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State of the art in the quantitative risk assessment of the CCS value chain

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ABSTRACT

Carbon Capture and Storage (CCS) emerges as a pivotal strategy in the global pursuit of achieving a net-zero society by 2050. CCS technologies may play a strategic role in the mitigation of greenhouse gas emissions in hard-to-abate industrial processes. However, assuring an excellent and enduring safety performance of the CCS value chain is of utmost importance to enhance its social acceptability. The early integration of inherent safety principles and of appropriate safety barriers and safety systems in design is thus paramount. Quantitative Risk Assessment (QRA) is a key tool to investigate and assess the safety performance of technologies. Actually, the unique thermodynamic characteristics of CO_2 cause specific safety issues throughout the value chain. This comprehensive review explores the state of the art of specific data, models, and tools for the application of QRA to CCS technologies, addressing each of the specific steps of the CCS value chain: CO_2 capture, conditioning, transport, injection, and storage into geological formations. Available models and data, as well as areas requiring further research to address knowledge gaps are highlighted. Offering a holistic perspective on CCS safety assessment, this review contributes to support informed decision-making based on QRA and advances in understanding the safety of CCS technologies.

1. Introduction

Carbon Capture and Storage (CCS) is regarded as a key enabling technology to support the transition towards a net zero society by 2050 (International Energy Agency, 2021). The CCS value chain consists in the capture of the CO_2 emitted from industrial and power generation facilities, and in its conditioning, transport, and injection in geological formations suitable for its long-term storage (Intergovernmental Panel on Climate Change, 2005). In the short term, CCS is among the few strategies able to reduce hard-to-abate greenhouse gas emissions in several industrial processes (International Energy Agency, 2019).

According to the latest available statistics, an average yearly CO_2 capture capacity of 1.42 Mt yr^{-1} is recorded for the 30 operational large-scale CCS projects (Global CCS Institute, 2022). In addition, there are 11 facilities in construction, 153 under development, and 2 non-operational. CCS value chains are mostly deployed in Europe, Canada, the Middle East, the Asia Pacific region, and the United States (US). The latter lead the large-scale deployment of CCS strategies, with 13 operational infrastructures out of the total 30 present worldwide (Global CCS Institute, 2022). CCS is also gradually gaining momentum in the European region, with about 70 projects at various stages of development in Europe and in the United Kingdom (UK) (Global CCS Institute, 2022). In this context, Norway pioneered the commercial development of CCS from 1970 to 2010, with the long-standing Equinor's Sleipner and Snøhvit fields having sequestered more than 25 Mt of CO_2 as of 2021 (Loria and Bright, 2021).

Despite the growing importance of CCS in the future energy scenarios, its large-scale deployment remains hindered by costs and other non-technical aspects, such as regulations and public perception (Budinis et al., 2018). In this context, addressing the safety aspects of new technologies since the early stages of the design lifecycle is pivotal to enhance their societal acceptability (Cipolletta et al., 2022; Zanobetti et al., 2023). Among all the tools available for safety analysis, quantitative risk assessment (QRA) is recommended for a rigorous and systematic assessment (Mannan, 2012).

General widely used methods and software tools are available for QRA (Mannan, 2012). All these, regardless of whether their nature is static or dynamic, rely on the identification of three key elements: i) the reference release scenarios, ii) the failure probabilities of the involved equipment, and iii) the expected consequences of the final outcomes of

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the relevant accident scenarios. Therefore, in order to address the risk assessment CCS projects, particular attention must be dedicated to the collection and assessment of CO_2-specific models and data needed to support the three key steps in the QRA process, rather than to the development of generic QRA techniques. In particular, the CO_2 thermodynamic peculiarities can directly or indirectly impact the three key elements aforementioned, thus calling for specific data and modeling approached to address the analysis of CO_2 release scenarios (Pham and Rusli, 2016; Vitali et al., 2021; Witlox et al., 2014a).

Indeed, except for the Capture step, CO_2 is preferably handled and transported in its dense phase. In this conditions, its viscosity is similar to that of a gas, but its density resembles that of a liquid (Intergovernmental Panel on Climate Change, 2005), thus higher volumes can be managed and a large-scale commercial infrastructure can be deployed with limited equipment footprints. However, since at ambient conditions CO_2 is below its triple point, in the event of a release, it undergoes a rapid depressurization leading to the formation of a gaseous cloud in which solid dry ice particles may be dispersed. Therefore, CO_2 represents not only a mildly toxic substance but also a physical stressor for humans, assets, and the environment. In fact, extremely low temperatures may be reached in the vicinity of the releases, that may harm humans causing cold burns. Moreover, the presence of abrasive solid particles may treat assets, causing erosion and/or cold embrittlement. Furthermore, CO_2 dissolved in water causes a decrease of pH, resulting in corrosive water solution (Mohammadian et al., 2023). In case of underwater releases, the decrease of pH in the seawater may affect the marine biota (Halsband and Kurihara, 2013; Ishida et al., 2013; Tamburini et al., 2023).

Previous studies and literature reviews (Mazzoldi et al., 2011; Oraee-Mirzamani et al., 2013) addressing the safety of CCS technologies mostly concern specific data sources (Duncan and Wang, 2014a), methods (Cleaver et al., 2015; Koornneef et al., 2010; McGillivray et al., 2014), and best practices (Teng et al., 2021; Vianello et al., 2016) for the risk assessment of CO_2 pipeline networks. To the best of the authors' knowledge, a review of QRA best practices for CCS systems, addressing systematically each stage of the CCS value chain, is still lacking.

In the present study, a comprehensive review of all the relevant aspects needed to carry out QRA studies within CCS projects is provided. The study aims at framing the topic by tracking a clear state of the art, enabling the identification of available and validated data sources and models, while identifying the knowledge gaps that need further investigation. A novel holistic approach is introduced, embracing all safety aspects related to CO_2 handling throughout the CCS value chain, from the capture to the transport, up to the injection in the reservoir. Furthermore, the study provides a detailed identification and analysis of gaps in the state-of-the-art, spanning each single step required to perform the QRA of CCS technologies.

In the following, Section 2 describes the methodological approach applied to carry out the literature review. In Section 3, the findings of the literature review are reported and discussed with respect to the different stages of the CCS value chain. Section 4 addresses an overview of the data available in supporting scenarios and release frequencies identification for the various stages of the CCS value chain. In Section 5, details regarding the consequence models and the experimental campaigns conducted to support CCS consequence models' validation are provided. Concerning Section 6, a gap analysis is reported, highlighting areas for improvement that may strengthen QRA approaches to CCS. Finally, conclusions are drawn in Section 7.

2. Methodology

In order to introduce an effective and comprehensive approach to the analysis of the QRA aspects available in the literature for CCS systems, Section 2.1 introduces a specific schematization of the CCS value chain, dividing it in four main steps. In Section 2.2, the methodological approach applied for the systematic review of available information required for the QRA of CCS systems is presented.

2.1. The CCS value chain

The CCS value chain entails four main conceptual steps, starting from CO_2 capture from the emission point source up to the final storage of CO_2, as shown in Fig. 1 (Intergovernmental Panel on Climate Change, 2005):

- *Capture*. This step is intended as the set of strategies enabling the separation of CO_2 emitted with the flue gases originating from industrial sources and power generation systems.
- *Conditioning*. In this stage, the captured CO_2 stream is processed to achieve the thermodynamic and purity conditions required for the subsequent transport mode.
- *Transport*. In this step, CO_2 is transported from the capture and conditioning site to the storage and injection site. Integration of different transportation mode is possible, ranging from pipeline, to ships or rail and road tankers.
- *Injection and Storage*. The CO_2 reaching the storage point is injected deep underground into geological formations such as depleted oil and gas reservoirs or saline aquifers where it is permanently stored.

2.2. Literature search and collection of relevant documents

In order to systematically assess all available input data for QRA, in accordance with the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) (Moher et al., 2009) approach, the method applied to each stage of the CCS value chain was divided into four sub-steps:

1. Definition of the scope and aim of the literature search;
2. Literature search: detailed definition of queries and selection criteria;
3. Grey literature search and integration of the results;
4. Data analysis.

The literature search addressing the QRA of the single stages of the CCS value chain was performed using Scopus, a widely recognized tool for data mining and scientific search. Grey literature, such as reports, standards, recommended practices, and documents from regulatory agencies was also considered in the analysis, in addition to journal papers and conference proceedings. Fig. 2 illustrates the queries, in terms of a set-theoretic representation of keywords, applied in the present review. Moreover, Table 1 lists all the keywords and sentences included in each query set (see Fig. 2).

The keywords considered were grouped into six query sets (tagged A to F in Table 1), each addressing two different fields of research, that are "Title" and "Title-Abstract-Keywords". Each query set is connected to the others by logic operators of union, intersection, and exclusion in order to identify all the literature results closely pertaining to the subject, as shown in Fig. 2.

More specifically, two main sets of keywords were defined and considered simultaneously through a logic union, which describe the two main combinations of words possibly composing the research areas:

A. QRA and SAFETY related terms (in green in Fig. 2);
B. RELEASE related terms (in pink in Fig. 2).

Focusing on "Title" as a field of research, for both query sets A and B, the identified titles must contain terms related to the field of CCS or CO_2. Therefore, in the data analysis, the intersection of query sets A and B with query set C (see Table 1) was performed. Furthermore, an intersection with query set E (see Table 1) was also carried out, in order to exclude misleading results pertaining to similar subjects in the context of monitoring, medicine, energy, biology, and politics. The same approach was applied to the field "Title-Abstract-Keywords", with the difference

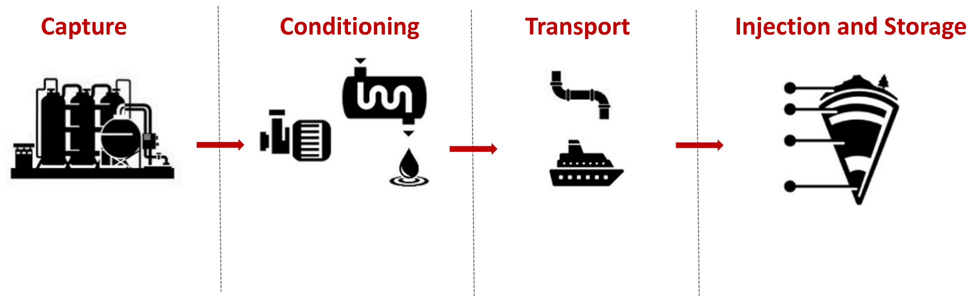

Fig. 1. Schematic representation of the CO_2 value chain in CCS projects.

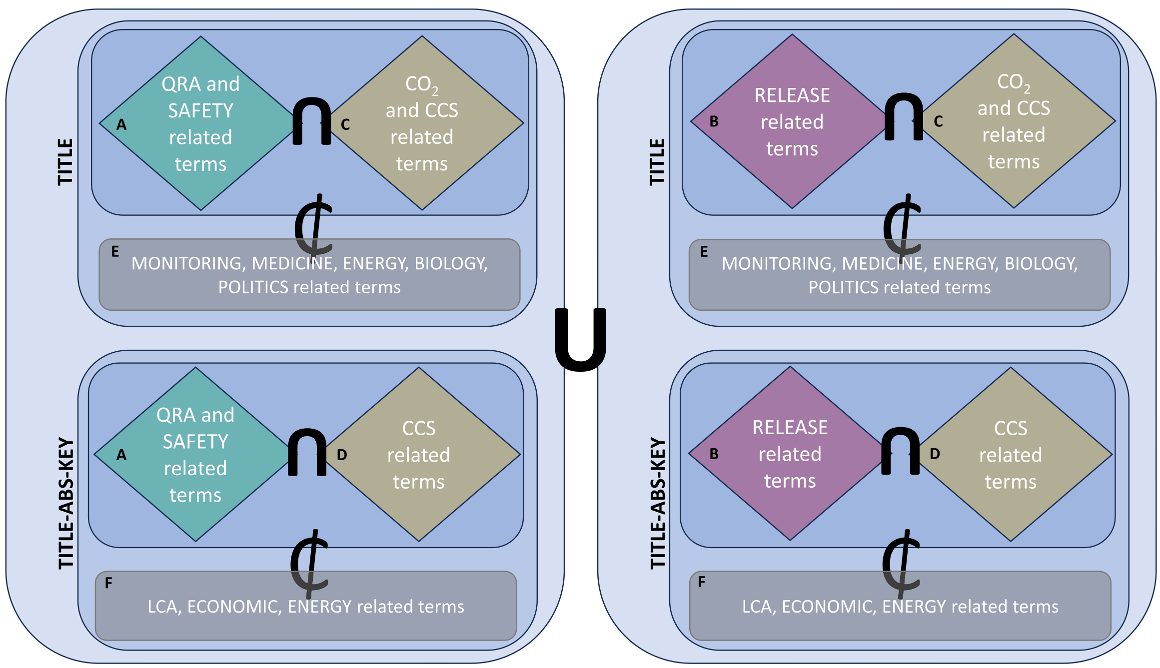

Fig. 2. Set-theoretic representation of the logic of the queries defining the literature review.

Table 1
Queries included in each set defined for the systematic review.

Query set	Query
A	*“risk assessment” OR “safety” OR “risk” OR “hazard” OR “assessment” OR “consequence” OR “impact”*
B	*“dispersion” OR “release’ OR “discharge” OR “leak” OR “modelling”*
C	*“carbon capture and storage” OR “CCS” OR “carbon capture storage” OR “marine CCS” OR “CO2” OR “carbon dioxide” OR ((“carbon” OR “CO_2”) AND (“storage” OR “transport” OR “capture” OR “sequestration” OR “conditioning” OR “capture and conditioning” OR “injection”))*
D	*“carbon capture and storage” OR “CCS” OR “carbon capture storage” OR “marine CCS”*
E	*“monitoring” OR “detection” OR “CCS” OR “measurement” OR “LNG CCS” OR “mitigation” OR “public acceptance” OR “bio-energy carbon capture and storage” OR “groundwater chemistry” OR “sediment” OR “adsorption capacity” OR “biological carbon sequestration” OR “economic optimization” OR “power sector” OR “opportunities” OR “sewage” OR “start-up” OR “regulation” OR “coal”*
F	*“life cycle assessment” OR “environmental assessment” OR “life-cycle assessment” OR “techno-economic” OR “economic assessment” OR “economic analysis” OR “economic evaluation” OR “economic feasibility” OR “energy modelling”*

that query set D (see Table 1) considers only CCS related terms and the exclusion of keywords in query set F (see Table 1) includes terms related to life cycle assessment (LCA) and economics.

Then, an in-depth web research targeting grey literature was carried out to identify technical reports and deliverables from industrial and scientific projects and other documents which deal with the aim of the current literature review.

Finally, the relevant documents collected were analyzed in two steps. In the initial phase, a comprehensive bibliometric analysis was performed using both statistical methods and text mining tools, aimed at outlining the general features of the gathered documents. The VOSviewer software (van Eck and Waltman, 2010a) was employed to construct and visualize bibliometric maps. VOSviewer relies on a built-in mapping technique for the preparation of distance-based maps, wherein the proximity between items indicates the strength of their relationship (van Eck and Waltman, 2023, 2010b). Specifically, VOSviewer was adopted to generate maps concerning authors' nationality and co-author relationships, as well as keywords co-occurrence plots both for author-selected and indexed keywords.

In the second step of the study, a more detailed analysis was carried out, addressing the three main elements required to conduct a quantitative risk assessment: scenarios, frequency data sources, and models for consequence analysis. Each stage of the CCS value chain, as shown in Fig. 1, was specifically examined to identify specific datasets and resources available in the literature pertaining to CCS. Non-specific general-purpose data and tools available for QRA were used to define a generic baseline for the QRA of CCS systems. In particular, baseline reference loss of containment scenarios were identified using standards and handbooks such as the TNO Purple Book (Uijt de Haag and Ale, 2005) and the MIMAH (Methodology for the Identification of Major Accident Hazards) procedure (Delvosalle et al., 2004a), proposed within the ARAMIS (Accidental Risk Assessment Methodology for Industries) project (Delvosalle et al., 2004b). Additionally, the TNO Purple Book (Uijt de Haag and Ale, 2005) and the MIRAS (Methodology for the Identification of Reference Accident Scenarios) procedure (Delvosalle et al., 2004b) were used to obtain baseline frequency reference data. By the same approach, generic event trees (ETs) were derived from MIRAS and the TNO Purple Book to define all possible end-point events following a loss of containment event. After the determination of end-point events, the TNO Yellow Book (Van Den Bosh and Weterings, 2005) was referenced to identify available models for consequence analysis.

The generic baseline for QRA obtained through this approach was then revised in the light of the documents collected, with two objectives: i) identifying specific and/or additional scenarios, models, tools, and data repositories specific for CCS systems and accident scenarios; and/or ii) provide a preliminary validation concerning the consistency of the application of the components of the generic QRA baseline to CCS systems using the data available in the literature.

3. General results of the literature search

In this section, a general overview of the results of the literature search described in Section 2.2 is provided. Table 2 reports the number of documents collected in the literature search conducted by the above-described methodological approach. As shown in the table, the identification phase based on the defined queries yielded 340 papers. After the application of filters (exclusion phase) and the inclusion of relevant grey literature, as suggested by the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) statement, a total of 347 documents were considered for the analysis.

Fig. 3 illustrates the different categories of publications collected. Scientific publications retrieved from the Scopus database are represented in blue tones, while documents originating from the grey literature are depicted in grey tones. Although scientific papers offer a wide base for the determination of the state-of-the-art of QRA of CCS technologies, grey literature also plays an important role in providing relevant information on the subject, comprising approximately 10 % of the collected documents.

Fig. 4 reports the time trend of publications addressing risk assessment of the CCS value chain. Data concerning year 2024 were not included in this figure, since they may not yet be consolidated in the Scopus database. The figure illustrates that the interest in the topic started in year 2005, with a significant increase in relevant publications over the following decade, peaking at 40 publications in 2014. Subsequently, there was a slowdown between 2015 and 2018. However, since 2019, there has been a consistent revival of publications on the topic, coherently with a growing interest in projects aimed at mitigating the effects of anthropogenic CO_2 emissions (Global CCS Institute, 2023).

Fig. 5, generated using the VOSviewer software, allowed the identification of the countries where the authors of the collected publications are located. The three countries most engaged in research on the topic are the UK, the US, and China. The second most important group of contributors are the European countries, as shown in Fig. 5. Actually, Europe stands out as the continent where most of the research contributing to CCS QRA has been carried out, with a share of the collected publications well above 50 %. This trend aligns with the stringent regulations promoted by the European Commission for the safety and the decarbonization of the industrial sector, notably through initiatives as the Emission Trading System (ETS). The contributions from China and the US are more recent, coherently with the more recent interest in the implementation of decarbonization policies in these countries (Department of Energy, 2023; International Energy Agency, 2023).

As previously mentioned, the VOSviewer software was also applied to the mining of the text included in the collected documents. This process facilitated the identification of the most frequently used keywords, distinguishing between author-selected and indexed keywords. The resulting keywords co-occurrence plots are presented in Fig. 6. Specifically, Fig. 6a) refers to author keywords and was obtained including only documents from authors co-authoring a minimum of five document, while Fig. 6b) refers to indexed keywords. Also in this case, only papers from authors co-authoring a minimum of five documents were considered. The software categorized the retained keywords into six main clusters, represented by different colors. No additional filters related to the total strength of the links were applied in the analysis.

In Fig. 6, the distance between two items is inversely proportional to the strength of their relationship, reflecting the co-occurrence frequency of two keywords. Keywords with numerous interconnections are denoted by larger labels. The figure evidences the high number of interdisciplinary issues relevant to the risk assessment of CCS systems, encompassing topics ranging from reservoir studies to numerical models and risk perception.

Fig. 7 shows the co-occurrence maps of author keywords (Fig. 7a)) and indexed keywords (Fig. 7b)), considering a different clustering approach, based on the average publication date of the documents. In this representation, a color scale is applied to indicate the time at which the keywords were mostly used. It may be observed that, in both panels, the keyword “carbon dioxide”, occurring most frequently, is associated with an average date of 2015. Prior to this date, predominantly generic keywords (in blue) such as “groundwater”, “atmospheric dispersion”, and “risk perception” were used. These keywords span a diverse range of semantic areas, indicating a broad distribution of research topics in the early period of CCS safety research. Since 2015, more specific keywords have emerged (such as “leakage”, “numeric simulation”, “monitoring”, “storage capacity”, “pipelines”, and so on), reflecting advancements in knowledge and tools, as well as in the investigation of more specific issues.

Based on the results of the literature search, the state of the art concerning the availability of specific data, models, and tools for the application of QRA to the CCS value chain is presented in the following sections. Table 3 reports the breakdown of collected QRA-related documents by focus on each step of the CCS value chain. Documents addressing multiple CCS steps were counted in each relevant category. An additional category, "Others," was included in Table 3 to classify studies not pertaining to any specific step of the CCS value chain. As shown in the table, the "Others" category accounts for the highest number of document counts, whilst “Transport” and “Injection/Storage” together account for nearly 60 % of the total count. This may be due to the greater operational experience with CO_2 transport and injection from Enhanced Oil Recovery (EOR) technologies, as well as the higher specificity of CO_2 transport and storage steps compared to other steps in the value chain (Intergovernmental Panel on Climate Change, 2005).

Table 2
Studies included and excluded in the systematic review according to the PRISMA statement.

Phase	Description	Records included	Records excluded
Identification	Records from Scopus with the defined queries	340	-
Exclusion	Additional non-relevant topic categories concerning social sciences, biochemistry, and genetics	321	19
Inclusion	Additional records identified	26	-
Total		347	19

4. Scenarios and release frequencies

In the following section, the state of the art concerning accident

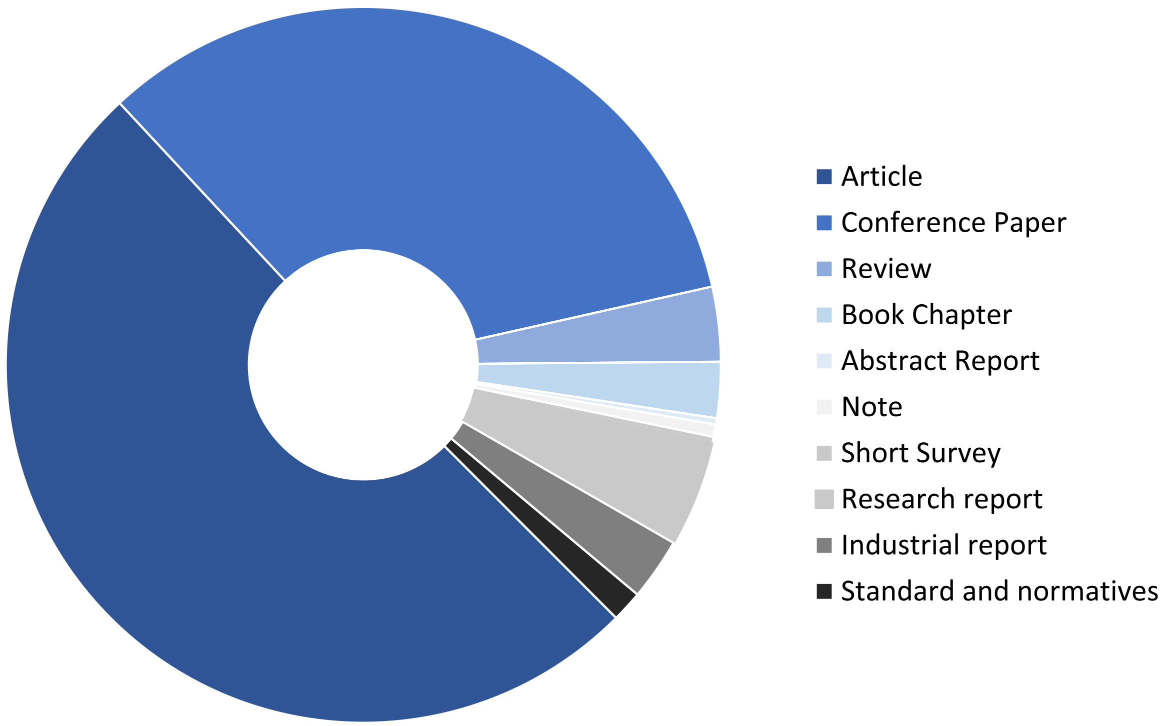

Fig. 3. Type of document classification of all the publications gathered from the literature review.

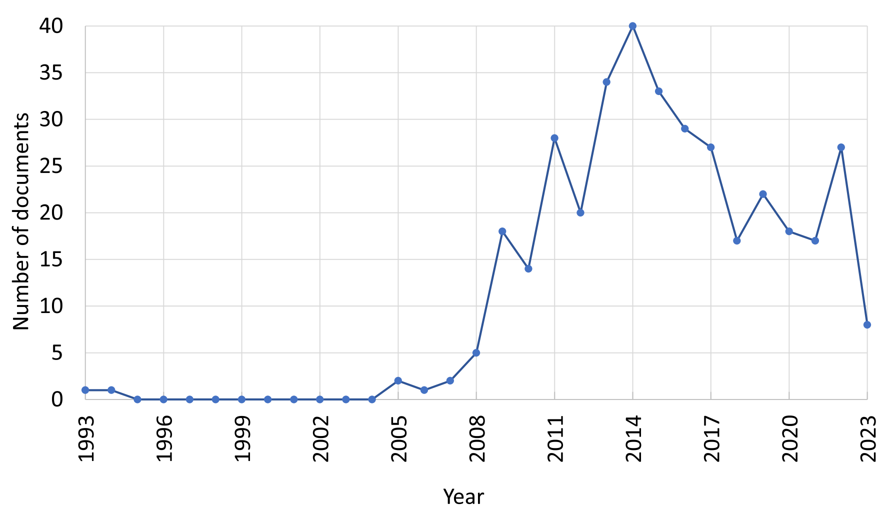

Fig. 4. Number of documents considered in the literature review by year.

scenarios and release frequencies is examined separately for each step of the CCS value chain, with the aim of identifying specific datasets and resources available in the literature for the QRA of CCS. Alternatively, where specific data were not present, information from non-specific sources was obtained to outline baseline reference scenarios and frequency data that may be considered as a starting point for the QRA of the CCS value chain.

4.1. Capture

The Capture stage involves implementing chemical or physical separation processes to selectively remove CO_2 from exhaust gases produced by power generation and industrial installations, preventing its release into the atmosphere. None of the documents collected in the present review provides neither a specific list of validated critical scenarios nor a dedicated set of failure frequencies for the processing and storage of CO_2 in capture facilities. Actually, the variety of concepts proposed for capture technologies and the limited operational experience with capture processes justify the current gap in the availability of specific data and tools for this step of the value chain.

Therefore, presently it is only possible to derive critical accident scenarios and failure frequency data from non-specific documents. As discussed in the methodology section (see Section 2) of the present study, the ARAMIS methodology (Delvosalle et al., 2004b) and the TNO Purple Book (Uijt de Haag and Ale, 2005) were considered to derive baseline reference data in areas where knowledge gaps are present in the specific literature. More specifically, baseline reference data for release frequencies may be derived from the TNO Purple book (Uijt de Haag and Ale, 2005). Reference baseline event trees may be derived from MIRAS procedure (Delvosalle et al., 2004b) and the TNO purple book (Uijt de Haag and Ale, 2005) to outline all possible end-point scenarios following the critical events identified for the capture unit. Nevertheless, other

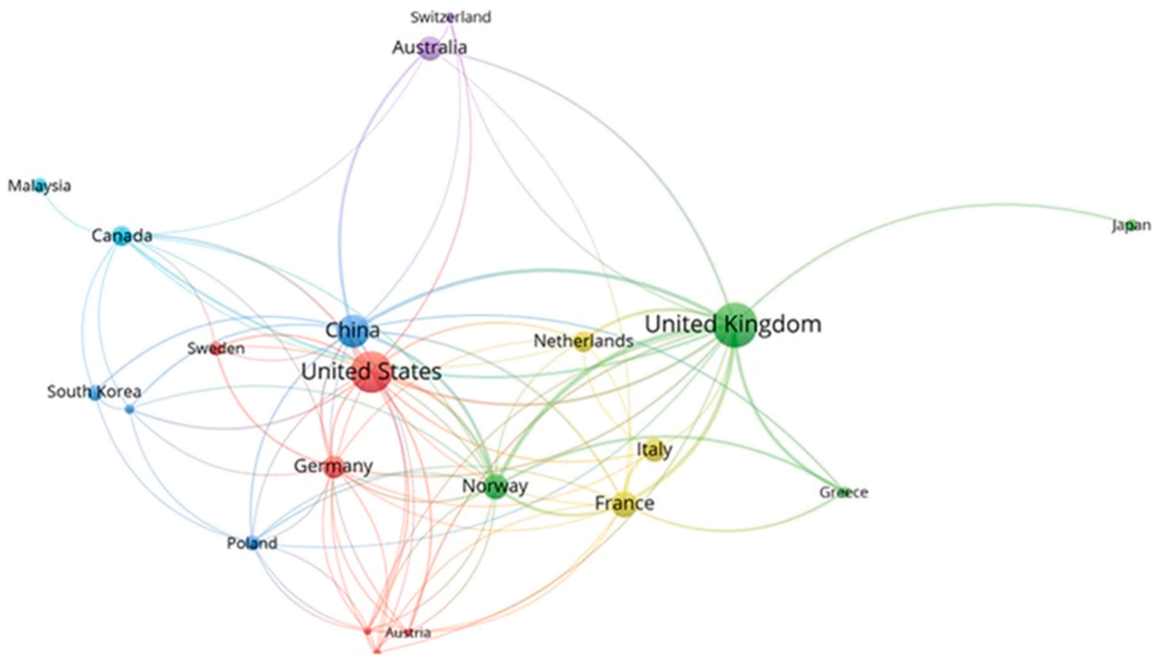

Fig. 5. Principal countries where the institutions to which the authors of the collected publications are affiliated and relationship among countries based on co-authorship (data obtained from (van Eck and Waltman, 2010a)).

non-specific literature sources may be considered as well to derive similar data (CCPS, 2000; Mannan, 2012; OREDA, 2015).

The variety of capture technologies proposed for application in CCS prevents obtaining a thorough identification of possible accident scenarios, since most scenarios are specific to the capture technology adopted. The same applies to the failure frequencies, which may differ due to the different substance hazards and operating conditions of the different capture technologies proposed (i.e., relevant differences may be present concerning operating temperatures, operating pressures, presence of corrosive agents, etc.). Thus, only process specific baseline data may be obtained from the literature. As an example, Table A.1 (in Appendix) summarizes the end-point scenarios and failure frequencies associated with critical events possibly originating from a representative reference process scheme for the amine scrubbing-based CO_2 capture process. Indeed, the latter is currently regarded as the most mature capture technology for a widespread large-scale implementation (Global CCS Institute, 2021). Reference guidelines provided in the technical literature (Delvosalle et al., 2004a, 2004c, 2004d; Uijt de Haag and Ale, 2005) were adopted to derive the data reported in the table. Table A.1 highlights, in addition to toxic dispersions of the processed CO_2, the potential occurrence of fires, such as flash fire and pool fire, for conventional systems based on amine scrubbing. The occurrence of fire accidents is related to the use of flammable substances such as monoethanolamine (MEA), triethanolamine (TEA), diethanolamine (DEA), and others in CO_2 capture (You and Kim, 2020). The physical effects and the targets impacted by the identified end-point scenarios for amine scrubbing-based CO_2 capture are reported in Appendix in Table A.2. As shown in the table, fire-related accidents possibly occurring in conventional amine scrubbing-based capture may also lead to effects on the environment and on assets. The latter, as in the case of blast waves, are expected as a consequence of domino effects (Cozzani and Reniers, 2021; Reniers and Cozzani, 2013)) and thus their inclusion in QRA studies is paramount.

Clearly enough, different critical scenarios may arise when alternative capture technologies are considered. As an example, oxy-fuel and pre-combustion capture processes have a higher efficiency at elevated pressure of around 10 ÷ 20 bar, unlike post-combustion capture systems, which typically operate at atmospheric pressure (Martynov et al., 2016). Thus, specific potential accident scenarios deriving from the processing of substances at high pressures should be considered. The data sources and the approach applied to obtain the data reported in Table A.1 and A.2 may be used to derive baseline frequency data and end-point scenarios for alternative CO_2 capture processes.

4.2. Conditioning

Also, in the case of CO_2 conditioning, no literature source reports specific critical scenarios and/or failure frequency data. Baseline event trees, end-point scenarios and failure frequency datasets can be obtained by the ARAMIS methodology (Delvosalle et al., 2004b), the TNO Purple Book (Uijt de Haag and Ale, 2005), the MIRAS procedure (Delvosalle et al., 2004b), and/or other literature sources. Table A.3 (in the Appendix) shows the baseline data obtained from these reference approaches for a CO_2 compressor. Indeed, the latter may constitute a highly safety-critical equipment type in CO_2 conditioning, due to its considerable proneness to loss of containment (Tugnoli et al., 2007). As can be seen from the table, the most significant end-point scenario is represented by toxic clouds associated with high-pressure releases of the processed CO_2-rich streams, since other hazardous substances are typically not present in relevant quantities. A further relevant end-point scenario to be considered is the potential catastrophic failure of pressurized liquid CO_2 buffer tanks following a Boiling Liquid Expanding Vapor Explosion (BLEVE) event (Energy Institute, 2013). Such accidents often occur as a result of domino effects triggered by external fires (Hemmatian et al., 2015).

The physical effects, the potential targets impacted, and the potential type of damage associated with the above-mentioned end-point scenarios are collected in Table 4. Findings in the table point out that toxic clouds possibly originating from conditioning facilities may be of much higher concern than in the capture stage, due to a larger variety of consequences and potential damages. The increased severity of toxic CO_2 releases in conditioning is to be attributed to the dense state in which CO_2 may be present. Specifically, the thermodynamics of the release of dense CO_2 (depressurization-driven rapid phase transition) may lead to the formation of a gas-solid fog, characterized by very low temperatures (up to −78.5 °C) in the vicinity of the release (Hamish

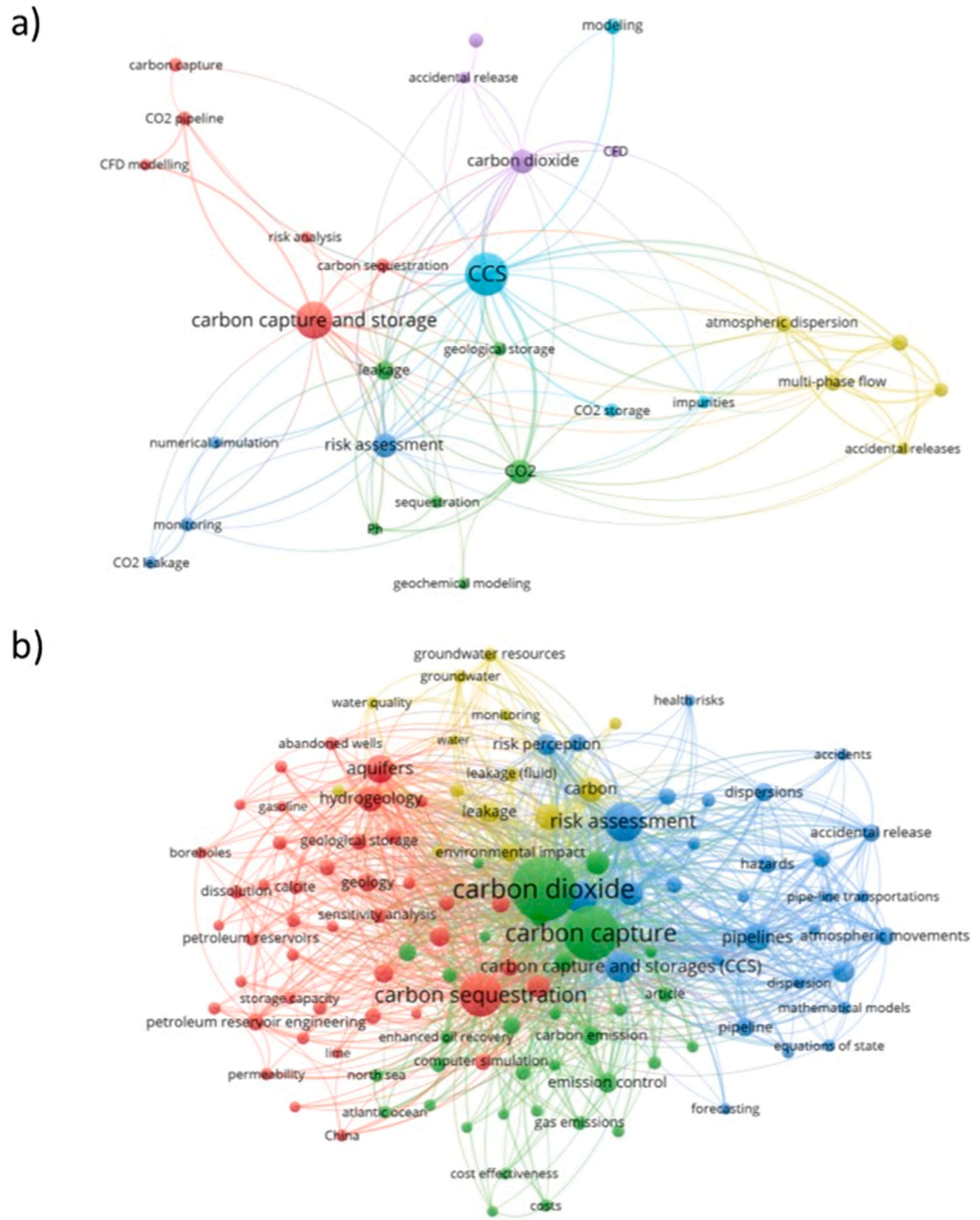

Fig. 6. Keywords co-occurrence in documents retained in the bibliometric analysis: a) author keywords; b) indexed keywords (data obtained from (van Eck and Waltman, 2010a)).

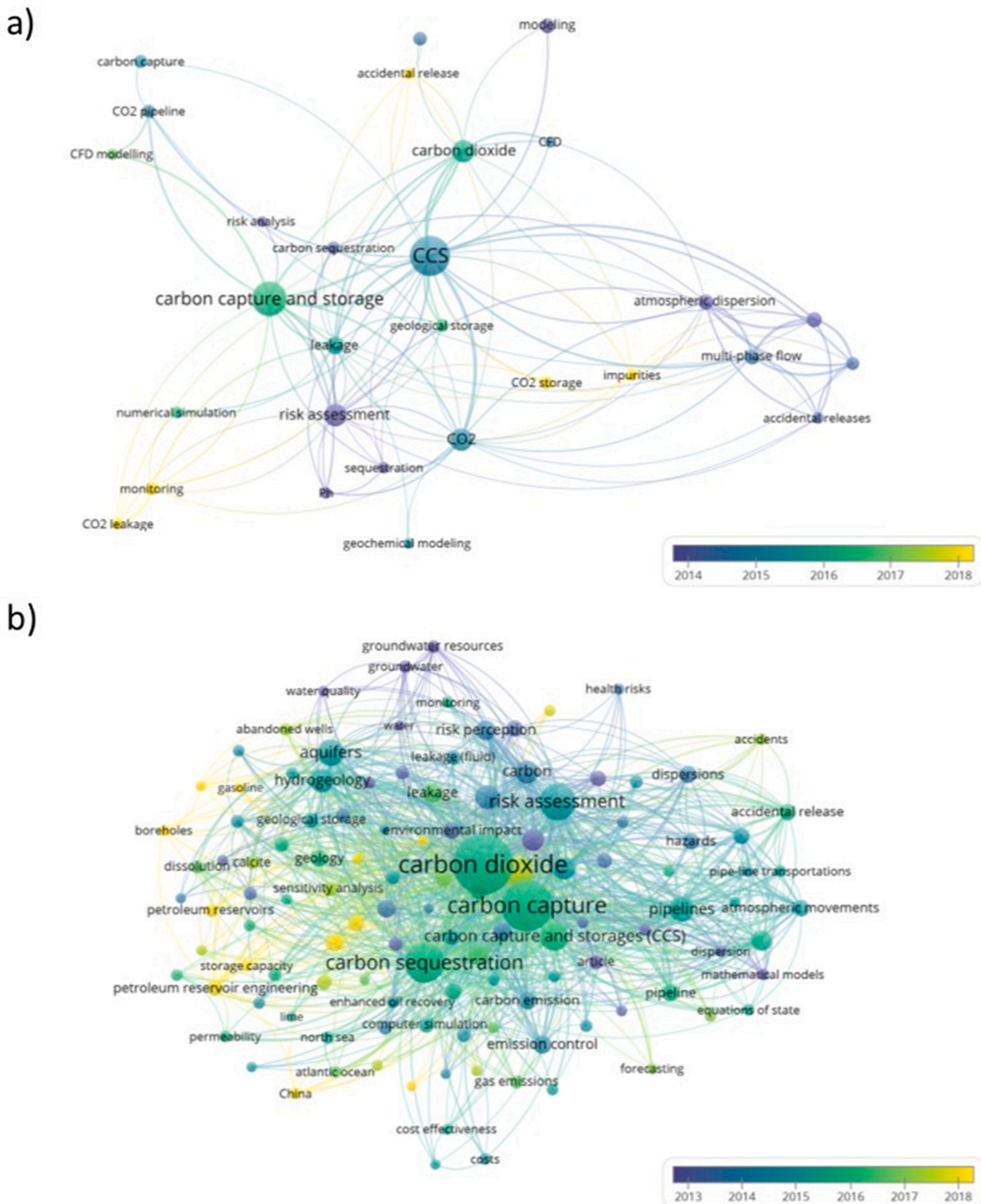

Fig. 7. Keywords co-occurrence according to the average publication year of the documents retained in the bibliometric analysis: a) author keywords; b) indexed keywords (data obtained from (van Eck and Waltman, 2010a)).

Table 3
Document counts per CCS value chain stage ("Others" includes documents unrelated to any stage). Documents covering multiple stages were counted in each relevant stage; thus, the sum of category counts may exceed the total number of collected documents presented in Table 2.

Category	Document counts
Capture	18
Conditioning	1
Transport	103
Injection/Storage	123
Others	145

et al., 2021). These effects may lead to additional damage modes for humans and assets. With respect to the human target, in addition to toxicity, the gas-solid CO_2 fog causes visibility issues which impair the ability to rapidly find and follow escape ways, while low temperatures may cause cryogenic burns through skin contact and cold burns to the airways and lungs after the eventual inhalation of solid CO_2 particles (Hamish et al., 2021). As far as assets are concerned, in the vicinity of the release point, the solid particles formed during the release may contribute to the erosion of metals and to cold embrittlement of materials (Benucci et al., 2022).

4.3. Transport

CO_2 transport may be categorized as onshore and offshore, depending on whether the transport is on land or on/under water, respectively. Clearly enough, accidents in onshore transport modes lead to atmospheric release scenario. On the contrary, in the case of offshore transport, the release scenario varies depending on the specific conditions. Table 5 summarizes the release scenarios expected in accidents involving CO_2 transport (Intergovernmental Panel on Climate Change, 2005).

A specific study addresses the identification of critical events concerning the failure of CO_2 pipelines and the expected occurrence frequencies, derived from the analysis of past accidents (Duncan and Wang, 2014a). In the study, the database of the US Pipeline and Hazardous Materials Safety Administration (PHMSA) (US Department of Transportation, 2024) for onshore CO_2 pipelines was investigated and the frequency of significant accidents (that is, of accidents resulting in a spill volume of the transported substance larger than 5 barrels) derived from the accidents occurred in the last three decades was estimated in the range $1.2 \times 10^{-4} \div 6.1 \times 10^{-4}$ $km^{-1}y^{-1}$. From the study, information regarding the occurrence probability of different equivalent diameters of release and causal factors along with the failure rate of leakages, ruptures, and system-component failures from 1990 through 2009 were obtained. However, the study is limited to onshore pipelines.

When considering CO_2 subsea pipelines, there is a lack of failure data in the open literature. However, (Duncan and Wang, 2014b) suggest that CO_2 sealines can be considered analogous to natural gas (NG) sealines for the purpose of identifying critical scenarios and estimating leakage frequency, due to the similarity of their features in terms of the operating pressure and the design characteristics. This statement is supported by similar failure frequencies observed in (Duncan and Wang, 2014a) when comparing onshore CO_2 and NG pipelines. Specifically, the failure frequency of significant accidents in onshore NG pipelines over the last three decades was found to be 1.3×10^{-4} $km^{-1}y^{-1}$, a value consistent with the range reported above for onshore CO_2 pipelines. Consequently, since onshore CO_2 pipelines exhibit a failure frequency akin to onshore NG pipelines, it is plausible that also offshore CO_2 pipelines share a similar failure frequency with offshore NG pipelines. However, it is noted that onshore and offshore frequencies generally differ, with offshore pipeline failure frequency being at least one order of magnitude higher than that of onshore pipelines. Once again, data from the US PHMSA corroborate this statement, showing a failure frequency of significant accidents in NG sealines over the last three decades equals to 1.5×10^{-3} $km^{-1}y^{-1}$. Data from (International Association of Oil and Gas Producers, 2010) confirm the latter value and offer critical scenarios and failure frequencies for both offshore NG pipelines and risers (refer to Section 4.4.1).

Table A.4 and A.5 (in the Appendix) report a summary of the critical events, release modes, baseline frequencies, and end-point scenarios identified and/or estimated for onshore CO_2 pipelines and 8-inch CO_2 sealines. In the case of subsea pipelines, data for different diameters are available in (International Association of Oil and Gas Producers, 2010).

Table 5
Release scenarios expected for different transport modes of CO_2.

Transport mode	Scenario type
Pipeline, onshore	Release to atmosphere
Road/Rail, onshore (both bulk and iso-tanks)	Release to atmosphere
Ship/Barge, iso-tanks, offshore	Release to atmosphere, release in water only in case of dropped iso-tanks and/or ship/barge wreckage
Ship/Barge, bulk, offshore	Release to atmosphere, possible limited release in water only in case of ship/barge collision and/or wreckage
Subsea, offshore	Subsea release, dissolution in water, possible partial release to atmosphere

Table 4
End-point scenarios, related physical effects, and targets impacted for CO_2 releases in conditioning, transport and injection. Both onshore and offshore releases are considered.

End-point scenario	Consequences (physical effects)	Targets impacted and type of impact		
		Human	Environment	Assets
Above-sea				
Blast	Overpressure	Injury	-	Structural damage
	Missiles	Injury	-	Structural damage
Toxic cloud	Toxic concentration	Acute intoxication	-	-
	Low temperatures in the near-field	Cold burns	-	Erosion Cold embrittlement
	Gas-solid fog	Impair escape ways due to visibility issues	-	-
Subsea				
Toxic plume (subsea)	Toxic concentration	Acute intoxication (mammals)	Acute intoxication (marine biota)	-
	Low temperatures in the near-field	Severe temperature changes	Severe temperature changes	Erosion Cold embrittlement
	pH alteration	-	Seawater acidification Calcification	-
	Density modification	-	-	Sinking of ships (Cone formation)
Toxic cloud (atmospheric)	Toxic concentration	Acute intoxication	-	-

In the case of road, railway, and ship transport, to the best of the authors' knowledge, no studies have neither specifically delved into critical scenarios nor documented historical accidents related to CO_2 transportation. However, when considering loss of containment scenarios and accident frequencies, data reported in the literature for hazardous material transportation can be reasonably assumed to be applicable with confidence as well to CO_2 transportation, since no significant difference is present in the type of vehicles and ships/barges used for the transportation. Thus, release scenarios and failure frequencies may be derived e.g. from (Saccomanno et al., 1993) for rail and road tankers and from (Flemish Government, 2009) for ships/barges' tanks. These literature sources suggest considering catastrophic ruptures or leakages from breaches and/or punctures of nozzles or pipework as main critical events. Table A.6, A.7 and A.8 (in Appendix) report a summary of the baseline critical events, release modes, baseline frequencies, and end-point scenarios for CO_2 tanks for road/rail/ship transportation. However, specific scenarios concerning CO_2 transport by road/rail/ship may arise when considering the possible failure of bulk containers due to corrosion phenomena or external fires, and the loading/unloading of bulk storage systems used for CO_2 transportation. Similarly, no specific data are reported concerning the probability of release given the accident that may derive from the specific design and operating conditions of storage systems used for CO_2 transportation. However, no specific studies in the literature to date address such phenomena.

In Table 4, the baseline reference end-points derived from the TNO Purple book to outline the physical effects of CO_2 releases during the transport stage of the CCS value chain (Uijt de Haag and Ale, 2005) are collected. Depending on the technology concept considered for large-scale CO_2 transportation in CCS systems, CO_2 releases during an accident scenario may lead to different final outcomes due to the different thermodynamic conditions inherent in the various technology concepts. Typically, dense phase (i.e., CO_2 pressure above 74 bar) is considered for pipeline or sealine transport (Intergovernmental Panel on Climate Change, 2005). Differently, cryogenic liquid is usually contemplated for transport concepts based on rail and road tankers and ships. In more detail, for tankers on trucks or railways, CO_2 is transported at a temperature of -20 °C and a pressure of 20 bar (Intergovernmental Panel on Climate Change, 2005), while for ships, CO_2 is characterized by pressures in the range 5.2 ÷ 11 bar and temperatures in the range $-56.6 \div -40$ °C (Turrell et al., 2022).

A dense gaseous cloud, in which solid dry ice particles may be dispersed, is expected to be formed following onshore releases to the atmosphere, i.e., when CO_2 in a dense or liquid phase is released. Indeed, at atmospheric condition, CO_2 is below its triple point: therefore, in case of releases, it undergoes an iso-entropic depressurization leading to solid formation (Munkejord et al., 2016). Besides the toxic effects of the cloud, in the near field, reduction of visibility, possibility of low temperatures causing cryogenic burns and material embrittlement, and possible erosion phenomena due to the impact of CO_2 jets entraining solid particles are expected (Hamish et al., 2021).

In the case of underwater releases, important differences are present. A bubble plume is formed, with features affected mostly by the initial pressure and water depth at the point where the release takes place (Oldenburg and Pan, 2019; Olsen and Skjetne, 2020). At water depths lower than 40 m - corresponding to the triple point pressure of 5.12 bar in the seabed (Intergovernmental Panel on Climate Change, 2005) - iso-entropic depressurization occurs, and a gaseous plume with solid particles is generated. At larger water depths, CO_2 is released as a liquid stream wherein solid particles are spread. In both cases, partial absorption and dissolution in the seawater is likely, leading to the formation of a gas cloud on the sea surface (Tamburini et al., 2023). However, in slow-speed releases and high-water depths, CO_2 tends to be completely absorbed in the seawater, without any degassing from the water surface (Helwig et al., 2016; Tamburini et al., 2024). Beside toxic effects of CO_2 clouds formed on the sea surface, dissolution of CO_2 in seawater may also cause damages to the environment due to pH alteration and local modification of the seawater density (Tamburini et al., 2024). Further consequences of subsea releases may be the induction of significant upward water motions due to the bubble plume formed, leading to the formation of cones where the density of seawater is reduced by the presence of gaseous CO_2 (Olsen and Skjetne, 2020). This phenomenon is often considered dangerous for navigation, due to its ability of causing vessel wreckage (Tamburini et al., 2024).

4.4. Injection and storage

Although storage and injection are strongly linked from the operational point of view, quite different accident scenarios may affect these two elements of the CCS value chain. Thus, in the following, the state of the art concerning critical event and failure frequencies are discussed separately.

4.4.1. Injection

In the injection phase a main release scenario can be identified: the blowout of the injection well. In case the injection well is offshore, also the riser failure may be considered (International Association of Oil and Gas Producers, 2010). All the scenarios involve the potential release of CO_2 from the reservoir. Table 6 reports the specific scenarios, the values for CO_2 release rates and the data on the typical duration of the outflow suggested for consideration for leaks from the injection wells. However, none of the documents collected in the literature reports a specific set of frequencies for release scenarios involving injection wells, due in part to the specificity of blow-out phenomena. Actually, only site-specific values from detailed studies or generic baseline frequency data are available.

With respect to the riser, the scenarios and failure frequencies discussed for subsea pipelines may be applied in the absence of specific data (International Association of Oil and Gas Producers, 2010). None of the collected documents addressed specifically riser failure in CCS systems.

4.4.2. Storage

When considering release scenarios from geological reservoirs used for the storage of CO_2, entail the storage phase, three specific scenarios are identified in the literature (European Commission, 2009): from abandoned wells, from faults and fractures, and from caprock hydro-fractures. Abandoned wells are manmade escape routes, while faults, fractures and hydro-fractures are defined as geological or natural leakage pathways.

Two further CO_2 release scenarios from geological reservoirs are suggested for consideration in the collected documents, even if they are deemed unlikely:

1. CO_2 leakage through locally absent or low permeability or degraded portions of the cap rock;
2. dissolution of CO_2 in the pore fluids and subsequent transport out of the reservoir by natural fluid flow (i.e., formation water).

All the scenarios may cause atmospheric or subsea releases, respectively in case of onshore or offshore reservoirs.

In ECO2 (2015), a semi-quantitative assessment is proposed to assess the propensity to leak of the reservoir (unlikely, possible and likely),

Table 6
Specific release scenarios for CO_2 injection wells and values suggested for the source term characterization in case of accident.

Scenario	Outflow rate (t/d)	Duration (y)	Reference
Minor leakage	0.1 ÷ 10	0.5 ÷ 20	(ClimateWise, 2012)
	7	100	(ETIP ZEP, 2019)
Severe leakage	5000	0.25 ÷ 0.5	(ClimateWise, 2012)
	6000	2	(ETIP ZEP, 2019)

while ClimateWise (2012) reports release frequency values for abandoned well releases. Other data can be obtained from ETIP ZEP (2019), where the probability of release occurrence from reservoirs is conveyed over 500 years. Table 7 summarizes the outflow data and the occurrence frequencies of CO_2 releases from geological storages obtained from the documents collected in the literature search.

Nevertheless, it should be highlighted that the final outcomes and the occurrence probability of such events are highly dependent on site-specific factors, also involving the characteristics of the reservoir. Thus, all the data reported in the tables should be considered as baseline data, preliminary to a more detailed geological survey of the storage site considered.

Table 4 reports the final outcomes of CO_2 releases during both the injection and storage phases. The end-point scenarios in general involve the dispersion of CO_2 in the atmosphere (in case of onshore reservoirs or failures of the onshore piping of the riser) or in seawater (in case of offshore reservoirs or failures of the subsea piping of the riser).

5. Models for consequence analysis

In the following, the models available for the analysis of the consequences of accident scenarios affecting the CCS value chain, suitable for the application in a QRA framework, are outlined. The discussion focuses on models addressing the specific end-point events affecting the CCS value chain (e.g., the CO_2 dispersion to the atmosphere or in the seawater), rather than on generic end-point events as fires and blast waves, that are widely discussed in the open literature and in handbooks (Mannan, 2012; Van Den Bosh and Weterings, 2005). Moreover, the discussion is limited to models suitable for the use in the specific QRA framework, where the analysis of a wide number of alternative scenarios is needed. Thus, this section is mostly oriented to the discussion of integral models rather than to Computational Fluid Dynamics (CFD) tools.

The description of the models was derived from the documents retrieved in the literature search carried out. The discussion was divided into three parts: source term models, dispersion models and damage models. The final part of the section deals with field tests and large-scale experimental data tests available for model validation.

5.1. Source term modelling

Source term models are required to assess the flowrate or amount of hazardous substance released as a consequence of a critical event. As discussed in the previous sections, most of the critical scenarios potentially affecting the CCS value chain involve the release of CO_2 from breaches or failing connections due to the loss of integrity of pipelines or storage/process equipment. In this framework, the different types of source terms models are presented, highlighting their peculiarities and fields of application.

Depending on the step of the CCS value chain involved, CO_2 storage and processing conditions might differ (i.e., physical state, temperature, pressure at which CO_2 is handled in the process/storage equipment item). During capture, CO_2 is mainly present in its gaseous state, while during conditioning and transport it is mostly in a dense phase. Moreover, in the case of subsea releases, external pressure may be different from the atmospheric one.

In order to assess the source term, three types of models are available: (i) CFD models, (ii) process simulators and multiphase dynamic flow simulators, and (ii) integral models. CFD models are usually a standard tool applied to assess the characteristics of the source terms, due to the need of considering the transient condition of extended and complex systems (i.e., equipment items and pipework, or extended pipeline sections) that would require the use of an extended simulation domains. However, they need high computational resources, usually not available in a QRA framework requiring the assessment of several different source terms.

Process simulators and multiphase dynamic flow simulators are mostly applied to address flow assurance issues. Therefore, in the present framework, they are useful to assess the source term features (i.e., the dynamic assessment of the outflow rate of CO_2 released after system failure). Among the available simulators, Aspen HYSYS is suitable for generic equipment items in the process industry (AspenTech, 2024), while OLGA (Schlumberger, 2023) and LedaFlow (Kongsberg Digital AS, 2024; Yang et al., 2021) are options to consider for transient pipeline flows.

Alternatively, several software tools developed for the consequence analysis of industrial accidents allow source term simulation. In particular, the PHAST software includes integral models for source term assessment along with EFFECTS and SHELL FRED (Cleaver et al., 2015; DNV GL, 2023; GEXCON, 2023a, 2023b; Mazzoldi et al., 2011; Sherpa Consulting, 2015; Witlox and Holt, 1999). ALOHA, despite its limitations related to the characteristics of the release (i.e., point-source releases with no outflow velocity), includes models able to handle dense gases as CO_2 (Mazzoldi et al., 2008; US Environmental Protection Agency, 2023).

It is worth noting that this last category of integral models is not suitable to accurately assess the source term in case of underwater releases (Tamburini et al., 2024). Indeed, source term simulations for subsea releases, due to their peculiar characteristics, such as the higher external pressure compared to atmospheric conditions, require the use of process simulators or multiphase dynamic flow simulators. These tools may account for the pressure gradient in the release present in subsea conditions (AspenTech, 2024; Kongsberg Digital AS, 2024; Schlumberger, 2023).

Focusing on subsea pipelines, the OLGA software (Schlumberger, 2023) is suggested for the evaluation of the source term features of underwater CO_2 leakages, since it is able to consider the presence of a two-phase flow of gas and ice (Sherpa Consulting, 2015). Alternative tools available are LedaFlow (Kongsberg Digital AS, 2024) for pipelines or Aspen HYSYS (AspenTech, 2024) for submerged process equipment.

Table 7
Summary of reported occurrence probabilities of CO_2 release applicable to the storage phase (ClimateWise, 2012; ETIP ZEP, 2019).

Source type	Scenario	Outflow rate (t/d)	% probability over 500 years	Duration (y)
Abandoned well	Minor leakage	0.6 ÷ 6	0.04 ÷ 0.08	1 ÷ 100
	Blowout	3000	0.10	1
Faults and fractures	Minor leakage	100	0.20	50
	Moderate leakage	700	0.05	12
	Sever leakage	5000	0.005	4
Cap rock hydro-fracture	Minor leakage	100	0.20	50
	Moderate leakage	700	0.05	12
	Sever leakage	5000	0.005	4

5.2. Atmospheric dispersion modelling

In the framework of QRA, integral models are mostly used for the simulation of atmospheric dispersion, although CFD models may also be employed. However, due to the high computational requirements, CFD simulations are mostly used to tackle the study of specific complex dispersion problems (e.g., the presence of obstacles). These simulations are resource-intensive and demand detailed input data on the release and on the layout under consideration for the dispersion. Thus, owing to computational constrains, CFD models in the present framework are predominantly adopted outside the specific QRA framework, to address system-specific problems in the near-field dispersion of CO_2 (Sherpa

Consulting, 2015; Tamburini et al., 2024).

Integral dispersion models represent a category of simplified semi-empirical models, validated against experimental data, tailored for simulating the far-field dispersion of CO_2 (Tamburini et al., 2024). Due to their flexibility and minimal computational demands, they are the standard tool used in current QRA practice. A review of the literature shows that four integral models are mainly used to assess the consequences of CO_2 releases into the atmosphere, each distinguished by unique features. In particular, ALOHA, thanks to the presence of a variant of the DEGADIS model, is able to handle dense gases including CO_2 (Mazzoldi et al., 2008; US Environmental Protection Agency, 2023). Similarly, EFFECTS and SHELL FRED include integral dense gas dispersion models, namely SLAB and HEGADIS, respectively, allowing them to simulate CO_2 dispersion (Cleaver et al., 2015; GEXCON, 2023a, 2023b; Mazzoldi et al., 2011; Sherpa Consulting, 2015). Lastly, PHAST incorporates the UDM (Unified Dispersion Model) validated against CO_2 experimental data, particularly for assessing the dispersion outcomes of major accidents in process equipment (DNV GL, 2023; Witlox and Holt, 1999).

Clearly enough, all these integral models are not able to take into account the effect of specific release conditions, as the effect of the crater in the case of the burst of an underground pipeline, or the effect of complex terrain slopes on dense cloud dispersions.

5.3. Subsea dispersion modelling

When addressing the complexities of subsea CO_2 releases and of the subsequent CO_2 dispersion and absorption in water, conventional integral models fall short in capturing all relevant features (DHI, 2023a). Specific software tools are available to simulate the near-field dispersion of CO_2 in the water column and the bubble plume formed. The TAMOC (Texas A&M Oilspill Calculator) software (Socolofsky et al., 2015), originally developed to address the simulation of subsea oil and gas releases (Tamburini et al., 2023), was extended to enable the modelling of the near-field dynamics of CO_2 releases (Oldenburg and Pan, 2019). TAMOC includes general modules for managing ambient seawater data, the dynamics of bubbles and droplets in the water column, and equations of state, allowing for steady-state simulations (Gros et al., 2018). Alternatively, CFD models offer valuable insights into near-field CO_2 dispersion effects, albeit their computational demands presently hinder their widespread application within QRA frameworks.

In order to simulate the mixing and dispersion of CO_2 in water, models based on the simulation of the ocean hydrodynamics shall be implemented. These models require the combination of three different modules: a hydrodynamic module to assess the 3D movement and mixing of marine systems under atmospheric, tidal, and geostrophic forcing, a biogeochemical module to define the flow of carbon and nutrients through inorganic and ecological processes, and a carbon system module to characterize CO_2 dissolution reactions. The MIKE software (DHI, 2023b) is among the more complete software tools presently available, coupling the hydrodynamic module MIKE 3 FM HD (DHI, 2017) with the biogeochemical module MIKE ECO Lab (DHI, 2023a), which in turn incorporates a specific module (derived from the CO2SYS program (National Oceanic and Atmospheric Administration, 2023)) for solving the reactions of the carbonate system.

5.4. Damage models

In this section, models available to quantify the damage to humans, assets, and marine biota as a consequence of the physical effects of the critical scenarios reported in the literature for the CCS value chain are discussed.

5.4.1. Damages to humans

Toxic effects of CO_2 on humans through inhalation are reported as dominant compared to asphyxiation effects related to oxygen substitution at ground level, owing to its nature as a heavy gas (Health and Safety Executive, 2013). Specifically, while asphyxiation starts at a CO_2 concentration of about 70000 ppm, the onset of the first toxic symptoms occurs at approximately 14000 ppm (Energy Institute, 2013). The Immediately Dangerous to Life or Health (IDLH) value of CO_2 is set at 40000 ppm (National Institute for Occupational Safety and Health, 2023), while other CO_2 threshold limits can be found in the technical literature (National Institute for Occupational Safety and Health, 2023; Occupational Safety and Health Administration, 2023; Sherpa Consulting, 2015).

A Probit equation (Eq. 1) is proposed in the literature for the quantification of the human death probability due to CO_2 inhalation, derived from the Specified Level of Toxicity (SLOT) and the Significant Likelihood of Death (SLOD) by the UK Health and Safety Executive (Health and Safety Executive, 2013):

$$Y = (C^{8} \quad t_{exp}) - 89.9 \tag{1}$$

where C represents the dose concentration and t_{exp} denotes the exposure time.

For what concerns cold and cryogenic burns, specific temperature thresholds or damage models are not available in the literature. According to US National Aeronautics and Space Administration (NASA), a value of −18 °C is considered as threshold temperature for damages to skin following the contact with cryogenic fluids. However, some studies argue that contact damage may occur even at higher temperatures, especially in the case of prolonged contact times (Ungar and Stroud, 2010). DNV GL suggests that cryogenic burns mainly arise from the contact with solid CO_2 particles, and recommended assessing the damage area according to the “CO2RISKMAN Guidance” (Hamish et al., 2021). This document is aligned with medical studies addressing cold burn injuries, which emphasize the importance of the affected surface in determining the extent of damage (Nizamoglu et al., 2016).

Clearly enough, when considering damage to humans due to non-specific physical effects, as fires and blast waves, conventional damage models as those proposed by Lees and the Green book may be applied (Mannan, 2012; Van Den Bosch, 1992).

5.4.2. Damages to assets

Three physical effects deriving from CO_2 unwanted releases may cause asset damage: low temperatures, abrasive dry ice particles formed during rapid CO_2 depressurization and phase change, and blast-waves.

Low temperatures caused by CO_2 releases promote the cold embrittlement of steel in process equipment and structural components (Connolly and Cusco, 2007; Energy Institute, 2013; Hamish et al., 2021; Institute, 2010). Although the phenomenon is well-recognized, there is a relevant variation of the embrittlement temperature depending on the material type. As an example, for structural steels used in fixed offshore structures, embrittlement temperatures range within −20 °C and −40 °C (BSI, 2001). Moreover, no specific models or simulations addressing this phenomenon for the components of the CCS value chain were found in the literature. Thus, the possible relevance of accident scenarios involving cold embrittlement in CCS systems needs to be further investigated considering specific data, although the theoretical possibility of such accidents is confirmed by the information collected.

Erosion is a further potential consequence affecting the structural components of assets when high-pressure CO_2 jets are released. Solid CO_2 particles formed on-site enable heavy-duty surface scouring, especially when supercritical CO_2 is used as a drilling fluid (Connolly and Cusco, 2007; Hamish et al., 2021). However, to date, no evidence is reported concerning accidental events in CCS systems caused by CO_2 jet erosion. As for the effects of low temperatures on assets, no specific simulations carried out by means of mathematical models are available to confirm the relevance of this potential hazard, neither the definition of parametric thresholds for damages was ever addressed in specific studies.

When considering fire and blast-wave damage, no system-specific effect is expected, thus the thresholds and the Probit equations usually adopted in the context of consequence evaluation of major accidents (Mannan, 2012; Van Den Bosch, 1992) or of escalation assessment (Cozzani and Salzano, 2004; Reniers and Cozzani, 2013) may be applied.

5.4.3. CO_2 damages to biota

CO_2 induces calcification in the marine environment, a phenomenon that harms the species living in the water column and on the seabed (Blackford et al., 2009; Widdicombe et al., 2015, 2013). The alterations in the concentration of chemical compounds caused by the calcification process can be modelled through Eqs. (2)-(3), which also allow for the quantification of the local variation of pH, representing a physical and/or toxic stressor for marine species (Lichtschlag et al., 2015):

$$2HCO_3^{-} + \quad Ca_2^{+} \rightleftharpoons \quad CaCO_3 + \quad CO_2 + \quad H_2O \tag{2}$$

$$CaCO_3 \quad \rightleftharpoons \quad Ca^{2+} + \quad CO_3^{2-} \tag{3}$$

For most species and most damage end-points, several studies report that it is not possible to distinguish between a physical and a toxic stressor (Blackford et al., 2020; Ellis et al., 2015). Therefore, a single threshold value is usually associated with a given organism and a given damage end-point (Blackford and Gilbert, 2007; Ulfsnes et al., 2013; Wallmann et al., 2015). Threshold values can be expressed as ΔpH or as a partial pressure of CO_2 (pCO_2, often given in μatm) and can be found in the scientific and technical literature, covering a wide spectrum of species and various damage end-points (Jones et al., 2015). These limits were determined during laboratory-scale, meso-scale, and real-scale experiments, as well as by studying the impact on ecosystems of natural seeps.

It is important to note that the majority of these research contributions focused on low-flowrate CO_2 seepage scenarios from the seabed, where the effects of the dissolved CO_2 are limited to few meters of water in the vicinity of the sea bottom, primarily affecting the benthos (Jones et al., 2015). Due to their scarce mobility and sensitivity to CO_2, benthic species are particularly exposed to anomalies in CO_2 concentration. A relevant amount of data is available for this type of biota (Hamish et al., 2021).

A specific study (Blackford et al., 2009) proposed a list of damage effects induced by modification of pH levels, summarized in Table 8. Even if the table does not consider the specific effects on deep sea ecosystems, it can be inferred from the reported data that a |ΔpH| value of 0.3 may be considered as a conservative baseline threshold above which the mitigation of potential eco-systemic damage effects shall be specifically considered in environmental risk assessment and management.

An approach to obtain substance-specific Species Sensitivity Distribution (SSD) was developed by (Iwasaki and Sorgog, 2021). These curves estimate the fraction of the ecosystem population affected by a given concentration of the substance. SSD curves for CO_2 can be found in (De Vries et al., 2013).

It should also be remarked that specific studies evidenced that in the environmental risk assessment of offshore CCS systems there is the need to account for the seasonal variation of pH levels, which are determined by several factors, with water depth being the more relevant (Blackford et al., 2009). The value of the maximum normal yearly pH variation $|\Delta pH_{max}|$ is site-specific. Therefore, in the context of risk assessment, the maximum natural seasonal variation of pH, $|\Delta pH_{max}|$, is generally adopted as the threshold value for the acceptable modifications due to CO_2 dissolution in seawater (Ulfsnes et al., 2013).

Table 8
Damage effects reported for a generic marine ecosystem as a consequence of changes in the pH value (Blackford et al., 2009).

|ΔpH|	Effect
< 0.1	No or minimal effect likely, perturbation minor than natural variability
0.1 – 0.3	Perturbation in the order of natural variability, potential small impacts not of systemic relevance
0.3 – 0.4	Some species and some biological processes experiencing significant impacts, possibly some systemic disruption
> 0.4	More wide-ranging and significant to severe effects predicted

As with other types of damage, the impact of a toxic substance on the ecosystem depends on both the intensity of the effect and the duration of exposure to the effect, as evidenced by several studies (Blackford and Gilbert, 2007; Jones et al., 2015; Lessin et al., 2016). These studies suggest that a ΔpH threshold of 0.3 is responsible for minimal eco-systemic impacts over the long-term (more than 3 years). In a conservative estimation of the damage to biota, an infinite exposure time is generally assumed. Hence, this threshold is also suggested as the value capable of damaging a given species in the absence of specific data on its response to CO_2 (Blackford and Gilbert, 2007; Jones et al., 2015; Ulfsnes et al., 2013; Wallmann et al., 2015).

With respect to birds and mammals living on the sea surface, as well as biota living on land, a CO_2 concentration threshold equal to 4 % vol (40000 ppm) was adopted in the environmental risk assessment of the Northern Lights storage site in Norway (Equinor, 2019). This limit corresponds to the IDLH concentration of CO_2 but lacks further evidence in the scientific and technical literature.

5.5. Experimental campaigns

Over the last twenty years, several experimental campaigns investigated the behavior of pressurized and unpressurized CO_2 releases into the atmosphere, with the aim of simulating accident or operational CCS release scenarios (Sherpa Consulting, 2015; Vitali et al., 2021; Wareing et al., 2015b).

The first experimental campaign (Kit Fox) dates back to 1995 and was part of the PERF (Petroleum Environmental Research Forum) 93–16 atmospheric dispersion modelling study which entailed short-duration CO_2 gaseous releases performed at ground level over a rough area during neutral to stable atmospheric conditions (Hanna and Chang, 2001; Witlox and Holt, 1999). As part of the same study, McQuaid wind tunnel tests using CO_2 as a dense gas were performed from a ground level line source (Sherpa Consulting, 2015; Witlox et al., 2014a). In the same year, another experimental campaign investigated gaseous CO_2 releases with the aim of validating heavy gas atmospheric dispersion models (Egami et al., 1995).

Other experimental campaigns were carried out in the following years, providing useful data. In years 2006 and 2007, data concerning both high-pressure steady-state (SS) cold releases (liquid storage) and high-pressure time-varying (TV) supercritical hot releases (vapor storage) were obtained as part of BP engineering project DF1 (made publicly available via CO2PIPETRANS joint industry project (JIP) initiated in 2009) (Witlox et al., 2015, 2014b). Then, in 2010 and 2011, SHELL integrated these tests with high-pressure time-varying cold releases (liquid storage) (Witlox et al., 2014b). Further work carried out by the CO2PIPETRANS JIP includes liquid phase CO_2 releases through large orifices (Ø 25–150 mm) and long pipelines (Holt et al., 2015; Witlox et al., 2015). In parallel to these two last campaigns, COSHER and COOLTRANS JIPs made available experimental data concerning punctures and ruptures of buried high-pressure dense phase CO_2 pipelines (Ahmad et al., 2015; Cleaver et al., 2015; Wareing et al., 2015a, 2014), while CO2QUEST and CO2PIPEHAZ projects involved unburied ones (Guo et al., 2018, 2017, 2016; Woolley et al., 2014). An additional project named SARCO2, ended in 2015, investigated both small and large-scale dense phase CO_2 releases from both buried and unburied pipelines (Di Biagio et al., 2017).

No experimental campaigns were carried out to date to assess underwater scenarios affecting offshore pipelines or other subsea facilities. The only available study concerns subsea seepage releases (Blackford et al., 2020, 2008).

Table 9 summarizes the documents collected that report data on experimental campaigns. The majority of the field tests described in the table collected useful data to validate source term and dispersion models for CO_2 in both vapor and dense phases (Brown et al., 2014).

Table 10 summarizes the available information concerning the validation of the models for CO_2 consequence assessment, that were outlined in Sections 5.1 and 5.2. As shown in the table, to the best of the authors knowledge, only the models included in the PHAST software by DNV GL were validated against experimental data involving dense phase releases. Specifically, four models simulating three different accidental scenarios were tested against data provided by CO2PIPETRANS, COOLTRANS and COSHER experimental projects. Even though reference literature related to the EFFECTS software mentions that the software is able to take into account the rain out of the solid dry ice particles generated from dense CO_2 releases, no specific information is openly available concerning the validation of the software with respect to field data (Koornneef et al., 2009). The same conclusions can be drawn for the ALOHA and SHELL FRED. Nevertheless, as shown in the table, the dispersion models of these three software codes and the PHAST UDM model were validated against the Kit Fox, McQuaid, and COOLTRANS tests.

6. Gap analysis

In this section, a gap analysis was carried out, based on the results of the literature review discussed in the previous sections. Table 11 shows the specific data and models available for the QRA of the different components of the CCS value chain. Per each step of the QRA and per and each component of the CCS value chain, the background color in the figure provides a qualitative indication concerning the availability of specific information and tools to carry out a QRA.

Table 9
List of publications reporting the description of CO_2 field tests and large-scale experimental campaigns.

Experimental study	Year/ Period	Description	Reference
Kit Fox	1995	Small-scale Ground level CO_2 gaseous releases	(Hanna and Chang, 2001; Witlox and Holt, 1999)
McQuaid (wind tunnel tests)	1995	Small-scale CO_2 dense phase releases	(Sherpa Consulting, 2015; Witlox et al., 2014a)
Egami	1995	CO_2 gaseous releases	(Egami et al., 1995)
CO2PIPETRANS	2006–2015	Medium-scale/Large-scale Dense phase CO_2 releases through large orifices and long pipelines	(Holt et al., 2015; Witlox et al., 2015, 2014b)
CO2PIPEHAZ	2009–2013	Small-scale/Large-scale Punctures and ruptures of unburied CO_2 dense phase pipelines	(Woolley et al., 2014)
COSHER	2011–2015	Large-scale Ruptures of buried CO_2 dense phase pipelines	(Ahmad et al., 2015)
COOLTRANS	2011–2015	Large-scale Shock tube, burst, venting, punctures and ruptures of buried CO_2 dense phase pipelines	(Wareing et al., 2015a, 2014)
SARCO2	2011–2015	Small-scale/Large-scale Dense phase CO_2 releases through long buried and unburied pipelines	(Di Biagio et al., 2017)
CO2QUEST	2013–2016	Small-scale/Medium-scale Impure CO_2 dense phase releases from pipelines	(Guo et al., 2018, 2017, 2016)

Table 10
Open data collected concerning the validation of integral models for the consequence analysis of CO_2 releases.

Software Tool	Scenario	Validated Model	Experimental study	Reference
Source term				
PHAST	Orifice, horizontal	DISC, TVDI	CO2PIPETRANS	(Witlox et al., 2015, 2014a)
	Long pipe, horizontal	PIPEBREAK	CO2PIPETRANS	(Holt et al., 2015)
	Buried long pipe	CRATER	COOLTRANS, COSHER	(Ahmad et al., 2015; Cleaver et al., 2015)
Atmospheric dispersion				
ALOHA	Vapour area source	DEGADIS	Kit Fox	(Mazzoldi et al., 2008)
EFFECTS	Vapour area source	SLAB	Kit Fox	(Hanna and Chang, 2001)
PHAST	Vapour area source	UDM	Kit Fox, McQuaid	(Witlox and Holt, 1999)
	Orifice, horizontal	UDM	CO2PIPETRANS	(Witlox et al., 2015, 2014a)
SHELL FRED	Vapour area source	HEGADAS	Mc Quaid, COOLTRANS	(Dixon et al., 2012; Witlox and Holt, 1999)

As shown in Table 11, to date specific studies addressing the critical scenarios that may affect CCS systems and the specific failure frequencies are still missing. This is reasonable, given the limited operational experience obtained so far with large-scale applications involving CO_2 capture, conditioning, and transport. However, as shown in the table, generic scenarios and baseline failure frequency data, derived from consolidated approaches widely used in the QRA framework, may be used as a starting point for the QRA of these steps of the CCS value chain (e.g. refer to Table A.1, A.3, A.5, A.6, A.7 and A.8). Conversely, specific data concerning both scenarios and failure frequencies are available when considering injection and storage systems (see Table 6 and Table 7), due to the relevant experience in EOR operations in the Oil&Gas sector, as well with onshore CO_2 pipelines (see Table A.4).

When considering end-point events associated to the critical scenarios, it should be remarked that, even though CO_2-specific event trees could only be obtained from generic approaches as those suggested by MIRAS (Delvosalle et al., 2004b) and TNO Purple Book (Uijt de Haag and Ale, 2005), the specific literature sources retrieved include information allowing the identification of the credible end-point scenarios, including those involving CO_2 subsea releases. More in detail, experimental tests concerning on-land CO_2 pipelines allow retrieving information regarding the impacts of atmospheric releases on humans, assets, and the environment. Clearly, this knowledge can be extended to all the categories of equipment potentially leading to CO_2 atmospheric dispersion, as, i.e., those involved in the capture, conditioning, and rail/road/ship transportation. However, it is worth noting that capture units may involve specific hazardous substances for which a limited operational experience is present, e.g. amine solvents, that may originate accident scenarios where a high uncertainty is present concerning the specific end-point effects.

Focusing on models for consequence analysis, the characterization of end-point scenarios and the modelling of their physical effects is not straightforward, in particular in the context of capture, transport via sealines, injection, and storage. In fact, while specific validated models are available for atmospheric release scenarios, this is not the case for underwater CO_2 releases.

With respect to atmospheric release scenarios, a relevant effort was devoted to carry out specific experimental campaigns simulating a variety of critical scenarios for CO_2. These enabled the validation of several models for atmospheric dispersion, which are nowadays included in commercial software tools for consequence assessment, as discussed

Table 11
Results of the gap analysis.

CCS step	Sub-step or alternatives	Critical scenario identification	End-point scenario identification	Release frequencies	Models for consequence analysis		
					Source term	Near-field	Far-field
Capture	-	orange	orange	orange	orange	orange	orange
Conditioning	-	orange	green	orange	green	green	green
Transport	Onshore pipeline	green	green	green	green	green	green
	Sealine	orange	orange	orange	orange	orange	orange
	Road (truck)	orange	green	orange	green	green	green
	Rail (tanker)	orange	green	orange	green	green	green
	Ship (vessel)	orange	green	orange	green	green	green
Injection and Storage	Injection	orange	orange	orange	orange	orange	orange
	Storage	green	green	green	orange	orange	orange

(green) = specific information available - specific validated scenarios/data/models

(orange) = incomplete or general information only - generic scenarios/data/models with no specific validation for CO_2

above. It should be remarked, however, that these integral tools stull have limitations when considering specific release modes (as craters) or the effect of terrain slope.

Differently, when considering subsea scenarios, the gap analysis highlights the existence of specific tools (as OLGA and TAMOC) that are still lacking a specific validation.

When focusing on the single stages of the CCS value chain, Table 11 shows that specific models are lacking for the capture stage. Contrarily, specific information is available for onshore pipelines. In the case of all the other steps, a jeopardized situation is present, with specific knowledge gaps. In particular, significant gaps exist for offshore sealines, concerning critical scenario identification, release frequency assessment, and models for consequence estimation. Similar knowledge gaps are present concerning the conditioning and the transportation of captured CO_2 via truck, rail, and ship, even if for the latter baseline data may be confidently used for scenario identification and accident frequencies (although not for release probabilities given the accident). When considering the CO_2 injection and storage steps, gaps affect mostly the consequence modelling, especially in offshore scenarios. Actually, as mentioned earlier, several models for consequence analysis addressing CO_2 subsea releases still lack a specific validation. In addition, integral or multi-target models are needed to support the quantification of the physical effects that may damage aquatic species, as density and pH variation, cone formations, calcification, erosion, cold embrittlement, toxic effects on aquatic marine animal and plant species.

The current assessment underscores the need for a coordinated effort among the different stakeholders to prioritize data collection, model validation, and scenario identification to improve the risk management in the CCS value chain. Addressing the identified gaps is paramount to enhance the reliability, safety, and public confidence in CCS technologies. The development of standardized methodologies for scenario identification and the development of robust models for consequence analysis is crucial in this framework.

7. Conclusions

A thorough literature review was carried out to shed some light on the available data and tools for the quantitative risk assessment of the Carbon Capture and Storage (CCS) value chain. The technological innovation required by systems handling CO_2 must be coupled with the awareness of the risks deriving from the handling, processing, and transportation of CO_2 across complex - and possibly extended - value chains. By means of a systematic analysis, synthesis, and organization of all the retrieved information, it was possible to identify the available documents reporting data on the characterization of release scenarios and release frequencies, as well as on methods and tools for the modelling of the physical effects of CO_2 releases. Additionally, a critical review of the damage models for targets affected by CO_2 releases was undertaken. The gap analysis carried out highlighted that the identification of critical scenarios and of specific failure frequencies are often overlooked in specific studies, that mostly rely on generic data. Moreover, offshore subsea pipelines, injection, and storage systems are the elements of the value chain where significant knowledge gaps exist, in particular with respect to the modelling of the consequences of the releases.

Overall, the results obtained outline the areas where specific data and tools for the QRA of CCS systems are available, as well as those needing future research efforts to address gaps in the available data and tools. Future research should target these gaps, focusing on the specific validation of existing models and on the development of new tools where necessary. Such efforts will enhance the safety, the efficiency, and the public acceptance of CCS as a viable technology to support a sustainable energy transition.

CRediT authorship contribution statement

Federica Tamburini: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft. **Francesco Zanobetti:** Conceptualization, Data curation, Investigation, Methodology, Writing – original draft. **Mariasole Cipolletta:** Formal analysis, Methodology, Writing – original draft. **Sarah Bonvicini:** Conceptualization, Data curation, Investigation, Methodology, Supervision. **Valerio Cozzani:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

Table A.1
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for amine scrubbing, a specific equipment type of interest for CO_2 capture. Data in the table were evaluated based on the guidelines provided in (Delvosalle et al., 2004b).

Equipment type	Key substance	Critical event	Release mode	Baseline frequency [yr^{-1}]	End-point scenario
Absorber	CO_2 (gas) MEA (liquid)	Breach on the shell in vapour/liquid phase	Continuous release (Ø 10 mm)	5.00×10^{-4}	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud
			Continuous release (Ø 35 mm)	5.00×10^{-5}	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud
			Continuous release (Ø 100 mm)	5.00×10^{-6}	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud
		Leak from liquid/gas pipe	Leak (Ø 10 % nominal diameter)	1.75×10^{-6}	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud
			Leak (Ø 22 % nominal diameter)	6.50×10^{-7}	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud
			Full bore rupture	1.18×10^{-7}	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud
		Catastrophic rupture	Instantaneous release of the inventory	$5.00 \times 10^{-6} \div 1.00 \times 10^{-5}$	Fire: Flash fire, Pool fire Blast: VCE, Physical explosion Toxic cloud
			Continuous release of the inventory in 10 min	$5.00 \times 10^{-6} \div 1.00 \times 10^{-5}$	Fire: Flash fire, Pool fire Blast: VCE Toxic cloud

Table A.2
End-point scenarios, related physical effects, targets potentially impacted and possible type of damage for CO_2 capture.

End-point scenario	Consequences (physical effects)	Targets impacted and type of impact		
		Human	Environment	Assets
Blast	Overpressure	Injury	-	Structural damage
	Missiles	Injury	-	Structural damage
Toxic cloud	Toxic concentration	Acute intoxication	-	-
Fire	Radiation	Burns	Air pollution	Structural damage

Table A.3
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for a CO_2 compressor in the conditioning step. Data in the table evaluated were evaluated based on the guidelines provided in (Delvosalle et al., 2004b).

Equipment type	Key substance	Critical event	Release mode	Baseline frequency [yr^{-1}]	End-point scenario
Compressor	CO_2 (gas/dense)	Leak from gas pipe	Leak (Ø 10 % nominal diameter)	1.00×10^{-3}	Toxic cloud
			Leak (Ø 22 % nominal diameter)	8.80×10^{-4}	Toxic cloud
			Full bore rupture	1.00×10^{-4}	Toxic cloud

Table A.4
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for onshore CO_2 pipelines. Data in the table were evaluated based on the guidelines provided in (Duncan and Wang, 2014a).

Equipment type	Key substance	Critical event	Release mode	Baseline frequency $[km^{-1} yr^{-1}]$	End-point scenario
On-land pipeline	CO_2 (dense)	Leak from liquid pipe	Leak (Ø 10 mm)	2.80×10^{-4}	Toxic cloud
			Leak (Ø 50 mm)	4.00×10^{-5}	Toxic cloud
			Leak (Ø 100 mm)	1.36×10^{-5}	Toxic cloud
			Full bore rupture	2.64×10^{-5}	Toxic cloud

Table A.5
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for an 8-inch CO_2 sealine. Data in the table were evaluated based on the guidelines provided in (International Association of Oil and Gas Producers, 2010).

Equipment type	Key substance	Critical event	Release mode	Baseline frequency $[km^{-1} yr^{-1}]$	End-point scenario
Sealine	CO_2 (dense)	Leak from liquid pipe	Leak (Ø 10 mm)	7.22×10^{-3}	Toxic plume
			Leak (Ø 50 mm)	8.49×10^{-4}	Toxic plume
			Leak (Ø 100 mm)	1.70×10^{-4}	Toxic plume
			Full bore rupture	2.55×10^{-4}	Toxic plume

Table A.6
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for onshore CO_2 road tankers.

Equipment type	Key substance	Critical event	Release mode	Baseline frequency	End-point scenario
Pressurized tank	CO_2 (liquid)	Puncture	Leak (Ø 10 mm)	3.86×10^{-8} km^{-1} [a]	Toxic cloud
		Breach	Leak (Ø 50 mm)	3.86×10^{-8} km^{-1} [a]	Toxic cloud
		Catastrophic rupture	Release of the mass equal to the nominal flow rates of all the inlet streams for 3 minutes	2.16×10^{-8} km^{-1} [a]	Blast Toxic cloud
		BLEVE	Instantaneous release of the inventory	8×10^{-5} yr^{-1} [b]	Blast Toxic cloud
		External impact	Case-specific	To be calculated based on case-specific release mode[c]	Toxic cloud

[a] (Saccomanno et al., 1993); [b] (Delvosalle et al., 2004c); [c] (Uijt de Haag and Ale, 2005).

Table A.7
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for onshore CO_2 rail tankers. Data in the table evaluated based on guidelines provided in (Saccomanno et al., 1993).

Equipment type	Key substance	Critical event	Release mode	Baseline frequency	End-point scenario
Pressurized tank	CO_2 (liquid)	Puncture	Leak (Ø 10 mm)	1.20×10^{-8} km^{-1} [a]	Toxic cloud
		Breach	Leak (Ø 50 mm)	1.20×10^{-8} km^{-1} [a]	Toxic cloud
		Catastrophic rupture	Release of the mass equal to the nominal flow rates of all the inlet streams for 3 minutes	6.69×10^{-9} km^{-1} [a]	Blast Toxic cloud
		BLEVE	Instantaneous release of the inventory	7×10^{-5} yr^{-1} [b]	Blast Toxic cloud
		External impact	Case-specific	To be calculated based on case-specific release mode[c]	Toxic cloud

[a] (Saccomanno et al., 1993); [b] (Delvosalle et al., 2004c); [c] (Uijt de Haag and Ale, 2005).

Table A.8
Assessment of critical events, release modes, baseline frequencies, and end-point scenarios exemplified for onshore CO_2 tanks on ships (f_0 represents a base accident failure rate and is computed as $6.7 \times 10^{-11} \times T \times t \times N$, where T is the total number of ships per year on the transport route or in the harbour, t is the average hourly duration of loading/unloading per ship and N is the number of transhipments per year).

Equipment type	Key substance	Critical event	Release mode	Baseline frequency	End-point scenario
Pressurized tank	CO_2 (liquid)	Puncture	Leak (Ø 10 mm)	3.06×10^{-11} km^{-1} [a]	Toxic cloud
		Breach	Leak (Ø 50 mm)	1.64×10^{-11} km^{-1} [a]	Toxic cloud
		Catastrophic rupture	Release of the mass equal to the nominal flow rates of all the inlet streams for 3 minutes	2.27×10^{-12} km^{-1} [a]	Blast Toxic cloud
		BLEVE	Instantaneous release of the inventory	Not available	Blast Toxic cloud

(continued on next page)

Table A.8 (*continued*)

Equipment type	Key substance	Critical event	Release mode	Baseline frequency	End-point scenario
		External impact	Small spill on liquid tank (continuous release of 20–30 m^3 in 1800 s)	$0.0015 \times f_0 \div 0.2 \times f_0$ yr^{-1} [b]	Toxic cloud
			Large spill on liquid tank (continuous release of 75 m^3 in 1800 s)	$0.006 \times f_0 \div 0.1 \times f_0$ yr^{-1} [b]	Toxic cloud
			Small spill on gas tank (continuous release of 32–90 m^3 in 1800 s)	$0.00012 \times f_0$ yr^{-1} [b]	Toxic cloud
			Large spill on gas tank (continuous release of 126–180 m^3 in 1800 s)	$0.025 \times f_0$ yr^{-1} [b]	Toxic cloud

[a] (Saccomanno et al., 1993); [b] (Uijt de Haag and Ale, 2005)

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