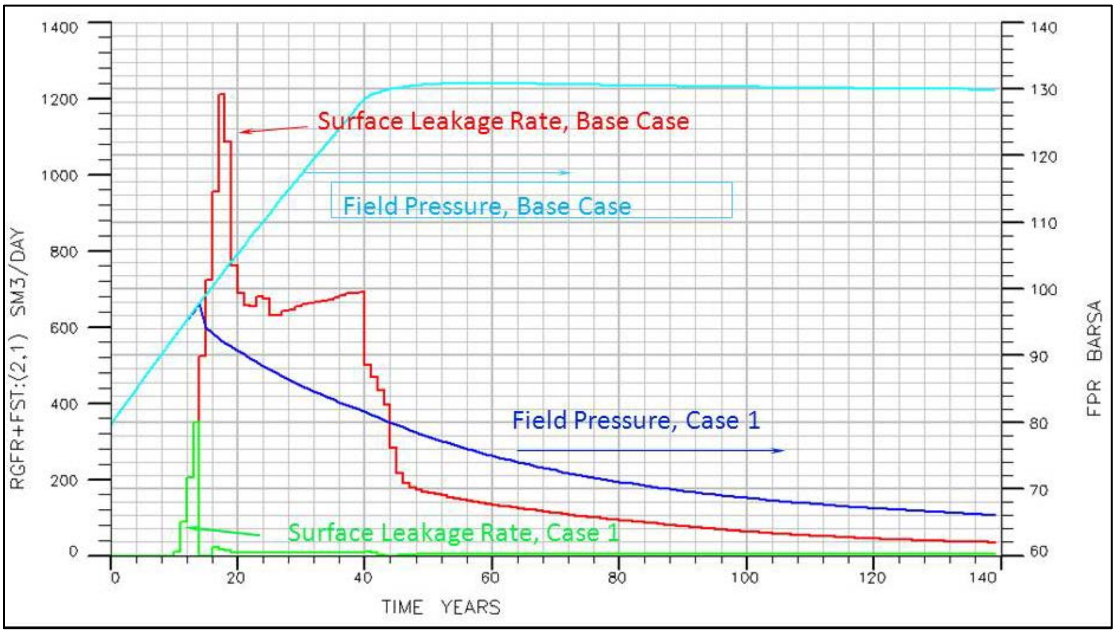

Figure A.3: Comparison of the surface leakage rate (/day) and pressure (bar) between the base case and case 1 of the Deep saline aquifer pressure reduction.

Effects of Increasing Groundwater Pressure

A significant difference in the leakage rates was observed for the Increasing Water Pressure scenarios considered in this study.

This is due to the delay in the frontal displacement and pressure communication over the leakage point. For the case of one well opened after 13 years of injection and continued its production for the whole 100 years of simulation considered after 40-years of injection period, the maximum leakage percentage reduced from 8.1% (base case) to 3.3% and leakage arrival time into the groundwater was observed at 32.5 years compared to 18 years for the base case**.**

The outcome of this strategy was not impressive, especially before the termination of injection and towards the end of the storage period, due to the low bottom hole pressure (BHP) target that was initially specified in the model for the groundwater horizon. Further sensitivity analysis was then performed on the BHP limit for the groundwater. The formation fracture pressure is crucial in this scenario and will greatly influence the viable BHP limit in reality. However, the sensitivity results suggested that injection of freshwater at 180 bar will give sufficient force to overcome leakage to a reasonable extent, irrespective of its buoyancy. With this approach, the maximum leakage rate was 0.93%, which is an indication of the fact that the BHP limit is the primary determinant of the rate of leakage, followed by well placement.

Reducing Saline Aquifer Pressure and Increasing Groundwater Pressure

The combined strategy, whereby freshwater was injected into the groundwater horizon at the same time as producing brine from the saline aquifer, resulted in no surface leak being observed. The location of the leaky path must be known for accurate water injection well placement in order to achieve this outcome.

Effects of Reducing Injection Rate

From simulation results it was evident that the higher the rate of injection into the saline aquifer, the higher the subsequent rate of leakage into the groundwater. In addition, the proximity of the injection well and the leakage pathway also contributes to the rate of leakage and the arrival time of in the groundwater. The latter was acknowledged but not investigated further. The results of the sensitivity analysis carried out on the injection rate are summarized in Table A.1.

Table A.1: Maximum leakage rate at various injection rates.

Case Index	arrival time @ surface (years)	injection rate (/d)	Maximum Leakage rate (/d)	Percentage leakage (%)
1	25.1	8000	605.8	7.6
2	24.0	9000	658.0	7.3
3	23.0	10000	785.5	7.9
4	20.0	13000	1144.9	8.8

A.4 CONCLUSIONS

From the four leakage mitigation scenarios examined here, the result obtained indicate that the combination of saline aquifer pressure reduction and groundwater pressure increase is the best mitigation strategy against leakage. In addition, having more than one well for controlling leakage can help continue to prevent/reduce leakage in the event that one of the well fails, although this approach has a cost implication.

Pressurizing groundwater to reduce/stop leakage and flow from the deep saline aquifer has the advantage of increasing the pressure and the supply of potable water but the question would be the availability, treatment and compatibility of the injected water with the water in situ to avoid altering the water quality. If these conditions are met then this strategy would be preferable compared to reducing the saline aquifer pressure, as production of brine from the deep saline aquifer is associated with production of either dissolved or free (plume).

Reducing the injection rate will prolong the injection phase of the project; this may necessitate the use of multiple wells distributed within the field and further simulation in order to understand dynamics and leakage in this situation.

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