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Abstract

Nowadays, we are observing a continuous rise in trends of greenhouse gasses' concentration in the atmosphere, especially of carbon dioxide, and this is, in great part, attributable to human activities. The first detrimental effects on climate have already been observed and ever more long-term changes in weather patterns should be expected if no concrete action to contrast these trends is put in practice. The scientific community is thus suggesting innovative and practical solutions for both mitigating climate change and adapting to its impacts: carbon capture and storage (CCS) is one such option. CCS involves capturing carbon dioxide (CO_2) from power plants, industrial activities and any other sources of CO_2 and storing it in a geological formation. The appeal of this technique resides in the fact that CCS is able to combine the use of fossil fuels, on which our society still relies a lot, with the environmental exigency to cut carbon dioxide's emissions. However, despite the interesting mitigation option offered by CCS, there is the impelling need, as for any other human activity, to assess and manage risk; this work is intended to do so.

The focus is, more precisely, on marine environmental risk posed by CO_2 leakages, as how this risk should be addressed still represents a largely debated topic. Specific risks can be associated to each of the stages of a CCS system (capture, transport and storage). The focus of this work is on the subsea engineering system, thus, offshore pipelines (transport) and injection / plugged and abandoned wells (part of the storage).

The aim of this work is to start approaching the development of a complete and standardized practical procedure to perform a quantified environmental risk assessment for CCS, with reference to the specific activities mentioned above. Such an effort would be of extreme relevance not only for companies willing to implement CCS, as a methodological guidance, but also, by uniformizing the ERA procedure, to begin changing people's perception about CCS, that happens to be often discredited due to the evident lack of systematized methods to assess the impacts on the marine environment.

The backbone structure of the framework developed sees the integration of ERA's main steps, which are the problem formulation, exposure assessment, effect assessment and risk characterization, and those belonging to the well-known quantified risk assessment (QRA). This, in practice, meant giving relevance to the identification of possible hazards, before the fate of CO_2 in seawater could be described (exposure assessment), and estimating the frequencies of the leakage scenarios, in order to finally describe risk as a combination of magnitude of the consequences and their frequency.

The framework developed by this work is, however, at a preliminary stage, as not every single aspect has been dealt with in the required detail, thus, several alternative options are presented to be used depending on the situation. Further specific studies should address their accuracy and efficiency and solve the knowledge gaps emerged, in order to establish and validate a final and complete procedure.

Regardless of the knowledge gaps and uncertainties, that surely need to be addressed, this preliminary framework can already find some relevance in on field applications, as a non-stringent guidance to perform CCS ERA, and, anyways, it constitutes the foundation of the final framework.

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1. Introduction

This thesis aims to develop an initial framework for the environmental risk assessment of CCS, with specific reference to its activities of subsea transport and injection.

1.1 Background

1.1.1 Climate change and sustainability

Nowadays, we live in an era in which the concept of sustainability is assuming an increasingly fundamental influence on human decisions for future evolution. With the term sustainability, it is meant the development without the compromission of future generations' opportunities (Lenton et al., 2008).

Sustainability first gained attention during the 20th century, when the unforeseen development of some countries, due to the industrial revolution, brought up environmental concerns. Some of these were, for the example, the increase in water demand due to intensive agriculture; the increase in demand for energy; the increase of carbon dioxide (CO_2) concentration in the atmosphere, which, being a greenhouse gas (GHG), is responsible for climate change; etc. Seen this evidence, during the 20th century, for the first time in history, doubts emerged regarding the capability of Earth to withstand and buffer, without negative implications, human development. This is when the consciousness of the necessity to protect the environment first rose.

1.1.2 What is climate change?

"Climate change is a long-term change in the average weather patterns that have come to define Earth's local, regional and global climates" (NASA, n.d.). Climate change could both be attributed to natural variability, meaning natural processes such as solar activity, plate tectonics, etc., but may also be caused by human-induced alterations of the natural environment. There is still uncertainty on the degree and extent of climate changes that can be attributed to human activities, however, there is no doubt that human activity is impacting climate (Lenton et al., 2008). The first concerns regarding climate change were brought to light in the early 19th century, when the greenhouse effect was first discovered. It was by the end of the 19th century that scientists advanced the hypothesis that human-caused emissions of gases and pollution could impact climate, locally and globally. When in the '60s, carbon dioxide's warming effects finally gained scientific consensus (Lenton et al., 2008), it was also agreed that human activities were strongly impacting climate: CO_2 levels have now reached the highest historical levels and the trend is in continuous rise (Figure 1.1).

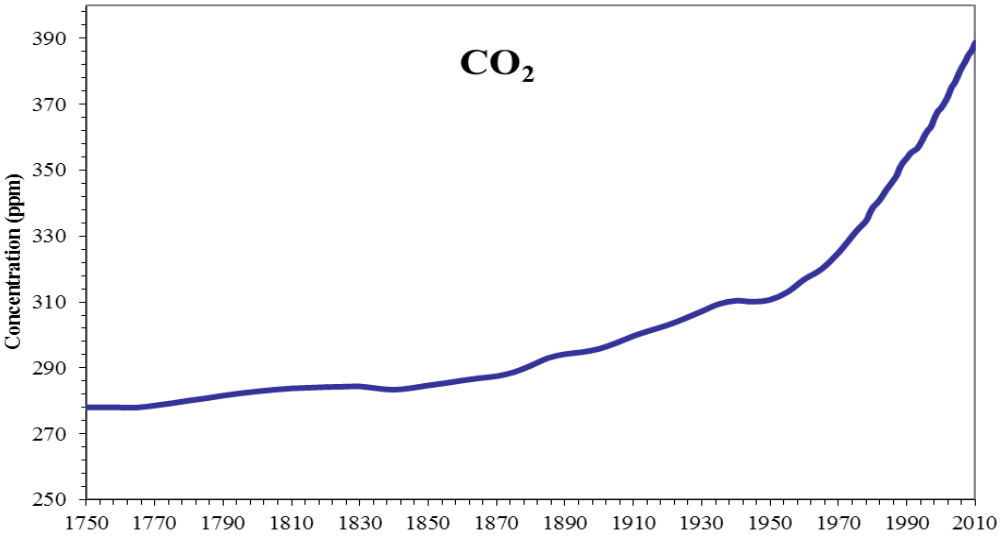

Figure 1.1: Atmospheric concentration of carbon dioxide (ppm) from 1750 to 2010.
From: "Atmospheric Concentration of Carbon Dioxide (Ppm)", 2011, European Environment Agency. CC BY 2.5 DK.
(https://www.eea.europa.eu/data-and-maps/figures/atmospheric-concentration-of-co2-ppm-1)

1.1.3 Greenhouse gas effect and tipping points

The greenhouse effect is the trapping of heat around Earth's surface due to the presence of greenhouse gases (GHGs). Some examples of greenhouse gases include carbon dioxide, methane, nitrous oxides, and water vapor. The infrared radiation, emitted from Earth's surface, is absorbed by these gasses and reradiated back. The greenhouse effect is a natural phenomenon, as GHGs are naturally present in the atmosphere, and it plays a fundamental role in making Earth a habitable planet, by keeping a mean of 15 °C at the surface. However, in the last centuries, humans have been interfering with the Earth's delicate climatic equilibrium, mainly through the burning of fossil fuels, that add carbon dioxide to the air. The concentration of carbon dioxide in Earth's atmosphere has therefore been consistently rising in the last decades and has led to exceptional levels of heat-trapping near the Earth's surface, with consequential temperatures' rise. Moreover, not only the slow environmental changes due to the rising of temperature (correlated to the increase of CO_2 concentration in the atmosphere) worry scientists, but also the possibility of crossing ever more 'tipping points' if no concrete and immediate action to abate the emissions' trends is put in practice (Lenton et al., 2008).

The definition given by Lenton et al. (2008) of a tipping point is a state of the system, the climate systems in our case, that could shift to a new equilibrium by means only of a tiny change. These alterations may not be reversible: think for example at a forest that, due to decreased rainfall, turns into brush. What scares the most is that there is still uncertainty on how tiny the change can be to be able to trigger a tipping point (Lenton et al., 2008). It is thus evident that remediation actions should be then applied immediately to prevent drastic and irreversible changes in our planet's system.

1.1.4 Actions for the reduction of GHGs emissions

Climate change is a global problem that has been addressed by many international and national political regulations. Policies to accomplish the goal of reducing future greenhouse gasses emissions can be divided into several categories listed below*:*

1. *Consumer incentives that reward people for taking steps that reduce their use of fossil fuels and, by extension, reduce their carbon footprint*
2. *Carbon pricing policies that require emitters to pay for their carbon emissions, such as a carbon tax (which would require carbon emitters to pay a tax for each ton of carbon they emit), or a cap-and-trade program (which would require businesses to have a permit for each ton of carbon they emit)*
3. *Regulations that require manufacturers to increase energy efficiency of their products, including automobiles, appliances, and buildings*
4. *Tax incentives that encourage manufacturers to increase the energy efficiency of their products*

(Krosnick & MacInnis, 2020, p. 1)

An example of a well-known international treaty is the Kyoto Protocol (11 December 1997), which entered into force on 16 February 2005 and currently involves 192 parties (UNFCCC, 2022b). It is an extension of the 1992 United Nations Framework Convention on Climate Change (UNFCCC) and it commits developed and developing countries to cut greenhouse gases emissions, based on the scientific consensus reached on the fact that global warming is currently happening and that human actions are playing a major role. Another example is the Paris Agreement, which is a legally binding international treaty on climate change. It involves 196 Parties that participated at COP 21 in Paris (12 December 2015). It entered into force on 4 November 2016 with the goal to limit global warming below 2.0 °C (preferably 1.5 °C) by 2100 (UNFCCC, 2022a).

These political actions are needed as, clearly, climate change is a controversial topic, indeed, the abatement of CO_2 emissions can potentially translate into an economic regression, however, now more than ever, there is the need to be objective: mitigation and adaptation are urgently needed. It is therefore important to identify clear targets and appropriate methods to promptly respond to this new challenge. Here is where the scientific and technical knowledge of engineering scientists is expected to suggest innovative solutions aiming both at mitigating climate change and adapting to its impacts (Lenton et al., 2008). Notice that by mitigation is meant an action aiming at reducing climate change, while with adaptation it is meant an action to limit the impact of climate change.

1.1.5 Greenhouse effect mitigation options

Some mitigation options to contrast the increasing trend of greenhouse gasses emissions are presented by Metz et al. (2005) and are listed below:

- Fuel switching: switching the focus towards renewable energy sources or at least preferring less polluting fuels;
- Energy efficiency: some examples are improving the efficiency of energy consumption in vehicles, reducing buildings’ energy request by improving insulating systems, etc.

- Carbon capture and storage: this technology involves capturing CO_2 from power plants, industrial activities and any other source of CO_2 and storing it in a geological formation. The interest towards this option finds its motivation in the fact that it combines the use of fossil fuels, on which our society still relies a lot, with the environmental exigency to cut carbon dioxide's emissions.

Carbon Capture and Storage is the focus of this work, its technology is therefore further explained, in a generic form, below.

1.2 Carbon capture and storage

A general CCS system is composed by three consequential processes: the capture, the transport and the storage. This chapter is meant to give a general overview of how each of these steps can be approached, from a practical point of view, seen the experience and progressing research deriving from already existing and upcoming CCS projects.

1.2.1 Capture

The purpose of the capture stage is to separate the highest percentage of CO_2 from a gaseous stream. This stream could either be the waste gas of a power / industrial plant, that needs to be purified before being emitted into the atmosphere, or natural gas just extracted that needs to be purified from CO_2 before being immitted into national pipelines (e.g., Sleipner field). The CO_2 stream then needs to be pressurized, so to be transported to the storage site. It is well known that separation techniques are economically demanding, however, high impurities concentrations could themselves negatively impact costs, from the transport point of view. A purity optimum needs therefore to be anyways achieved.

The capture techniques (very simply resumed in Figure 1.2) can be divided into three main categories, based on at what stage of the process the separation takes place; these are post-combustion, pre-combustion and oxy-combustion (Berge et al., 2016). Post-combustion separation is the first CO_2 separation process developed. The separation is realised by means of chemical solutions that create a reversive bond with CO_2 and are thus able to extract it from the stream. For what concerns pre-combustion, it contemplates that the hydrocarbon stream is converted into CO_2 and H_2 before combustion. The reactor is then fed with H_2 only, having already removed the CO_2. This results in having only water vapour as the combustion product. At last, oxy-combustion consists in using pure O_2, extracted from air, as comburent. This guarantees that only CO_2 and water vapour are produced during the combustion, which can be easily separated by condensation. Each of these techniques is further dealt with below.

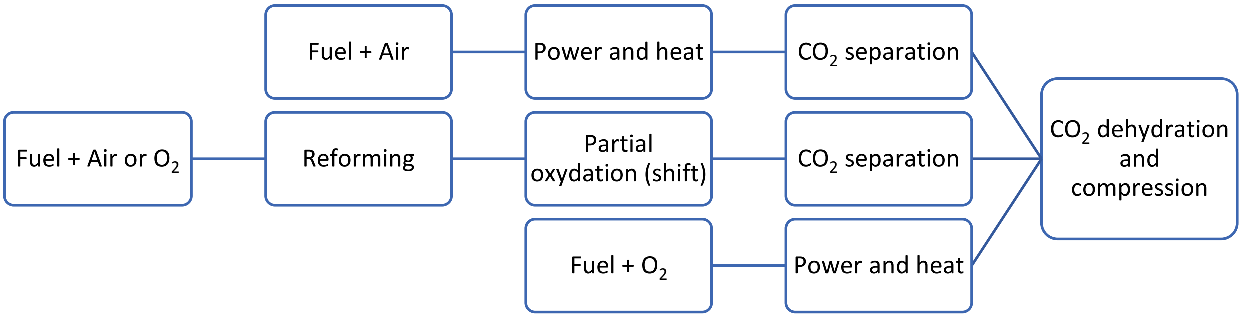

Figure 1.2: Schematic representation of capture techniques: from post-combustion at the top to oxy-combustion at the bottom.
Adapted from: "Carbon capture and storage", by Berge, U., Gjerset, M., Kristoffersen, B., Lindberg, M., Palm, T., Risberg, T., & Skriung, C. S., 2016, Zero Emission Resource Organization (ZERO), p. 13. (https://zero.no/wp-content/uploads/2016/06/carbon-capture-and-storage.pdf)

Post-combustion

This separation method is the most versatile as *"it can be fitted to many different types of emitters – both power plants and industrial plants – and separation equipment can be post-fitted on existing emission sources"* (Berge et al., 2016, p. 16).

The degree of CO_2 removal achieved strictly depends on economic resources available, indeed, as CO_2 concentration in the stream decreases, its removal gets more complicated, thus more expensive. A solution of water and amines can be used as absorption fluid in the absorber: amines form weak bonds with CO_2. This reversible bond consents to remove CO_2 from the stream, in the absorption phase, and to regenerate the amines in the stripping tower. Generally, the degree of CO_2 removal reached with amines is around 85% of the carbon's total concentration in the stream, but as said, higher capture rates can be reached (Berge et al., 2016). Ammonia can also be used instead of amines, and its advantage is that the regeneration process requires less energy.

Pre-combustion

In the pre-combustion separation, the fuel is initially transformed, in presence of water vapour and air, or oxygen, into carbon monoxide (CO) and hydrogen (H_2), which is the classical reforming process (Berge et al., 2016). It requires high temperatures and pressures. The syngas ($CO+H_2$) is then further processed with water into a shift reactor: the output is a CO_2 and H_2 stream. CO_2 is then removed, using amine absorption, and hydrogen is combusted. Despite being a more expensive solution, if compared to the previous one, the CO_2 stream obtained is usually purer and already pressurized, which is a great advantage for the subsequent CCS transport stage (Mocellin, 2013).

Oxy-fuel combustion

Oxy-fuel combustion consists in using pure O_2 as comburent, rather than air (Berge et al., 2016). Only water vapour and CO_2 will be then produced in the combustion, and these can be separated by condensation. Notice that air separation, despite being a consolidated technology, is still very expensive (Mocellin, 2013).

1.2.2 Transport

Once captured, CO_2 needs to be transported to the offshore storage site. Given the high volumes of CO_2 involved in CCS, the only feasible and economic transport options are pipeline and ship (Berge et al., 2016).

Transport via pipelines

Subsea pipelines for the transport of CO_2 are recently gaining increasing attention. There are some applications already, some of which are located (Snøhvit and Sleipner in Table 1.1) or will be located (Norther Lights project (Equinor, 2019)) in Norway.

Pipeline	**Capacity (Mt/yr)**	**Length (km)**	**Diameter (mm)**	**Pressure (bar)**	**Year**
Sleipner	1	160	n/a	n/a	1996
Snøhvit	0.7	153	200 (8’’)	100	2006

n/a - not available

Table 1.1: Main existing CO_2 transport projects for the scope of CCS in the North Sea
From: “Carbon dioxide pipelines for sequestration in the UK: An engineering gap analysis”, by Seevam, P. N., Race, J. M., & Downie, M. J., 2007, The Journal of Pipeline Engineering, 6. Referred in (Serpa et al., 2011, p. 3)

Onshore and offshore pipelines for CO_2 transport have a similar design to that of hydrocarbons’ pipelines. They can travel for hundreds of kilometres, reaching depths of thousands of metres (Mocellin, 2013).

Operative temperature and pressure

The CO_2 physical state that guarantees the most efficient transport by pipeline is the high-density phase (Figure 1.3), thus meaning liquid or supercritical state (dense phase). By efficient transport is meant that minimum values of friction loss along the pipeline, per mass unit of CO_2, are observed.

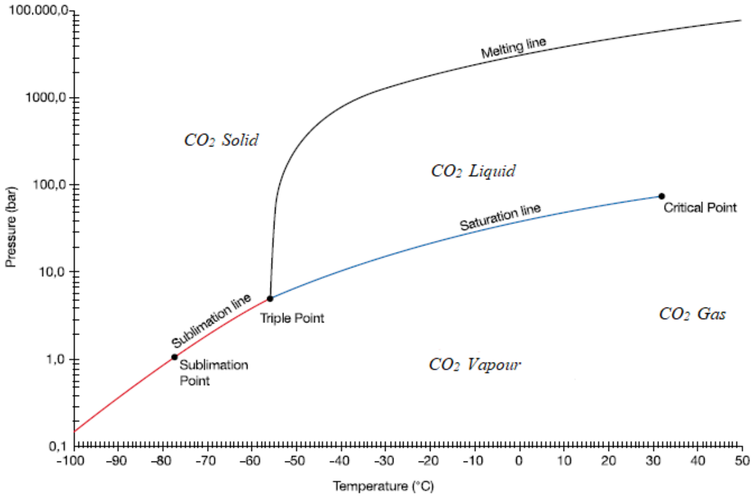

Figure 1.3: Carbon dioxide phase diagram.

The most efficient state of CO_2 for pipeline transport is the dense phase, as densities are high and, if one among pressure or temperature are kept above the critical ones (Table 1.2), there is no risk of phase change. Notice that near the critical point, small changes in temperature or pressure could lead to abrupt changes in the density and the potential formation of two phases, which has drastic implications on the correct functioning of the whole system (Serpa et al., 2011).

Property	**Unit**	**Value**
Molecular weight	g mol^{-1}	44.01
Critical pressure	bar	73.8
Critical temperature	°C	31.1
Critical density	Kgm^{-3}	467
Triple point pressure	Bar	5.2
Triple point temperature	°C	-56.5
Gas density (at 0°C and 1.013 bar)	Kgm^{-3}	1.976
Liquid density (at -20 °C and 19.7 bar)	Kgm^{-3}	1032

Table 1.2: Carbon dioxide properties
From: "Technical and economic characteristics of a CO2 transmission pipeline infrastructure", by Serpa, J., Morbee, J., & Tzimas, E., 2011, European Commission. Joint Research Centre. Institute for Energy., Publications Office of the European Union, p. 8. Copyright 2011 by European Union.
(https://data.europa.eu/doi/10.2790/30861)

Notice that offshore pipelines can withstand pressures up to 300 bars both because they are not near population and also because of the compensative effect of the hydrostatic pressure, which increases with depth (Mocellin, 2013).

Stream composition

The composition of the stream depends on the source from which CO_2 has been extracted and on the capture technique. Impurities could be water vapour, H_2S, N_2, CH_4, O_2, Hg and other hydrocarbon. Composition limit values are reported in Table 1.3, while a general composition example is reported in Table 1.4.

Component	**Concentration limit value, ppm (mol)**
Water, H2O	≤ 30
Oxygen, O2	≤ 10
Sulphur oxides, SOx	≤ 10
Nitrogen oxide/nitrogen dioxide, NOx	≤ 10
Hydrogen sulphide, H2S	≤ 9
Carbon monoxide, CO	≤ 100
Amines	≤ 10
Ammonia, NH3	≤ 10
Hydrogen, H2	≤ 50
Formaldehyde	≤ 20

Component	**Concentration limit value, ppm (mol)**
Acetaldehyde	≤ 20
Mercury, Hg	≤ 0.03
Cadmium, Cd Thallium, Tl	≤ 0.03 (sum)

Table 1.3: Limit values for the composition of carbon dioxide to be stored.
Adapted from: "EL001 Northern Lights—Receiving and permanent storage of CO_2. Plan for development, installation and operation Part II - Impact Assessment", by Equinor, 2019, p. 52.
(https://northernlightsccs.com/wp-content/uploads/2021/03/RE-PM673-00011-02-Impact-Assessment.pdf)

		Coal fired power plant			**Gas fired power plant**		
Component	**Comment**	**Post-combustion**	**Pre-combustion**	**Oxy-fuel**	**Post-combustion**	**Pre-combustion**	**Oxy-fuel**
N_2 / O_2	Non-toxic	0.01	0.03 - 0.6	3.7	0.01	1.3	4.1
H_2S	Flammable, strong odour, extremely toxic at low concentrations	0	0.01 - 0.6	0	0	< 0.01	0
H_2	Non-toxic	0	0.8 - 2.0	0	0	1	0
SO_2	Non-flammable, strong odour	< 0.01	0	0.5	< 0.01	0	< 0.01
CO	Non-flammable, toxic	0	0.03 - 0.4	0	0	0.04	0
CH_4	Odourless, flammable	0	0.01	0	0	2.0	0

Table 1.4: Indicative compositions of CO_2 streams from coal and gas power plants, in % by volume.
Adapted from: "Technical and economic characteristics of a CO2 transmission pipeline infrastructure", by Serpa, J., Morbee, J., & Tzimas, E., 2011, European Commission. Joint Research Centre. Institute for Energy., Publications Office of the European Union, p. 9. Copyright 2011 by European Union.
(https://data.europa.eu/doi/10.2790/30861)

The composition clearly has an influence on the properties of the stream and, consequently, on the design procedures. For example, the critical pressure of the fluid changes if impurities are present, thus, as most impurities are low-boiling, higher pressures might be required to maintain a single-phase supercritical or dense-phase. Furthermore, if H_2 or N_2 are present in the stream, pressure and temperature drops increase and this can not only itself cause damage to materials, but also lead to the formation of hydrate (ice crystals), which can damage the pipeline as well (Serpa et al., 2011).

Ship transport

Nowadays there are a very few CO_2 transport dedicated ships, and their dimensions go from small (1000 m^3) to medium (1500 m^3) (Mocellin, 2013). Equinor (2019) is recently assessing the feasibility of using LPG transport ships, or food industry ships, with higher tank capacity (7500 m^3) and operating conditions of 15 barg and - 26 °C. In any case, the key elements for ship transport are liquefaction, intermediate storage, loading, unloading, that can either happen onshore (e.g., Northern Lights (Figure 1.4)) or offshore.

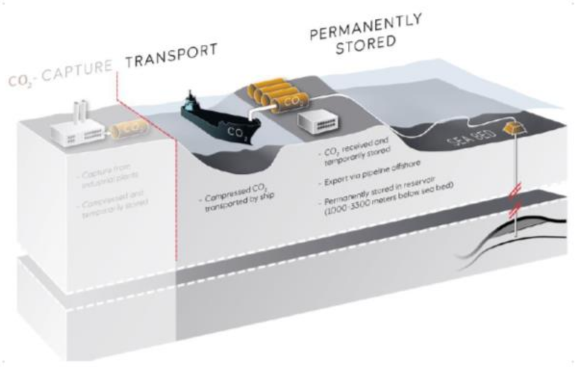

Figure 1.4: Schematic representation of Equinor's Northern Lights project: the unloading of the ship happens onshore. From: "EL001 Northern Lights—Receiving and permanent storage of CO_2. Plan for development, installation and operation Part II - Impact Assessment", by Equinor, 2019, p. 24. (https://northernlightsccs.com/wp-content/uploads/2021/03/RE-PM673-00011-02-Impact-Assessment.pdf)

1.2.3 Storage

The arriving point of the CO_2 transport line is the storage, which takes place in a deep geological formation as sedimentary basins, depleted oil / gas fields, saline formations and coal seams (Serpa et al., 2011). Once injected, CO_2 mixes with the fluids present in the geological storage (formation waters or any residual natural fluids) and migrates upwards due to buoyancy. It is a fundamental prerequisite of any type of CO_2 storage to have an impermeable cap rock formation above: this prevents CO_2 from migrating out (ZEP, 2019). Being unable to migrate upwards, CO_2 spreads sideways under the cap rock. Therefore, this impermeable layer should have a sufficient side extension to contain the spreading of the CO_2 plume (Figure 1.5).

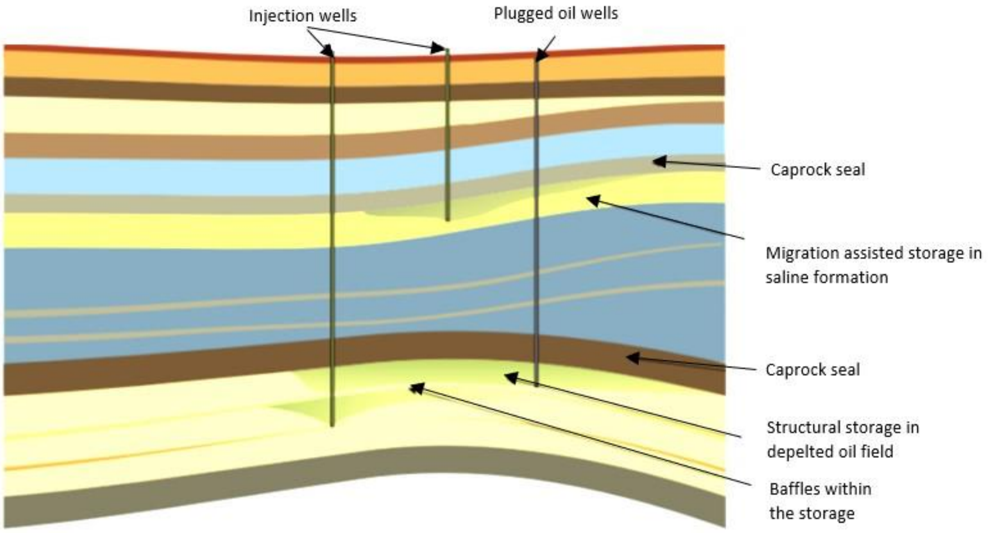

Figure 1.5: Schematic representation of carbon dioxide's storage in a geological formation. Adapted from: "CO_2 Storage Safety in the North Sea: Implications of the CO_2 Storage Directive", by ZEP, 2019. Zero *Emissions Platform, p. 12. (https://zeroemissionsplatform.eu/wp-content/uploads/ZEP-report-CO2-Storage-Safety-in-the-North-Sea-Nov-2019-3.pdf)*

1.3 Environmental risk associated to CCS.

Despite the interesting mitigation option that CCS offers, CCS risk should also be addressed. Past industrial experience has helped in developing necessary safety measures to protect both the operators of the plant and population around. However, how environmental risk associated to CO_2 leakages should be dealt with is still a debated topic, especially for what concerns the marine environment. The focus of this work is therefore on this new burning topic: the risk posed by CCS towards the marine environment. Notice that specific risks can be associated to each of the stages of a CCS system (capture, transport and storage). This work's attention is on leakage scenarios taking place under the sea surface, which could either be related to subsea engineering systems, meaning pipelines (transport) and injection / plugged and abandoned wells (storage). Anyways, the information related to the impact assessment still hold true for reservoir leakages.

In the following paragraph a qualitative overview of the impacts of CO_2 on marine environment is presented, so to let the reader understand why there is a great urgency to address this topic.

1.3.1 Adverse impact of CO_2 on marine environment

When CO_2 is released in seawater, it dissolves (Eq. 1) and forms H_2CO_3, that dissociates into HCO_3^- and H^+ (Eq. 2) that, in turn, reacts with CO_3^{2-} to form HCO_3^-. These reactions' net result is an increase in the concentrations of H_2CO_3, HCO_3^-, H^+, and a decrease of CO_3^{2-} and pH levels (Eq. 3). The chemical balances of these reactions are illustrated below (Kim et al., 2016):

$$CO_2\,(g) \leftrightarrow\ CO_2\,(aq) +\ H_2O \quad [1]$$

$$CO_2\,(aq) +\ H_2O\ \leftrightarrow\ H_2CO_3 \leftrightarrow\ H^+ +\ HCO_3^-\ \leftrightarrow 2H^+ +\ CO_3^{2-} \quad [2]$$

$$pH =\ -\log[H^+]\ [3]$$

As Wallmann et al. (2015) underlines, CO_2 impacts on marine species are '*complex and situation-specific'*. The first evident impact on the species level involves calcifying organisms that have a $CaCO_3$ shell (e.g., corals, coccolithophores, corallaine algae, molluscs, echinoderms, and crustaceans). These organisms are impacted, in the normal production of their shell, not only by the lower availability of CO_3^{2-} ions, but also by the enchanted dissolution of $CaCO_3$ shells (Kim et al., 2016). Apart from calcifying organisms, impacts are recorded also on other species, as low seawater pH can cause "acidosis": *"a pH decrease of the extracellular body fluids, such as blood, haemolymph, or coelomic fluid"* (Wallmann et al., 2015, p. 35), that if uncompensated leads to metabolic depression.

1.3.2 Impacts of seawater acidification on a species level

In this paragraph some examples of impacts on marine species, identified by Kim et al. (2016), are briefly reported:

- Phytoplankton: Kim et al. (2016, p. 142) record alterations in "*growth rates, respiration, carbon fixation, photosynthesis, and C:N:P stoichiometry";*
- Calcifying organisms: not only showed a decrease in the calcification rates, as CO_3^{2-} concentration decreased, but also an increase in shell dissolution;
- Zooplankton: Both calcareous (e.g., foraminifera, pteropods) and non (e.g, copepods) zooplankton showed stress responses to increased CO_2 levels (e.g., reduced egg production and hatching success);
- Bacteria: experiments show that N and P bacterial cycles can be altered by pH changes;
- Marine invertebrates: deep sea marine invertebrates seem to be more affected by CO_2 dissolution, which can cause changes in *"acid–base regulation, calcification, growth, respiration, energy turnover, and mode of metabolism"* (Kim et al., 2016, p. 145);
- Fish: some stress responses recorded are *"decreased sperm motility, motility, fertilization, metabolism, cardiac output, and increased ventilation"* (Kim et al., 2016, p. 145).

Notice that impacts of increased CO_2 in seawater can be recorded also on a marine community level, meaning there can be effects on *"composition, diversity, and relative abundance of phytoplankton and of microbial communities"* (Kim et al., 2016, p. 145).

1.4 Thesis objectives

According to what reported in Section 1.3, there is the evident need to assess and manage marine environmental risk associated to CCS projects. Complete and standardized practical guidelines to perform CCS environmental risk assessment should, therefore, be made available. There are already some existing ones, however, these are not covering in detail the engineering systems of our interest or characterize risk only in a semi-quantitative way. The aim of this work is thus that of start setting the way for the development of a complete and standardized procedure to perform a quantified environmental risk assessment for the engineering systems involved in the activities of subsea transport and storage. Further specific studies should address the accuracy and efficiency of the approaches here proposed and solve the knowledge gaps emerged, in order to establish a final and complete procedure. All the aspects just mentioned are also explained more in-depth during the work itself.

Before moving into the heart of the work, the structure of the thesis is presented as well as some basic concepts on risk.

1.5 Thesis Structure

This work is composed by ten chapters, the first of which was the ‘Introduction’ (Chapter 1) itself, where information regarding the background and scope of the work has been given. The remaining chapters are articulated as follows:

- Chapter 2 - Method and Approach: the approach used to develop the framework is explained, in terms of method used, structure adopted, inspiring reference works and the criterion applied in the review process;
- Chapter 3 - Problem formulation: the goal of the framework is stated out and an overall view of how it will be dealt with in the procedure is presented;
- Chapter 4 - Hazard identification and characterization: potential leakage causes and credible failure scenarios are identified and characterized;
- Chapter 5 - Exposure assessment: alternative approaches to model and analyse the fate of released CO_2 in water, and the subsequent pH spatial distribution, are presented;
- Chapter 6 - Effect assessment: several methods to quantify the degree of impact of CO_2 on the marine environment are reported;
- Chapter 7 - Frequencies estimation: methods to estimate the frequencies of the final failure scenarios are reported, with the assumptions they are based on;
- Chapter 8 - Risk characterization: approaches to determine risk are presented and considerations regarding acceptance criteria are mentioned in the end;
- Chapter 9 - Discussion and recommendations: an overview of what has been done in this work is reported and suggestions for future research are highlighted;
- Chapter 10 - Conclusion: conclusive comments on the whole work itself and main gaps in knowledge are briefly dealt with.

1.6 Basic concepts on risk

Before reporting some risk and risk description definitions, the meaning of some key terms needs to be presented first:

- *Risk source: Element (action, sub-activity, component, system, event, etc.) which alone or in combination with other elements has the potential to give rise to some specified consequences (typically undesirable consequences)*
- *Hazard: A risk source where the potential consequences relate to harm.*
- *Harm: Physical or psychological injury or damage*
- *Damage: Loss of something desirable*
- *Adverse consequences: Unfavorable consequences*
- *Impacts: The effects that the consequences have on specified values (such as human life and health, environment and economic assets)*
- *Severity: The magnitude of the damage, harm, etc*

(SRA, 2018, p. 6)

There are many *qualitative* definitions of risk, as exemplified by the list from the Society of Risk Analysis glossary (SRA, 2018):

1. *Risk is the possibility of an unfortunate occurrence*
2. *Risk is the potential for realization of unwanted, negative consequences of an event*
3. *Risk is exposure to a proposition (e.g., the occurrence of a loss) of which one is uncertain*
4. *Risk is the consequences of the activity and associated uncertainties*
5. *Risk is uncertainty about and severity of the consequences of an activity with respect to something that humans value*
6. *Risk is the occurrences of some specified consequences of the activity and associated uncertainties*
7. *Risk is the deviation from a reference value and associated uncertainties ISO defines risk as the effect of uncertainty on objectives.*

(p. 4)

Examples of quantitative risk descriptions in use are also reported by SRA (2018):

1. *The combination of probability and magnitude / severity of consequences*
2. *The combination of the probability of a hazard occurring and a vulnerability metric given the occurrence of the hazard*
3. *The triplet* (s_i, p_i, c_i)*, where si is the* i^{th} *scenario, pi is the probability of that scenario, and ci is the consequence of the* i^{th} *scenario,* $i = 1, 2, \ldots N$.

4. *The triplet (C’, Q, K), where C’ is some specified consequences, Q a measure of uncertainty associated with C’ (typically probability), and K the background knowledge that supports C’ and Q (which includes a judgment of the strength of this knowledge)*

(p. 4)

With reference to the last definition, notice that probability is a *“measure for representing or expressing uncertainty, variation or beliefs, following the rules of probability calculus”* (SRA, 2018, p. 5). A probability is defined for a specific time interval, sometimes called the mission time.

In this thesis we will be referring to frequency when sometimes also the term probability could have been used. To clarify, a frequency is the expected number of occurrences per time unit, so it applies when the event can occur more than once, while a probability is used if the event may occur only once. If a frequency is sufficiently small, for example less than 0.1, it can be interpreted approximately as a probability (as the probability of more than 1 occurrence is then negligible) (Aven, 2006).

2. Method and approach

2.1 CCS framework development

In recent years, carbon capture and storage has seen a rapid increase in its implementation due to the spreading consciousness of its benefits, from both an environmental point of view, by means of the abatement of GHGs' emissions, and economical point of view, for what concerns the major producers of CO_2. However, this sudden interest towards the mitigation option, for greenhouse gas reduction, offered by CCS is now posing different questions to worldwide risk experts: many are indeed finalizing their studies at finding these answers. The reason behind this is that, as for any other industrial process, there is the impelling need to assess and manage risk, for humans and the environment. As mentioned in the introduction, for what concerns the environmental aspects especially, being CCS such a new-born field of study, it carries the weight of not having worldwide shared and common practical guidelines concerning risk assessment. At the state of the art, some procedures do exist (for example Wallmann et al. (2015)), but usually they have a limited field of applicability and tend to use a semi-quantitative characterization of risk.

Koornneef et al. (2011), already back in 2011, brought out the topic (with reference to the storage part), underlining the absence of a methodological standard to assess whether and how representative scenarios should be modelled to quantitatively estimate risk, and recommending the development of guidelines for risk assessment.

Having set the contest, the driving interest behind the present work is now becoming evident: there is not only the challenge, but the necessity to develop a standardised and robust procedure to perform carbon capture and storage environmental risk assessment.

The structure on which the methodological framework for CCS' environmental risk assessment, that this work aimed at developing, is based upon the results emerged in McMeekin et al. (2020). First of all, the definition, given in the last-mentioned article, of 'methodological framework' is: *"a tool to guide the developer through a sequence of steps to complete a procedure. Methodology is defined as the group of methods used in a specified field, and framework is defined as a structure of rules or ideas"* (McMeekin et al., 2020, p. 2).

McMeekin et al. (2020) identifies three fundamental phases in which the procedure, to build a methodological framework, can be divided into:

- *Phase 1 – identifying evidence to inform the methodological framework: This phase is split into two; the first is identifying previous frameworks or guidance which are used for the foundations of the new methodological framework, the second is identifying new data to help develop the methodological framework.*

  (p. 6)

- *Phase 2 – developing the methodological framework: In this phase the frameworks or guidance identified in Phase 1 are adapted, combined with other guidance and built upon to create the foundations of the new methodological framework.* […] *Once the information*

> *is extracted it should be analysed, synthesised, and grouped or amalgamated into categories to inform the new framework* […].
>
> [The process is iterative:] *"after grouping or amalgamation of the new data, it should be brought back to key experts and the study team for refinement. This iterative approach should be followed until consensus is reached on the proposed methodological framework".*
>
> (pp. 6-7)

- *Phase 3 – evaluate and refine: In this final stage the proposed methodological framework should be evaluated and refined.*

  (p. 7)

The present work is not intended to solve the detail of each knowledge gap that could emerge during the development of a framework, but, at least, to group, and, by this, shed light, on some existing possible ways to perform CCS' risk assessment and point out the aspects that would require better and specific insights. This is the reason why we will refer to the work as a 'preliminary' framework, meant to set a base, a starting point, for future studies oriented towards this direction.

What will thus follow in the next chapters is the result of a literature review regarding existing approaches to characterize environmental risk associated to subsea CO_2 pipelines and injection / plugged and abandoned wells. Overall, the integration and comparison between different points of view has permitted the definition of a preliminary framework's structure for environmental risk assessment associated to CCS' activities of transport and injection, meaning the well in its active and inactive life.

2.2 ERA’s structure and necessary integrations

The preliminary framework, this work is intentioned to develop, in part follows the four phases structure of the general environmental risk assessment (ERA). For each of the phases, some relevant elements have been shortlisted by Vora et al. (2021) and used here to suggest the ERA framework for CCS. The reasons behind the choice of these relevant aspects are extensively explained in the article (Vora et al., 2021): their conclusions have been considered applicable here, being EOR a really close field to CCS. A brief summary is also reported below.

The four phases are defined by Vora et al. (2021) as follows:

> • *Problem formulation: This is the first step in any ERA process where information about goals, hazard sources, contaminants of concern, assessment endpoint and methodology for characterizing exposure and effects is collected for an explicitly stated problem.*
>
> • *Exposure Assessment: It is a process of measuring or estimating the exposure in terms of intensity, space and time in units that can be combined with effects assessment to characterize risk.*
>
> • *Effects Assessment: The purpose of the effect’s assessment is to characterize the adverse effects by a contaminant under an exposure condition to a receptor.*
>
> • *Risk characterization: The process of estimating the magnitude of adverse ecological impacts based on the information collected from exposure and effects assessment.*
>
> (p. 3)

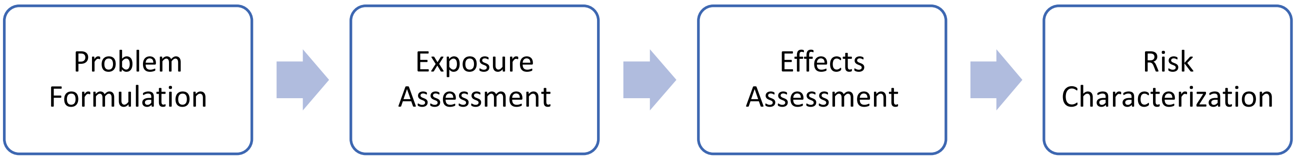

Figure 2.1: Key steps in the environmental risk assessment.

For each one of the steps (Figure 2.1), some significant elements have been identified. Among these, the ones of our interest are the following:

a) Problem Formulation:
   - Management goals: setting the goal;
   - Regulatory context: legislative framework that applies to the aspect analysed (storage / transport / injection);
   - Review of existing site information: guidance on how to select a site and how to collect all the information needed to complete the environmental risk analysis;
   - Contaminants of potential concern (COC): identification of all contaminants which may cause and adverse effect (‘stress’) to the site’s environment. Some examples referred to CO_2 releases in seawater are CO_2 itself, impurities that might be present in

the stream and heavy metals dissolved from the sediments (due to an increase in seawater acidity caused by CO_2 dissolution);

- Factors controlling the stressor: identification of all the factors that affect the spatial distribution of the stressors, which, in the case of CCS, are meant as all those factors that have an influence on, for example, the degree of variation of acidity, induced by a release of CO_2, the degree of dissolved CO_2, etc.;

  With the scope of only showing some examples, these factors could be water currents, the size of the leakage, the velocity of the release, etc.;

- Receptors of concern (ROC): identification of all the organisms that could suffer from the presence of a potential 'stressor' in their habitat. In the context of the framework this means the procedure that needs to be followed to perform this ROCs identification;
- Exposure pathways: identification of the ways by which a ROC can enter in contact with a stressor (water, sediment…);
- Conceptual model: explanation of the connections between key information regarding contaminant sources, their fate through the exposure pathway, their contact with receptors of concern, and how efficiently this is given relevance in the modelling approach;
- Protection goals and acceptable effects level;
- Assessment endpoint: explicit expression of the environmental value (meant as specific fitness level) to be protected, with reference to a precise receptor. Endpoint properties could include population demographics, biomass, genetic variability, physical condition, chemical and biological parameters (i.e., biological effects often used as biomarkers) etc;
- Measurement Endpoints: measure of effects, meant as changes in an assessment endpoint, reported by a ROC. Examples could be NOEC, PNEC, LC_{50}, EC_{50}, etc. thresholds or directly chemical and biological information (e.g., biomarkers).

b) Exposure assessment:

- Stressor information:
  - Release: identification of all the necessary information associated to the release;
  - Dispersion: identification of COC's dispersion patterns and accuracy of the approach used. In our case, the outputs should be the pH spatial distribution, the dissolved CO_2 spatial distribution, etc.;
- Exposure media information: identification of all the useful information related to the exposure pathway. In our case this means, for example, water currents, tides, seawater temperature, salinity etc.

Notice that: the release may not be continuous in case of an accidental release.

c) Effects assessment:

  - Types of effect assessment measures: degree of negative impact on organisms' fitness levels, which can result, for example, in changes in reproduction rates, in death or chemical or biological parameters, etc.;
  - Linkage of measures of effect to an assessment endpoint: how the fitness level of organisms can be measured;
  - Stressor - response analysis: how response results are analysed, which, in other words, means if the results are interpreted in a qualitative /semi-quantitative / quantitative way.

  Notice that: the assessment also needs to account for whether or not the organisms are present in the area at risk at the time of the release.

d) Risk characterization:

  - Risk description: how risk is being defined;
  - Approaches for risk estimation: procedure used to estimate risk and whether the result is in a qualitative / semiquantitative / quantitative form;
  - Risk evaluation: criteria used to compare the results computed against limit thresholds, with the aim to determine risk's significance.

Notice that, for the development of the framework, some integrations to this general ERA structure needed to be made. First of all, relevance has been given, with a dedicated step of the framework (previous to the exposure assessment), to the 'hazard identification', that is the process of identification of what 'can go wrong' in the analysed system and for which causes. This information will then be used as input to describe the expected consequences that could arise from each leakage scenario.

The other observation concerns the risk characterization. Risk can be described in different ways, for instance, when initially pointing out the four steps of the process, risk characterization was defined by Vora et al. (2021) as "*the process of estimating the magnitude of adverse ecological impacts based on the information collected from exposure and effects assessment"* (p. 3). It has to be noticed that, in this definition, no reference is made to the uncertainty of the scenario, measured by its frequency or probability, but only to its magnitude. That is, much of the focus and modelling effort in an ERA is typically placed on assessing the impact magnitude of a release and less on modelling and assessing the occurrence uncertainty of the release scenario. To clarify, the uncertainty associated with the parameters of a release, determining its magnitude, such as the flowrate or pollutant concentration, may be low. Accordingly, the comment above concerns the uncertainty about the occurrence or not of the release scenario in the first place. Neglecting this uncertainty assessment is something that often happens in environmental risk assessments, however, in drafting this framework, we did not consider it being an option, thus, modifications to the ERA's structure have been made, with the aim of considering the frequency assessment. This work is indeed consistent with the definitions of risk that combine both the influence of the magnitude of a damaging event and its uncertainty (measured by frequency or probability).

To sum up, the final approach followed to develop the framework sees the combination of the general ERA structure and the general Quantitative Risk Analysis (QRA) structure briefly reported in Figure 2.2 below. Notice that the analysis of the consequences, in the QRA, includes both the exposure assessment and the effect assessment, however, in this work we preferred to dedicate two different chapters respectively to the exposure and effects assessment.

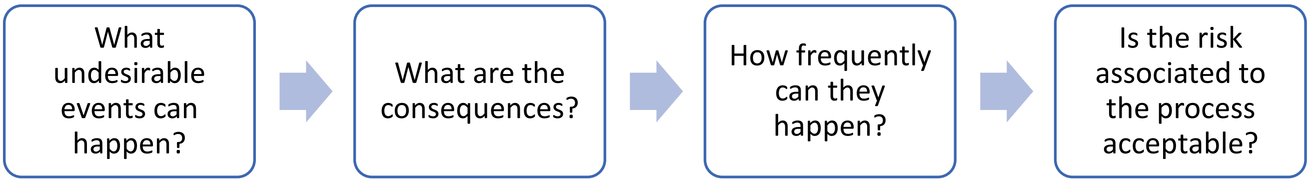

Figure 2.2: Key steps in the quantitative risk analysis.

2.3 Existing ERA procedures

As said in Section 2.2, the starting point of the present work is based on the analysis of already existing procedures for environmental risk assessment of CCS. This has been fundamental to acquire knowledge on CCS' ERA procedures developed up to present and, by comparing them to the scheme above exposed, to start thinking of possible modifications / integrations that could have been made. Among the existing ERA procedures, two representative ones have been selected as this work's 'starting point', due to their specific focus on CCS and their completeness:

- The European project ECO_2 (Wallmann et al., 2015);
- DNV GL risk assessment of the "Northern Lights" Equinor's project (DNV GL, 2019).

2.3.1 ECO_2

The ECO_2 project was funded by the EU to assess the environmental risks associated with the sub-seabed storage (reservoir and wells) of CO_2 and to provide practical guidelines on environmental practices. A remark has to be made on the fact that ECO_2's focus is on all of those aspects related to storage leakages only, which are not of our interest for what concerns the reservoir, but only for the aspects concerning injection wells. However, apart from the scenarios' characterization, the rest of the approach is of extreme relevance to our work, thus ECO_2 is here presented among the 'starting points'.

For its development, comprehensive offshore field programmes at the Norwegian storage sites Sleipner and Snøhvit were conducted. This helped not only identify potential pathways for CO_2 leakage through the overburden, but also analyse the benthic biota response to CO_2. Moreover, ECO_2's guidelines have been developed in compliance with the legal framework for CCS. As stated in Wallmann et al. (2015):

> *ECO_2 developed a generic approach for assessing consequences, probability and risk associated with sub-seabed CO2 storage based on the assessment of i) the environmental value of local organisms and biological resources, ii) the potentially affected fraction of population or habitat, iii) the vulnerability of, and the impact on the valued environmental resource, iv) consequences (based on steps i – iii), v) propensity to leak, vi) environmental risk (based on steps iv and v).*
>
> (p. 1)

At last, it is worth being noticed that ECO_2 consortium was very diversified: 24 research institutes took part in it, in addition to one independent foundation (DNV GL) and 2 commercial entities (Statoil AS and Grupa Lotos). A total of nine European countries participated (Germany, Norway, U.K., Italy, The Netherlands, Poland, Belgium, Sweden, France).

2.3.2 DNV GL risk assessment for Equinor

This environmental risk assessment has been conducted by DNV GL for the Northern Lights project. The Northern Lights project's aim is to study the feasibility of CCS implementation on the continental shelf, and is guided by Equinor in collaboration with As Norske Shell and Total E&P (DNV GL, 2019). The approach used in this ERA is divided in the same six phases of ECO_2. The risk analysis includes possible leakages from injection well and from transport pipelines.

2.3.3 Evaluation against selected ERA – QRA steps

The two above mentioned approaches were then compared to the selected ERA's relevant points, complete of the necessary integrations, related to the hazard identification and frequency assessment, presented in the previous paragraph. The 'hazard identification step' has here been divided into two steps ('causes and techniques' and 'characterization of failure scenarios') to distinguish between how the identification of leakage causes and the failure scenarios characterization have been dealt with in the two procedures. As said at the beginning of this Section (2.3), this comparison was useful to start thinking of necessary modifications and integrations in the perspective of developing the framework, object of this study. The results of this comparison are qualitatively reported in the Table 2.1, where colours indicate how well each of the steps was dealt with. Notice that: for simplicity, in Table. letter A and B refer, respectively, to ECO_2 project (Wallmann et al., 2015) and DNV GL project for Equinor (DNV GL, 2019). The legend, that explains the meaning of the different colours used, is presented under the table.

One note has to be made regarding the criterion used to assess the colour of the cells: some cells may have been given a colour corresponding to a low or medium level of detail either because that specific aspect was not mentioned or was neglected in some of its parts, or either because the result was not relevant to our work. To let the reader better understand, the following example is presented: ECO_2's focus, as stated above, is the storage (reservoir and wells), thus some of its results might not be consistent with the aspects we are considering in the present work.

Problem formulation	**A**	**B**
Management goals	■	■
Regulatory context	■	■
Review of existing site information	■	■
Contaminants of potential concern	■	■
Factors controlling the stressor	▨	
Receptors of concern	■	■
Exposure pathways	■	■
Conceptual model	■	■
Protection goals and acceptable effects level	■	■
Assessment endpoint	▨	▨
Measurement Endpoints	▨	▨

Hazard identification and characterization		
Causes and Techniques	■	▨
Characterization of failure scenarios	■	■
Exposure assessment		
Stressor information: Release	▨	■
Stressor information: Dispersion	■	▨
Exposure media information	▨	
Effects assessment		
Assessment measures and linkage to measurements endpoints	▨	▨
Stressor - Response analysis	▨	▨
Frequencies assessment	■	■
Risk characterization		
Risk description	■	■
Approaches for risk estimation	▨	▨
Risk evaluation	▨	▨

Legend: Level of detail covered	
Considered in substantial detail	■
Considered in limited detail	▨
Not considered	

Table 2.1: Qualitative evaluation of projects A (ECO$_2$) and B (DNV GL for Equinor) against the selected ERA – QRA steps.

The reason behind each value assigned is briefly reported below and will, anyways, appear clearer during the development of the framework, where, each of the steps mentioned, will be analysed in greater detail.

The reasons behind the assignation of each box's colour are the following:

a) Problem Formulation:

- Management goals: both projects clearly set their goals (mentioned in Sections 2.3.1 and 2.3.2);
- Regulatory context: both projects were developed in agreement to the relevant regulatory contexts;
- Review of existing site information: only project A presents techniques to approach the selection of the site, as in project B the site has already been selected. Both projects efficiently collect all the information needed for what concerns the ROCs (through ESBA methodology (Wallmann et al., 2015));

- Contaminants of potential concern (COC): both projects focus their attention only on CO_2, which, as will be explained in Chapter 3, is the only stressor considered in this work as well;
- Factors controlling the stressor: project A considers both the specific site's hydrodynamic (see for example the work by Ulfsnes et al. (2015)), through a dedicated model, and all the other possible parameters that could influence the release, that appear as factors in the transport models used (see the work by Dewar, Chen, et al. (2013)). By contrary, project B does not account either for the hydrodynamic or other specific factors controlling the stressor, indeed the dispersion modelling is performed in a very conservative way (see Chapter 5);
- Receptors of concern (ROC): both projects follow ESBA approach (Wallmann et al., 2015), which has proven to be an efficient method to screen out the site in terms of ROCs;
- Exposure pathways: both projects identify water as a potential exposure pathway and, in addition, project A identifies the sediments as well (which is not in the scope of our work, as explained in Section 1.4);
- Conceptual model: both projects well explain the connections between key information regarding contaminant sources, their fate through the exposure pathway and their contact with receptors of concern;
- Protection goals and acceptable effects level: project A clearly defines protection goals through acceptable effects and risks levels and they are used by project B as well;
- Assessment and measurements endpoint: both projects use available literature data in order to identify a limit threshold value of the concentration of the COC to which the organism ca be exposed without reporting any adverse effect. However, nowadays, approaches that permit to obtain more detailed information regarding organisms' responses to the stressors are available.

b) Hazard Identification and characterization:

- Causes and Technique: Project A identifies possible failure scenarios by means of a site-specific model, thus all possible specific causes, that Wallmann et al. (2015) were able to identify, are considered inside the modelling. In Project B, wells' failure scenarios are the result of a specific analysis of the site, while for pipelines standard holes' size were used;
- Characterization of failure scenarios: both projects, through the approaches mentioned above, are able to identify a wide range of failure scenarios. In both project a good characterization of the release is performed, in terms of diameter of the leakage and / or mass flowrate released.

c) Exposure assessment:

- Stressor information:

    - Release: project A focuses on releases from the storage and associates to them a mass flowrate based on model calculations. Project B, whose focuses is on pipelines and wells, uses a specific software to calculate the parameters related to the release;
    - Dispersion: project A has developed a specific modelling approach to simulate the dispersion, while project B, for the case of wells releases, simply scales up or down the results computed in a case study performed by project A (Ulfsnes et al., 2015) and, for pipelines' releases, uses a very simplified and conservative model.
- Exposure media information: project A accounts for useful information related to the exposure pathway (water currents, tides, seawater temperature, salinity etc.) through the hydrodynamic model, while project B does not account for them.

d) Effects assessment:

- Assessment measures and linkage to measurements endpoints: both projects use ESBA methodology and, depending on what type of data is available in literature, they identify a threshold value of the concentration of the COC to which the organism can be exposed without reporting any adverse effect;
- Stressor - Response analysis: both projects use the approach by Wallmann et al. (2015), which, identifies the degree of impact depending on the value of the resource being assessed. The criteria for assigning value are qualitative, e.g., an area of 'medium value' is an *"[a]rea with regional importance for species and habitats, and/or having national Red List species/habitats classified as data deficient (DD) or nearly threatened (NT)"* (Wallmann et al., 2015, p. 19). Still, as Wallmann et al. (2015) say, there is a rational behind the assignation of the value to each resource, which must be traceable and documented.

e) Frequencies assessment: project A develops a specific approach to determine the propensity of storage leaks, based on Bayesian networks. Project B uses data sources for wells and a specific approach (based on data sources) for offshore pipelines, developed by DNV GL (2017).

f) Risk characterization:

- Risk description: in both projects risk is defined with reference to the severity of the consequences and the uncertainty associated to the final failure scenario (in compliance with risk descriptions given in Section 1.6);
- Approaches for risk estimation: both projects use the same semi-quantitative approach, developed by Wallmann et al. (2015);
- Risk evaluation: acceptability criteria are defined by Wallmann et al. (2015) and results are evaluated against them. These criteria are in a risk matrix format. If a fully quantitative risk characterization is made in the form of a release frequency and a numerical impact/magnitude prediction, these numbers can be plotted in the risk matrix if the frequency/probability and impact severity categories used in the matrix

are associated with clearly defined numerical values. Alternatively, fully quantitative acceptability criteria should be established.

Notice that, in the development of the framework, the most logical way of presenting each topic has been followed, thus not every step of the procedure is precisely articulated following the exact same points reported here. More specifically:

- The ‘problem formulation’ follows exactly the points listed here and in the exact same order because it appeared to us the most logical way to structure it;
- The ‘hazard identification and characterization’ is divided in two parts: a first one where failure causes are identified, and linked to credible leakage scenarios (that should be modelled during a risk assessment), and a second one quantitative, where failure scenarios are characterized in terms of mass flowrate released or leakage hole size, etc.;
- The ‘exposure assessment’ is divided in release and dispersion modelling, as the exposure media information, meaning hydrodynamic aspects, is already integrated in the discussion of carbon dioxide’s dispersion;
- The ‘effects assessment’ is developed in two parts: first the identification of both the area to be examined and both of the most representative organisms living there and, then, the selection of endpoints to quantify the degree of impact;
- The ‘frequencies estimation’ is articulated in only one chapter;
- The ‘risk characterization’ deals only with risk estimation as, for what concerns risk description, it is developed in Section 1.6, as some basic knowledge on risk needed to be recalled before the presentation of the framework, and, for what concerns risk evaluation, only general considerations have been made, as the definition of acceptance criteria was out of the scope of this work.

2.4 Review approach

It is important, before presenting the work, to make explicit the review approach that has been used to develop the framework.

The starting idea has been set by the two works mentioned in Section 2.3 (ECO_2 project and DNV GL project for Equinor) and, in compliance with the key ERA's points underlined above, additional suggestions and approaches have been introduced. It is thus fundamental to explain why and how additional material has been collected, and most of all used.

The principal reasons are three. First of all, there was the interest to find the newest solutions to approach environmental risk analysis for the case of CCS. Moreover, there was the urge to add more details to the method, to generalize its applicability to any new CCS' project. And finally, our true interest was to be able to express risk in a quantified way: this implied expressing both the environmental impact of the failure scenario and its frequency in a fully quantified way. In both of the projects mentioned above, the risk characterization is made using a risk matrix format, with qualitative labels being used for the impact severity (e.g., 'major'), for the frequency/probability (e.g., 'unlikely') and for the final risk classification (e.g., 'severe negative'). Not surprisingly, quantifying risk has indeed, also in this work, represented a major obstacle. The reason has to be attributed to the fact that only a few quantified approaches (for the different steps) exist, many of which have not been fully developed or validated yet. Despite the evidence of knowledge gaps, this framework tried to comprehend more approaches as possible, even if some absolutely need to be further improved. Thus, to summarize, every step has been added in most details possible and quantified approaches have been proposed.

2.5 Utility and limitations of the framework

The scope of this work has been briefly discussed in Section 1.4, but some other observations are due.

As explained above, the framework developed by this work is at its preliminary stage, it is therfore meant to set the way for future studies and research. However, in the meanwhile, albeit being incomplete, it can already be useful in some on field applications. To clarify, its incompleteness resides in the fact that not every single aspect has been treated in the required detail, because this could have implied years of experts' research, and also that, for the same reason, alternatives are only presented, and not a final selection of how to perform each procedure's step is given (end of phases 2 and phase 3 of McMeekin et al. (2020) are not covered). However, this work could potentially be already useful to companies, willing to implement CCS, at least to guide in the risk assessment from a methodological point of view, through a step-by-step approach, and to help in the choice of risk assessment's procedures, as several of them are proposed. The real scope and strength of this framework, indeed, is not to propose a final and complete methodology, as this was not feasible with such a limited amount of time, but to collect, summarize and, when possible, to compare and combine what has been done since now in terms of risk assessment procedures for CCS, which is something that has not been undertaken before. Thus, despite not being a final solution, it could already provide a reduction of costs / human-work invested by companies for CCS' risk assessment, helping improve the consistency, robustness and reporting of the activity.

Moreover, methodological guidelines for CCS risk assessment could also contribute to the development of more accurate monitoring techniques, enabling a finer integration of environmental risk considerations in the operational activities of the plant. This aspect will be further discussed in Section 6.2.4, dedicated to the biomarkers-based SSDs.

For what concerns knowledge gaps, these will emerge during the drafting of the framework, and will be discussed in Chapters 9 and 10, so to give some evidence of the need for targeted future studies.

3. Problem formulation

The first step of the ERA consists in the problem formulation. Its fundamental aspects have been highlighted previously and are here articulated in detail.

3.1 Management goals

If a final goal has to be clearly stated out this would be to guarantee that the environmental risk associated to undesired leakages from subsea CO_2 pipelines and CO_2 injection and plugged and abandoned wells, in the context of CCS, lies within acceptable limits. Being risk a function of frequency and impacts' magnitude of a failure event, the aim can both be identified in assuring that the extent of damaging effects on the marine environment, in case a leakage could happen, is smaller than acceptability impact thresholds, and that risk itself, that combines magnitude and frequency, is lower than risk acceptability thresholds. These threshold values quantify to which extent a certain damage / risk is acceptable, which is associated to external factors as society's risk perception. Therefore, in order to be applicable to real case scenarios, this framework has to be coupled with, more preferably, risk acceptance criteria.

3.2 Regulatory context

CCS risk assessment must satisfy the regulatory requirements set by the legal context that holds both on a global level, meaning international or European, and on the local one, meaning the state jurisdiction, which is usually more stringent. Some examples of CCS / subsea pipelines' / wells' regulations are:

- EU Directive on geological storage of CO_2 2009/31/EC (usually referred to as the CCS Directive): it is the *"primary and only dedicated piece of European legislation for CCS"* (Wallmann et al., 2015, p. 6). A fundamental aspect, dealt with in the directive, is the necessity for obtaining an exploration and CO_2 storage permit. It focuses on the obligatory components of a storage permit, meaning *"site selection procedures, site characterisation, monitoring plans, financial security and liability transfer protocols"* (Wallmann et al., 2015, p. 6). Moreover, it strengthens the fact that the scope of reaching effective offshore CCS regulations cannot be achieved by the EU alone, but only in the perspective of a wider legal framework, through:

> *The obligations arising out of the 1996 London Protocol to the 1972 Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (1996 London Protocol) and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention).*
>
> (Wallmann et al., 2015, p. 8)

- International Agreements (London Protocol, OSPAR Convention): these international agreements deal with the protection of the marine environment. Wallmann et al. (2015) reminds that *"the OSPAR Convention and the London Protocol have developed a framework for risk assessment and management for CO2 sequestration in sub-seabed geological structures, abbreviated to FRAM"*(p. 8).
- Environmental liability Directive 2004/35/EC (ELD): it focuses on the "*damage to protective species and habitats, water and land, caused by a specified list of economic activities"* (Wallmann et al., 2015, p. 9). A relevant aspect, that the procedure deals with, is that, if in the CCS site, some protected species / ecosystems are identified, according to ELD, the risk in case of leakage is higher and the accurate establishment of baseline conditions is recommended.
- EU Emission Trading Scheme – Monitoring and Reporting 2003/87/EC: it determines the method "*to take into account any CO_2 that is either purposely vented (i.e. for maintenance or safety) or can be considered as fugitive emissions"* (Wallmann et al., 2015, p. 10).
- Pipelines Safety Regulations 1996 (PSR): these apply, with only a few exceptions, to all pipelines in Great Britain and in territorial waters of the UK Continental Shelf (*A Guide to the Pipelines Safety Regulations 1996*, 1996). They express general duties for all pipelines and additional ones for major accident hazard pipelines (MAHPs) that transport dangerous fluids.

Also, some regulations for the offshore oil and gas industries can have direct relevance to CCS applications, some examples are presented by the Energy Institute (Great Britain) (2013).

3.3 Review of existing site information

A fundamental step lies in the selection of the site: already established procedures are reported in literature (see for example Wallmann et al. (2015)) and will not be extensively explained here as storage aspects are not dealt with in this work. Whereas attention is given to the collection of site information around the storage area (in which the injection well is located too) and the area surrounding the pipeline. The reason behind this is that data collection is essential to have a precise map of the area, in terms of site characteristics and marine environment. A precise and detailed technical map of the offshore CCS field and the transport pipelines' should be available, with the addition of information on the hydrodynamic of the site, of the conditions of temperature and pressure at various water depths, of the pipelines' dimensions / depths / inclinations, of the baseline values of pH / pCO_2 (refer to Wallmann et al. (2015) for further details on how to perform baseline studies), etc. While, for what concerns data on the marine environment, the marine organisms, living in the area at risk, should be identified and their environmental value / vulnerability be assessed based on clear criteria, so to not overlook any type of receptor of concern. A possible approach is, for example, the one suggested by ECO_2 project, applied also by DNV GL for the Northern Lights project, which is explained in the chapter dedicated to the impacts assessment.

3.4 Contaminants of potential concern (COC)

The contaminants of potential concern in the case of CO_2 release in seawater, due to transport and injection failure scenarios, are, first of all, CO_2 itself and, secondly, H^+, deriving from the reaction of CO_2 with water. Other COCs can be identified in the impurities present in the CO_2 stream and heavy metals that could dissolve into water from the sediment, due to the increase in seawater acidity. These last two are not further deepened in the present work for some specific reasons that are discussed below.

For what concerns the concentration of impurities in the CO_2 stream, it is generally neglectable with respect to that of CO_2, as the composition must be conform to legislative constraints. Different upstream processes are indeed devoted to the purification of the stream before transport, meaning the removal of impurities. We can thus assume that the composition of CO_2 stream is strictly monitored to be consistent with the legislation in place. Therefore, if a release happens, the effects caused by impurities on the environmental habitat can be neglected. Clearly, if in the real case-study this general hypothesis does not apply, which could happen, due to economic constraints, as the removal of impurities from a stream is a very expensive operation, the effect of impurities on the habitat has to be assessed as well.

A similar reasoning applies to heavy metals: their dissolution from the sediments into water is strictly related to the presence of heavy metals in the soil and the degree of variation of the pH. Generally, during the selection of the site, attention is paid to the composition of the soil, and especially to the presence of heavy metals. If the sediments of a specific site are rich in heavy metals, that site is usually left out from the potentially interesting ones. In addition to that, the dissolution of heavy metals, if present, is only associated to major changes in pH with respect to the baseline pH, thus meaning only extreme case scenarios. To conclude, heavy metals' weight on the environmental impact can be generally neglected for the case of CCS' failure scenarios, with the exception of those situations in which the site's sediments are rich in them.

3.5 Factors controlling the stressor

The factors that affect the spatial distribution of the stressors are associated both to the characteristics of the release, meaning the depth of the release, the hole's size, the mass flowrate released and physical state, and both to the hydrodynamic of the site, thus, the presence of water currents, the temperature, the salinity, etc. All these parameters are inputs to either release or dispersion models and are therefore dealt with in more detail further on in the exposure assessment.

3.6 Receptors of concern (ROC)

The identification of the organisms, living in the area of interest, that could suffer from the presence of one of the above-mentioned stressors in their habitat, has to be done based on clear criteria. Valuable and vulnerable site-specific organisms have to be identified. This means that, once having screened out all the organisms present in the area, some prioritization has to be done to narrow the analysis. A possible method to prioritize could be to assess the sensitivity, intended as exposure thresholds, for each of the present species; otherwise, their value could be identified. Available methods to draft a prioritization are, for example, ESBA methodology presented by ECO_2 (Wallmann et al., 2015) and also used by DNV GL (2019). As for the site information, this as well will be explained during the effect assessment.

3.7 Exposure pathways

The exposure pathways by which a ROC can enter in contact with one of the stressors are essentially water and sediment. In this study attention is focused only on the water exposure pathway, as the releases analysed take place directly in water. The reason for this is that sediment's pathway is only associated to CO_2 leakages deriving from faults and fractures in the reservoir (carbon storage), thus here not considered.

A note has to be made: having assumed water as the only possible pathway for ROC-stressor contact does not imply that, when identifying the ROCs, organisms living on the seabed (for example bivalves, molluscs, etc…) can be neglected, because acidified water, generated by the release of CO_2, can get in contact with the seabed as well. It is evident that the identification and modelling of the transport mechanisms behind water exposure pathway is a key point of this work: the detail of it is not reported in the framework but can be found in the literature related to each model (that either simulates the release or the dispersion) presented.

3.8 Conceptual model

The conceptual model consists in the links and relations between contaminant sources, their fate, trough the specific exposure pathway, and the contact with the receptors of concern. The conceptual model thus represents the reasoning on which the full method is based upon, by 'full' meaning complete in all its consequential steps.

In practice, these connections, from a methodological point of view, are given relevance in the framework through the use of several consequential models that account for each of the above-mentioned aspects. However, before any model can be applied, hazards need to be clearly identified, which means answering to the question: 'What can go wrong? What undesirable events can happen?'.

After that, a characterization of the credible failure scenarios has to be performed, as credible failure scenarios are those that should be simulated, within a risk assessment, in order to understand the level of risk the environment is exposed to, and eventually introduce required safety measures. Failure scenarios can either be characterized directly in terms of mass flowrate released or by the expected failure holes' dimension. In this last case, a release model has to be applied to derive the mass flowrate released. Having collected all the necessary information regarding the release (mass flowrate and other information at the point of the release) and the surrounding site (depth, temperature, salinity, hydrodynamic etc.), the fate of the COC (CO_2) through the exposure pathway (water) can be described through dispersion models. Dispersion models compute the spatial distribution of the physical effect arising from the release. In the case of a CO_2 release in water, the physical effect can be seen as a DIC concentration (dissolved CO_2 in water), as CO_2 is soluble in water. The dissolution of the CO_2 plume will cause changes in dissolved carbon, pCO_2, pH (usually pH is considered a good proxy for pCO_2 (Ulfsnes et al., 2015; Wallmann et al., 2015)), etc. More precisely, the dissolution of CO_2 in seawater forms H_2CO_3, that quickly dissociates into H^+ and HCO_3^-. H^+, in turn, reacts with CO_3^{2-} to form HCO_3^-. The net effect of CO_2 dissolution causes an increase in H_2CO_3, HCO_3^-, H^+ concentrations and a decrease in CO_3^{2-} and pH levels. The spatial distribution of pCO_2 or pH can then be correlated to dose-response curves to identify the spatial distribution of the impacts on the selected ROCs. To obtain accurate dose-response curves, it is fundamental, first of all, to understand how marine species might be influenced by altered external CO_2 levels and changes in marine carbonate chemistry: Kim et al. (2016) reports that elevated CO_2 levels in seawater can impact marine organisms "*via decreased $CaCO_3$ saturation (which is directly related to calcification rates), or through a disturbance in acid–base metabolic physiology*" (p. 141). Having identified the type of impact, it has to be analysed how these organisms might respond to different levels of the stressor, therefore, reliable measurement endpoints should be selected, and dose-response curves be drawn.

This study, by combining different sources of information and several methods, is aiming at strengthening the robustness of the logical pathway that connects the accidental release of CO_2 to its dispersion, dissolution in water and impact on marine environment. Attention has indeed been paid not only to the identification of valid methods to approach each of the steps, but also at not overlooking any relevant parameter, that could have an influence on release, dispersion or impact. Only further, in the discussion, connections will be explained in detail.

3.9 Protection goals and acceptable effects level / Assessment endpoint / Measurement endpoints

The 'potentially affected fraction' (PAF) threshold is usually assigned at 5%, which aims to protect 95% of the species. Percentage of deaths is usually referred to when using this criterion in traditional ERA. However, more sensitive environmental values (meant as fitness level) can be used, and can provide an early warning signal, to avoid irrecoverable damages of the ecosystem. Endpoint properties could include for example population demographics, biomass, genetic variability, physical condition, biomarkers. Measure to identify the change in the attribute of an assessment endpoint could be NOEC, PNEC, LC_{50}, EC_{50}, etc.

After a general overview of the effects assessment methods already in place for CCS (for example the one presented by ECO_2 (Wallmann et al., 2015)), we will be oriented towards the newest technologies available in the field of environmental impact assessment, meaning the use of biological markers (known as biomarkers) as an instrument to finer describe, assess and monitor the impact.

4. Hazard identification and characterization

In order to be able to assess CCS environmental risk, initially, all the credible failure scenarios need to be identified. The first step of the hazard identification is qualitative and consists in the identification of the possible failure causes and the credible failure scenarios that could arise from them, which means answering to the question: ‘What undesirable events can happen?’. The credible failure scenarios represent those events that should be modelled when performing the risk assessment, in order to evaluate the risk to which the environment is exposed to. Credible failure scenarios need, thus, to be further characterised in a quantitative way, in terms of mass flowrate released or leakage hole size. As mentioned in Section 3.8, the information on the mass flowrate released or leakage hole size serves than, in the exposure assessment, as input to either the release model, if data refer to the hole sizes distributions (which computes the mass flowrate released), or directly to the dispersion model, if data refer already to mass flowrates. Given information on the characteristics and hydrodynamic of the site, the dispersion model is then able to trace the spatial distributions of pH / pCO_2 caused by the leakage.

The role of the hazard analysis is therefore to shed awareness on the possible hazards of the system, with the final aim of allowing any possible knowledge / experience application to manage safety. Hazard identification methods (e.g., historical analysis, ‘What if?’, ‘How can?’, ‘Hazard and operability study’ (HAZOP), FMEA / FMECA, etc) are required to identify the possible undesirable events, with reference to the specific case in analysis: the Energy Institute (Great Britain) (2013) warmly suggests their use in addition to the historical analysis of happened incidents, in relation to the field analysed.

Therefore, to clarify, what is presented in the following chapter is not the result of the application of a hazard identification method, as this is strictly case specific, but only general information on possible causes, that should be taken into account when practically performing a hazard identification, are provided. To these, the most credible scenarios reported in literature sources are associated, first in a qualitative way then quantitative, as explained above. Again, to clarify, the suggestion, for the most complete risk assessment, is to model the potential releases identified by this work in addition to the system-specific releases pointed out by the hazard identification methods. For each of the steps, possible alternative approaches found in literature will be presented, so to provide the user with practical options to complete the procedure.

As a last observation, ECO_2 project and Equinor’s have been ideally set as starting points and integrations have been made in compliance with what stated in Section 2.4. Notice that by ‘ideally setting’ is meant that, despite taking the works by Wallmann et al. (2015) and DNV GL (2019) as starting points, each section will be structured in the most logical way, thus if, for example, the approaches used by ECO_2 or Equinor are too case-specific, or not in compliance with our applications, they will be respectively presented after the more general methods found in literature or not mentioned.

4.1 Qualitative analysis: Causes and linkage with failure scenarios

4.1.1 Subsea pipelines

As anticipated, failure causes emerged in literature reports need to be pointed out. The review done showed commonly agreed causes for losses of containment associated to subsea pipelines: some examples of the primary concerns that should be addressed during a CO_2 pipeline risk assessment are presented in Table 4.1, with reference to the source.

Notice that these failure causes are associated to general pipelines, but also to pipelines or risers directly connected to wells, thus a situation in which the driving force of the release comes directly from the reservoir.

Literature source	Causes identified
(C. Smyth & D. Hovorka, 2018)	• Internal corrosion; • External corrosion; • Mechanical and material failure; • Operator and maintenance errors; • Unplanned product release; • Construction accidents and impact; • Natural disasters.
(Energy Institute (Great Britain), 2013)	• Third party damage (e.g., anchor being dropped and then dragged, vessels or objects hitting the pipeline, etc.); • Corrosion: according to the Energy Institute (Great Britain) (2013), internal corrosion does not represent the main problem, while external corrosion could (due to corrosion protection system failure); • Mechanical failure; • Damage associated to construction; • Natural hazards.
(Spinelli & Ahmad, 2015) *(Derived from oil and gas experience and projects phasing)*	• Operational / construction related damage; • Third party interference; • Corrosion: Spinelli & Ahmad (2015) believe internal corrosion should not be expected to occur if the composition of the stream lies within acceptable criteria, while external corrosion could occur; • Natural hazards.

Literature source	Causes identified
(DNV GL, 2017)	• Corrosion; • Third party activity; • Production (Design and construction failures); • Material or weld; • Operation and maintenance; • Environment.

Table 4.1: Examples of primary concerns (with reference to the sources) that should be addressed during CO_2 pipelines' risk assessment.

As anticipated, there is a good agreement, between literature reports, on the causes of pipelines' failure scenarios.

Having pointed out the possible causes that could lead to a leakage, credible scenarios need to be associated to them. The reason behind the identification of credible scenarios is that these events are, with reference to their cause, the ones that might be expected to truly happen, thus the ones that should be modelled when performing the ERA.

The Energy Institute (Great Britain) (2013) links to the causes, reported in Table 4.1, the possible failure scenarios expected for offshore carbon capture platforms and pipelines. The failure on subsea pipelines could be either a pinhole leak, a hole or a rupture (a rupture is a pipeline failure resulting in a large leakage flow rate: more than 10 kg/s (Oldenburg & Pan, 2020)). The Energy Institute (Great Britain) (2013) divides the offshore chain into two parts: the pipeline that goes from the beachhead to the wellhead and the platforms. The table, not reported here for copyright constraints, can be found in 'Annex A - Hazard analysis: credible events' of the work by Energy Institute (Great Britain) (2013).

Another detailed analysis of credible scenarios has been done by DNV GL in 'Appendix B – Failures, failure modes and causes' of a report by DNV GL (2017), whose failure causes were listed as well in Table 4.1. It is useful to recall the definitions of some specific terms mentioned in DNV GL (2017) Appendix B's tables:

- A cause is the event that leads to a failure mode; according to DNV GL (2017), it can be related to project, production and operations;
- A failure mechanism is the process initiated by a cause; it could be: corrosion, fatigue, etc.;
- The defect or damage is the result of a failure mechanism (e.g., fractures, loss of wall thickness, etc.);
- If a certain limit is crossed, a damage can result in failure (e.g., leakage).

In Table B.1 of DNV GL (2017) an overview of causal relations that can result in failures of a pipeline is given. DNV GL (2017) divides the causes into general groups, that coincide with the groups found in the failure databases:

- Corrosion: internal corrosion depends both on the composition of the stream and the presence of possible impurities, e.g., water. Water concentration, especially, must be known and monitored during the process. According to DNV GL (2017) opinion, external corrosion is efficiently prevented through the use of the corrosion preventive systems. Notice that this in not in agreement with what reported by the other literature sources in the Table above, that identify external corrosion as the main problem;

- Third party activity is directly linked to the intensity of the activities in the area. This means that, in strictly controlled areas, the failure frequency for pipelines is reduced if compared to less controlled areas;
- Production (Design and construction failures), as DNV GL (2017) states, accounts for failures caused by unacceptable strains or the pipeline being bent;
- Material or weld related failures are usually proportional to the volume of material and welds, thus, they increase with increasing diameter / wall thickness / length of the pipeline. This type of failure frequency can be reduced by suitable testing and monitoring of the pipeline;
- Operation and maintenance related failures occur when adequate monitoring of operational activities is lacking;
- Environment: Storm damage, earthquake, landslide, etc.

Notice that general groups are identified as individual cause reports are not easily accessible (DNV GL, 2017). To each cause mentioned above, the most extreme consequence scenario, that is believed to have the potentiality to arise, is associated (see Table B.1 of 'Appendix B – Failures, failure modes and causes' by DNV GL (2017)).

4.1.2 Injection wells

Existing wells, meaning active, inactive or abandoned (when using hydrocarbon fields for CO_2 storage), have the potentiality to be or can become leakage pathways. It is believed that "*abandoned or active wells that penetrate the storage formation pose the greatest risk for CO_2 leakage*" (Gaurina-Međimurec & Novak Mavar, 2017, p. 24). Especially with age, the casing / tubing strength and the cement behind casings start deteriorating due different factors, for example: corrosion, thermal changes, fatigue due to production or injection, etc.

For what concerns new CO_2 injection wells, mandatory technical requirements for CO_2 injection wells (US EPA, 2015) have to be followed to ensure that there is no possibility of leakage related to incorrect drilling. CO_2 migration is prevented through the use of corrosion-resistant materials and through the casing and cement, which are designed for the life expectancy of the well.

However, no matter if new, inactive or abandoned, each well's long-term integrity should be ensured: various methodologies are available for evaluating long-term integrity of wells. Examples of these techniques are: data mining, FEP based analysis, Performance & Risk Management Technology, etc. (Patil et al., 2021).

Potential leakage pathways from wells, with the exclusion of the leakage from the pipeline directly connected to the well (which has been mentioned in the previous paragraph), which generally leads to a blowout, are presented in Figure 4.1. Figure 4.1 is an immediately understandable summary of potential seepages, along active (right) injection wells and abandoned (left) wells. These include leakages:

> *Through deterioration (corrosion) of the tubing (1), around the packer (2), through deterioration (corrosion) of the casing (3), between the outside of the casing and the cement (4), through deterioration of the cement in the annulus (cement fractures) (5), leakage in the annular region between the cement and the formations (6), through the cement plug (7), and between the cement and the inside of the casing (8).*
>
> (Gaurina-Međimurec & Novak Mavar, 2017, p. 18)

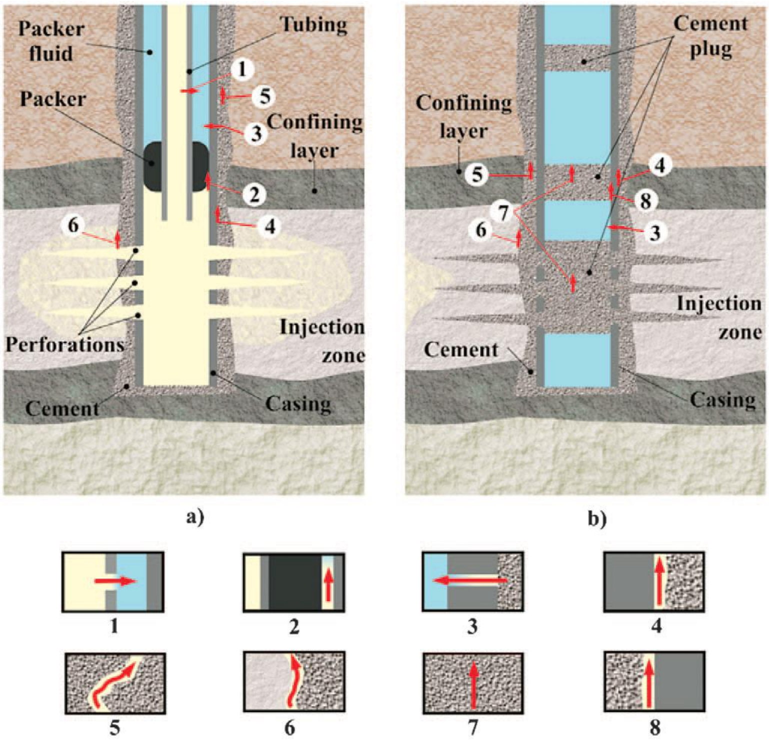

Figure 4.1: Potential seepages along active injection wells (right) and abandoned wells (left). From: "Depleted hydrocarbon reservoirs and CO_2 injection wells –CO_2 leakage assessment", by Gaurina-Međimurec, N., & Novak Mavar, K., 2017. The Mining-Geology-Petroleum Engineering Bulletin, 32(2), p. 18. Copyright 2017 by Rudarsko-geološko-naftni zbornik. (https://doi.org/10.17794/rgn.2017.2.3)

The internal integrity of the well should be assessed to avoid corrosion of tubing and casing (leading to cases 1, 2, 3 in Figure 4.1). Corrosion can happen on: "*equipment parts that come into contact with CO_2, the tubing and the part of the casing string below the packer*" (Gaurina-Međimurec & Novak Mavar, 2017, p. 18). To avoid internal corrosion of tubing and casing, corrosion-resistant material are required, for example: "*316 stainless steel (SS), glass reinforced epoxy (GRE) or lined carbon steel*" (Gaurina-Međimurec & Novak Mavar, 2017, p. 18). Moreover, packers and valves should be "*nickel-plated or made of other high nickel alloys*" (Gaurina-Međimurec & Novak Mavar, 2017, p. 18).

For what concerns external integrity, its lack could lead to cases 4, 5, 6 in Figure 4.1. External integrity is ensured by properly cementing the casing, which "*protects the casing string from stress and corrosion, as well as preventing CO_2 migration by sealing the annulus*" (Gaurina-Međimurec & Novak Mavar, 2017, p. 19). Cement is also used to plug the casing in case of well abandonment (cases 7 and 8 in Figure 4.1). Notice that Portland cement not stable in CO_2-rich environments, form a thermodynamic point of view. CO_2 forms carbonic acid (H_2CO_3) if water is present: over time, chemical reactions (Carroll et al., 2016) cause its degradation, thus the compressive strength decreases, while porosity and permeability increase. Cement degradation can be prevented through the utilisation of "*CO_2 resistant Portland cement or cement with a greater proportion of pozzolan*" (Gaurina-Međimurec & Novak Mavar, 2017, p. 19).

Another literature source (Patil et al., 2021) analyses the causes behind leakages from wells. Potential leakages identified by Patil et al. (2021) can happen: *"(1) between cement plug and casing interface and between casing and annular cement interface, (2) between annular cement and formation interface, (3) through corroded casing wall, (4) through cement plug, and (5) through annular cement*" *(p. 4).* Patil et al. (2021) identify some characteristics associated to crucial P&A elements (leakage point e.g., casing, casing-cement interface, cement, cement-formation interface): their functions, the failure risk, causes, effects, and mitigation plans.

One last source identifies the main functions of wells and associates, to each of them, failure models (Le Guen et al., 2009). According to Guen et al. (2009), wells' main functions can be summarized into five groups: *"(I) resist formation-fluids pressure; (II) ensure sealing with respect to formation fluids; (III) resist CO2 pressure and temperature; (IV) ensure sealing with respect to injected CO2; (V) resist formation pressure*" *(p. 89).* For each component's function, specific failure modes exist that could alter / impede the functioning of the component itself (e.g., loss in mechanic resistance, overpressure, etc.). These different failure modes can be associated with causes (e.g., corrosion, erosion, etc.) and effects (e.g., breaking and collapse, loss of bond between casing and cement, etc.).

4.2 Quantitative analysis - Characterization of the releases

As said, a fundamental aspect when performing a risk assessment is the selection of representative failure scenarios induced by the causes presented in the previous chapter, to be further modelled in the analysis. The modelling enables the understanding of the spatial extension of a damaging event and the quantification of the magnitude of its impact, which permits to properly select and dimension the required safety measures.

There are different levels of detail by which representative failure scenarios can be found reported in literature: some sources directly associate to each failure scenario a total mass released or a mass flowrate being released, while other sources report a distribution of holes' sizes and for each of them, by means of a release model, the mass flowrate released is evaluated. Notice that, in the second case mentioned, in which a release model is used, not only the mass flowrate released (specifically dependant on the conditions of the case study) can be calculated, but also other information can be obtained, for example regarding the physical state, conditions of temperature and pressure at the point of the release, duration of the release etc. Thus, the second case, when available, represents the best alternative, as a higher level of detail, concerning the release, can be achieved.

The characterization of the releases will be divided in three sections: the first subchapter is called general scenarios, meaning that it comprehends both pipelines and well leakages, while the second and third subchapters refer respectively only to subsea pipelines and wells. Table 4.2 summarizes the literature sources found for each case.

	Literature Sources
General	(J. Blackford et al., 2009)
	(J. C. Blackford et al., 2013)
	(Dewar, Wei, et al., 2013)
Pipelines	(DNV GL, 2017)
	(DNV GL, 2019)
Wells	(ZEP, 2019)
	(DNV GL, 2019)

Table 4.2: List of literature sources that characterize the releases from CO_2 subsea engineering systems.

4.2.1 General scenarios

In this first case a mass flowrate being released is directly associated to each failure scenario. We chose to start with a work, that is often recalled in CCS risk analysis studies, by J. Blackford et al. (2009). J. Blackford et al. (2009) investigates three forms of CO_2 release that cover the possible mechanisms of leakage. Little information is reported for each failure scenario because, as Blackford et al. (2009, pp. 270–271) states, "*parameterizing the rate and duration of a stochastic leak event is speculative; there is little information available to guide towards realistic scenarios"*. Data are obtained from:

- Estimates of seepage from a terrestrial EOR sequestration project in Colorado, USA, of <3800 tonnes CO_2/a over an area of $78km^2$ with rates of <170 tonnes CO_2/a, that provide a baseline for the diffuse type of scenarios;
- For the ‘catastrophic’ scenarios, the baseline used is, for example, the typical capacity of the pipelines used to deliver CO_2 to well systems, 100–250 mmscfd (million standard cubic feet per day).

The three leakage scenarios identified by J. Blackford et al. (2009) are, thus, the following:

- Long-term, diffuse seepage (3.02×10^3 – 3.02×10^5 tonnes CO_2 yr^{-1}): *“a constant low-level seepage of CO2, which spreads homogeneously across the area of one model box (49km2) is assumed, representing a notion of porosity in geological formations”.*

  (p. 271)
- Short-term, point source leak (1.49×10^4 – 1.49×10^5 tonnes CO_2 yr^{-1}):

  This is analogous to a fracture in a pipeline that persists for 1 day (and assuming some delay in automatic shutdown of the pumping systems). Two input rates are described, 1.49×10^4 and 1.49×10^5 tonnes CO_2, approximately 5 and 50 times a typical pipeline daily flow capacity.

  (p. 271)
- Long-term, point source leak (5.43×10^6 tonnes CO_2 yr^{-1}): *“an unmitigable fault in a well-casing or some catastrophic geologic fissure,* [with] *an outgassing rate of ~5.43×10^6 tonnes CO_2 over 1 year”.*

  (p. 271)

As reservoir leakages are not in the scope of the present work, only the scenarios referred to pipelines and wells are taken into account. The three scenarios identified by J. Blackford et al. (2009) were further modified as part of the European RISCS project (J. C. Blackford et al., 2013):

- Dissolved CO_2 point source low flux (8.99×10^4 tonnes yr^{-1});
- Dissolved CO_2 point source high flux (1.35×10^8 tonnes yr^{-1});
- Pipeline leak (2.8×10^{11} tonnes yr^{-1}).

Another literature source that identifies possible leakage scenarios is by Dewar, Wei, et al. (2013). It states that:

> *An extreme case would be a well blowout or burst pipeline, this could create a leakage of up to 578 kg/s (50 ktons/day) (IEA GHG, 2008). Other leakages are estimated to be of a far lower order, with predictions of rates below 0.006 kg/s (200 tons/year) (IEA GHG, 2008). One leakage that had a rate estimated to be within this range was to be somewhere between 170 and 3800 tons/ year (0.1207 kg/s). This rate was suggested by Klusman (2003) when taking observations from seepage from the Rangely enhanced oil recovery (EOR) field in the USA.*

(Dewar, Wei, et al., 2013, p. 510)

4.2.2 Subsea Pipelines

The intensity of the damaging consequences of a leak from a pipeline is strictly dependant on the hole size distribution. As DNV GL (2017) highlights, there are many factors that could influence the holes' size: the mechanism causing failure, the operative pressure, the pipeline dimensions, the physical state of the transported fluid etc. DNV GL (2017) suggests the following recommended hole sizes distribution (Table 4.3), based upon PARLOC database for offshore pipelines.

Hole size	**Offshore pipelines - Steel pipelines**
Small (<20mm)	79%
Medium (20-80mm)	5%
Large (>80mm)	5%
Rupture	11%
Total	100%

Table 4.3: Recommended failure hole size distribution for offshore steel pipelines
Adapted from: "Recommended failure rates for pipelines", by DNV GL, 2017, (No. 2017–0547, Rev. 2). DNV GL, p. 5. Copyright 2017 by DNV GL.

This hole size distribution is furthermore used by DNV GL in the case study of the Northern Lights project (DNV GL, 2019), as shown in Table 4.4.

Leakage category	**Leak size (mm)**	**Distribution (%)**
Small (< ø20mm)	2	79
	5	
	10	
Medium (ø20 - ø80mm)	20	5
	50	
Large (> ø80mm)	80	5
	100	
Full bore rupture	2 x ø239	11
Total	-	100

Table 4.4: Failure hole size distribution used by DNV GL for Northern Lights offshore pipelines' risk assessment
Adapted from: "Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2", by DNV GL, 2019. (No. 2019–0746, Rev. 1), p. 38. DNV GL. Copyright 2019 by DNV GL.
(https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)

One additional observation has to be made on the geometry of the release: Dissanayake et al. (2021) have proven its relevance on the impacts by simulating the same release, in terms of mass flowrate released, through a point source and a line source, which is a possible scenario from a pipeline fracture. The aim was to identify the linkage of the geometry of the release to the amount of CO_2

dissolved in water: the difference between the two results (see Dissanayake et al. (2021) for details) clearly shows that, for a detailed risk analysis, the geometry of the release should also be considered.

4.2.3 Wells' scenarios

Some literature sources, like ZEP (2019), identify a list of potential leakage scenarios from wells. ZEP (2019) refers to an aquifer storage site in the North Sea, and data are derived from experience of CO_2 storage projects (e.g., Statoil's Sleipner project and Total's Lacq project), published and unpublished risk estimates for North Sea storage sites and further evaluation by CO_2 storage experts. ZEP (2019) observes that the containment risks (meaning leaks from the storage, tush the reservoir itself or the wells) are:

> *Site-specific, influenced by storage site type* […] *Additionally, the risk is dependent on the planned development* […]. *Despite this inherent variability the risks quoted* [in Table 4.5] *below are representative of the approximate scale of the containment risk for a general* CO_2 *storage project*.
>
> (p. 29)

The case analysed by ZEP (2019) is a storage site:

- injecting 100 Mt at 2000-3000 m depth, over a period of 50 years;
- including one injection well and one abandoned well.

The probabilities (Table 4.5) express the likelihood of occurrence of the events during the lifetime of the project (500 years).

Notice that not all of the scenarios presented by ZEP (2019) were relevant to this work, as some refer to reservoir leakages or installations, thus only wells' leakages have been reported.

Scenario	**Probability of leakage (%)**	**Peak Leakage Rate (t/d)**	**Duration (in years or days)**	**Total Mass Lost to surface (tonnes)**
Active well leakage	0.5	50	250 days	12500
Active well blowout	0.15	5000	250 days	1250000
Abandoned well blowout	0.1	3000	1 years	1095000
Seepage in abandoned well	0.5	7	100 years	255500
Severe well problem, no repair successful	0.005	6000	2 years	4380000

Table 4.5: Leakage parameters for wells' failure scenarios in a North Sea storage.
Adapted from: "CO_2 Storage Safety in the North Sea: Implications of the CO_2 Storage Directive", by ZEP, 2019. Zero *Emissions Platform, p. 30.*
(https://zeroemissionsplatform.eu/wp-content/uploads/ZEP-report-CO2-Storage-Safety-in-the-North-Sea-Nov-2019-3.pdf)

In contrast to ZEP's (2019) results and assumptions, DNV GL project for Equinor (2019) identifies the site specific (the Northern Light's site) wells' leakages: these are reported in Table 4.6. The estimation of wells' failure probabilities and mass flowrates released are based on the report *"Input to ERA Memo May 2019"*, with reference to the supplementary report *"Northern Lights (Aurora*

Complex) Subsurface Containment Bowtie Analysis, Issue 3.0". The failure scenarios pointed out are specific for the Northern Lights project, thus they are not general, and therefore, not applicable to different cases other than the Northern Lighs one. What is worth being mentioned, of this section of DNV GL project for Equinor (2019), is the approach, meaning environmental risk analysis guidelines, adopted in the selection of relevant wells' leakage scenarios. The initial assumption is that a leakage scenario requires modelling, in the perspective of assessing CCS' risk, if it is potentially able to cause a negative environmental impact. Therefore, to be able to select these relevant scenarios, among the ones identified, a minimum threshold value for the CO_2 mass flowrate released, which is the minimum mass flowrate able to cause an observable negative effect to the environment, needs to be set. This threshold can assume two different values, depending on the case studied (DNV GL, 2019):

- If ESBA analysis (Wallmann et al., 2015), whose aim is to assess an environmental value to the site (it will be explained in detail in the effect assessment chapter), shows no overlap between the vulnerable environment and CO_2 plume, the minimum threshold value can be taken at 50 kg_{CO2}/m^2 per day. This value was proven to be causing negligible / low harm to the surrounding marine environment at Sleipner during the environmental risk analysis conducted by Ulfsnes et al. (2015). According to DNV GL's opinion (2019), this value is representative for the area above Sleipner as well, meaning that a similar release will have a comparable environmental impact.
- In case of overlap between the vulnerable environment and CO_2 plume, the threshold limit is set according, mainly, to the sensitivity of organisms present in the environment towards changes in pH.

All well failure scenarios identified for the Northern Lights project are supposed to have a maximum leakage flowrate of $< 1\ t_{CO2}/m^2$ (except for the first case that has an even greater maximum leakage flowrate ($< 10\ t_{CO2}/m^2$)), which means that 50 kg_{CO2}/m^2 can be reached if the leakage area is smaller than 20 m^2. Therefore, they have all been modelled in the Northern Lights risk assessment (see Table 4.6).

Scenario	Probability	Mass-flowrate released	Duration
CO_2 leakage via injection wells during the injection period	< 1%	≤ 10 ton/day	≤ 1 year
CO_2 leakage via bean heads after the injection period	< 1%	≤ 1 ton/day	≤ 100 year
CO_2 migrates from the well to the overlying sediment packet ("overburden") during the injection period	< 1%	≤ 1 ton/day	≤ 1 year
CO_2 migrates vertically under Drake roof rock in Aurora, for example towards fault zones in NW / SW, migrates north towards Troll, and leaks out of existing well (s)	< 1%	≤ 1 ton/day	≤ 100 year
CO_2 migrates north to the Troll area through the Johansen / Cock formations, passes the Svartalv fault, and leaks out of existing well (s)	< 1%	≤ 1 ton/day	≤ 100 year

Scenario	Probability	Mass-flowrate released	Duration
CO_2 migrates north to the Troll area through the Johansen / Cock formation, and leaks out of existing well (s)	< 1%	≤ 1 ton/day	≤ 100 year

Table 4.6: Leakage parameters for wells' failure scenarios, in relation to Northern Lights project. Adapted from: "Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2*", by DNV GL, 2019. (No. 2019–0746, Rev. 1), p. 32. DNV GL. Copyright 2019 by DNV GL. (https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)*

5. Exposure assessment

The purpose of the exposure assessment is to *"characterize the mechanisms by which receptors are exposed to COCs, and to quantify the magnitude of those exposures"* (Federal Contaminated Sites Action Plan (FCSAP), 2013, p. 3.1). In other words, this means to associate to possible failure scenarios their 'physical effect distribution', that, for the case of CO_2 releases in seawater, can either be defined in terms of change of pH or pCO_2 values. The results of the previous chapter, as already said, are the inputs first to the release models, if the failure scenarios are referred to leakage holes sizes, and then to dispersion models. Dispersion models, given also the information on the hydrodynamic and specific characteristics of the site, are able to compute the spatial distributions of pH / pCO_2 caused by a leakage. This chapter of the framework will identify a step-by-step procedure to perform a CCS' exposure assessment and, for each of the steps, possible approaches found in literature will be presented.

The first part of this chapter will be dedicated to release models, that compute the mass flowrate released if only information on the dimension of the hole is available, and not directly the mass flowrate released itself. The second part is then dedicated to the dispersion models, whose inputs are the mass flowrate released, the hydrodynamic and other characteristics of the site or of the release.

5.1 Release modelling

Release models are the mean used to describe the release, in terms of mass flowrate released and other characteristics. Depending on their level of detail, release models can have all or some of the following input:

- The leakage hole size;
- The length and characteristics of the pipeline section, which also depend on the inter-distance between block valves;
- The conditions of temperature and pressure in the pipeline or reservoir (in case of well leakage);
- The properties of the fluid;
- The depth of the leakage;
- Model specific parameters.

Notice that this models, are not only able to calculate the mass flowrate released, with reference to the specific case studied, but can also evaluate other relevant information e.g., the physical state, the conditions of temperature and pressure at the point of the release and the duration of the release, if it is not stopped by human intervention.

Release models can therefore account for the influence of different parameters, thus enabling a finer description of the release, which is of extreme relevance, as Dewar et al. (2013) indeed states:

> *Changing individual leakage parameters, such as the depth or current while maintaining other properties across leakage scenarios, can have a great affect, with clear differences* [, for example,] *between bubbles and droplets. Droplets have a density at least 100 times that of a bubble of the same volume, therefore take more time and distance to dissolve. Due to the lower density of gas, there will be a larger number of bubbles than that of droplets at the same leakage flux, increasing the interfacial surface area enhancing dissolution rates, producing lower terminal heights along with greater pH changes and concentrations.*
>
> (p. 512)

Table 5.1 summarizes the sources found for each case.

	Literature sources for release models
Pipelines	(DNV GL, 2019)
	(Xinhong et al., 2018)
Wells	(Oldenburg & Pan, 2020)
	(Patil et al., 2021)

Table 5.1: List of literature sources that used or developed release models for carbon dioxide's spills from subsea engineering systems.

5.1.1 Pipelines

As it was mentioned in Section 4.1.1, possible leakages from CO_2 subsea pipelines should be divided in two cases: the first one concerning leakages on general traits of a transport pipeline, while the second one referring to leakages on pipelines directly connected to wells (e.g, hole on a pipeline 10 m from the well), thus where the driving force for CO_2 release comes from the reservoir and not from the pipeline itself. This clearly means that two different type of release models have to be applied to describe the two different cases. In this first paragraph, release models for general transport pipelines only are listed, while the second case mentioned will be analysed in the following paragraph dedicated to well leakages.

DNV GL (2019) calculates the mass flowrate released by means of a software called OLGA, using as input the corresponding dimensions of the leakage. Results for Northern Lights specific case are shown in Table 5.2.

Leakage category	**Leak size (mm)**	**Initial leakage rate (kg / s) ***	**Time for detection**	**Duration after detection**
Small (< ø20mm)	2	0.6	6 months	1 month
	5	4	24 h	1 month
	10	15	24 h	1 month
Medium (ø20 - ø80mm)	20	58	12h	26 days
	50	255	15 min	6 days
Large (> ø80mm)	100	411	15 min	3 days
Full bore rupture	2 x ø239	700	15 min	1 day

*(*the numbers represent the average of the first 30 minutes)*

Table 5.2: Northern Lights' pipelines' release characteristics, computed by means of OLGA software. Adapted from: "Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2", by DNV GL, 2019. (No. 2019–0746, Rev. 1), p. 40. DNV GL. Copyright 2019 by DNV GL. (https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)

DNV GL (2019), for the scope of his project, also calculated the time required to identify the leakage and the duration of human intervention to fix it (both reported in Table 5.2). Notice that these values are strictly case specific, they thus cannot be generalised to other applications. Some case specific dependences are, for example:

- Human's decisions: it is within the plant's owner's choice to decide whether, for example, for the case of minor releases, the leakage should be fixed immediately or only after some time from its detection. Notice that, if fixing takes place, the line needs to be stopped and depressurized, thus causing an economical loss due to work interruption. Clearly the same cannot be applied to major leakages, as the mass flowrate released is of relevant entity and constitutes itself the economic loss. The repair works thus get started as soon as the leakage is identified (almost immediately as major leakages are the easiest ones to be identified).

- Distance between valves: not only the mass released, but also the duration of the release, depend on the inter distance between block valves, which is something that can vary from case to case
- Reaction time of the emergency shut down system

Equinor’s results are shown in Table 5.3.

		Before leak detection		**After leak detection**		**Total**	
Leakage category	**Leak size ø (mm)**	**Duration (days)**	**Released CO_2 (ton)**	**Duration (days)**	**Released CO_2 (ton)**	**Duration (days)**	**Released CO_2 (ton)**
Small (< ø20mm)	2	180	9331	30	778	210	10109
	5	1	7880	30	5184	31	5512
	10	1	31311	30	20218	31	21522
Medium (ø20 - ø80mm)	20	0.5	2513	26	6757	27	9270
	50	0,01	220	6	6757	6	6977
Large (> ø80mm)	100	0.01	355	3	6757	3	7112
Fullbore rupture	2 x ø239	0.01	605	1	6757	1	7362

Table 5.3: Duration and volumes released before and after the detection of the leak (with reference to the Northern Lights project).

Adapted from: “Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2”, by DNV GL, 2019. (No. 2019–0746, Rev. 1), p. 41. DNV GL. Copyright 2019 by DNV GL. (https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)

Alternative release models are the CFDs, an example is presented by Xinhong et al. (2018), where a short pipeline model is built and used to estimate underwater gas (CH_4) release rate. Parameters considered by the model are:

- The hole size, assumed to be of circular shape;
- The pipeline pressure and temperature inlet and outlet;
- The wall thickness;
- The water depth.

Boundary conditions used for the simulations include pressure inlet and outlet, no-slip wall, velocity inlet, roughness of the pipeline and outflow.

Moreover, Xinhong et al. (2018) make an interesting observation concerning leak position: due to the uncertainty of accident, a leak may happen on different positions of a pipeline. Leak position determines the initial jet direction of gas plume, but it only affects the initial jet direction of gas plume, not its final distribution.

5.1.2 Wells

Release models identified in our literature review are able to describe two types of failure scenario: the first one is the leakage from a pipeline directly connected to the well (active well), mentioned in the previous paragraph; the second one is seepage from the well (inactive well).

The first failure scenario, which involves CO_2 leaking from a hole in a pipe directly connected to a well (e.g., 10 m away (Oldenburg & Pan, 2020)), can be referred to as a major well blowout because the source of CO_2 is the reservoir (connected via the well) rather than the pipeline, which is assumed to be immediately shut off following the detection of the leak. Some clarity on the term major blowout has to be made:

> *Note that while the term "blowout" in the oil and gas context is defined as any uncontrolled leakage of fluids, a major blowout is usually understood to imply large flow rates (>10 kg* s^{-1}*) from a localized leakage pathway up a well.*
>
> (Oldenburg & Pan, 2020, p. 17)

The release model applied by Oldenburg & Pan (2020), to describe this scenario, is T2Well, which couples well and reservoir flows. Given the dimension of the pipe, size of the hole, the roughness of the wall, the initial pressure of the reservoir, seawater characteristics (e.g., temperature, currents, salinity, etc.), T2Well is able to calculate the mass flow rate, the velocity, the pressure, the temperature, and CO_2 density at the point of leakage.

For what concerns the second type of release model, an example found in literature is given by Patil et al. (2021), where the seepage from the cement of a P&A well is analysed. The leakage is modelled based on Darcy's law and can be estimated for a "*leak through bulk cement, cracks and micro annuli through the plugs and annular cement as well as around the plugs and annular cement"* (Patil et al., 2021, p. 11). Equations for the gas flowrate are based on the models developed by other research works, mentioned in the article. In Patil et al. (2021) a range of values for the parameters was selected during the modelling, with the aim to understand the effects of "*cement permeability, crack size and micro-annulus on* CO_2 *leak migration from subsurface to surface"* (p. 12).

5.2 Dispersion modelling

Having set the whole context for what concerns possible failure scenarios, the dispersion of CO_2 in seawater needs to be modelled, so to be able to identify the area of impact to be analysed during the effect assessment. Several alternative dispersion models will be proposed in this chapter. The modelling of the dispersion is complex and computationally demanding, as it requires several model components. These have been well identified by Jones et al. (2015) and are listed below:

- Hydrodynamic models;
- Bubble plume models;
- Carbonate system models.

The hydrodynamic models simulate the "*3D movement and mixing of marine systems*" (Jones et al., 2015, p. 364), which are key components for understanding the dispersion of dissolved CO_2. Jones et al. (2015) stresses on the fact that:

> *Realistic atmospheric, tidal and geostrophic forcing are essential in order to correctly estimate dispersion characteristics. Initial studies of leakage used available models, often with a relatively coarse resolution (e.g. Blackford et al., 2008, ~7 km horizontal resolution), and were only able to address large scale leakage events. In the last decade the resolution of hydrodynamic models has improved, as a result of advances in computational systems. Shelf wide models can now reach resolutions of 1 km horizontally (e.g. Phelps et al., 2015) whilst local models can resolve at least part of the domain with resolutions of a few metres (e.g. Blackford et al., 2013).*
>
> (p. 364)

For what concerns Bubble plume models, Jones et al. (2015) further states that:

> They *are necessary to properly understand the characteristics of the leak epicentre, in terms of the gas phase plume and the near field dissolved plume. Bubble size (larger bubbles are more buoyant and dissolve slower) is the key determinant of the elevation of a plume from the sea floor and consequently the vertical profile of chemical change and the patterns of dispersion; with implications for both monitoring strategy and environmental impact. As with the hydrodynamic models, emission form, topography and currents impart a large variability on the outcome of a given emission scenario. Plume models have made progressive improvements to the parameterisation of processes, based on observations of natural and man-made leakage analogues (Dewar et al., 2015).*
>
> (p. 364)

And, at last:

> *Carbonate system models are an essential component of all leakage simulations as they can derive pH, pCO_2, CO_3^{2-} and HCO_3^- ion concentration and saturation state from given concentrations of dissolved CO_2* [e.g., HALTAFALL model used in (J. Blackford et al., 2009)]. *These parameters are necessary to understand both impact and detectability. Whilst carbonate system models have been available for decades, since 2005 international agreement on the parameterisation of reaction constants (Dickson et al., 2007) and a far better treatment of alkalinity (e.g. Artioli et al., 2012) has improved the realism of these models, especially when applied to shelf and coastal systems.*

(Jones et al., 2015, pp. 364–365)

Some more recent advances have been made, for what concerns the bubble plume model, by Pham et al. (2020). In this study a comparison between existing models is carried out and awareness is raised on the relevance of, both, considering the breakup and coalescence of bubbles and on the greater modelling accuracy that could be achieved by integrating the chemical reaction in the numerical modelling (thus taking into account the enhanced transport of CO_2, between gas and liquid phase, due to its consumption in the liquid) (Figure 5.1).

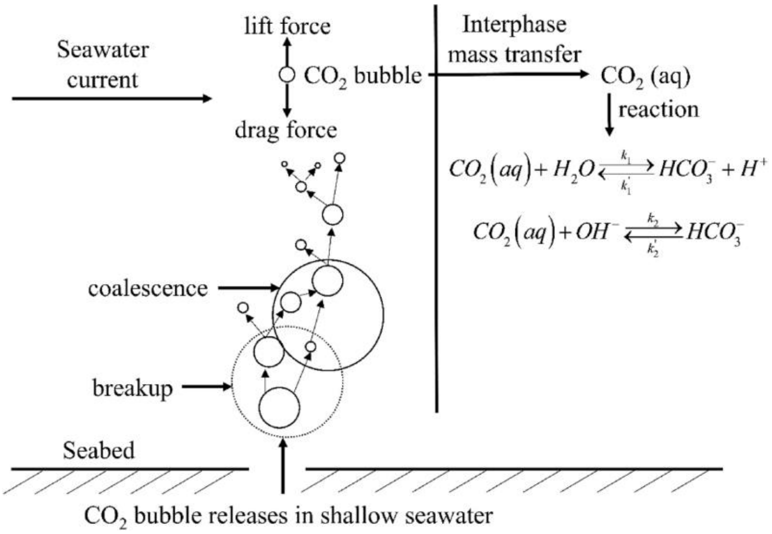

Figure 5.1: Schematic representation of the release and dispersion process of CO_2 bubbles in shallow seawater. From: "Dispersion of carbon dioxide bubble release from shallow subsea carbon dioxide storage to seawater", by Pham, L. H. H. P., Rusli, R., Shariff, A. M., & Khan, F., 2020, Continental Shelf Research, 196(104075), p. 2. Copyright 2020 by Elsevier Ltd. (https://doi.org/10.1016/j.csr.2020.104075)

The models analysed by Pham et al. (2020) are reported, in their work, in 'Table. 1', with information on their missing aspects (with reference to the coalescence and reaction aspects mentioned above). Through the comprehension of the state of the art and lates research's discoveries, Pham et al. (2020) developed and validated, against published experimental data, a updated transport model:

> *An integrated dispersion model of the CFD-Fluent and the PBM model established by Pham et al. (2016) was improved to fully understand release behaviour of CO2 gas in shallow seawater. The only CFD model was improved by including chemical reaction. The improved CFD model was implemented to perform hydrodynamic, mass transfer as well as reaction of the CO2 bubbles in both of low and high tides at the shallow seawater condition. In order to calculate breakup and coalescence phenomena, the PBM model was integrated with the improved CFD model.*
>
> (p. 14)

Having set the contest of the key components required in the modelling, some other examples of dispersion modelling strategies are presented: refer to each article mentioned for further details. The first approach that we want to mention is the one applied in the ECO_2 project (Dewar, Chen, et al., 2013). It makes use of three classes of models: a marine chemistry model, two different Near-field two-phase plume models (NFTPM) and a regional scale general circulation model (BOM, Bergen Ocean Model). Dewar, Chen, et al. (2013) reports:

> *Near-field multiphase model (NFMPM) is the model to predict the acute impact of leaked CO_2 on the marine environment. The space scale is ranging from centimetres to several kilometres and time scale from seconds to days. The data of porosity of the sediments, the topography of seafloor, the vertical (and horizontal if available) distribution of local current, temperature, salinity and background pCO2, are requested for reconstruction of a near-field scale turbulent ocean. Those data can be the field observation data or the data predicted from up-scale model (regional OGCM). The CO_2 leakage flux and sites (area) are the data for generation of plume of dispersed phase. The outputs from this NFMPM, such as the pH/pCO2 changes, can be applied for prediction of acute biological impacts* [...].
>
> (p. 11)

For reasons of completeness, DNV GL (2019) dispersion modelling approach is mentioned as well, despite being very conservative and 'rough', especially for what concerns wells' releases. CO_2 plumes arising from pipelines' releases are modelled through a software developed by DNV GL itself, called DNV GL PLUMERO, which estimates the radius of the bubble area at the sea surface (Figure 5.2). This approach is based on very conservative assumptions (see DNV GL (2019) for details), that guarantee simplicity in computations (e.g., neglecting the currents and tidal effects along the pipeline). For what concerns wells' releases, the dispersion modelling is performed by simply scaling up or down the results, in terms of pH spatial distribution, obtained by ECO_2 in Sleipner case study (Ulfsnes et al., 2015).

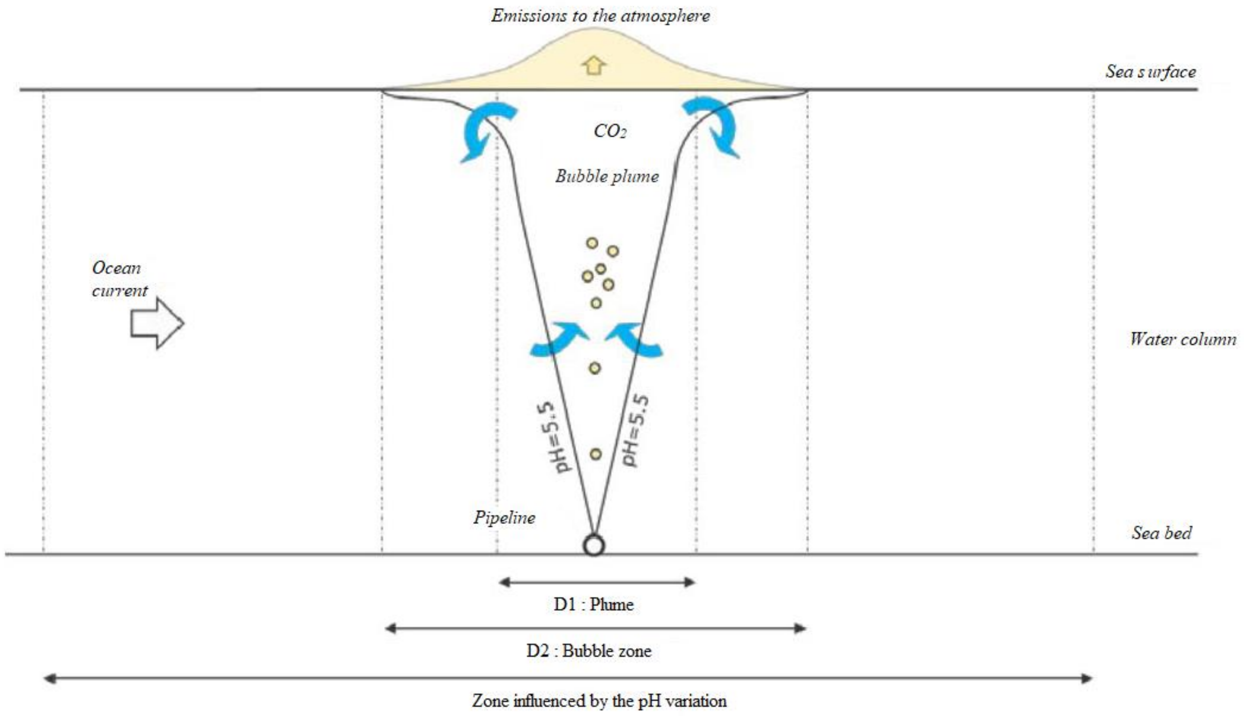

Figure 5.2: DNV GL description of CO_2 plume diffusion in seawater due to a pipeline leakage.
Adapted from: "Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2", by DNV GL, 2019. (No. 2019–0746, Rev. 1), p. 46. DNV GL. Copyright 2019 by DNV GL. (https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)

Another modelling option found in literature is given by Amir Rashidi et al. (2020) where, to quantify the coupled physical (bubbles volume changes as a net difference between the volume loss from gas dissolution and the volume gain from reduction in hydrostatic pressure) and chemical reactions ($CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^++HCO_3^- \rightleftharpoons 2H^++CO_3^{2-}$):

> *A combined Lagrangian-Eulerian modelling approach has been established, using the open-equation solver MIKE ECO Lab to predict the environmental fate of leaked CO_2 gas bubbles in the marine environment. Mathematical expressions describing the physical fates of CO2 gas bubbles have been based on the works by Zheng and Yapa (2000) and Zheng and Yapa (2002) while calculations for the DIC speciation and pH have been based on the CO2SYS model by Lewis and Wallace (1998) in the MIKE ECO Lab template.* […] *As the MIKE ECO Lab template was fully coupled to the MIKE 3 FM HD model, the model was further able to describe the advection and dispersion of pH plume under transient flows, which allows for a more accurate and realistic estimate of the plume excursion with time.*

(Amir Rashidi et al., 2020, pp. 9–10)

Moreover, in another report by Jeong et al. (2020), the behaviour and convection-diffusion of CO_2 was described by means of a multi-scale ocean model which is an improved version of the original Maritime Environment Committee (MEC) ocean model developed by the Japan Society of Naval Architecture and Ocean Engineers (JASNAOE). A modified version of the MEC (named "MEC-CO_2 model") was used in Jeong et al. (2020) study.

Generally, software developed for natural gas and oil could also be used to simulate the dispersion of a CO_2 release, in terms of bubble plumes spread, "*provided an option exists to use an equation of state for CO_2 as an alternative to natural gas and oil*" (Oldenburg & Pan, 2020, p. 17). A model with this capability is the Texas A&M oil spill (outfall) calculator (TAMOC). As Oldenburg & Pan (2020) states:

> *TAMOC is a multipurpose modeling suite for multiphase offshore oil and gas spill simulations, natural gas underwater releases, and single-phase plumes. TAMOC includes capabilities to model major blowouts or ruptures and the transition to a buoyant bubble or droplet plume as entrainment and ebullition occur.*[31,34] *[...] TAMOC uses an integral approach to model the buoyant bubble plume and entrained sea water*[34,44,45] *and models the dissolution processes by a discrete particle model.*[46,47]

(p.19)

Moreover Dissanayake et al. (2021) explains that:

> *The multi-phase plume models in TAMOC are integral models that consider the conservation of mass, momentum, and buoyancy, and provide estimates of cross-sectional averages of these parameters along the plume trajectory. The models track the mass transfer of gas from bubbles to the ambient, and expansion as the pressure drops when the plume rises in the water column.*

(p. 384)

Differently from CFD models, integral models do not suffer from having long computational times, as they are more simple and efficient (Oldenburg & Pan, 2020). TAMOC, in particular, has been tested and validated in several case studies, both in laboratory and on field. Inputs to TAMOC include CO_2 leakage rate, the diameter of the orifice, the water depth, temperature, and salinity of the seawater at the leak point, the temperature and salinity profiles in the water column and the background cross current in the water column. Moreover, being TAMOC an integral model simulates the behaviour of various size classes of bubbles, not of a single one, therefore inputs on bubble size and bubble-size distribution are required (Oldenburg & Pan, 2020). Notice that, as Dewar et al. (2013) states:

> *The initial bubble and droplet size (or equivalence diameter) is vital as it determines the rate at which the* CO_2 *rises and the rate of dissolution. Leakages of larger bubbles or droplets have more buoyancy and therefore rise faster, whereas smaller bubbles and droplets have more interfacial area at given leakage rate, so will dissolve quicker.*
>
> (p. 508)

There are different examples of TAMOC's application in literature, from point sources releases to major blowouts:

- Dissanayake et al. (2021) simulate releases form a point source releases and a line source release (which is a possible scenario from a geological fault-line or from a pipeline fracture). Dissanayake et al. (2021, p. 387) state that, to date, "*a well validated bubble size prediction model for subsea gas blowout plumes is only available in the literature for idealized scenarios (circular orifice)*" and has been developed by Wang et al. (2018), and this is indeed the model used in this work.
- Oldenburg & Pan (2020) simulate a major well blowout due to the failure of a pipeline directly connected to the injection well. Inputs come from the outputs of T2Well (see Section 5.1.2) and consists of the mass flow rate, pressure, temperature, and CO_2 density at the point of leakage. The approach used by Oldenburg & Pan (2020, p. 19) for the initial bubble size and distribution estimation is generated from a "*combination of scaling laws and empirical results*" based on Wang et al. (2018), as above. Results of TAMOC's modelling are CO_2 flowrate emitted at the sea surface and the fraction of CO_2 that dissolves in the water column. The higher the quantity of CO_2 that dissolves in seawater, the higher the potential harm caused to the marine environment by the release.

At last, notice that in the case of seepage, as seen through the cement plug / casing of wells, a different bubble-size distribution model has to be used, as the release does not possess an intrinsic velocity. One such model is presented in (Dewar, Chen, et al., 2013).

6. Effects assessment

The scope of the effect assessment is the quantification of the degree of the environmental impact caused by the contaminant of concern, which in the present work, as already explained in Section 3.4, is assumed to be solely CO_2.

Before presenting the possible methods to quantify the impact, the area to be examined has to be identified, as well as the most representative species living there. Ideally, the protection of the representative species should ensure the protection of all the organisms living in that specific environment, which, in other words, enables to analyse the impact assessment parameters only on these species and not on all of the organisms populating the site. The identification and selection of the representative species is thus a fundamental step. To such scope, ESBA methodology (used by Wallmann et al. (2015)), which is an approach to first identify the area and then assess the value of the resources, is here presented.

6.1 Identification of the area and of representative organisms

6.1.1 Ecologically or Biologically Significant Marine Areas (EBSA)

As ECO_2 states, the sites biology and habitats need to be described in a systematic way, calling attention to important species / habitats, to whom a measure of value should be assigned.
One such already established method, recognized by the Norwegian Environmental Agency, is the EBSA (Ecologically or Biologically Significant Marine Areas) approach (Wallmann et al., 2015), which has already been used in several DNV GL's risk analysis, including DNV GL (2019). ESBA's points of strength lie in its logic and transparency: this should ensure that no valued ROC is overlooked. ESBA establishes seven criteria (reported in Table 6.1) to identify ecologically or biologically important areas in the sea.

CBD COP 9 Decision IX/20		
Criteria	**Definition**	
Uniqueness or rarity	(i)	unique ("the only one of its kind")
		rare (occurs only in few locations)
		endemic species/populations/communities
	(ii)	unique/rare/distinct habitats
		unique/rare/distinct ecosystems
	(iii)	unique/unusual geomorphological features
		unique/unusual oceanographic features
Special importance for life history stages of species	Those areas required for a population to survive and thrive.	
Importance for threatened, endangered or declining species and/or habitats	Area containing habitat for the survival and recovery of endangered/threatened/declining species.	
	Area with significant assemblages of endangered/threatened/declining species.	
Vulnerability, fragility, sensitivity, or slow recovery	Relatively high proportion of sensitive habitats/biotopes/species that are functionally fragile	
	Habitats/biotopes/species with slow recovery	
Biological productivity	Area containing species/populations/communities with comparatively higher natural biological productivity	
Biological diversity	Area contains comparatively higher diversity of ecosystems/habitats/communities/species/diversity.	
Naturalness	Area with a comparatively higher degree of naturalness as a result of the lack of or low level of human-induced disturbance or degradation.	

Table 6.1: The seven criteria used in ESBA approach to identify ecologically or biologically important areas in the sea. Adapted from: "Best practice guidance for environmental risk assessment for offshore CO2 geological storage", by Wallmann, K., Haeckel, M., Linke, P., Haffert, L., Schmidt, M., Buenz, S., James, R., Hauton, C., Tsimplis, M., & Purchell, M., 2015, (265847 (D14.1)). ECO2 Project Office, p. 18. CC BY 3.0. (https://doi.org/10.3289/ECO2_D14.1)

To assign the environmental value to the site-specific resources, three steps need to be followed (Wallmann et al., 2015):

1. "Identify the area to be examined

2. Determine appropriate data sets, and identify valued resources

3. Assign environmental value"

(p. 18)

Notice that, during CCS ERA, the first two steps must be performed no matter what approach to identify the representative species is chosen; while the third point, through which ESBA assigns the value to the ROCs, is (for the reasons stated below) presented in this work as a possible technique to identify representative organisms, then subject to further detailed assessment.

Identifying the area to be examined

Wallmann et al. (2015) first assess the value of receptors in a wider geographical area and then positions the potential area at risk of CO_2 leakage, in our case based on the location of the CO_2 storage / pipeline path and on dispersion features, inside it (Figure 6.1).

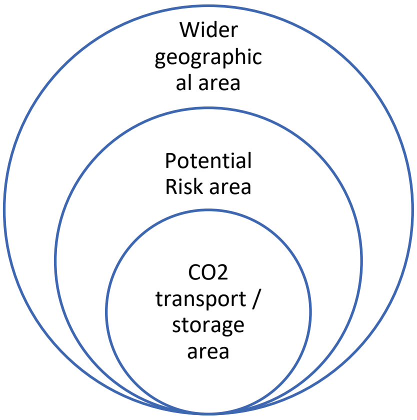

Figure 6.1: Schematic representation of how the wider and risk areas are located in respect to one another. Adapted from: "Report on environmental risks associated to CO2 storage at Sleipner", by Ulfsnes, A., Møskeland, T., Brooks, L., Flach, T., de Bruin, G., Jedari Eyvazi, F., & Geel, K., 2015, (265847 (D5.1)). ECO2, p. 16. CC BY 3.0. (https://oceanrep.geomar.de/id/eprint/29081/1/D5.1[1].pdf)

Determine appropriate data sets and identify valued resources in the area

All sources of biota and habitat information available for the wider area are consulted and documented. The data collected is evaluated against the seven aspects illustrated in Fig. (Refer to Wallmann et al. (2015) for further details). This should make available not only an overview of the ecological / biological components, but also an environmental map that traces the distributions of each identified species / habitat.

Assign environmental value

The value of the receptors identified in the wider geographical area is assigned using the following criteria (Wallmann et al., 2015):

> - ***Low value:*** *Area with local importance for species and habitats*
> - ***Medium value:*** *Area with regional importance for species and habitats, and/or having national Red List species/habitats classified as data deficient (DD) or nearly threatened (NT).*
> - ***High value:*** *Area with national importance for species and habitats, and/or having national Red List species/habitats classified as vulnerable (VU), endangered (EN), critically endangered (CR) or regionally extinct (RE).*
>
> (p. 19)

As mentioned in Section 2.3.3, Wallmann et al. (2015) underline that sufficient and traceable documentation should be made available to explain and support the reasoning used in the assignation of the value to a ROC. Wallmann et al. (2015) suggest that the value assigned by recognized frameworks (international, national and regional) can be first of all applied and, in case highly detailed data are available, it can be further adjusted. Notice, therefore, that the value assigned to each resource is case specific and dependent on the available information and the interpretation of the criteria by the assessor. A given value assignment may therefore not be 100% reproducible.

The value of the ROC is then used by ECO_2, combined with the information on the vulnerability, to determine the degree of magnitude of the consequences (approach presented among the impact assessment methods below). If a fully quantitative approach is taken, the use of this method to assign the value to the ROCs is here only recommended as a way to select representative organisms, which will then be subject to further detailed quantitative assessments.

Another approach to determine representative organisms is the PEC-PNEC ratio, which is presented in the impact assessment, for reasons that will be clearer then.

6.2 Impact assessment

The impact can be calculated in several different ways, some of which are more detailed and accurate than others. Thus, what follows is the presentation of four possible approaches, where the last one is the result of the latest research discoveries in the field of environmental risk assessment.

6.2.1 ECO$_2$ approach

What follows in the ECO$_2$ approach is the analysis of the overlap between the pH / pCO2 distribution, traced by the dispersion model, and each valued resource identified. This enables to quantify the potentially affected valuable population or habitat (expressed as a proportion of a population, number of individuals, or size of an area).

To be able to assess the degree of the consequences, however, another step is still required, which entails to evaluate the vulnerability of each valuable resource. This is done by means of a 'threshold value', which represents a *"level to which it is believed a species can be exposed without adverse effects"* (Wallmann et al., 2015, p. 20), using verifiable data sources.

The threshold values identified are then used as cut-off in the modelled pH / pCO2 distribution, meaning that no adverse effect on that specific resource is expected to happen outside that cut-off value. Based on this information, Wallmann et al. (2015) then assess the degree of the impact on each identified resource following the criteria reported below:

- ***Small degree:*** *The impact can impair/reduce species and habitats on an individual level.*
- ***Moderate degree:*** *The impact can impair species and habitats at the population level.*
- ***Large degree:*** *The impact can reduce/remove species and habitats at the population level.*

(p. 21)

The result, again, depends on the specific valuable resource considered. At last, the information on the environmental value is combined with the degree of impact assessed, and the result is used to identify the magnitude of the consequences (semi-quantitatively) through a consequence matrix (Table 6.2). The outcome value is than used as input in the risk matrix (semi-quantitative representation of risk), jointly with the result of the frequency assessment.

Value Degree		**Environmental value**		
		Low	*Medium*	*High*
Degree of impact	*Small*	Incidental	Incidental	Moderate
	Moderate	Incidental	Moderate	Major
	Large	Moderate	Major	Critical

Table 6.2: ECO_2 consequences matrix.
From: "Best practice guidance for environmental risk assessment for offshore CO2 geological storage", by Wallmann, K., Haeckel, M., Linke, P., Haffert, L., Schmidt, M., Buenz, S., James, R., Hauton, C., Tsimplis, M., & Purchell, M., 2015, (265847 (D14.1)). ECO2 Project Office, p. 22. CC BY 3.0.
(https://doi.org/10.3289/ECO2_D14.1)

DNV GL (2019) use the same approach used by Wallmann et al. (2015).

6.2.2 PEC/PNEC method

Kita & Watanabe (2008) use the PEC-PNEC ratio as value for risk assessment, where PEC stands for predicted environmental concertation and PNEC for predicted no effect concentration (Smit et al., 2004). According to this criterion, if PEC-PNEC ratio is higher than 1, there is a risk and it is likely that negative adverse effects on organisms occur, and this likelihood increases as the ratio increases. It is also assumed that, when the PEC is equal to the PNEC (PEC-PNEC ratio equal to one), the probability that a species is affected by the stressor is equal to 5% (Smit et al., 2004). However, the same Smit et al. (2004) argue against the reliability of PEC-PNEC ratio as an approach to quantify the impact, stating that, according to how risk is defined, it should quantify the likelihood and the degree of damaging effects, and the PEC-PNEC ratio does not comply with this definition. The PEC-PNEC ratio does neither provide, indeed, any characterisation of the impacts and does not quantify the likelihood. In the opinion of Smit et al. (2004), PEC-PNEC ratio can only be used for prioritisation, but not as a quantification of the degree of impact.

This prioritisation among organisms could serve to identify the most representative (site-specific) species, in terms of vulnerability to the stressor. Thus, the PEC-PNEC method can help identify the site's representative species, whose responses to the stressors are analysed when quantifying the impact, as already explained above. Therefore, it could be good practice to identify representative species based on both, ESBA methodology, that assesses the value, and PEC-PNEC ratio, that assesses the vulnerability. The use of both methods would validate ESBA results, and also guarantee more robustness to the selection of the representative species done.

6.2.3 SSD WOR method

The species sensitivity distribution (SSD) is a method that quantifies the degree of impact on the receptors of concern by describing the variation of the hazard, caused by a stressor, to the organisms (Smit et al., 2004). In other words, SSDs show the fraction of species affected by a certain level of the stressor. Generally, the variability is represented through a frequency distribution of NOEC values for the representative ROCs and the procedure to build the SSD is based on the log transformation of toxicity data and their fitting into a distribution (Smit et al., 2004). Therefore, SSDs commonly report the potentially affected fraction of species (PAF) on the x-axis against the log of the concentration of the pollutant (y-axis) (Sanni, Björkblom, et al., 2017). Notice that, among the main assumptions behind the use of SSDs as a tool to quantify the impact, in the context of effect assessment, there is that the selected representative species are representative for all species (Smit et al., 2004).

The SSDs approach has been used to quantify the degree of impact of pH on ROCs by Azevedo et al. (2015). Azevedo et al. (2015) developed SSDs based on the responses to ocean acidification for whom he considered to be representative organisms (calcifying species). These responses were categorized by Azevedo et al. (2015) in three life processes: growth, reproduction, and survival. This is the most common categorization, as growth (growth rates, body size / weight, etc.), reproduction (fertility, percentage of normal larvae, etc.) and survival (mortality and survival rates) are good indicators of the fitness of species; these are referred to as whole organisms' responses (WOR). The SSDs built by Azevedo et al. (2015) report the potentially affected fraction of species on the y-axis corresponding to different pH scenarios, on the x-axis. The change in PAF, for each life process, was calculated through Eq. 4:

$$\Delta PAF_S = PAF_S - PAF_0 \quad [4]$$

Where PAF_0 is the control PAF and PAF_S is the PAF in the new scenario (S).

Another possible impact assessment approach, derived from the one above, has been suggested by Smit et al. (2004) and consists in the usage of the SSDs to translate the PEC values into risk values. The assumption behind the development of this method is the fact that, if when the PEC-PNEC ratio is equal to one the PAF is equal to 5%, it can then be assumed that at any other level of exposure the probability that a species is affected by the toxicant is equal to the corresponding PAF in the SSD.

6.2.4 SSD biomarkers method

In ERA's regulatory context, which aims at sufficiently protecting the structure and functions of the ecosystems, reference is always made to adverse whole-organism responses, meaning, as said in the previous paragraph, survival, reproduction, or growth (Smit et al., 2009). However, a limitation related to WORs is that *in situ* measurements are really difficult (Sanni, Lyng, & Pampanin, 2017) and thus no proper monitoring can be performed during the operational activities. Monitoring is essential to guarantee that everything is working properly: this is indeed the first reason that pushed towards something that had never been done before (Sanni, Björkblom, et al., 2017), meaning the introduction of chemical and biological parameters, which are more practically measurable, in ERAs. This has been done through 'biomarkers', defined as "*detectable biological changes in organisms*" (Sanni, Lyng, Pampanin, et al., 2017, p. 11) measured in bioindicators ("*species used to evaluate biotic and abiotic environmental characteristics throughout a short or a long period*" (Zebral et al., 2019, p. 4)), after exposure to pollutants. Biomarkers can be measured at various levels of biological organisation (Sanni, Lyng, Pampanin, et al., 2017); some examples could be "*the expression of genes, the activity of enzymes, the concentration of proteins, growth, behavioural patterns, reproductive success, and many other biological processes*" (Zebral et al., 2019, p. 5).

Biomarkers are not only easily measurable in field obtained samples, which enables improved monitoring in the site, but also, they are highly sensitive to stressors (sensitive endpoints), meaning that responses occur at very low concentrations, before effects can be recorded at a higher level of biological organisation (Sanni, Björkblom, et al., 2017). Thus, they are also early impact assessment warning tools, which is very useful during the monitoring activities to identify low stressor concentrations in the area, that eventually means to help detect unplanned leaks.

It is however clear that, to be useful in the risk assessment context, biomarker responses and WOR need to be in some way related, as effects acceptability criteria in force refer only to WORs. In recent years, Sanni, Björkblom, et al. (2017), Sanni, Lyng, Pampanin, et al. (2017), Sanni, Lyng, & Pampanin (2017) suggested a relation through SSDs (alias biomarker bridges). By the SSDs, biomarker values can be related to the acceptance limits provided in ERA (commonly set at the level where 95% of the species are protected) and, by this, sub-lethal limit biomarkers' thresholds can be identified. As stated by Sanni, Lyng, Pampanin, et al. (2017): *"the rationale of this approach would be to enable the definition of threshold values of relevant parameters for different toxicities, and thereby provide more early warning capability of possible dynamic impact development than WORs can provide"* (p. 21).

By this, biomarkers can thus be used for hazard identification (early detection of biological imbalance), for assessing general ecosystem / organism health (Sanni, Björkblom, et al., 2017) and for quantifying the degree of impact of the stressor on the ROCs.
Thus, this last impact assessment approach suggested is the result of what has been reported above: after having selected the site-specific representative bioindicators, done through the combination of the information on the value of the organisms (ESBA methodology) and the one on their vulnerability (PEC/PNEC approach), pH-sensitive biomarkers (for those bioindicators) can be identified, and relative dose-response curves be plotted. This permits the translation of the outcome of the distribution model, that is the pH variation caused by the CO_2 leakage, in terms of quantified effects on the marine environment. This means to identify the spatial distribution of biomarkers levels and, through significant biomarkers-based effects thresholds, identify what type of safety measure should be introduced. As already said, the advantage of working with biomarkers would be that these could be efficiently monitored at any time on the field, so to make sure no limit threshold is overcome.

By pH-sensitive biomarkers it is meant tested biomarkers that showed variations, in their value, due to changes in pH. The ones identified in literature are reported in Table 6.3, with reference to the source, the range of pH for which they were tested and the corresponding bioindicator on which they were measured.

Acronyms reported in Table 6.3 stand for:

- AChE: Acetylcholinesterase
- CA: carbonic anydrase
- CAT: Catalase
- CBO: Carbonyl groups
- CEA: Cellular energy allocation
- EROD: CYP1A enzyme activities
- Est: Esterase
- ETS: Electron transport systemactivity
- GLY: Glycogen content
- GPx: Glutathione peroxidase
- GSH: Reduced glutathione
- GST: Glutathione S-transferase
- CBH: Total carbohydrate levels
- Hm: Hemocyte mortality
- LDH: Lactate dehydrogenase

- LIP: Lipids content
- LPO: Levels of lipid peroxidation
- Lyso: Lysosomal content
- MDA: Malondialdehyde
- PC: Protein carbonylation
- PROT: Total soluble protein content
- ROS: Reactive oxygen species
- SOD: Superoxide dismutase
- THC: Total hemocyte counts

Biomarker results can also be implemented in impact assessment models e.g., DREAM (Dose-related Risk and Effect Assessment Model)) that, taken the information of the pH spatial distribution computed by the dispersion model, are able to trace the spatial distribution of the impact (Sanni et al., 2018).

Species	**Organism**	**pH levels**	**Duration of exposure (days)**	**Biomarker group**				**Reference**
				PAH Metabolites	***Oxidative stress***	***Immunotoxicity***	***General parameters***	
Flounder larvae (fish)	Paralichthys olivaceus	8.1 7.7 7.3	49		CAT GST GPx GSH MDA			(Cui et al., 2020)
Herbivorous gastropods	Trochus niloticus	8.1 7.6	28		CAT GST LPO SOD		AChE CEA	(Zhang et al., 2021)
Thick shell mussel	Mytilus coruscus	8.1 7.7 7.3	14			Hm Est THC Lyso ROS		(Wu et al., 2016)
Polychaete, Onuphidae (bivalve)	Diopatra neapolitana	7.8 7.5 7.3 7.1	28		LPO GSH CAT SOD GST Glycogen and protein content			(Freitas et al., 2016)
Flounder larvae (fish)	Paralichthys olivaceus	8.1 7.7 7.3	49		CA	Content of LZM Content of IgM Content of HSP70 Na+/K+-ATPase Ca2+-ATPase		(Cui et al., 2022)
Mussel	Mytilus galloprovincialis	7.8 7.3	28	ETS	SOD CAT CA LPO		GLY PROT LIP	(Freitas et al., 2017)
Atlantic halibut	Hippoglossus hippoglossus	8 7.6	96		CAT GST	ROS	AChE EROD	(Carney Almroth et al., 2019)

Species	**Organism**	**pH levels**	**Duration of exposure (days)**	**Biomarker group**				**Reference**
				PAH Metabolites	***Oxidative stress***	***Immunotoxicity***	***General parameters***	
					GPx PC			
	Portunus pelagicus	8.1 7.5 7 6.5 5.5			CAT MDA GST GR	ROS	Level of total protein AChE	(Jeeva Priya et al., 2017)
Sand smelt larvae	Atherina presbyter	8 7.9 7.6	15	CBH ETS LDH Isocitrate dehydrogenase enzyme activities	SOD CAT LPO DNA damage Superoxide anion production			(Silva et al., 2016)
Baltic calm	Limecola balthica	7.7 7 6.3	50		GPx CAT GST MDA CA SOD		AChE CBO	(Sokołowski et al., 2021)
Calcifyng organisms	Mussel Mytilus edulis	7.7 7 6.5	21		CA			(Zebral et al., 2019)
	Mussel Mytilus edulis	7.7 7.5 7.4 7.3 7.2	30					
	Two oyster species from Crassostrea genus (C. gigas and C. angulata)	7.3	28					
	Coral Mussismilia harttii	7.5 7.2	15 35					

Table 6.3: pH-sensitive biomarkers, with references to the bioindicator, the range of pH in which they were tested, the duration of the exposure and the reference.

7. Frequencies estimation

Risk is often quantitatively expressed as a combination of frequency and the magnitude of the failure scenario. This chapter addresses frequency estimation.

Before the presentation of the possible methods to estimate the frequency, an observation needs to be made: data on frequencies usually referr to the release scenarios and not directly to the final scenarios, meaning the CO_2 dispersion in water. However, in this perecise context, no distintion beween the frequencies of the release and final scenario is needed, as the CO_2 dispersion in water is the only final scenario that can arise from a CO_2 subsea release. Attention needs to be paid only in the case of pipelines, where holes' size distribution are available, because the freqency of the final scenario corresponds to the product of the release frequency and the probability of occurrence of the specific hole considered (reported in the Tables of Section 4.2.2)

Failure rate data for release scenarios can be obtained in a multiple number of ways (Energy Institute (Great Britain), 2013):

- From databases and literature sources;
- By sample testing;
- From plant experience;
- By predictive techniques (e.g., by using fault tree analysis or by Bayesian Belief Networks (Wallmann et al., 2015)).

Just as an example, Wallmann et al. (2015) have developed:

> *A prototype Bayesian Belief Net (BBN) that implements the first method of aggregating expert opinion* [refer to Wallmann et al. (2015) for further details] *and evidence. The* ECO_2 *project tested one of these by building a prototype PTL model based on a BBN software tool which implements the basic mathematics of Bayesian inference using a graphical interface and representation of causal linkages. There are several advantages to the BBN platform, but here we mention the main one for estimating the PTL* [(propensity to leak)]. *The BBN can combine qualitative, quantitative, statistical and expert opinion data in a way that represents the main evidence for each site-specific FEP, and the evidence can include ambiguity, i.e. can be inconclusive or point in contrasting directions.*
>
> (p. 23)

Clearly, a predictive method, like the one proposed by Wallmann et al. (2015), that is strictly based on site-specific information / considerations, could bring greater specificity in the final frequencies' estimates. However, for the scope of the work, in alternative, or in addition (as a confront to validate the results), to this approach, we are also presenting the frequencies' reports found in literature, even if, as said, they might be less specific, being generally based on natural gas historical data (especially for what concerns pipelines).

7.1 Failure frequencies for pipelines

7.1.1 Influencing Parameters

There are numerous factors that influence pipelines' failure frequency: DNV GL (2017) provides an overview (summarised below) of the relationships between failures and influencing factors. However, it is complicated to isolate each parameter's influence on the failure frequency: it is done uniquely when detailed risk analyses are performed. Therefore, only qualitative considerations on influencing parameters are here reported. DNV GL (2017) itself stresses on the fact that effects, on failure frequency, from one parameter would be taken into account several different times when trying to identify its specific effects. DNV GL (2017) therefore believes that frequencies should rather be discussed with reference to failure modes, thus according to their causes, rather than in relation to influencing parameters.

Process medium

As reported by DNV GL (2017), several sources believe that oil pipelines have higher failure frequencies than the corresponding gas pipelines, but notice that, often, gas pipelines have higher design pressures, thus a larger wall thickness. This could be an explanation to why gas pipelines seem to be less prone to leakage than oil pipelines. Thus, what DNV GL (2017) deduces is that, from the available data, it is not possible to prove a relevant influence of the process medium, as an isolated parameter, on the failure frequency.

Installation

Pipelines with small diameters are typically buried during the installation process, which is something that can, itself, threaten the integrity of the pipeline. However, the bury reduces the chances of damage caused by dropped objects, thus the net result is beneficial for what concerns the risk of loss of containment (DNV GL, 2017).

Corrosion prevention

Corrosion prevention is a fundamental aspect during the design phase of pipeline. Sources (see DNV GL (2017) for details) report that internal corrosion is dominating for offshore pipelines, indeed, for what concerns external corrosion, offshore pipelines' corrosion prevention system is effective and reliable (moreover the surrounding seawater contributes by providing stable conductivity).

Pipeline material

For steel pipelines, the failure frequency increases with increased material strength. The reason behind this is that increased material strength permits to reduce the wall thickness, but this translates into a reduction in the ability to withstand corrosion (shorter time period for an corrosion to reach critical levels) and external interference (see DNV GL (2017) for details).

Material utilization factor

The material utilization factor indicates the relationship between the tangential / circular tension, due to the pressure difference between the pipeline’s inside and outside, and the material strength (DNV GL, 2017). For offshore pipelines this value is within a range that goes from 0.72 to 0.85 (DNV GL, 2017). If corrosion is limited to a local area, the material utilisation factor will not impact on the pipe’s ability to withstand the pressure difference, thus, the utilization factor will not have any impact on this failure mechanism (the leak before rupture can be fixed). By contrary, for corrosion over larger areas, a large utilization factor will lead to a shorter time period for corrosion to result in failure.

Age

DNV GL (2017), after a literature review, concludes that existing reports are quite uniform when assessing the impact of pipeline age on failure frequency. Pipelines normally go through an initial period of time (from 1-2 years to 10 years depending on the case) in which higher failure frequency are recorded, if compared to the remaining part of their design life, where the failure frequency is almost constant. The reasons for this have to be searched into external interference, operational issues, material failure and defect welds. For example, when the pipeline system is fist used, an increase in surrounding activities in the area is expected, which translates into higher frequency for falling objects. Moreover, most of fabrication defects in material or welds will be revealed in the first years of activity of the pipeline. Therefore, for what concerns the influence of the aging of the pipeline on the failure frequencies, the Concawe reports (2016, as cited in DNV GL, 2017) conclude that there is no evident relation between the ageing of the pipeline system and the risk of leakage.

Size

As DNV GL (2017) says, several sources believe that, as the diameter increases, pipelines’ failure frequency decreases. A large diameter is usually associated to a larger wall thickness, which permits to have more resistance against external interference and against corrosion. However, some sources reported by DNV GL (2017) believe that the real reason why frequencies have this trend with the diameter is that large diameters are often used over long distances, while smaller diameters are usually found in the pipelines near the platform zone (higher activity intensity). Thus, it is impossible, with the data available for the moment, to prove the existence of a negative correlation between pipeline diameter and failure frequency.

Length of line

The isolated effect of the length of the subsea line on failure frequencies is hard to determine as the increased corrosion / material defects with the length of the pipeline could be also due to two aspects, rather than simply being correlated with the length of the pipeline:

- In shorter pipelines flow rates are higher;
- Longer pipelines have got larger diameters and wall thicknesses.

Location

For what concerns offshore pipelines, the highest failure frequencies are found near the platform, where activities are more intense. Therefore, when calculating the frequencies, local conditions must be considered too.

As a conclusion of this qualitative introduction to the influencing parameters, it can be stressed out again that the parameters can be often linked to each other, in several different ways, thus the effect of isolated factors is hard to assess.

7.1.2 Data banks and literature sources for pipelines

Some literature sources concerning CO_2 pipelines failure frequencies are reported in this paragraph with their own assumptions and observations to justify the usage of specific sets of data.

A detailed study has been done by Duncan & Wang (2014), where safety records of natural gas pipelines have been used as an analogue for CO_2 pipelines based on the following similarities (refer to Duncan & Wang (2014) for further details):

- Generally, the same grades of carbon steel are used (API 5 X55 to X70 or higher);
- The welding and installation techniques applied are the same;
- The internal and external coatings are similar if not the same;
- If the gas is not properly dehydrated or contains impurities (CO_2, H_2S, NO_2 or other acid) the corrosion issues encountered are the same;
- External corrosion is mitigated through the same cathodic protection;
- In many jurisdictions the same ASME design code applies for both pipelines.

However, Duncan & Wang (2014) also remind that not all the design requisites for natural gas and CO_2 pipelines are exactly the same: for example, ‘anthropogenic CCS CO_2’ could contain impurities that can strongly contribute to corrosion mechanisms. Despite this observation, Duncan & Wang (2014) conclude that the ‘natural gas – CO_2 analogy’ has no more value only if no satisfactory dehydration of the CO_2 stream is performed, or if the concentrations of the contaminants are not kept at very low levels. Therefore, in all the other general offshore CO_2 pipelines' cases, the following applies:

> *In the absence of any information on pipeline failures* […], *the use of information from an analogue, such as offshore natural gas pipelines, seems the most useful approach to understanding the likelihood and consequences of failure of future sub-sea CO_2 pipelines for sequestration.*
>
> (Duncan & Wang, 2014, p. 137)

Duncan & Wang (2014) work is based on information from a database on natural gas pipeline incidents from the U.S. Pipeline and Hazardous Materials Safety Administration (PHMSA). Using historical data has its pros and cons, Duncan & Wang (2014), indeed, state that:

> *The implicit assumption in this approach is that historical incident rates (and the temporal trends in these rates) can be extrapolated to predict future outcomes. This approach assumes that a complete spectrum of types of accidents is represented in the data. The problem with this assumption is that the data sets may be too limited to accurately predict the future occurrence of low-frequency but high-consequence events. These kinds of events that may not be represented in our actuarial data set are sometimes referred to as the "unknown-unknowns".*
>
> (p. 132)

Moreover, historical data many not be able to predict future events due to improvements in technologies and materials used.

PHMSA defines three types of failure:

- Leaks (pinhole or puncture failure);
- Ruptures (longitudinal or circumferential crack);
- System-component failures (malfunction of valves, failure of mechanical joints, breaks in fittings, or flaws in compressors).

In PHMSA database, each of these failures has been attributed several causes: internal corrosion, external corrosion, outside forces and defects in construction or materials. However, Duncan & Wang (2014) state that generally causes are linked with one another, thus it might be hard to divide the failure data in neat categories.

Another literature report that deals with CO_2 pipelines' failure frequencies is the Energy Institute (Great Britain) (2013), which has already been mentioned in the hazard identification. The premise made by this article, similarly to the work by Duncan & Wang (2014), is that frequency data for risk assessment coming from data banks and literature sources might carry drawbacks in terms of accuracy. First of all, historical data can be incomplete or not up to date, thus not applicable to present processes. Moreover, the most accurate risk prediction consists in calculating the failure rate for the cause of the specific failure scenario. However, as CCS is an emergent technology, there is a lack of data on CO_2 pipelines' failures and it is thus difficult to collect such information in great quantity. Therefore, more generalised sources of data are commonly used for CO_2 pipelines risk calculations, with eventual readaptations (Energy Institute (Great Britain), 2013). Otherwise, these generalised data can be used to calculate the frequency of the worst-case scenarios. Databases mentioned by Energy Institute (Great Britain) (2013) are:

a) PARLOC 2001: the most comprehensive database for offshore gas pipelines available (report published by UK HSE entitled PARLOC 2001 Pipeline And Riser Loss Of Containment). In its most recent version, incidents from the 1960s until 2000 are covered. Data geographically come from the UK, Norway, the Netherlands, Denmark and Germany;

b) European Gas Pipeline Incident Data Group (EGIG): cooperation of 12 major European gas transmission system operators and owner of an extensive data base of pipeline incident (information collected since 1970);

c) UKOPA report: collaborative pipeline and product loss incident data from onshore Major Accident Hazard Pipelines (MAHPs) operated by National Grid, Scotia Gas Network, Northern Gas Network, Wales and West Utilities, Shell UK, BP, Huntsman and E-ON UK, (information up to the end of 2006);

d) CONCAWE: inventory that covers European pipelines failures from, in its latest version, 1971 to 2019;

e) Pipeline and Hazardous Material Administration (U.S. Department of Transport): collection of data specifically related to transmission of compressed supercritical CO_2 (used by Duncan & Wang (2014) as well).

A summary of the pipeline failure data is reported in 'Table A.2 – Annex A' by the Energy Institute (Great Britain) (2013), in incidents per 1000 km/year (it could not be reported here for reasons of copyright). According to Energy Institute (Great Britain) (2013), PARLOC 2001 data are the most relevant, as they are exclusively related to offshore incidents.

At last, in the alredy mentioned DNV GL's report (2017) the case of CO_2 pipelines is considered as well. According to the authors' opinion, if sufficient operations' monitoring is performed, in compliance with procedures, failure frequencies for hydrocarbons pipelines can be used for CO_2 pipelines. In case there are doubts associated to the adequacy of monitoring or of procedures, hydrocarbons' pipelines failure frequencies cannot be used and a detailed, case specific, analysis of the CO_2 pipeline is necessary. However, it is always better practice, when estimating failure frequencies, to consider all information on the specific pipeline (operational experience, inspection results etc.) and involve experts in the evaluation.

Data sources used in DNV GL's report (2017) to assess offshore pipelines' failure frequencies are (details reported in DNV GL's report (2017)):

- PARLOC 2001, issued in 2003 (5th edition);
- PARLOC 2012, issued in 2015 (6th edition);
- NCS.

DNV GL (2017) finally develops a specific failure frequency model for offshore transport pipelines, based on data of North Sea pipelines, that have been divided into categories with reference to their dimensions, area of operation and transported medium. Only some of these groups, identified by DNV GL (2017), are here relevant, as CO_2 for CCS is a processed fluid (its composition ensures that acceptance criteria for corrosion rates are respected):

- Steel pipelines transporting processed fluid, with diameter ≤24"
- Steel pipelines transporting processed fluid, with diameter > 24"

The offshore transport pipelines model, by DNV GL (2017), to estimate failure frequency consists of three elements: a first length dependent element, a second length independent, which results from pipeline characteristics and surrounding conditions, and a last one that accounts for anchors being unintentionally dropped and dragged on the pipeline (see Appendix E of DNV GL (2017) for details). This model has also been used in DNV GL (2019) to assess subsea pipelines failure frequencies. The frequency calculated by the model is thus expressed by Eq. 5:

$$Frequency = f_{km} \cdot Pipeline\ Lenght + f_{Score} \cdot Pipeline\ Characteristics + f_{Dragged\ Anchor} \quad [5]$$

And the value of the parameters, depending on the case analysed, can be taken from DNV GL (2017) and are reported in the table below (Table 7.1).

Factor	**≤ 24”**	**>24”**	**Unit**
Length dependent failures (f_{km})	$1.7 \cdot 10^{-5}$	$5.5 \cdot 10^{-6}$	Per km year
Length independent failures (f_{Score})	$7.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	Per score grade-year
Failures related to dragged anchors from ships underway ($f_{Dragged\ Anchor}$)	To be evaluated according to appendix E.	To be evaluated according to appendix E.	Per year

Table 7.1: DNV GL’s recommended failure frequencies for offshore pipelines containing processed fluid. From: “Recommended failure rates for pipelines”, by DNV GL, 2017, (No. 2017–0547, Rev. 2). DNV GL, p. 36. Copyright 2017 by DNV GL.

The score is used to account for length independent parameters and its value is assessed considering the operational experience and the knowledge of the loads that could impact the pipeline (see 5.2.3 of DNV GL (2017) for details).

One last observation is that DNV GL (2019) identifies ranges of probabilities’ values corresponding to three failures frequencies’ categories (Table 7.2) set by ECO_2 (in reference to storage leakages). The attribution of the frequencies’ class is then implemented, with the information regarding the degree of impact, in a risk matrix (developed by Wallmann et al. (2015)). More details on this risk matrix are presented in Chapter 8.

Category	**Description**
Unlikely	Less than 1% probable over the project period of 25 years Exposure rate less than $2 * 10^{-4}$ per year.
Possible	Between 1% and 10% probable over the project period of 25 years Exposure frequency between $2 * 10^{-4}$ and $2 * 10^{-3}$ per year.
Likely	Between 10% and 100% probable over the project period of 25 years Exposure frequency between $2 * 10^{-3}$ and $2 * 10^{-2}$ per year.

Table 7.2: DNV GL’s classification of the probability. Adapted from: “Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2”, by DNV GL, 2019. (No. 2019–0746, Rev. 1). DNV GL, p. 39. Copyright 2019 by DNV GL. (https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)

7.2 Failure frequencies for injection wells

For what concerns the assessment of the failure frequencies associated to wells' failures, the methods presented at the beginning of the chapter still hold true. As anticipated, the following reasoning, concerning wells' leakages, applies:

> *[H]undreds of thousands of wellbores in the oil and gas industry have provided deep insight into why and how frequently wellbores leak both during active operations and after they have been plugged and abandoned. However, the overall impression of these subsurface industrial analogues is that although they have large statistical databases of performance, these have limited relevance for predicting future performance of* CO_2 *geological storage sites. The reasons are varied, but the conclusion is clear. It is considered best practice to estimate probability for a given* CO_2 *geological storage site leakage scenario based on site-specific geological and engineering system descriptions. This entails constructing a structural model* [(refer to Wallmann et al. (2015) for further details on the models used)] *of the specific storage site subsurface based on seismic and wellbore data and subsurface engineering description of the specific storage complex and injection project, complete with the relevant uncertainties including those implied in forward modelling.*
>
> (Wallmann et al., 2015, p. 15)

However, as it has been done with pipelines, the literature sources' alternative is here presented as well. The sources that deal precisely with CO_2 wells are ZEP (2019) and DNV GL (2019).

7.2.1 ZEP

The origins of ZEP's (2019) data, and other related observations, have already been mentioned in Section 4.2.3. The table reporting the probability associated to each failure scenario is here recalled (Table 7.3).

Scenario	**Probability of leakage (%)**	**Peak Leakage Rate (t/d)**	**Duration (in years or days)**	**Total Mass Lost to surface (tonnes)**
Active well leakage	0.5	50	250 days	12500
Active well blowout	0.15	5000	250 days	1250000
Abandoned well blowout	0.1	3000	1 years	1095000
Seepage in abandoned well	0.5	7	100 years	255500
Severe well problem, no repair successful	0.005	6000	2 years	4380000

Table 7.3: Leakage parameters for wells' failure scenarios in a North Sea storage.
Adapted from: "CO_2 Storage Safety in the North Sea: Implications of the CO_2 Storage Directive", by ZEP, 2019. Zero *Emissions Platform, p. 30.*
(https://zeroemissionsplatform.eu/wp-content/uploads/ZEP-report-CO2-Storage-Safety-in-the-North-Sea-Nov-2019-3.pdf)

7.2.2 DNV GL for Equinor

The estimation of wells' failure probabilities, done by DNV GL for the Northern Lights project (2019), is based on the report *"Input to ERA Memo May 2019"*, with reference to the supplementary report *"Northern Lights (Aurora Complex) Subsurface Containment Bowtie Analysis, Issue 3.0"* (DNV GL, 2019). Notice that these data are case-specific and could, if practically possible, find a more general applicability only after expert and specific evaluations.

As for ZEP (2019), the table is recalled (Table 7.4).

Scenario	**Probability**	**Mass-flowrate released**	**Duration**
CO_2 leakage via injection wells during the injection period	< 1%	≤ 10 ton/day	≤ 1 year
CO_2 leakage via bean heads after the injection period	< 1%	≤ 1 ton/day	≤ 100 year
CO_2 migrates from the well to the overlying sediment packet ("overburden") during the injection period	< 1%	≤ 1 ton/day	≤ 1 year
CO_2 migrates vertically under Drake roof rock in Aurora, for example towards fault zones in NW / SW, migrates north towards Troll, and leaks out of existing well (s)	< 1%	≤ 1 ton/day	≤ 100 year
CO_2 migrates north to the Troll area through the Johansen / Cock formations, passes the Svartalv fault, and leaks out of existing well (s)	< 1%	≤ 1 ton/day	≤ 100 year
CO_2 migrates north to the Troll area through the Johansen / Cock formation, and leaks out of existing well (s)	< 1%	≤ 1 ton/day	≤ 100 year

Table 7.4: Leakage parameters for wells' failure scenarios, in relation to Northern Lights project. Adapted from: "Miljørisiko for EL001, Northern Lights, mottak og permanent lagring av CO_2", by DNV GL, 2019. (No. 2019–0746, Rev. 1). DNV GL, p. 32. Copyright 2019 by DNV GL. (https://cdn.sanity.io/files/h61q9gi9/global/d7d0d989ebb7229e00b1e0a93863c042914ff672.pdf?miljoerisiko-for-el001-northern-lights-mottak-og-permanent-lagring-av-co2-equinor.pdf)

The three categories for failures frequencies, identified by DNV GL (2019) (Table 7.2), are applied by DNV GL (2019) to wells' failures frequencies too, and the attribution of the frequency class is then implemented in the risk matrix (Wallmann et al., 2015).

8. Risk characterization

In the previous chapters approaches to assess the severity of the environmental impacts caused by potential CO_2 releases in seawater have been presented (Chapter 6), and for each scenario, methods to estimate the frequency have been identified (Chapter 7). Having collected these data, risk can be characterized. First of all we are briefly mentioning the method to characterize risk developed by Wallmann et al. (2015), and used by DNV GL (2019) as well, having taken them as reference works. Afterwards, quantified metrics are introduced for a finer description of risk.

8.1 ECO_2 approach

Wallmann et al. (2015) (i.e., ECO_2 project) characterize risk by means of a risk matrix (Table 8.1).

Severity measured in Environmental Value / Propensity to Leak	**Severity of environmental impact**			
	Incidental	*Moderate*	*Major*	*Critical*
Unlikely	Negligible / small negative	Negligible / small negative	Moderate negative	Large negative
Possible	Negligible / small negative	Moderate negative	Large negative	Severe negative
Very Likely	Moderate negative	Large negative	Severe negative	Severe negative

Table 8.1: ECO_2 risk matrix.
From: "Best practice guidance for environmental risk assessment for offshore CO2 geological storage", by Wallmann, K., Haeckel, M., Linke, P., Haffert, L., Schmidt, M., Buenz, S., James, R., Hauton, C., Tsimplis, M., & Purchell, M., 2015, (265847 (D14.1)). ECO2 Project Office, p. 27. CC BY 3.0.
(https://doi.org/10.3289/ECO2_D14.1)

The information required to enter in the risk matrix are, for what concerns the severity of environmental impact, obtained through the methods used by ECO_2 to assess the impact on the valuable organisms presented in Section 6.2.1 and, for what concerns frequency's range, the three categories are dealt with in the report by DNV GL (2019), which readapts them to the case of pipelines / wells (Section 7.2.2).

Notice that, in Table 8.1, Wallmann et al. (2015) have established criteria for the acceptability of risk: categories have indeed been set on the base of the value of both the severity of the environmental impact and the frequency of the scenario.

ECO$_2$'s method has already found on field applications (DNV GL, 2019; Ulfsnes et al., 2015) and has proven to be a valid way to approach the thematic of risk characterization for CCS; however, it must be noticed that it is a risk matrix-based characterization of risk, not a fully quantitative approach based on quantitative risk metrics as described in the following.

8.2 Risk metrics

As presented in Section 1.6, quantified expressions for risk can be established, assuming that quantified values, and not only ranges, for expressing both the impact of the consequences and the frequency of the failure scenario, are available. This is the case, as quantitative methods to assess both impact and frequency have been identified in the framework. One such approach to express risk in a quantified way is through risk metrics. Johansen & Rausand (2012) have made available an overview of existing risk metrics, for damages referred both to humans and to the environment. Before the relevant ones are presented, some terms' meanings have to be clarified:

- *"Individual risk: The risk to an actual or hypothetical individual related to single or multiple events.*
- *Societal risk: The risk to a society or population related to a single event that may affect multiple persons."*

(Johansen & Rausand, 2012, p. 1)

The risk metrics, in relation to environmental damage, identified by Johansen & Rausand (2012) are:

1. Potential environmental risk (PER): It represents the *"frequency of a defined consequence category for a certain organism, population, habitat or ecosystem within an area"* (Johansen & Rausand, 2012, p. 3). PER is an individual risk (whose 'loss of life analogous' is the individual risk per annum - IRPA) and it is calculated as follows (Eq. 6):

   $$f = \lambda_S \cdot \Pr(E|S) \cdot \Pr(C|E) \quad [6]$$

   Where λ_S is the frequency of the spill S per year, E is the exposure to the spill for the area ('a') and C is the undesired consequence associated to that release scenario. Notice that reference is made to the frequency of the spill, meaning the initial release scenario, but for our case, this coincides with the frequency of the final scenario. Moreover, the probability that, given the exposure to the spill, organisms encounter undesired effects (Pr $(C|E)$) can be seen as the value of PAF, obtained from the SSDs, either WOR or biomarkers related. The undesired effects to which the consequence scenario (C) is referring are those to which the PAF used is referring to.

   As for the 'loss of life' case, where the localized individual risk (LIRA) is defined from the IRPA neglecting the probability of presence of the individual in the area of impact (Pr (E|S)), which is indeed difficult to estimate, the same reasoning could be applied for the environmental case. This would permit, as the LIRA does with the IRPA, to conservatively estimate the PER in those cases in which the parameter Pr (E|S) is not available.

2. Recovery time (RT): It represents *"the probability per year of having an accident that exceeds the time needed by the ecosystem to recover from damage"* (Johansen & Rausand, 2012, p. 3). It is an individual risk and it is calculated as follows (Eq.7):

$$f = \lambda_S \cdot \Pr\,(D_d > RT) \quad [7]$$

Where λ_S is the frequency of the spill S per year, D_d is the damage duration and RT is the required recovery time. This metrics is however of limited applicability, as the recovery time may be impossible to establish in advance (Johansen & Rausand, 2012).

3. FE diagram: It is a *"diagram displaying the relationship between the frequency and environmental /- economic loss in a single accident"* (Johansen & Rausand, 2012, p. 3). It expresses a societal risk (whose 'loss of life analogous' is FN diagram) and is represented through a plot which has on the x-axis the environmental damage (E) and on the y-axis the cumulate frequency (F_e), meaning the frequency of all of the accidents that cause a loss of at least 'E'. The environmental damage (E) can be calculated, for example, by multiplying the value of PAF with the total number of organisms living in the area of impact: this computes the number of organisms affected. Notice that, if the PAF is not constant over the whole area of impact, an integral should be used, where the value of PAF depends on the location (Eq.8):

$$E = \int_{A1} PAF(A) \cdot \rho(A) \cdot dA \quad [8]$$

The advantage of this risk metrics is in its capability to distinguish between high consequence - low probability and low consequence - high probability events (Johansen & Rausand, 2012).

For what concerns acceptability criteria, as it has been done with the 'loss of life analogue', they should be set for these environmental parameters as well. Environmental thresholds for these values should be set referring to PAF's value in relation to WORs (notice that WORs, for example, the number of deaths, are universal parameters). These can then be translated into biomarkers' PAFs, reported on the y-axis of the biomarkers based SSD, through the method presented by Sanni, Lyng, Pampanin, et al. (2017) and Sanni, Lyng, & Pampanin (2017), being the biomarkers, and their correlated effect (to which the biomarker-PAF is referred), stressor-specific (thus not universal).

Limit thresholds are generally defined by international /national governments, which, in other words, is out of the scope of this work. However, efforts should be made to define these criteria in the near future, so to be able to apply this quantified risk analysis also to the environmental aspects of CCS.

9. Discussion and recommendations

The aim of this work, discussed in Section 1.4, was, briefly, to suggest several alternative approaches to perform each ERA's step applied to CCS (confined to the activities of transport and injection) and to be able to quantitatively determine risk.

As already mentioned in Section 2.5, for reasons of time, not every single aspect has been treated in the required detail and alternative approaches have only been presented, without performing a final selection. Despite the immediate utility of this work as a guidance in the risk assessment, as it provides a step-by-step procedure, a final and complete methodology should be developed, by performing the end of phase two and phase 3 of McMeekin et al. (2020), regarding, respectively, the optimization of each steps and the reaching of experts' consensus on the techniques selected to complete the procedure. Future studies should therefore address the accuracy and efficiency of the methods here suggested and, by that, identify a definitive and standardized approach to perform CCS ERA, for the activities of transport and injection.

A general comment on what has been done in each section is here presented and, in addition to that, some recommendations for future advancements are suggested, in relation to refinements needed and knowledge gaps that should be addressed:

1) Problem Formulation: In this first step of the ERA, the goal of the ERA has been clearly stated out and contextualised. Moreover, in the conceptual model, the logical pathway followed throughout the work has been summarized. To introduce our future recommendation, we need to stress once more on the identification of the COCs. Only CO_2 has been considered in this work, however, for a more complete risk assessment procedure, the impact of impurities, that could be present in the stream, should also be considered. Future researche should therefore work towards the integration of the relevant information, concerning how environmental risk posed by impurities should be dealt with, inside this framework.

2) Hazard identification and characterization: The results emerged in this second step are a series of potential causes, that could lead to pipelines' or wells' failure, and the corresponding most credible failure scenarios that could arise from them. Credible scenarios were then quantitatively characterized, either by means of a mass flowrate released or by a hole size. The suggestion is, in order to perform the most complete environmental risk assessment, to apply a hazard identification technique to the specific system and identify, through that, a series of possible failure scenarios to be simulated, and add to those the general scenarios identified by this work.

3) Exposure assessment: In this part of the ERA, carbon's fate in the exposure pathway (water) has been addressed. Several alternative approaches have been proposed and some relevant points have been highlighted, for example, the higher accuracy in the description of the release achievable through release models, or, moreover, important aspects, related to transport (Pham et al., 2020), that should be taken into account for a finer modelling of the dispersion. However, an important selection of the most accurate and efficient models should be performed, both for what concerns the description of the release and both for the dispersion,

and adjustments on the procedure chosen should be done to give relevance to the observations done by Pham et al. (2020). Moreover, other knowledge gaps still need to be addressed as well. There are already some research projects, that will be available in the recent future, that are oriented towards the solving of uncertainties. One such study Spinelli & Ahmad (2015) is already taking place. As Spinelli & Ahmad (2015) state:

> *The lack of knowledge on CO_2 subsea release behavior must be filled with a scientific approach; this would help in growing the chances for an industrial deployment of CCS-EHR technologies and its acceptance. The Joint Industry Project Sub- CO_2 will explore CO_2 subsea releases by generating data from well-defined experiments under different conditions of leak size, pressure, water depths and direction of the release. The purpose is to generate knowledge for models improvement and to provide guidance for "model developers" in undertaking leak consequence assessments. Information is needed about what happens when CO_2 is released underwater, the behavior of plumes and bubbles and how the CO_2 disperses above water. Better understanding is also needed of the CO_2 outflow, at the leak point, for different sizes of release, at different release depths. The effect of CO_2 release on water acidity will be measured in various failure scenarios including different release rates and water depths.*
>
> (p. 1113)

4) Effect assessment: quantitative approaches have been suggested for this step of the ERA, by means of the SSDs. Moreover biomarkers-based SSDs have been given relevant attention due to the substantial advantages offered by the use of biomarkers in the field of environmental risk assessment (see Chapter 6 for details). What we would suggest for future research works is to officialise the utilization of certain pH-biomarkers and to start implementing this information inside effect assessment software (e.g., DREAMS).

5) Frequencies estimation: In this step of the procedure, we have mainly dealt with frequency's data sources and some other alternative approaches have only been mentioned, for example, predictive approaches (e.g., Wallmann et al. (2015)). For what concerns pipelines' historical data, we have seen that, in certain cases, there could still be some uncertainty on whether natural gas failure frequencies accurately apply to the case of CO_2, thus, further verifications should be done in this sense. While, in relation to predictive models, that, as said in Chapter 7, are more case specific, further tests should be performed to either be able to obtain more accurate frequency values, than the analogue historical data (based on natural gas), or as a validation of the last ones.

6) Risk characterization: For what concerns this conclusive part of the ERA, approaches to quantitatively determine risk, caused by a failure scenario, have been proposed, by means of risk metrics. As said at the end of Chapter 8, there is the impelling need to define standardized limit thresholds, in relation to risk metrics, above which risk must be reduced. This would finally permit to extend the application field of the quantitative risk assessment also to the environmental aspects of CCS.

It is thus hoped and, in part, expected that, seen the urgency of this issue, this work will be taken as a helpful starting point for the development, by means of the adjustments and recommendations listed above, of a final and complete methodological framework for the environmental risk assessment of CCS (with reference to transport and injection only).

The availability of such standardized practical guidelines should guarantee the performance of the best structured and stricter environmental risk assessment of CCS, which is a fundamental step towards the gain of social consensus, and thus the diffusion, of this GHGs mitigation strategy.

10. Conclusion

To conclude, the preliminary methodological framework developed by this work is our answer to the impelling need to define complete and standardized practical guidelines to assess and manage marine environmental risk associated to CCS projects, for the aspects concerning the subsea engineering systems.

To briefly retrace this work's steps that led to the final achievement of the scope of this work, which was to start setting the way for the development of a complete and standardized procedure to perform a quantified ERA for the subsea engineering systems, we have to initially recall that a structure for the framework has been identified. This has been done by selecting the general ERA aspects that could have been relevant to our case and integrating them with the knowledge on quantified risk assessment. Two reference works have than been selected (DNV GL, 2019; Wallmann et al., 2015) and integrations have been made with the aim to: extend the application field of these guidelines, suggest newer solutions and being able to quantitatively describe risk. By means of a vast literature review, alternative methods to approach each of the framework's steps have been proposed and, when possible (as not all approaches and theories have been analysed in sufficient detail), some comparisons and considerations have been made, despite not arriving to a final and definitive selection of the best methods to be used.

The aim, during a risk assessment, is to simulate potential credible failure scenarios, associate to those a risk level and, by the evaluation against acceptance criteria, identify appropriate risk measures to either reduce risk or maintain it acceptable. Notice that the description of risk adopted in this work both accounts for the magnitude of the impact and the frequency / probability associated to the occurrence of the failure scenario.

An overview of failure causes, and associated credible leakage scenarios, has been presented in the 'hazard identification and characterization' (Chapter 4). Then, in order to describe the fate of CO_2 in seawater, credible failure scenarios have been characterized, in terms of mass flowrate released, or hole size of the leakage, and have been modelled by means of release and dispersion models. Several alternative approaches have been proposed, however, for the purpose of developing definitive methodological guidelines for CCS environmental risk assessment, a selection of the most accurate and efficient methods should be performed.

Given the results of the dispersion model, the effects could be described. Various methods to describe the degree of impact are available, however, argumentations have been played in favour of biomarkers-based SSDs, as they provide a quantified information on the degree of impact with reference to biomarkers, that are sensitive and easy to measure endpoints.

Moreover, techniques to assess frequencies have been presented. Predictive approaches have been just mentioned, as an alternative to historical data, but have not been dealt in detail. While, for what concerns historical data, databases or reference literature sources have been cited. In the case of pipelines, whatever technique one decides to apply, the usage of the method by DNV GL (2017) to assess subsea pipelines failure frequencies is strongly recommended, as it separately gives relevance to different influencing factors. Regardless, further research should be carried out in relation to frequencies estimation, in order to collect more accurate and case-specific data.

At last, having identified procedures to assess the degree of impact and methods to estimate frequencies, risk has been quantitatively characterized by means of risk metrics. Our focus has been mainly on risk metrics as they not only comply with the description of risk used in this work, but they also provide a quantitative characterization of the level of risk. There is, however, still much work to be done to consolidate their use, as limit threshold for these values, applied to the environmental risk posed by CCS, still need to be defined.

Despite the knowledge gaps and uncertainties that still need to be addressed, we, in conclusion, believe that, through this work, a starting step towards the development of a methodological procedure, to assess environmental risk of CCS, has been made. Further studies are undoubtedly required to compare the accuracy and efficiency of the approaches proposed and solve the remaining knowledge gaps, but, in the meanwhile, this preliminary framework can already find some on field applications, as a guidance to perform CCS ERA, and, anyways, it constitutes the foundation of the recommended future dedicated studies.

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