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Development of a Comprehensive Framework for the Assessment of Technological Scenarios Triggered by Natural Events (Natech) in the Chemical and Process Industries

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Abstract

The interaction between natural hazards and chemical and process installations might lead to severe technological accidents involving hazardous materials. Examples of such scenarios are fires, explosions, or toxic releases that can heavily impact the nearby population and cause damages to valuable assets and to the environment. In the literature dedicated to risk management and process safety, these events are usually termed as Natech accidents. There are manifold peculiarities of Natech events that fall beyond the features of industrial accidents caused by internal factors. Indeed, natural events can simultaneously trigger multiple technological scenarios, leading to complex situations hard to be managed by emergency teams. Moreover, natural hazards can impact the site at the systemic level, affecting also utilities and lifelines required to guarantee the correct operation of processes and of safety measures implemented to prevent or mitigate accidents. As the analysis of several past accidents confirmed, this impairment can have a role in producing peculiar scenarios in case some specific classes of substances are handled. In addition, it can influence the possibility of accident escalation and propagation through domino effect, eventually leading to cascading scenarios with extremely severe consequences. This thesis work is aimed at developing the tools for a more comprehensive and robust quantification of the risk related to Natech scenarios, with a specific focus on the possibility that utilities and safety barriers will be impacted as well during the accident. A novel paradigm will be presented for the description of the dynamics of Natech events, to highlight the central role of auxiliary systems, utilities, and safety barriers in accident chain progression. Subsequently, a complete approach to assess the modification of barrier performance during natural hazards will be described. Moving from the results obtained from an expert elicitation, the methodology will be used to assess the modification of Natech escalation likelihood given barrier depletion. Then, a set of quantitative risk assessment methodologies will be presented, which have been developed to enable the evaluation of Natech risk accounting for the possibility of barrier depletion and accident escalation also via domino effects. The tools developed within this research project will hopefully enhance the comprehension of complex Natech events and foster the development of effective strategies for risk reduction and management, pivotal issues to be addressed to improve the resilience of chemical and process sites to natural hazards also in the light of the possibility that in the foreseeable future their severity will be inflated by the effects of climate change.

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Chapter 1. Introduction

As a consequence of the industrialization of the last two centuries, increasingly complex technological systems have been developed and a great share of the technologies required to achieve the target welfare state of modern societies involves the handling and storage of hazardous substances. Clear examples of such types of technological installations are oil&gas infrastructures (whether offshore or onshore), production and storage sites belonging to the chemical, process, and pharmaceutical sectors, and energy production plants. All these typologies of critical installations might lead to severe consequences in case they are exposed to natural hazards. Indeed, besides the direct damages and the business interruption that can lead to relevant economic losses, secondary scenarios following the release of substances can be also triggered. Fires, explosions, and toxic clouds following the impact of natural disasters as earthquakes, floods, and storms can pose a threat to personnel and population, and cause relevant damages to company assets and to the surrounding environment. Moreover, technological scenarios constitute an additional burden for the emergency management teams performing the necessary operations in the aftermath of natural disasters. This specific class of technological accidents is typically defined as Natech (Krausmann et al., 2017). Quoting the first publication where the term "*Natech*" was coined, "*the dynamic processes that take place during a natural disaster can act as a catalyst for the creation of a hazardous material (hazmat) release.* […] *Mitigation preparations for natural disasters that create technological emergencies (hereafter referred to as "na-tech events") are complex, therefore, it is important to confront the issue before a significant na-tech event takes place*" (Showalter and Myers, 1994). This sentence on the one side evidences the complexity of dealing with Natech accidents, while on the other it highlights the importance of fostering preparedness before scenarios of such kind take place. Indeed, whereas the initial steps on the research on Natech accidents can be dated back to the nineties (Lindell and Perry, 1997, 1996; Showalter and Myers, 1994), only relatively recently this issue has been recognized as an emerging risk, mainly as a consequence of natural disasters like the Tohoku earthquake and tsunami (2011) that triggered several technological scenarios, demonstrating that plant operators were often not ready to face the challenges posed by such complex situations (Salzano et al., 2013).

Nowadays, Natech risk management has become an important topic in process safety (Khakzad and Cozzani, 2020; Reniers et al., 2018), and its relevance has been recognized by international organizations and regulatory agencies. For instance, considering the case of the European Union, the control of the risk related to major accidents involving industrial activities handling or storing relevant quantities of hazardous substances is regulated by the Seveso Directive. In 2012 the regulation was specifically amended in its current version as to explicitly address Natech risks and plant owners are required to identify natural hazards that can be the cause of hazardous outcomes and include them in the safety reports (European Commission, 2012). In 2015, in a worldwide effort towards the reduction of the risks related to disasters, governments agreed on the definition of the Sendai Framework for disaster risk reduction 2015 – 2030 (UNDRR, 2015). The framework was developed with the support of the United Nations Office for Disaster Risk Reduction (UNDRR) and evidences the need for an all-hazard approach to disaster risk management, thus directly addressing the issue of Natech accidents (UNDRR, 2015; WHO, 2018). In 2019, for the first time, the UNDRR included Natech risks in the Global Assessment Report (UNDRR, 2019), possibly the most important reference on international efforts for disaster risk reduction. In the report, it was remarked the importance of addressing Natech scenarios in the efforts to minimize the cascading impact of disasters and to foster the implementation of the Sendai Framework (UNDRR, 2019). In 2020, recognizing that Asia-Pacific region is particularly exposed to natural disasters as earthquakes, floods, tsunamis and volcanic eruptions, UNDRR developed a specific regional framework for Natech risk management. Ten guiding principles extracted from lessons learnt from a set of past accidents were defined therein with the aim of supporting the development of strategies to make societies of the region more resilient to cascading disasters (UNDRR-APSTAAG, 2020).

Despite these initiatives, our understanding of the dynamics of these accidents is still rather limited and consequently the tools developed hitherto to assess the risk of Natech events might not be fully capable of reproducing their cascading nature and catching their specificities. This limitation is clearly critical in a landscape of possible enhancement in the exposure and vulnerability of technological infrastructures to natural hazards resulting from climate change. Nowadays it is recognized that some categories of natural hazards (e.g., extreme weather events, storms, tropical storms) have experienced a severity increase in the last decades as a consequence of the changing climate, and are expected to be further exacerbated in the foreseeable future (IPCC, 2018, 2021). Addressing the risks related to the impact of this enhancement is a top priority at the global level (WEF, 2022). As a part of this effort, working towards the reduction of the Natech risk is pivotal. A recent study evidenced that over 95% of Natech events in the last 70 years have been caused by climate-related hazards (Ricci et al., 2021). Therefore, as recognized in the Global Assessment Report, it is clear that in case mitigative actions are not conceived, Natech risk is expected to trend upwards due to a combination of the aforementioned effects of climate change and factors as the growth in industrialization and urbanization (UNDRR, 2019).

Therefore, my thesis work was intended at solving some of the limitations of current Natech risk assessment approaches, enabling more realistic modeling of accident dynamics. Indeed, to enhance the resilience of chemical and process facilities to the possible effects of climate change, it is necessary to develop effective mitigation strategies supported by risk assessment methodologies capable of reproducing the complexities of the Natech issue.

To accomplish this task, first of all, the methodologies developed so far to quantify Natech risk were analyzed to identify possible gaps in light of the lessons that can be learnt from relevant past accidents and literature information. In particular, in Section 2.1 relevant past events will be presented along with some statistics on the incidence of this typology of events in major industrial accident databases, while the state of the art of the available approaches to quantify the risk posed by Natech accidents will be outlined in Section 2.2. Particular attention will be posed to the description of the quantitative approaches available to assess Natech risk, evidencing the main steps needed in the calculations. In addition, an essential description of the similarities between the tools for Natech quantitative risk assessment and the ones proposed to quantify the risk related to domino effects will be provided. Indeed, as it will be later shown in Section 2.2, due to their cascading nature, these two typologies of accidents share several similarities from the point of view of the risk assessment. Then, the main gaps identified in the state of the art of risk assessment methodologies will be presented in Chapter 3, together with the related research questions that motivated the activities carried out during the three years of my Ph.D. program. The research questions will be used to introduce the main topics that I sought to address and that will be extensively discussed in Chapters 4, 5, and 6. A thorough description of the contents of these chapters would not be effective before the presentation of the state of art, thus it will be provided directly in Chapter 3 with the support of the gaps identified. At this stage, it might be sufficient to say that Chapter 4 will be dedicated to the conceptualization of an updated framework for Natech risk assessment and that Chapters 5 and 6 will be dedicated respectively to the presentation of a dedicated approach to assessing the performance of safety systems during natural hazards, and to its inclusion in comprehensive risk assessment frameworks capable of modeling the cascading nature of Natech accidents.

Finally, the overall conclusions of the project will be given in Chapter 7, along with the summary of the main findings and an outline of the future research needs identified during the research activity.

Chapter 2. Technological accidents triggered by natural hazards (Natech)

This chapter is intended to provide the necessary background on Natech events and a concise state of art focused on the available tools to assess the risk related to this category of industrial accidents. The context will be introduced presenting some relevant past Natech events and briefly discussing significant statistics obtained from past accident analysis (see Section 2.1). This introduction should provide an idea of the complexity of the Natech issue and of the main features of these typologies of scenarios. Then, the attention will be devoted to the description of the main methodologies developed in the last decades for Natech risk assessment (see Section 2.2). It should be noted that the research work presented in this thesis is focused on themes related to the quantitative assessment of Natech risk, hence this topic will be dealt with in detail. Nevertheless, for the sake of completeness also qualitative and semi-quantitative methodologies will be described, even if with a lower detail. Finally, a discussion on the cascading nature of Natech accidents and on their similarities with the adjacent topic of domino effects in chemical and process industries will be provided.

2.1 Overview

As mentioned in Section 1, a common definition of Natech events might be that of technological accidents involving the release of hazardous materials that are triggered by natural hazards (Krausmann et al., 2017). In order to increase the understanding of Natech accidents, two complementary strategies have been mainly pursued in the literature. On the one side, several major events that had a clear public echo were analyzed looking for detailed information mainly to drive the definition of lessons to be learnt. On the other side, several publications tried to quantify the incidence of Natech events on accident databases and other available sources to extract useful statistics and identify possible recurrent accident patterns. To give the reader an idea of the complexity of the issue, first of all, some relevant Natech events will be briefly presented in the next subsection. Then, significant results and lessons obtained from past accident analysis will be provided.

2.1.1 Examples of Natech events

Recent natural disasters that stroke several countries worldwide evidenced the criticality of Natech accidents, raising awareness on this emerging risk (Salzano et al., 2013). Indeed, these severe scenarios highlighted on the one hand the vulnerability of technological installations to natural phenomena, and on the other the substantial lack of preparedness of facility operators and authorities in dealing with such complex events (Salzano et al., 2013). In the following, a set of relevant Natech accidents will be described to provide an overview of the main features of the overall threats posed by the interaction between nature and technological installations handling hazardous substances.

Northridge earthquake (U.S., 1994)

Whereas several previous earthquakes reportedly caused significant hazmat releases, the Northridge earthquake of 1994 can be considered among the first natural events that were systematically studied to assess their impact in these terms. The seismic event was classified as a moderate earthquake, although it caused more than fifty fatalities and more than nine thousand serious injuries. Moderate to severe damages were reported to 12500 structures for an overall cost of more than twenty billion dollars (Lindell and Perry, 1998, 1997, 1996; Young et al., 2004).

Many Natech events were identified following the earthquake. Nine petroleum pipelines ruptured during the strong ground shaking, leading to the spill of more than 870000 l of hydrocarbons that contaminated soil and groundwater and required an intense cleaning effort with a cost exceeding $15 million. More than 750 leaks involving the natural gas transmission and distribution networks were reported. One derailment event probably caused by the earthquake-induced track deformation was also reported involving 13 tank cars handling sulfuric acid. Luckily, besides the diesel fuel spilled from the locomotive, only one of the tank cars lost part of the sulfuric acid inventory, releasing about 7500 l of the chemical. An extended survey involving about 2300 industrial and commercial facilities was carried out, determining that releases of hazardous substances were experienced in 134 locations (Lindell and Perry, 1997). It was evidenced that in the high-impact area (surveyed by the Santa Clarita command post) 20% of the industrial facilities experienced hazmat releases (Lindell and Perry, 1998, 1997).

San Jacinto River flood (U.S., 1994)

The description of the accident has been made according to what was reported in (Krausmann and Cruz, 2017; NTBS, 1996). As a consequence of the heavy rainfall brought by Hurricane Rosa (8^{th} – 15^{th} October 1994), the San Jacinto River floodplain was flooded, requiring the evacuation of more than 14,000 people.

The plain is located near Houston, Texas, and at the time of the flooding was the crossroad of about seventy pipelines operated by several companies. Floodwaters caused the failure of eight pipelines with diameters ranging from 200 mm to more than 1m, leading to the release of several hydrocarbons (e.g., LPG, gasoline, natural gas). The released substances mixed with floodwater and accumulated in low-velocity areas, while some spilled gasoline created a sheen floating over water that eventually caught fire. More than 540 people were injured, experiencing burns and respiratory distress. Some of the pipeline operators managed to interrupt the operations, although it was reported that many could not access the main shut-down valves because they were submerged. Cleaning operations required a relevant effort, involving the displacement of oil booms to isolate the floating hydrocarbons and the implementation of in-situ burning strategies to dispose of the chemicals. The losses of petroleum products and natural gas were estimated at 5.7×10^3 m^3 and 2×10^8 m^3, respectively. The cost for the spill response operations exceeded $US 7 million while the losses related to property damage have been estimated at $US 16 million.

Kocaeli earthquake (Turkey, 1999)

The Kocaeli earthquake was a strong seism that hit Turkey in August 1999, affecting an area of more than 40000 km^2 and severely impacting one of the most industrialized regions of the country (Krausmann and Cruz, 2017). The seism featured Modified Mercalli Intensity values ranging from VIII to X (the most severe value in the scale). Civil and industrial facilities in the area were severely impacted by the intense ground motion, and severe damages to roads, bridges, utilities, and ports were reported (Cruz and Steinberg, 2005; Steinberg and Cruz, 2004).

Several Natech events were triggered during this natural disaster (Girgin, 2011; Steinberg and Cruz, 2004). About 50000 kg of light fuel was released in the Izmit Bay after the failure of a loading arm in a petroleum product storage facility. In a refinery located close to Izmit, fires broke up in three different locations. While one of them involved a warehouse and was successfully extinguished in few minutes, the other two fires were particularly severe. Indeed, one of the fires involved a process plant and was triggered by the release of hydrocarbons following the failure of more than sixty product and utility pipes caused by the collapse of a concrete stack tower due to the seismic load. Shut-off valves were not sufficient to interrupt the flux of flammable materials and the fire could not be interrupted. The other severe fire involved the tank farm area of the refinery. Indeed, right after the shaking, four floating-roof tanks storing naphtha caught fire. The ignition was caused by the sparks produced by the metal-to-metal contact between the roof and the lateral tank courses during the seism. Additionally, one of the tanks featured the failure of a flange connection, releasing naphtha in the drainage system of the area. The fire eventually reached the broken flange and propagated through the open ditch igniting other tanks located about 200m far from the first one. Firefighting operations lasted hours and due to the multiple simultaneous scenarios, the loss of electricity and the shortage of foam, could not be effective. Eventually, the firefighting operations were interrupted and an evacuation radius of 5km was implemented around the facility (Krausmann and Cruz, 2017). Six tanks in the naphtha storage area were destroyed, with a loss of more than 30000 t of burnt fuel, while in total thirty tanks were damaged. The severity of the scenarios was also due to the inadequacy of accident mitigation systems and emergency plans that could not be effective in managing the complexity of the events triggered by the seism (Girgin, 2011).

Another severe Natech involved an acrylic fiber plant in Yalova. Indeed, three steel tanks storing acrylonitrile underwent severe damages during the earthquake, and eventually, more than 6.5×10^6 kg of the highly toxic and flammable volatile liquid were released. The catch basins surrounding the tanks to avoid liquid spread were concurrently damaged by the intense seismic load and could not contain the spill, which eventually reached Izmit Bay (Girgin, 2011). The site suffered also severe damages to lifelines as power connection and water supply, making the emergency operations particularly complex. Indeed, electricity could not be restored because power generators could not be started as well since acrylonitrile could have caught fire and the application of foam to limit the evaporation of the chemical was significantly hampered due to water shortage. Moreover, emergency responders were not equipped with appropriate individual protection devices to carry out operations in contaminated areas. Severe intoxication symptoms were experienced by emergency responders and by neighboring residents. The chemical caused also the death of the vegetation and the fauna in the areas adjacent to the plant, contaminating the soil and causing long-term environmental damages. As a necessary measure to avoid risks for the population, the sale of agricultural products harvested in the region was prohibited due to the high concentration of acrylonitrile (Girgin, 2011).

Hurricanes Katrina and Rita (U.S./Mexico, 2005)

Hurricanes Katrina and Rita were two Category 3 storms that impacted the Gulf of Mexico during the 2005 Atlantic hurricane season, one of the most intense ever recorded (Knabb et al., 2011b, 2011a).

The two natural disasters impacted both oil&gas infrastructures off the coasts of Texas and Louisiana and fixed installations located onshore in the area. Indeed, more than 600 releases were directly triggered from offshore platforms and pipelines (Cruz and Krausmann, 2009). Most of the releases were of crude oil, lubricants, fuels, and natural gas, although in many cases the substance type and quantities were unknown. The storms impacted a particularly wide area, and more than 4000 platforms and 50000km of pipelines were exposed to the hurricanes leading to the interruption of oil and gas production and refining in the Gulf of Mexico (Krausmann and Cruz, 2017), impacting overall U.S. economy (e.g., it was estimated that the impact of Hurricane Katrina affected about 20%. Of overall U.S. refining capacity (Godoy, 2007)). Overall, 276 offshore platforms, 24 rigs, and 457 pipelines were heavily damaged or destroyed (Cruz and Krausmann, 2008). Regarding onshore facilities, several major releases from petrochemical product storage tanks were identified following the storms (Godoy, 2007). For instance, during Hurricane Katrina, ten releases featuring more than 38,000 l of spilled hydrocarbons caused by the impact of storm surges on storage tanks were identified (Santella et al., 2010). Catch basins were overtopped by the surge, and the oil spread to vast areas floating over floodwaters (Santella et al., 2010). Several releases of hazardous gases were also caused by the necessary shutdown operations in preparation for the storms and to the start-up operations in their aftermaths (Ruckart et al., 2008; Santella et al., 2010).

Tohoku earthquake and tsunami (Japan, 2011)

The Tohoku earthquake, also known as the Great East Japan earthquake, was a M_w 9.0 megathrust earthquake that occurred on March 11th 2011 off the Pacific Coast of Japan (Okada et al., 2011). The epicenter of the seism was estimated at 77km far from Honshu Island, while the hypocentre was located about 32km depth underwater. The earthquake triggered a massive tsunami wave that reached the north-eastern coast and exacerbated the destruction brought by the seism. The tsunami wave reached up to 24m in height and reached inland areas located up to 10km from the coast (Okada et al., 2011). The two events caused unprecedented destruction. The most updated official figures released by the Japanese firefighting agency report more than 19700 deaths, about 6200 injured, and more than 2500 people still missing to date (FDMA, 2021). The Great East Japan Earthquake and Tsunami (GEJET) had an unprecedented cost, which has been estimated to peak at more than US$211 billion related to direct damages, and to measurable impact on Japanese GDP reduction (Kajitani et al., 2013)

The events impacted also hazmat installations triggering a series of releases and causing damages to assets and infrastructures. The Japanese Fire Disaster Management Agency (FDMA) determined that 3341 facilities handling hazardous materials, corresponding to 1.6% of the sites located in the 16 prefectures surveyed underwent damages during the disaster (FDMA, 2011). The cause of damage in 42% of the cases was related to the earthquake, and in 55% to the tsunami wave, while the cause of the remaining 3% was not clear. Moreover, the investigation highlighted that several facilities experienced damages to measures that were implemented for accident prevention and mitigation. For instance, 46 establishments had implemented secondary containment measures to avoid oil spreading in case of a spill (e.g., catch basins, retention bunds, dikes) and 10 out of them reported their damage during the GEJET (FDMA, 2011). Out of 179 hazmat facilities that had implemented outdoor firefighting systems, 33 experienced damages to such protection measures as a consequence of the earthquake and the tsunami wave and in several cases also onsite fire trucks were damaged (FDMA, 2011). In a later study, focused on a sample of 48 hazmat facilities, it was found that almost 70% of them had to shut down, mainly due to direct damages and loss of electricity (Yu et al., 2017). Several facilities reported also damages to backup power generation measures that could not be used to restore operations. The situation was dramatic and emergency teams were employed in tremendous efforts in many regions of Japan. Moreover, national and international attention was mostly directed towards the management of the nuclear crisis in Fukushima prefecture, which was of incredible complexity and posed serious concerns about the long-term effects of the tragedy. These are the reasons why detailed information on many chemical releases was not collected unless they posed a serious concern for the population (Krausmann and Cruz, 2017). Nevertheless, some Natech accidents triggered by the GEJET were particularly severe and had been thoroughly documented.

For instance, in a refinery in Chiba, owned by Cosmo Oil Co., during the first shocks of the earthquake the braces withstanding a spherical tank designed to store flammable LPG were severely damaged (Cosmo Oil Co., 2011). During the seism, the tank was under maintenance and filled with water. Under the seismic loads the braces could not withstand the weight of the equipment (i.e., water features 1.8 times the weight of LPG considered in seismic verifications), and the structure collapsed breaching the pipework beneath and around it and leading to the release of flammable LPG in the area, that promptly ignited. The storage area was engulfed by fire, and several tanks exposed to intense heat loads exploded in severe BLEVEs, generating fireballs of up to 600m diameter (Nishi, 2012). Eventually, all the 17 LPG tanks were involved in the accident and destroyed. Remarkably, the accident propagated through domino effect involving other areas of the refinery and of neighbouring facilities (Cosmo Oil Co., 2011; Krausmann and Cruz, 2013). Indeed, the debris resulting from the explosions impacted the asphalt tanks located on an adjacent area of the refinery and triggered fires in two petrochemical companies leading to the release of methyl ethyl ketone and propylene (Krausmann and Cruz, 2013). It should be noted that the company declared that one of the emergency shutoff valves was fixed in open position due to a malfunctioning in the instrumental air circuit identified in the previous days, which could have led to valve closing during normal operations (Cosmo Oil Co., 2011). Thus, during the accident, the valve could not be operated, neither automatically nor manually, to stop the LPG release from the pipework.

Another severe Natech accident involved a refinery in the Sendai area (Krausmann and Cruz, 2013). In this case, the majority of damages were caused by the tsunami. Indeed, the plant automatically shut down when the seismic sensors detected a PGA higher than 0.25g. Right after, the tsunami wave hit the site, with inundation depth estimated at up to 3.5m. Multiple releases were triggered in different parts of the refinery. In the loading area, a tanker truck was displaced by the water and broke a gasoline pipe. The fuel ignited and the fire involved the entire area, engulfing also asphalt, sulfur, and gasoline tanks that were severely damaged and destroyed. In the same area, many other pipelines were damaged by the tsunami, with the consequent release of hydrocarbons that were involved in the blaze. In addition, heavy oil was release also from a damaged ship-loading arm and from a small tank that floated due to the severe inundation depth. The earthquake instead, caused only minor releases due to pipe movement and tank roof vibration (Krausmann and Cruz, 2017). The emergency management was particularly complex. Indeed, debris and rubbles brought by the tsunami interrupted all the access roads to the site and onsite firefighting equipment could not be used because was severely damaged during the inundation, forcing emergency teams to bring mobile equipment to the site. Moreover, the fire involved several substances and firefighters needed to use self-contained breathing apparatuses to enter the facility. The burning sulfur led also to the formation of toxic fumes that required issuing an evacuation order for an area of 2km radius around the refinery to prevent citizens from being exposed to the cloud.

Besides these two major Natech events that involved refineries, it is worth recalling another severe technological accident that received great public attention during GEJET, the aforementioned Fukushima nuclear disaster (Tokyo Electric Power Company Inc., 2012; Weightman, 2011). Indeed, as a consequence of the earthquake, the Fukushima Dai-ichi nuclear power station was isolated from the national power grid and the subsequent tsunami wave damaged the backup power systems in place to avoid the station blackout. As a consequence, all the cooling functions to remove decay heat and reach cold shutdown were lost and this safe condition could not be achieved. Eventually, three reactors underwent to core meltdown, and two out of them were involved in severe hydrogen explosions that exposed radioactive materials to air, resulting in a major nuclear accident according to International Atomic Energy Agency (IAEA) (IAEA, 2011). This accident will be described in further detail in Chapter 4.

Hurricane Harvey (U.S., 2017)

Hurricane Harvey was a Category 4 tropical storm that occurred during the 2017 Atlantic storm season, one of the most intense ever recorded (Landsea et al., 2019; Trenberth et al., 2018). Hurricane Harvey brought record-breaking rainfall that led to catastrophic flooding over extensive areas in Texas and Louisiana (Blake and Zelinsky, 2018; Risser and Wehner, 2017). Indeed, besides extreme wind damages, Harvey caused an unprecedented rainfall volume (Robinson and Thomas, 2018), which was declared the most significant rainfall event in the U.S. since 1880 (Watson et al., 2018). The most heavily affected area was between Houston (TX) and Lake Charles (LA), where about 1300 mm of rain were recorded in various locations, with few spots peaking at 1500 mm (Murphy, 2018). It should be noted that this record-breaking intensity of the precipitation level has been interpreted as an effect of climate change (Trenberth et al., 2018). In addition to rainfall, storm surge made a great contribution to flooding caused by Harvey. For instance, in coastal areas near Palacios (TX) surge height surpassed 2.5 m above ground due to the rise of sea level (NWS, 2018). The flooding impacted millions of people in the surroundings of Houston (TX), and damaged over 200’000 homes and businesses (Murphy, 2018). Floodwater height peaked at about 1.3 m in the area of Highlands (TX) (NERC, 2018). Lifelines were severely impacted (e.g., more than 2 million customers experienced power outages during Harvey (NERC, 2018). Moreover, as for the case of Hurricane Katrina (see the previous section), several refineries of the area had to shut down operations because of hurricane severity, with an estimated decrement in U.S. refining capacity of about 18% and a severe reduction in the production of building block chemicals.

Clearly, the business interruption was not the only issue for industrial installations and Hurricane Harvey caused relevant damages to assets and triggered several Natech accidents. The quality of information on chemical releases caused by the hurricane is not homogeneous, and detailed records are not available for the majority of the cases. Nevertheless, it is possible to obtain an overview of the damages and chemical releases from the comparison and integration of information from different sources (Misuri et al., 2019a). In the study, the information extracted from various database sources was integrated with the results of an ad-hoc survey administered to facilities exposed to natural disaster. In particular, the search on the National Response Center (NRC) database led to the identification of 81 records reporting releases caused by the hurricane (National Response Center (NRC), 2019). Most of these releases were from tanks and flares (i.e., 70% of releases from flares were scheduled due to operations to secure the plant during Harvey landfall), and involved several types of liquid and gaseous hydrocarbons and other dangerous substances (e.g., ammonia, hydrogen sulfide, methanol) (Misuri et al., 2019a). It is worth noting that not in all the cases the identification of the released substances was possible since it might have been hampered by the complexity of release scenarios, leading to possibly elevated amounts of unidentified hazardous chemicals spreading over vast and densely populated areas (Environmental Integrity Project, 2018). Searching on the Texas Commission on Environmental Quality (TCEQ) database instead, a total of 115 records were identified concerning massive releases to air due to shut down operations before hurricane landfall, emission events due to process upsets (e.g., power outage), or damages to equipment (e.g., floating roof sinking and hydrocarbon exposure to air), and start-up operations after the storm passed. The great incidence of releases from flaring and shutdown/start-up operations is consistent with Hurricanes Katrina and Rita (2005), as reported in (Ruckart et al., 2008). In a different study focusing only on those records in NRC and TCEQ databases reporting releases following equipment damages

(Qin et al., 2020), 43 Natech events were identified, showing that rainfall and floods were the main triggers of such accidents.

Besides the Natech accidents caused by the direct damage to tanks and process equipment and the releases due to shutdown and start-up operations, Hurricane Harvey caused also several damages to auxiliary equipment, systems dependent on the electric power supply as pumps, firefighting systems, compressors, and to site transformers and backup power generators, as evidenced in (Misuri et al., 2019a). Remarkably, the failure of auxiliary systems did not have safe outcomes in all cases. In particular, in a peroxide manufacturing site owned by Arkema (Crosby, TX), the power outage and the related unavailability of the cooling systems made it impossible to keep the reactive chemical under safe storage conditions. In addition, floodwaters made unavailable also all the backup power systems and the emergency cooling systems available at the site, finally leading to a severe accident due to peroxide decomposition (U.S. CSB, 2018). The accident required the implementation of an evacuation radius in an area already severely hit by the flood brought by Harvey, further complicating disaster management activities. This accident will be discussed in further detail in Chapter 4.

2.1.2 Statistics and lessons from past accident analysis

In addition to the accidents listed in the previous subsection, many others were identified in accident databases. In fact, several previous publications moved from the analysis of database records on Natech accidents to estimate their incidence on the totality of (reported) major industrial accidents, to identify vulnerable equipment types and their most common failure modes, and in general to support the development of strategies for Natech risk mitigation (e.g., see (Krausmann et al., 2011; Rasmussen, 1995; Young et al., 2004)). One of the first studies aimed at estimating the incidence of Natech events was based on the analysis of two European databases on major industrial accidents (Rasmussen, 1995). More than 230 accidents related to natural events were identified, with a 1% to 5% share on the totality of the records. It was also highlighted that atmospheric phenomena (mostly lightning strikes) were the most frequent natural events reported in the dataset (Rasmussen, 1995). These figures were similar to the ones obtained in other studies based on database analysis (Krausmann et al., 2011; Sengul et al., 2012). Indeed, according to (Krausmann et al., 2011) Natech events feature a share between 2% and 5% of the totality of records available in five major European industrial accident databases. On the other hand, in (Sengul et al., 2012) the authors analyzed the records reported in the U.S. NRC database between 1990 and 2008, identifying more than 16600 Natech events. This number roughly corresponds to 3% of the totality of the reported records, while analyzing data on yearly basis it fluctuates between 1% and 7%. These figures were substantially confirmed in a recent work based on a screening of more than 826000 records available in the US

NRC database between 1990 and 2017 (Luo et al., 2020). A semi-intelligent system was designed to aid researchers in the analysis of great amount of data, and leverages a machine learning algorithm to classify accident records available in U.S. NRC database. The results demonstrate that 3.98% of the extracted accidents (about 33000 records) can be classified as Natech events (Luo et al., 2020).

Another aspect investigated by recent research is the spatial distribution of Natech events worldwide and a possible link with the local incidence of natural disasters. A recent comprehensive work based on the analysis of more than 9000 entries from multiple database sources from the last 70 years provides some indications on this matter (Ricci et al., 2021). As shown in Figure 2.1. 1, a correlation between the number of Natech events and the number of natural disasters (i.e., according to the EM-DAT database (CRED, 2020)) can be spotted for some areas of the World (Ricci et al., 2021).

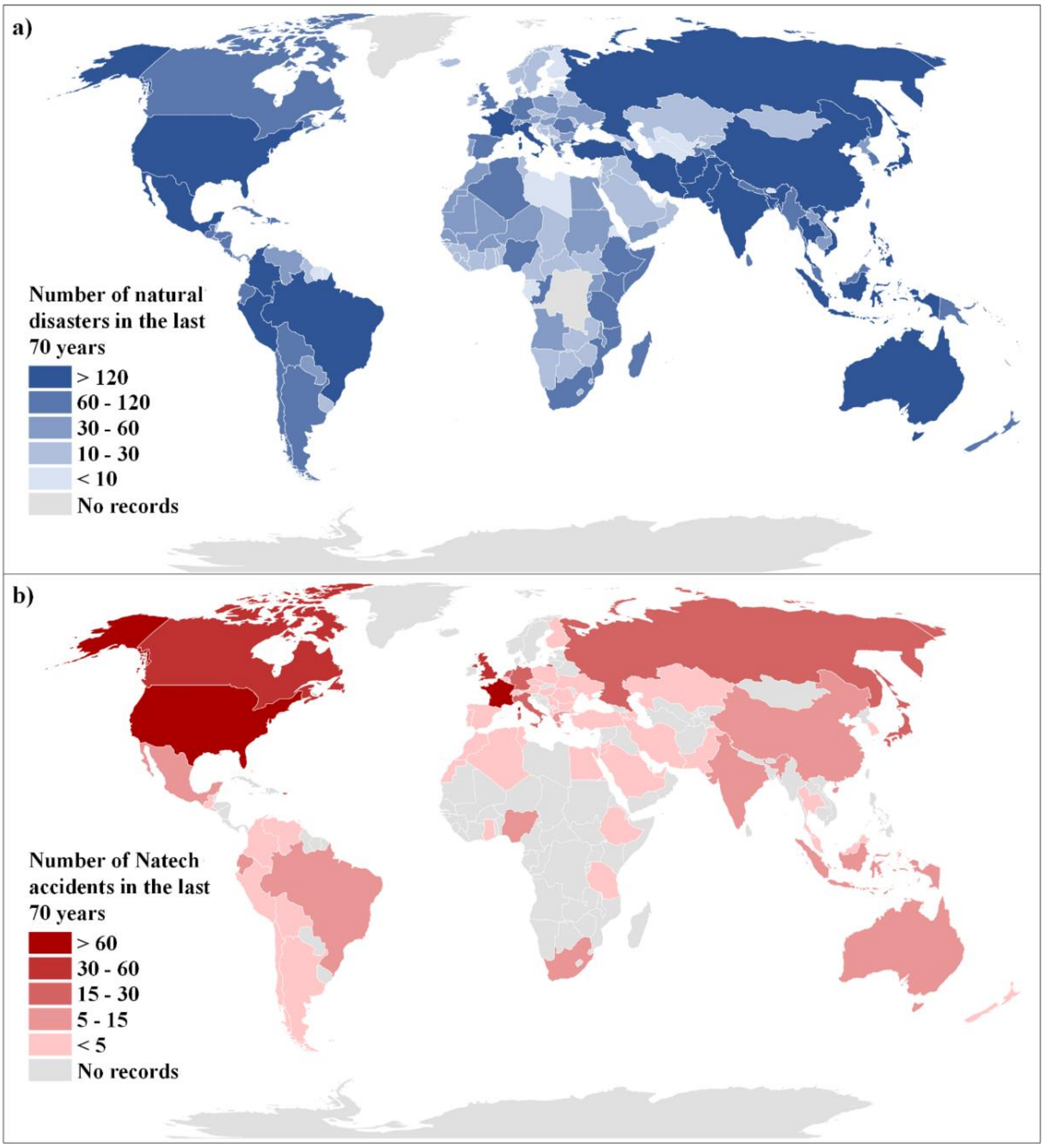


Figure 2.1. 1: Geographical distribution of natural disaster recorded in the EM-DAT database (CRED, 2020) *(panel a) and of Natech events recorded in the database developed by* (Ricci et al., 2021). *Adapted from* (Ricci et al., 2021).

It is thus not surprising if North America has been identified as a hotspot: the highly industrialized U.S. region bordering the Gulf of Mexico is impacted by Atlantic tropical storms recurrently generating several Natech events (Cruz and Krausmann, 2009, 2008; Misuri et al., 2019a; Sengul et al., 2012). In North America each natural disaster has been estimated to have generated on average 3.5 Natech events (Ricci et al., 2021), giving indications on the broad impact of meteorological hazards as hurricanes and tropical storms. The second most impacted area according to the study is Europe with more than 900 Natech accidents in the last 70 years (Ricci et al., 2021). In this case, the ratio between the number of Natech accidents and the number of natural disasters is significantly lower, at about 0.5. In all the other areas of the World, the number of Natech events is significantly lower, in total below 70 events in the last 70 years (Ricci et al., 2021). These results can be attributed to several factors as possible underreporting issues or to the lower industrialization of some countries (Ricci et al., 2021).

Besides general statistics on the Natech incidence and distribution, research effort was devoted to determine which natural hazards are associated with a greater share of records (Ricci et al., 2021).

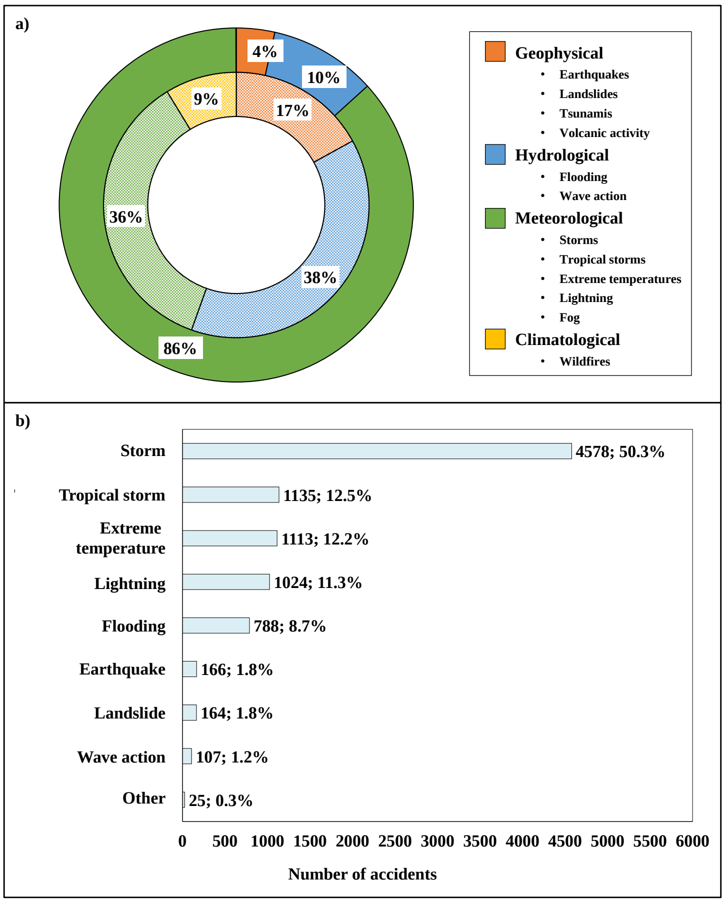


Figure 2.1. 2: a) Comparison between the distribution of Natech events according to the four macro-categories of natural events considered (outer ring) and the distribution of the occurrence of each macro-category according to the EM-DAT database (CRED, 2020) (inner ring); b) Distribution of Natech events per typology of natural hazard. The category "Other" indicates volcanic activity, tsunami, fog and wildfires. Adapted from (Ricci et al., 2021).

In particular, as shown in Figure 2.1. 2, grouping natural hazards into four macro-categories, that is, geophysical (i.e., earthquakes, landslides, tsunamis, volcanic activity), meteorological (i.e., storms, tropical storms, extreme temperatures, lightning, fog), hydrological (i.e., flooding, wave action) and climatological (i.e., wildfires) hazards, it becomes clear that the majority of Natech events has been caused by meteorological hazards, with 86% of the records retrieved in (Ricci et al., 2021), followed by hydrological hazards with a lower 10% of the records (i.e., outer circle of the chart of Figure 2.1. 2-a). The relevant share of Natech events caused by meteorological hazards is in line with the findings obtained by the analysis of the U.S. NRC database performed by the semi-intelligent system in (Luo et al., 2020). Interestingly, this distribution is not consistent with the distribution of the occurrence of natural hazards according to the data extracted from the EM-DAT database (CRED, 2020), where meteorological and hydrological hazards have a share of about 36% and 38% of the available records, respectively. This is an indicator that infrastructures handling hazardous materials might undergo damages and situations leading to Natech scenarios (possibly affecting also multiple sites simultaneously) during meteorological hazards more probably than during other macro-categories of natural events. This feature is confirmed also by the observation of the distribution of Natech events per typology of natural hazards. As shown in Figure 2.1. 2-b, it was found that overall less than 22% of Natech accidents were caused by lightning (11.3%), floods (8.7%), and earthquakes (1.8%), that is by the three typologies of natural events most studied in previous literature (Krausmann et al., 2011), and about 75% of the records were related to storms (50.3%), tropical storms (12.5%) and extreme temperatures (12.2%) (Ricci et al., 2021).

Nonetheless, research on the assessment of risk due to Natech events caused by meteorological phenomena, apart from the case of lightning strikes, is still at the initial stage. Therefore, the following subsections will be focused on the description of the main lessons learnt from past accident analysis concerning Natech events triggered by the three main natural hazards studied to date, that is, earthquakes, floods, and lightning strikes (Krausmann et al., 2011). These three typologies of natural hazards have been the main focus of Natech research for several reasons (Krausmann and Salzano, 2017). Indeed, technological scenarios caused by earthquakes had been prioritized in previous research to their higher severity (Antonioni et al., 2009a), while floods and lightning were also considered due to their high frequency in causing Natech scenarios in OECD member countries and in European Union (Krausmann and Baranzini, 2012). Then, a specific section devoted to the description of recent findings concerning the possible link between Natech events and climate change together with their implications will be provided.

Natech events triggered by earthquakes

Interesting information has been retrieved from the analysis of database records on earthquake-related Natech events (Campedel, 2008; Krausmann et al., 2011). The analysis of nearly 80 accident entries related to the impact of earthquakes allowed the authors to determine the categories of equipment more vulnerable to seismic events (Campedel, 2008). As can be noticed from Figure 2.1. 3, pipework and pipelines seem to be particularly vulnerable, totalling about 65% of equipment involved, followed by atmospheric tanks with a 33% share of the totality of items involved.

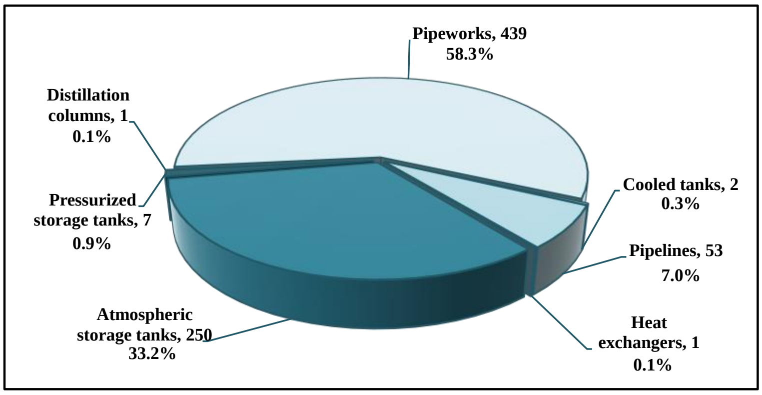


Figure 2.1. 3: Distribution of categories of equipment involved in Natech accidents triggered by flood (based on 78 accident records). Data from (Campedel, 2008).

It should be noted that the number of total equipment involved is substantially higher than the number of records extracted, indicating that during a single Natech event several elements of the site were damaged and destroyed simultaneously. The vulnerability linked to the structural features of these two categories of plant equipment has been clearly recognized, and consequently, they were prioritized in the research effort devoted to approaches to assess the possibility of their failure during seismic events (e.g., see (Lanzano et al., 2015, 2014, 2013; Phan et al., 2018; Salzano et al., 2003)). On the contrary, the failure of pressurized tanks has been reported only in few cases (0.9% of the totality of equipment involved according to Figure 2.1. 3), probably due to their mechanical resistance given their significant shell thickness and curvature required for design pressures typically higher than the one adopted for atmospheric storages (Mannan, 2005). The analysis of 32 detailed records provided also useful information on the type of damage equipment might undergo during earthquakes. As can be noticed from Figure 2.1. 4, in about 73% of the records a hazmat release was observed, while in the remaining 23% of the cases equipment underwent structural damages only (Krausmann et al., 2011). The data indicate that chemical equipment during earthquakes is more likely to suffer damage leading to substance release, rather than structural damages only, although these results might have been influenced by the possible underreporting of low-severity situations which consequently generated a reporting bias towards more severe scenarios (Krausmann et al., 2011).

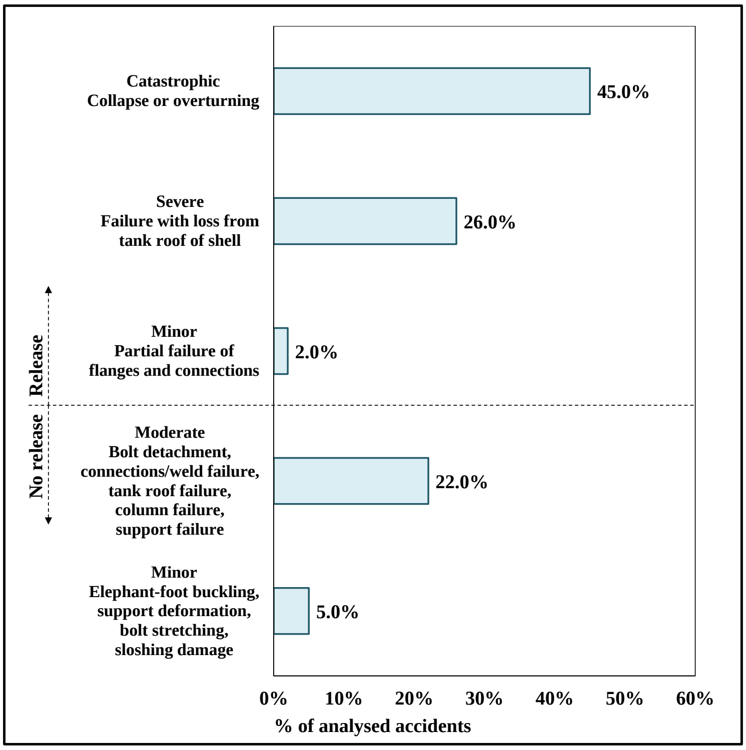


Figure 2.1. 4: Distribution of earthquake-related accidents per damage severity (based on 32 accident records). Data from (Krausmann et al., 2011).

The records allowed also to identify three subcategories of damages possibly leading to release (i.e., three uppermost categories in Figure 2.1. 4), and two expected not to lead to loss of containment (i.e., two lowermost categories in Figure 2.1. 4). The damages identified are consistent with what was evidenced by the analysis of damages during recent severe earthquakes (e.g., see (Krausmann et al., 2010; Krausmann and Cruz, 2013; Zama et al., 2012)).

Information on typical accidental scenarios initiated by earthquakes was also extracted from database records, as reported in Figure 2.1. 5.

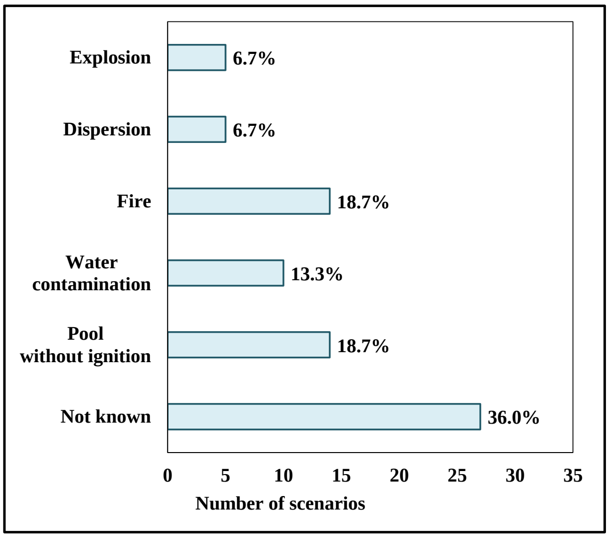


Figure 2.1. 5: Distribution of accidental scenarios caused by earthquakes (based on 78 records). Data from (Campedel, 2008).

As might be noticed, in a significant share of the records (about 36%) useful information on accident scenarios was provided, while an equal number of accidents involving fires and liquid release without ignition was assessed (18.7% of the records each) (Campedel, 2008). Water contamination was also reported several times (13.3% of the records). This result might be justified considering the elevated vulnerability of atmospheric tanks and pipelines (see Figure 2.1. 3) that are usually employed to store and transport liquid hydrocarbons that in case of release might pose serious concerns for environmental contamination of aquifers and shallow waters (e.g., see (Bonvicini et al., 2018, 2015; Pilone et al., 2021)). Considering only the records of accidents involving the release of flammable substances from atmospheric tanks (29 records out of the total, with more than 250 equipment damaged) it was possible to estimate a value of 0.76 as the probability of ignition specific for the case of Natech events during earthquakes (Campedel, 2008). Nevertheless, this value should be interpreted only as an upper limit given the possible reporting bias toward high-severity accidents mentioned above (Krausmann and Salzano, 2017). In fact, a recent comprehensive database analysis based on a higher number of records allowed to perform a more reliable evaluation, leading to 0.058 for liquid releases and 0.321 for gases (Ricci et al., 2021).

Natech events triggered by floods

According to accident databases, floods caused several Natech events in the last decades (Campedel, 2008; Cozzani et al., 2010; Ricci et al., 2021). More than 780 technological scenarios initiated by floods were identified in a recent paper (Ricci et al., 2021). It should be noted also that severe floods are the most recurrent natural disasters in Europe, thus this high number of events might be not surprising (The French Ministry of Ecology Sustainable Development, 2013; The French Ministry of Ecology Sustainable Development and Energy, 2015). This relatively high frequency pushed the research toward the systematic analysis of accidents triggered by floods, with the aim of distilling lessons learnt and useful recommendations (e.g., see (Campedel, 2008; Krausmann and Mushtaq, 2008)). One of the most insightful studies on flood-triggered Natech events was published in 2010 and was based on the analysis of 272 records extracted from major accident databases considering the period between 1960 and 2007 (Cozzani et al., 2010).

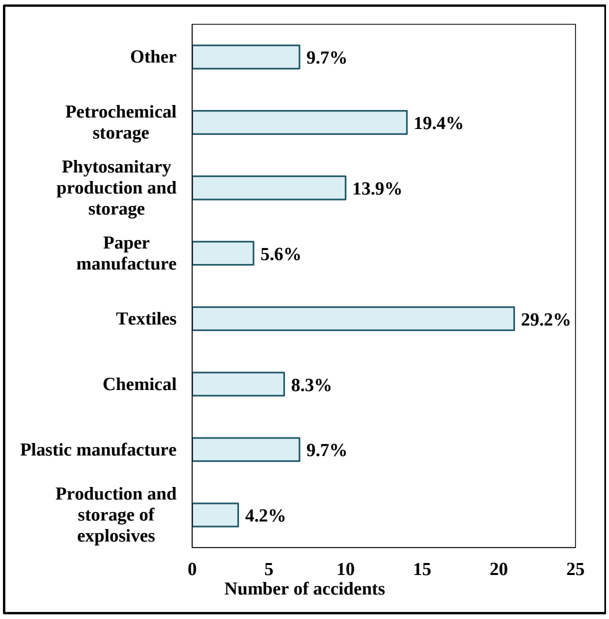


Figure 2.1. 6: Industrial activities involved in Natech events caused by floods (based on 72 records). Data from (Campedel, 2008; Cozzani et al., 2010).

As can be noticed from Figure 2.1. 6, a variety of industrial sectors have been involved in Natech events following flooding. Besides the textile industry (29.2%), petrochemical storage sites (19.4%) and phytosanitary production and storage facilities (13.9%) were the most recurrently impacted activities.

More importantly, the authors managed also to obtain a clear picture of the more vulnerable typologies of equipment during floods. Indeed, as can be seen in Figure 2.1. 7-a, storage tanks are by far the most vulnerable class of industrial equipment, featuring more than 330 items involved in the 272 records analyzed (more than 70% of the totality of equipment damaged in the considered dataset).

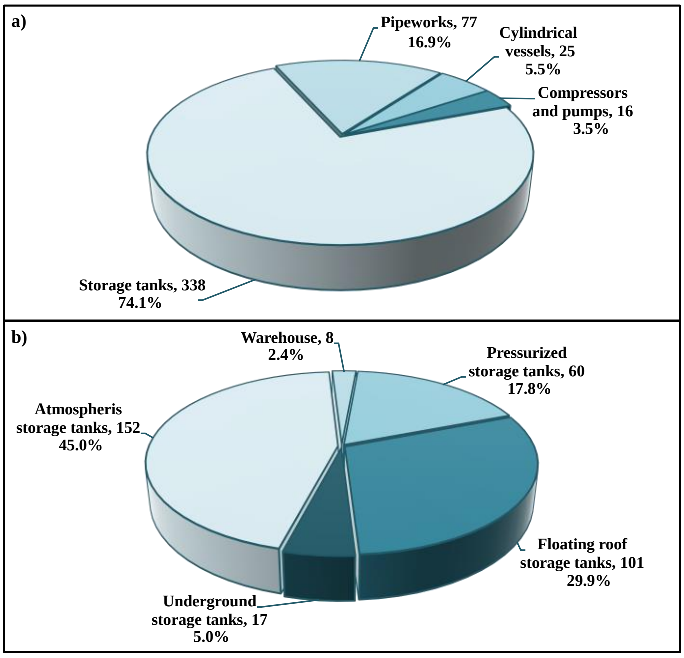


Figure 2.1. 7: a) Distribution of equipment categories involved in flood-triggered Natech events (based on 272 records); b) distribution of subcategories of storage tanks involved in flood-triggered Natech events. Data from (Cozzani et al., 2010).

This number clearly evidences the possibility of multiple simultaneous failures during flooding events. Pipework also showed a high vulnerability, with about 17% of the totality of equipment damaged in the analyzed records. Considering the distribution of storage tank categories involved instead (see Figure 2.1. 7-b), it can be noted that atmospheric storages are about 75% of the 338 identified items, confirming that they are by far the most vulnerable types of storage. Also pressurized storages show a not negligible vulnerability, with 60 items out of 338 (about 17%). Therefore, it is not surprising (as will be presented later in Section 2.2.2) that research on models to assess equipment vulnerability to floods started from such categories of items (e.g., see (Landucci et al., 2014, 2012)). In addition, the authors of the study identified a subset of accidents triggered by floods that involved substances reacting violently with water, producing toxic clouds, explosions, and flash fires (Cozzani et al., 2010). Remarkably, even if these final scenarios are typical of the process industry, during floods they might become particularly relevant and might be brought by non-conventional causes due to the presence of floodwater in the area where the loss of containment (LOC) happens (Cozzani et al., 2010). Finally, event trees were developed and validated with the accident records isolated in the study, which can be effectively applied in Natech risk assessment approaches (see Section 2.2.2).
Other authors managed to retrieve useful lessons and recommendations based on the analysis of available accident records. For instance, (Krausmann and Mushtaq, 2008) developed a qualitative damage scale for seven selected types of industry (e.g., petrochemical installations, tailing dams, metal processing facilities) to help authorities and practitioners to identify the scenarios that can be expected during low, intermediate, and high severity flooding events. More specific lessons and related recommendations can be found instead in (Krausmann et al., 2011). For instance, the authors identified the expected failure modes that can lead to hazmat release from process equipment as a qualitative function of flood severity, from the partial failure of connections and debris impact during minor severity flooding to the complete failure of connections and the possibility of tank floating or structural collapse due to buoyancy and shear forces during severe to catastrophic flooding events (Krausmann et al., 2011). Important indications on possible damages to auxiliary systems were also given. Among the others, the authors highlighted the possibility that flooding of electrical equipment leads to power outages, failure of cooling systems, or pumps and power-dependent safety systems, suggesting to implement strategies to protect such systems from floodwaters and to provide the adequate means to ensure safe emergency shutdown (Krausmann et al., 2011).

Natech events triggered by lightning strikes

Several previous studies have recognized technological accidents triggered by lightning strikes as one of the most frequent types of Natech events (Krausmann et al., 2011; Rasmussen, 1995). For instance, 61% of the Natech events involving processing and storage units identified in (Rasmussen, 1995) were related to lightning strikes. More than 67% of the 1072 Natech events considered in (Krausmann et al., 2011) were caused by keraunic phenomena.

Some of the most relevant lessons on Natech events triggered by lightning were retrieved in two relatively recent studies based on the analysis of more than 700 database records (Krausmann et al., 2011; Renni et al., 2010). Some interesting insights obtained from this analysis are reported in Figure 2.1. 8 and Figure 2.1. 9. As can be noticed from Figure 2.1. 8-a, more than 90% of lightning-triggered Natech events involved oil and gas and petrochemical facilities (Renni et al., 2010). In addition, it was evidenced that the majority of equipment categories involved in accidents triggered by lightning strikes are by far storage tanks (about 60% of analyzed records, as clear from Figure 2.1. 8-b).

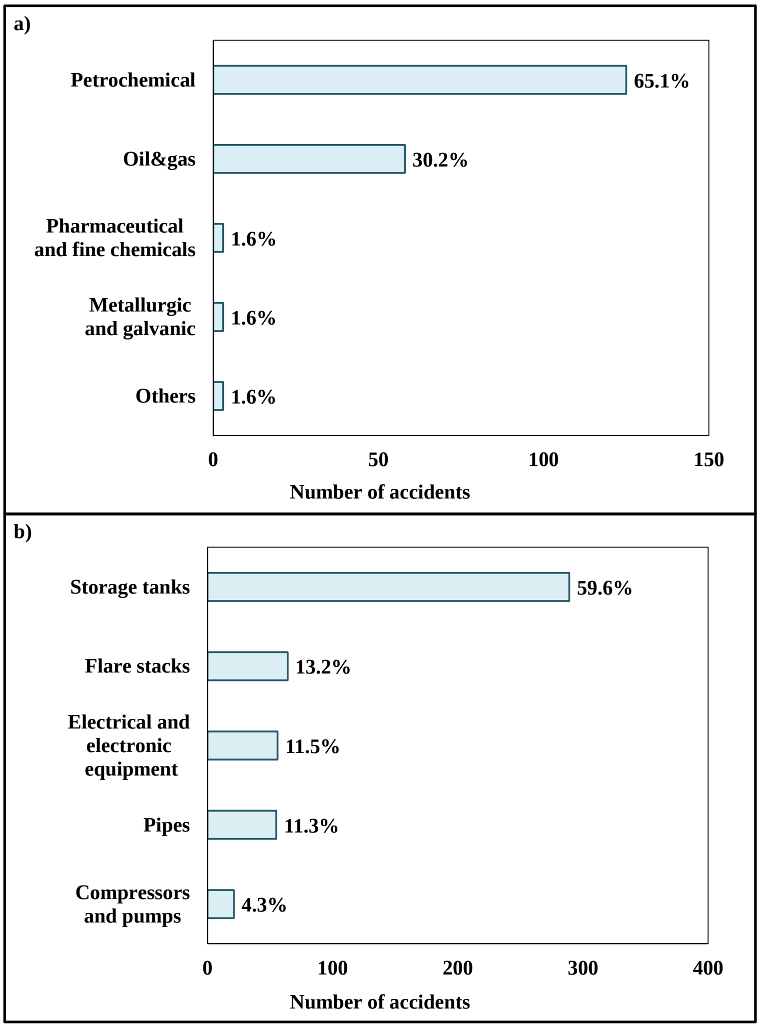


Figure 2.1. 8: a) Industrial activities involved in Natech events caused by lightning (based on 190 records), and b) equipment categories involved in Natech events triggered by lightning (based on 485 records). Data from (Renni et al., 2010).

In particular, the greatest share of the 289 accidents related to this category is composed of large atmospheric storage tanks usually employed to store liquid hydrocarbons, while just in really few cases pressurized tanks were involved (probably due to their limited dimensions and greater mechanical resistance) (Renni et al., 2010). The significant vulnerability of atmospheric storage tanks to keraunic phenomena was also evidenced in other research papers, confirming that lightning strikes are among the most recurring cause of accidents involving this category of industrial equipment (Argyropoulos et al., 2012; Chang and Lin, 2006).

Moreover, the authors retrieved information on the types of accident scenarios that were more recurrent in this typology of Natech events, as can be seen in Figure 2.1. 9 (Renni et al., 2010). Considering all the 721 records extracted from the databases, it was determined that about 58% of Natech events led to the release of hazardous substances, 35% led to fires, and about 7% to explosions (see Figure 2.1. 9-a).

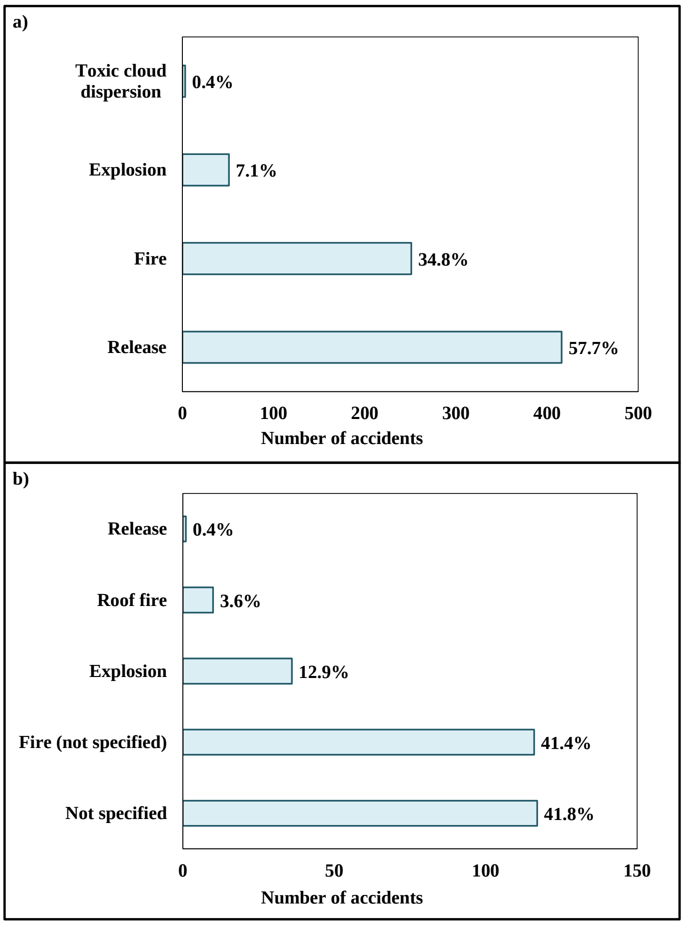


Figure 2.1. 9: a) Distribution of technological scenarios initiated by lightning strikes (based on 721 records) and b) distribution of technological scenarios in Natech events involving storage tanks (based on 280 records). Data from (Renni et al., 2010).

The situation is different considering the subset of accidents involving storage tanks (see Figure 2.1. 9-b). Indeed, in this case, final scenarios as fires and explosions were shown in a great part of the records. Clearly, the final scenarios following lightning strikes depend on several factors as the geometry of the tank, the inventory and the properties of the stored substances, the attachment point, and the safety measures implemented. General event trees were proposed considering the lessons obtained from the analysis of these records (Renni et al., 2010), while successive studies focused on the development of validated approaches for the specific case of atmospheric storage tanks (Necci et al., 2014b). Finally, some useful lessons and recommendations were distilled with the aim of supporting practitioners in developing strategies for the prevention and mitigation of accidents caused by lightning strikes (Krausmann et al., 2011). Among the others, the rim-seal area of floating roof tanks storing flammable products was recognized as a frequent initial point of accident development following lightning attachment. Thus, regular maintenance should be performed to reduce the possibility of vapor escape and the localized formation of flammable mixtures.

The implications of climate change

The possibility that the vulnerability of the industrial sector to natural hazards will be affected by the effect of climate change has been recognized in several works (Cruz et al., 2006; Cruz and Krausmann, 2013; Mahan and Liserio, 2018; UNDRR, 2019). Indeed, as recently stated by the United Nations in the Global Assessment Report, Natech risk is expected to trend upwards due to combined effects of climate change and of industrialization and urbanization growths (UNDRR, 2019).
From database analysis, it is unclear whether this acceleration is already ongoing. Indeed, as already shown at the beginning of Section 2.1.2 (see Figure 2.1. 2), recent research highlighted that the vast majority of Natech events in the last 70 years has been caused by meteorological and hydrological hazards (i.e., more than 95% of the retrieved records) (Ricci et al., 2021). Given that the frequency and intensity of most of the natural hazards belonging to these two macro-categories might be influenced by the effects of climate change (IPCC, 2021, 2018), it is legitimate to suppose that this will have serious implications for the future trend of Natech events. The same authors studied also the temporal distribution of Natech events reported in accident databases, trying to identify possible trends and assess whether climate change has already detectable effects: a globally growing trend of Natech events was evidenced, although the results suggest this increase is not homogenous worldwide. Some interesting indications on this trend can be obtained considering the number of Natech events normalized by the number of active industrial sites per year, for Europe and the U.S., the two most impacted regions according to (Ricci et al., 2021). As shown in Figure 2.1. 10-a, the ratio for Europe has grown in the time span between 2000 and 2017, with an average representative frequency value of about 3.5×10^{-5} events per year per site. On the contrary, for the case of the U.S., a higher average frequency of Natech accidents is obtained, with about 2.3×10^{-3} events per year per site, but a clear trend is hardly identifiable given the peaks in 2005 and 2008 (i.e., generated by Hurricanes Katrina and Rita in 2005 and Gustav and Ike in 2008), and just a slight increase in the numbers can be spotted overall (see Figure 2.1. 10-b).

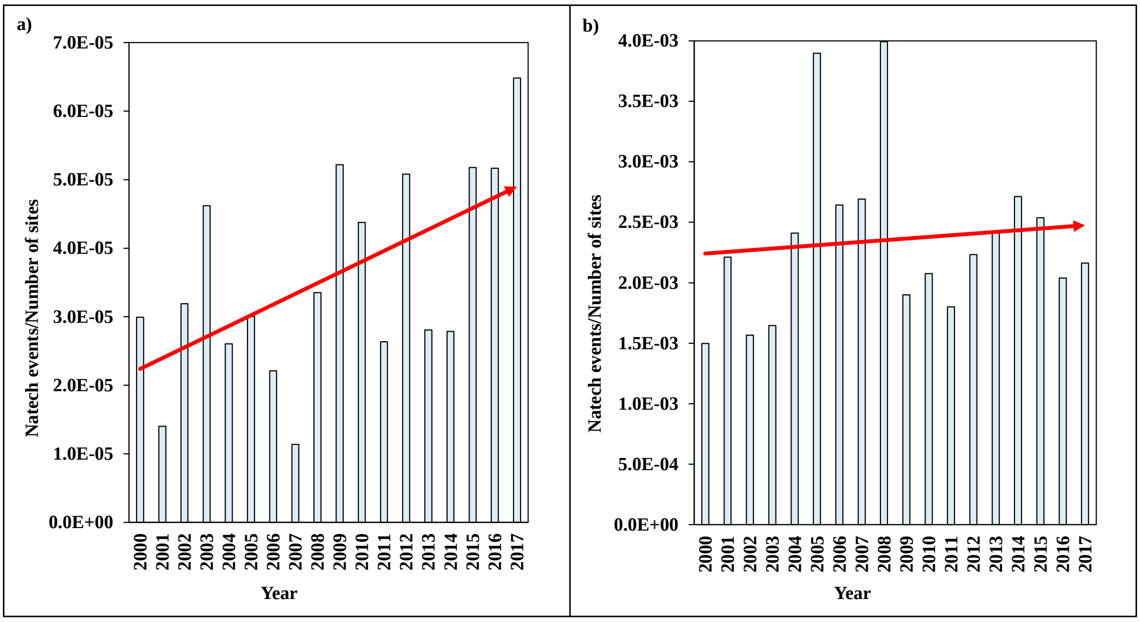


Figure 2.1. 10: Trend of Natech events normalized by the number of active industrial sites for Europe (panel a) and for the U.S. (panel b) between 2000 and 2017. Adapted from (Ricci et al., 2021).

Nonetheless, even if according to the study the probability that industrial sites experience Natech accidents has grown in the last two decades for the two most exposed regions (i.e., see Figure 2.1.1), it is not possible to clearly attribute this variation to climate change.

Other authors focused on the study of the subset of Natech events triggered by tropical storms (Luo et al., 2021). Analyzing data from the U.S. NRC database it was observed that while accidents triggered by tropical storms in the U.S. constituted about 6% of the Natech records in the period between 1990 and 2005, this number rose to 20% considering accidents between 1990 and 2008, and further to around 24% between 1990 and 2017 (Luo et al., 2020). In addition, it was observed that the monthly number of Natech events triggered by tropical storms in the U.S. has a statistically significant increase between 1990 and 2017 (Luo et al., 2021). This variation is shown to be correlated with two widely-used climatic indices indicating that climate change might have indirectly affected the incidence of these accidents by affecting tropical storm activity (Luo et al., 2021). These results are particularly relevant since the work of Luo et al. (2021) is the first study explicitly suggesting that climate change in fact led to an increasing number of Natech events triggered by meteorological disasters in the U.S. between 1990 and 2017. Whereas this should be considered just a preliminary exploration of the topic, possibly suffering from limitations related to the quality of entries of the U.S. NRC database, it paves the way for further exploration of the issue. What is clear to date is that tropical storms and extreme weather events are affected by climate change and expected to feature a severity increase in the foreseeable future (IPCC, 2021, 2018), and that the vulnerability of the infrastructures located in the region (e.g., the facilities belonging to the oil&gas sector located in coastal areas) will be consequently enhanced in case dedicated adaptation strategies accounting for possible hazard modification will not be implemented (Cruz and Krausmann, 2013; Luo et al., 2021). Also the analysis of some recent Natech accidents suggests that climate change is potentially playing a role in modifying site exposure and vulnerability to meteorological and hydrological events. For instance, in August 2019 a downpour of unprecedented severity hit south-western Japan, flooding an extended area and leading to the spill of a massive amount of metal-working oil from an ironworks factory (Misuri et al., 2021a). The presence of oil hampered crisis management operations and produced damages to dwellings and crops. Remarkably, the area has been interested by a long series of previous flooding events, and also by a previous flood-triggered oil spill from the same ironworks in 1990: this event was used as a design basis by the company to implement specific measures to prevent oil spills from happening again (Misuri et al., 2021a). Nevertheless, the intensity of the flooding of August 2019 was unexpected and all the measures were not effective, indicating that the severity of flood hazard of the area might have grown in the last decades (Misuri et al., 2021a). Other similar Natech accidents happened recently also in other parts of Japan (Araki et al., 2020; Kumasaki and King, 2020), suggesting that the oil spill of August 2019 is not an isolated event and that the region is potentially undergoing a modification of the hydrometeorological hazards that is revealing its first outcomes.

As shown, research is currently active in trying to evaluate the present and the future impacts of climate change on the likelihood of Natech events, and even though results obtained up to date might suffer from limitations related to the quality of records extracted from database sources, some interesting indications have been obtained. Indeed, on the one hand, the increase in the number of Natech accidents reported in databases in recent years has been highlighted (Ricci et al., 2021), while on the other some indications of a potential correlation between this growing trend and the changing climate have been also provided for some areas of the World (e.g., see (Luo et al., 2021)). Hence, if adaptation strategies to mitigate this growth will not be promptly developed and implemented, involving all the relevant stakeholders, the vulnerability of the industrial sector is likely to increase dramatically in the immediate future, and climate change together with the ongoing industrialization and urbanization will probably inflate future Natech risks (Krausmann et al., 2019; Krausmann and Necci, 2021; Pilone et al., 2021).

2.2 Natech risk assessment: State of the art

Considering the heterogeneity of the Natech examples described in the previous sections, it might be clear that assessing their risk is all but an easy task. Nonetheless, several approaches were proposed in the years to address this issue, and nowadays established methodologies are available. Not all the methodologies share the same degree of details and not all the methodologies are suitable in general for all the situations. Nevertheless, it is possible to group the main methodologies available in two main categories: the qualitative and semi-quantitative methodologies, and the quantitative methodologies (e.g., the tailored Quantitative Risk Assessment frameworks). Methodologies belonging to the former group usually require a relatively limited amount of data to be applied and provide results with a satisfactory level of detail particularly for screenings and preliminary analysis. On the contrary, quantitative methodologies generally require a significantly greater amount of input data and might be particularly calculation-intensive, although enable a more detailed description of Natech risk. In the following, these two main categories of approaches will be described along with the most relevant tools proposed. It must be said although that since the research work described in the rest of this thesis is focused on quantitative risk assessment of Natech events, only a concise description of the qualitative and semi-quantitative methods will be provided, while more attention will be dedicated to the thorough description of the Quantitative Risk Assessment rationale applied to the case of Natech accidents.

2.2.1 Qualitative and semi-quantitative approaches

Among the earliest shortcut methodologies, it is worth mentioning the approach for preliminary assessment of Natech risk (RNRA) proposed in (Cruz and Okada, 2008). The methodology has been specifically developed to support authorities in the identification, quantification, and analysis of the risk related to the presence of installations handling hazardous chemicals in urban areas exposed to natural hazards. In particular, the methodology is based on the evaluation of Natech risk indices (NRIs) associated with storage tanks with a relevant inventory of hazardous materials, which can drive the prioritization of risk reduction measures and the evaluation of the residual risk after their implementation. The methodology was tested against a case study defined in the Kocaeli region, Turkey. A significant number of sample industrial facilities were selected, and the results obtained applying the RNRA methodology were validated using data from the Natech events triggered by the 1999 Kocaeli earthquake (Cruz and Okada, 2008).

In the same period, another methodology for Natech risk assessment has been proposed by (Galderisi et al., 2008). The methodology is thought to support the definition of proper strategies for land-use planning and Natech risk reduction in urban areas. The method is implemented in a Geographical

Information System (GIS) tool and takes the advantage of a multi-attribute decision-making approach to process information from Safety Reports, from natural hazard maps and from databases of statistics related to the territory where the plant is located, and to provide a Natech risk index that can be used to rank territorial units and prioritize interventions.

A different approach to simplified risk assessment of Natech was followed by (Krausmann and Mushtaq, 2008). In their work, the authors propose a qualitative Natech damage scale for floods for seven relevant industrial sectors identified consulting major accident databases, and for three flood severity levels. It should be noted that this approach was originally intended to raise awareness on the issue of Natech events triggered by floods, although it can also be used as a qualitative tool to support emergency intervention planning activities providing a description of likely damages and scenarios during floods.

Another possibility to perform a qualitative screening is the short-cut methodology proposed by (Busini et al., 2011; Marzo et al., 2012). The methodology is based on the application of the Analytical Hierarchy Process (AHP) proposed by Saaty (Saaty, 2008, 1990) and exploits a predefined semantic scale to perform the binary comparisons between the elements of a set of alternatives, eventually enabling a rational choice between the options. This screening process aims to answer the question "*the Natech risk level associated to process plant A (or to item A) is larger than that associated to process plant B (or to item B)?*", thus its final objective is to provide a ranking for plants/items according to the Natech risk they are related with, which is identified through a set of Key Hazard Indicators (KHIs) representing the risk of fires, explosions or toxic releases as consequence of natural hazards (Busini et al., 2011).

Finally, it is worth mentioning the semi-quantitative methodology for rapid Natech risk assessment (RAPID-N) proposed in (Girgin, 2012; Girgin and Krausmann, 2013). The RAPID-N methodology has been developed by the Joint Research Centre (JRC) and has been implemented in an online software suite that is accessible from the European Commission website. The tool enables quick analysis of the Natech risk related to single installations or multiple assets requiring only a minimum amount of data. The tool is organized in modules addressing several aspects related to the Natech risk assessment process, from the site hazard evaluation to the estimation of substance properties, to the application of fragility curves and definition of risk states. Finally, the evaluation of the consequences of Natech scenarios is performed utilizing a simplified and well-established approach (U.S. EPA, 1999). The tool allows rapid estimation of Natech risk, and even if it is mainly focused on large storage tanks and is affected by some limitations, it has the primary aim of providing authorities with a valid support tool for decision-making in land-use and emergency planning processes.

2.2.2 *Quantitative approaches*

Besides the qualitative and semi-quantitative approaches presented in the previous section, there is a substantial line of research that investigated the applicability of QRA to the issue of Natech, tailoring this tool to accomplish this task. In the following, some of the most relevant works available in the literature will be briefly presented.

The earliest approaches proposed in the literature are focused on the quantitative risk assessment of technological scenarios triggered by earthquakes. One of the first methodologies to perform the quantitative risk assessment of scenarios that can arise from the release of hazardous substances during earthquakes was proposed in the work of (Seligson et al., 1996). In this publication, a simplified approach, yet spanning from the hazard assessment, through the application of generic seismic vulnerability models, to the consequence assessment was proposed with the aim of providing authorities with a cost-effective tool to be applied on a regional basis. A more detailed approach to the Quantitative probabilistic seismic risk analysis (QpsRA) has been proposed for the first time in (Fabbrocino et al., 2005). The authors analyzed an oil storage site located in south Italy coupling of the seismic hazard characterization resulting from the application of the Probabilistic Seismic Hazard Analysis (PSHA) (Baker, 2008), with empirical fragility curves and probit functions (e.g., see (Salzano et al., 2003)) to assess the main equipment failure frequencies and the related hazardous material releases, obtaining eventually the expression of the local risk in the area of the site connected to technological scenarios caused by earthquakes.

Following a similar approach, a specific procedure for seismic QRA was conceptualized in (Antonioni et al., 2007), where the possibility of multiple simultaneous failures due to seismic load was also included. The procedure was implemented in a specific tool for risk recomposition that had been developed within the ARIPAR project (Egidi et al., 1995; Spadoni et al., 2000), and was tested against several case studies showing how the inclusion of Natech scenarios caused by earthquakes modifies individual risk and societal risk figures.

In a subsequent work, the methodology proposed in (Antonioni et al., 2007) was applied to three case studies realized considering the layout of Italian refineries in Milazzo, Rome, and Livorno (Campedel et al., 2008). The authors carried out a thorough analysis of the influence of technological scenarios generated by earthquakes in risk figures and assessed also the effect of different types of equipment (e.g., atmospheric tanks, pressurized vessels) on the societal risk adopting the Potential Life Loss (PLL) indicator as a useful measure to summarize the substantial risk shift caused by Natech scenarios.

The framework conceptualized in these two works for the specific case of earthquakes was then generalized embedding also the case of floods (Antonioni et al., 2009a). The authors proposed also some preliminary criteria for the identification and ranking of critical target equipment based on the storage features, operating conditions, and maximum expected length of the damage distance of potential releases. Differently from the case of earthquakes, at that time simplified models for the vulnerability assessment of process equipment were not available, thus the author proposed a short-cut methodology for the preliminary estimation of equipment damage probability as a function of the maximum floodwater height and the squared maximum floodwater velocity.

In (Salzano et al., 2013), starting from the description of the events that led to the growth in public and academic awareness of Natech risks (e.g., Kocaeli earthquake, Wenchuan earthquake, Tohoku earthquake, and tsunami), the authors propose the integration of qualitative and quantitative methodologies for the assessment of scenarios triggered by natural hazards, proposing in particular to include the approach proposed by (Busini et al., 2011) in a consolidated version of the QRA methodology described in (Antonioni et al., 2009a).

In order to solve the limitation posed by the lack of approaches to assess the damage probability of process equipment during floods, in the following years, extensive work has been done in the development of simplified vulnerability models for this case (e.g., see (Landucci et al., 2014, 2012)). The models developed were then implemented in an updated version of the Natech QRA procedure focused on the risk related to flood-triggered scenarios (Antonioni et al., 2015). The methodology embedding the updated vulnerability models was tested against a case study defined considering the layout of a major chemical and petrochemical site in Italy. The comparison between the figures obtained considering hazardous scenarios from internal failures and the ones obtained considering the flood-induced scenarios evidenced a severe risk shift toward more frequent and more severe outcomes. This effect is related to the relatively higher frequency of natural hazards compared to internal failures and to the high severity of simultaneous scenarios and demonstrates that overlooking the Natech contribution might lead to the severe underestimation of the risk related to technological installations in flood-prone areas.

In parallel to these studies, the similarities between Natech accidents and domino effect were recognized and a procedure that evidences the similarities between the two typologies of accidents was proposed in the literature (Cozzani et al., 2014).

Another research line dealt with the development of appropriate tools for the evaluation of the risk related to technological scenarios triggered by lightning strikes. Specific models were defined to enable the simplified estimation of the likelihood that items present in a site are hit by a lightning strike and lead to technological scenarios (Necci et al., 2014a, 2014b, 2013). These models were developed for the context of the Natech QRA, and were implemented in a complete procedure to assess the risk related to major accidents triggered by lightning strikes (Necci et al., 2016).

Finally, it should be remarked that only a part of the available approaches to Natech quantitative risk assessment has been reported, whereas other approaches have been proposed in the literature, in particular for the case of earthquakes (Alessandri et al., 2018; Caputo et al., 2019). Performing a complete review of the available methodologies is out of the scope of the present section, thus for further information, the reader is referred to comprehensive reviews recently published on this topic (Mesa-Gómez et al., 2020b, 2020a; Suarez-Paba et al., 2019).

Looking at the described publications on Natech QRA, it might be noticed that apart from few exceptions (e.g., see (Antonioni et al., 2009a; Cozzani et al., 2014)), the majority of the approaches are hazard-specific, in the sense that they have been developed considering one natural hazard at time. For instance, in (Antonioni et al., 2015), the QRA procedure is defined for the case of flood-related scenarios only. Since the rationale behind this section is to give an overview of the current approach to the quantitative assessment of Natech risk, without strictly focusing on a specific type of natural hazard, a general procedure for QRA has been depicted in Figure 2.2. 1. The procedure has been mainly inspired to (Antonioni et al., 2009a), although many of its steps are a generalization of those belonging to most of the QRA approaches discussed above. Nevertheless, for the sake of clarity, the procedure will be discussed also pointing out the specificities related to the main types of natural hazards usually considered in the literature, that is, earthquakes, floods, and lightning strikes.

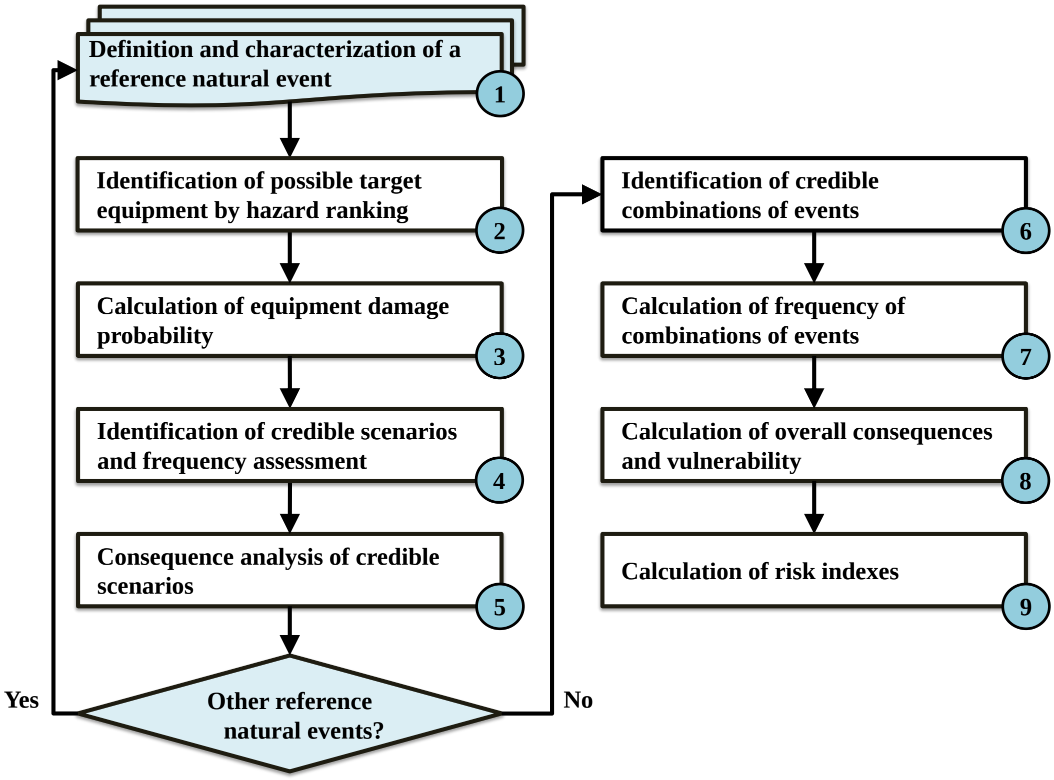


Figure 2.2. 1: Generic procedure for Natech Quantitative Risk Assessment. The procedure is a generalization of the methodologies available in the literature for the cases of accidents triggered by earthquakes, floods, and lightning strikes.

As can be noticed from Figure 2.2. 1, Natech QRA methodologies start with the analysis of natural hazards in the site where the process installation is located (step 1 in Figure 2.2. 1). To this aim, a sufficiently simple approach, suitable for risk assessment studies, should be adopted to perform the characterization of the frequency and of the severity of reference natural events. In practice, a limited number of reference natural events are identified, each having a given intensity and an expected frequency f_{nh} (i.e., or a return time). The intensity of reference natural events might be expressed with impact vectors, that is, tuples of one or more intensity parameters. Clearly, this step is not intended to provide a detailed characterization of the natural hazard at the site, but only to obtain the necessary input data for the evaluation of equipment vulnerability through simplified damage models, as will be later explained (Antonioni et al., 2009a).
The parameters commonly adopted in Natech QRA for earthquakes, floods, and lightning strikes are summarized in Table 2.2. 1.

Table 2.2. 1: Summary of the parameters adopted for the characterization of the three main types of natural hazards usually considered in the QRA of Natech scenarios.

Natural hazard	Data	Example of data source
Earthquake	Peak ground acceleration (*PGA*) [g] Peak ground velocity (*PGV*) [m/s] Frequency f_{nh} [y^{-1}] (or return time [y])	Exceedance probability curves from: - Local studies (e.g., PSHA) - National and international databases (e.g., INGV, EFEHR)
Flood	Maximum water depth h_w [m] Maximum water velocity v_w [m/s] Frequency f_{nh} [y^{-1}] (or return time [y])	Flood hazard maps from: - Local studies - National databases - Empirical correlations
Lightning	Flash density at ground level n_g [flashes/km^{2}year]	Flash density at ground level from: - National databases (e.g., CEI) - Local studies - Empirical correlations

As can be seen from the table, for the characterization of earthquakes a return time and two severity parameters are adopted in the context of QRA, the Peak Ground Acceleration (PGA), which is the peak of the horizontal component of the seismic acceleration at ground obtained from accelerometer measurements and the Peak Ground Velocity (PGV), which is the peak value of the horizontal component of the velocity. For what concerns the severity, whereas the PGA and PGV do not enable a detailed assessment of the effects of a seism on structures, they can be directly related to the structural damage to above ground and underground installations respectively (Lanzano et al., 2013), thus they are considered sufficiently accurate for Natech QRA (Antonioni et al., 2007; Lanzano et al., 2015; Salzano et al., 2003). For what concerns the return time associated with a certain earthquake with a given severity, this parameter can be usually obtained from historical data, for instance from exceedance probability curves obtained from local studies based on Probabilistic Seismic Hazard Analysis (PSHA) (Baker, 2008), or from data provided by national and international databases. As an example, the European Facilities for Earthquake Hazard and Risk (EFEHR) network provides a database of hazard maps realized to complement the dataset ones provided by national authorities (Woessner et al., 2015), whereas for the specific case of Italy, seismic hazard maps for several values of exceedance probability in 50 years have been developed by the National Institute of Geophysics and Volcanology (INGV), which can be freely consulted through a dedicated online tool (Meletti and Montaldo, 2007).

In the case of floods, a couple of intensity parameters are used in Natech QRA, the maximum water depth (h_w) and the maximum water velocity (v_w) expected at the industrial site (Antonioni et al., 2015). These two parameters depend on the selected flood scenario. Hence, different return times are usually assessed and one or more reference flooding events should be selected from the flood hazard maps available from local or national databases (de Moel et al., 2009). In many situations, flood hazard maps show only the maximum extent of the flooded area, thus in case of detailed hydrological studies cannot be performed, simplified correlations might be adopted for an estimate of the required intensity parameters (Krausmann et al., 2017). Clearly, the consultation of sectorial experts should drive the selection of the most appropriate methodologies, considering the uncertainties and the context of the analysis.

Lastly, for the characterization of lightning hazard, a single parameter is usually adopted (Misuri et al., 2020a; Necci et al., 2016). This parameter is the flash density at ground level (n_g) defined as the average number of strikes reaching ground level per area per year, and it is widely employed in the literature on lightning risk assessment and lightning protection systems (Cigré Working Group, 2013; IEC, 2019, 2010). Reference values for n_g can be assessed by the consultation of flash density maps (Cecil et al., 2014; CEI, 2021; IEC, 2019), or employing simplified approaches based on the number of thunderstorm days or hours perceived in a certain region per year (Huffines and Orville, 1999; IEC, 2010).

Once the characterization of identified natural hazards is completed, a preliminary screening procedure should be performed to identify the relevant equipment to be included in the analysis. This task is commonly performed also in conventional QRAs, since including all the equipment would possibly overburden the calculations and it is usually preferred to limit the scope of the analysis to a restricted number of items expected to be relevant in determining site risk level (CCPS, 2000; Uijt de Haag and Ale, 2005).

Clearly, among the relevant factors to be considered in performing a screening the most relevant are the type of equipment, the inventory, the hazardous properties of the substance involved, and the operating conditions. Various approaches to equipment ranking have been proposed in the literature. For instance, an analysis of the types of units most frequently involved in Natech events caused by earthquakes and floods has been performed in (Antonioni et al., 2009a). This analysis was based on 78 accidents triggered by earthquakes and 272 accidents induced by floods and demonstrated that atmospheric tanks were in both cases the most frequently impacted equipment category, respectively with 80.3% and 60.2% share of the records. Large diameters were involved in both cases in about 17% of the records, while in the case of floods also pressure vessels feature a relevant share of the records (13.4%). In the same publication, the authors suggest also a consequence-based criterion derived from the evaluation of damage distances related to releases of substances under various operating conditions from various types of equipment, considering similar equivalent diameters for all the equipment categories (Antonioni et al., 2009a).

Another example of criteria for equipment ranking can be found in (Krausmann et al., 2017). The criteria are summarized in Table 2.2. 2, and can be used for a preliminary risk-based screening developed considering the inventory of hazardous substances, their physical state, and the expected structural vulnerability of each type of equipment considered.

Table 2.2. 2: Matrix for a preliminary screening of equipment based on technological hazard. Scores are in increasing order (e.g., from 1 corresponding to low hazard, to 5 corresponding to high hazard). Adapted from (Krausmann et al., 2017).

Type of equipment	Liquefied gas	Compressed gas	Cryogenic liquid	Liquid	Fine dust
Pressurized vessel (above ground)	5	4	4	2	1
Pressurized vessel (underground)	2	3	2	2	1
Atmospheric equipment	n.a.	n.a.	5	3	3
Pipeline (above ground)	3	2	3	1	1
Pipeline (underground)	3	2	3	1	n.a.

For what concerns the case of lightning, past accident analysis evidenced that storage tanks are the items most frequently involved in Natech scenarios (Renni et al., 2010) (see Section 2.1.2). This category of equipment is usually employed to store significant quantities of liquid hydrocarbons, and it is not surprising that the impact of a lightning strike can thus lead to severe technological scenarios. It has been also demonstrated that the likelihood that a lightning strike is captured by a structure depends on the structure dimensions (Necci et al., 2014a), and atmospheric storage tanks might feature relevant capture areas due to their relevant diameter (e.g., according to API650 standard, large-capacity oil storage tanks can typically feature a diameter of more than 60m (API, 2007)). On the other hand, pressurized vessels are not usually prioritized in lightning Natech QRA, since are generally smaller (i.e., and thus linked to lower capture frequency), and due to their significantly greater shell thickness compared to atmospheric storage, the likelihood of being punctured is also significantly lower. It should be noted that this result has been somehow also confirmed by past accident analysis since in (Renni et al., 2010) it was shown that pressurized vessels have been involved only in about 1% of Natech accidents triggered by lightning strikes.

Lastly, as already pointed out, another option to perform a preliminary screening of the equipment to be included in the QRA is to exploit one of the qualitative or semi-quantitative methodologies presented above. In particular, the methodology based on AHP and KHI definition proposed by (Busini et al., 2011) has been indicated in the literature as a valid approach to this task (Salzano et al., 2013).

After a restricted set of critical equipment is identified and selected, the next step is to assess the likelihood that the natural hazard will lead to certain damage connected to a LOC (step 3 in Figure 2.2. 1). This task is usually accomplished through observational fragility models or simplified vulnerability models.
A non-exhaustive list of models is reported in Table 2.2. 3, for the cases of earthquakes, floods and lightning strikes. The common trait that all the models share is their suitability to support QRA studies, allowing the estimation of equipment failure probability as a function of the natural hazard characterization parameters assessed in step 1 of the procedure (see Figure 2.2. 1) and of a relatively limited amount of equipment information.

Table 2.2. 3: Sample list of some vulnerability and fragility models available in the literature to assess the likelihood of equipment failure due to three types of natural hazards (floods, earthquakes, and lightning).

Reference	**Equipment**	**Description**
Flood		
(Landucci et al., 2012)	Vertical atmospheric storage tanks	Model to assess the probability of failure of atmospheric storage tanks to floodwater load based on buckling failure mechanism.
(Landucci et al., 2014)	Horizontal storage vessels	Model to assess the probability of failure of horizontal storage vessels to floodwater load based on the mechanical failure of anchoring bolts to torque and buoyancy loads.
(Khakzad and Van Gelder, 2018, 2017)	Vertical atmospheric storage tanks	Models based on Bayesian networks to assess the failure probability of atmospheric tanks to flood scenarios.
(Zuluaga Mayorga et al., 2019)	Vertical atmospheric storage tanks	Models to assess the probability of storage tank failure due to buckling or floatation during flood scenarios.
(Kameshwar and Padgett, 2018a)	Vertical atmospheric storage tanks	Model to assess storage tank failure probability considering the cases of buckling and floatation related to storm surge scenarios.

Earthquake		
(Salzano et al., 2003)	Vertical atmospheric storage tanks	Observational fragility model for atmospheric storage tanks to assess their failure probability as a function of seismic PGA.
(Salzano et al., 2009)	Vertical atmospheric tanks, horizontal storage vessels, pressurized reactors, pumps	Observational fragility models for storage and process equipment to assess their failure probability as a function of seismic PGA.
(Lanzano et al., 2013)	Pipelines	Observational fragility models to assess the probability of failure of natural gas pipelines as a function of seismic PGV.
(Lanzano et al., 2014)	Buried pipelines	Observational fragility models to assess the probability of failure of buried pipelines carrying gases or liquids as a function of PGV during strong ground shaking, and as a function of PGA in case of ground failure.
(Moschonas et al., 2014)	Spherical pressure vessel	Model to assess the probability of failure of industrial spherical vessels as a function of seismic PGA.
Lightning		
(Necci et al., 2013)	All	Model to assess the probability lightning strikes impacting process equipment creates a hole in the containment and its expected dimensions.
(Necci et al., 2014a)	All	Model to assess the lightning capture frequency for process equipment, based on their geometrical features.

As can be seen looking at the table, models differ depending on the type of input required, on the simplifying assumptions, and on the approaches followed for their development. Indeed, some are based on observational analysis, others on mechanical models, while in some cases also advanced statistical tools as Bayesian networks are employed.

For instance, the vulnerability model developed by (Landucci et al., 2014) for horizontal vessels during floods was developed starting from a detailed mechanical model for anchor bolt failures, which was then used to provide the simplified correlations summarized in Table 2.2. 4 that are thought specifically for the application on QRA studies.

Table 2.2. 4: Example of vulnerability model for horizontal vessels during floods (Landucci et al., 2014). **Reference values have been calculated considering vessels built for 2MPa design pressure.*

Item	Definition	Value/Equation
Vulnerability model equations		
CFL	Critical Filling Level for horizontal vessels (pressurized or atmospheric)	$CFL = \frac{(\rho_{ref} \cdot A)}{(\rho_l - \rho_v)} \cdot (h_w - h_c) + \frac{(\rho_{ref} \cdot B - \rho_v)}{(\rho_l - \rho_v)}$
$v_{w,c}$	Flooding critical velocity	$v_{w,c} = E \cdot (h_w - h_c - h_{\min})^F$
P_{nhd}	Vessel vulnerability due to flooding	If $v_w \geq v_{w,c}$, $P_{nhd} = 1$ If $v_w < v_{w,c}$, $P_{nhd} = (CFL - \phi_{min})/(\phi_{max} - \phi_{min})$
Input parameters		
C	Vessel capacity	Small capacity < 10 m^3 Medium capacity 10–30 m^3 Large capacity > 30 m^3
W_t	Vessel tare weight*	900-2200 kg (Small capacity) 3000-7200 kg (Medium capacity) 9900-63000 kg (Large capacity)
D	Vessel diameter	1.3-1.6 m (Small capacity) 1.6-2.4 m (Medium capacity) 2.3-3.8 m (Large capacity)
L	Vessel length	3–3.5 m (Small capacity) 4.5–11.1 m (Medium capacity) 8-24 m (Large capacity)
A	First *CFL* correlation coefficient	$A = 1.339 \cdot D^{-0.989}$
B	Second *CFL* correlation coefficient	$B = -1.21(W_t - 374.4)^{-0.107}$
E	$v_{w,c}$ correlation factor	$E = 5.497 \cdot L^{-0.692}$
F	$v_{w,c}$ correlation exponent	$F = -0.06 \cdot \ln(L/D) - 0.375$
v_w	Flood water speed	0 – 3.5 m/s
h_w	Flood water depth	0 – 4 m
ρ_w	Flood water density	1100 kg/m^3
h_c	Height of concrete basement (flooding protection)	0.25 m (assumed)
h_{min}	Minimum flooding height able to wet the vessel surface	$h_{\min} = \lambda - D/2$
λ	Saddle height parameter (vessel axis height from the ground anchorage point)	0.98 m (Small capacity) 0.98–1.38 m (Medium capacity) 1.38-1.98 m (Large capacity)
ρ_l	Stored liquid density	500-1100 kg/m^3
ρ_v	Stored vapor density	1.25-20 kg/m^3
ρ_{ref}	Reference density used for the definition of *CFL* correlations	1000 kg/m^3
ϕ_{min}	Minimum operative filling level	0.01
ϕ_{max}	Maximum operative filling level	0.90

On the contrary, most of the models for seismic risk assessment presented in Table 2.2. 3 have been developed directly from the analysis of past events and provided observational fragility curves applicable to a broad set of similar equipment. An example of fragility curves obtained in (Salzano et al., 2003) for atmospheric storage tanks is shown in Figure 2.2. 2. As shown in the figure, this approach allowed to include different LOC intensities. Indeed, in this case two curves are available, one for moderate LOC (i.e., the continuous line in Figure 2.2. 2), and another for extensive LOC (i.e., the dashed line in Figure 2.2. 2) that is possible as a result of the complete loss of mechanical integrity of the containment.

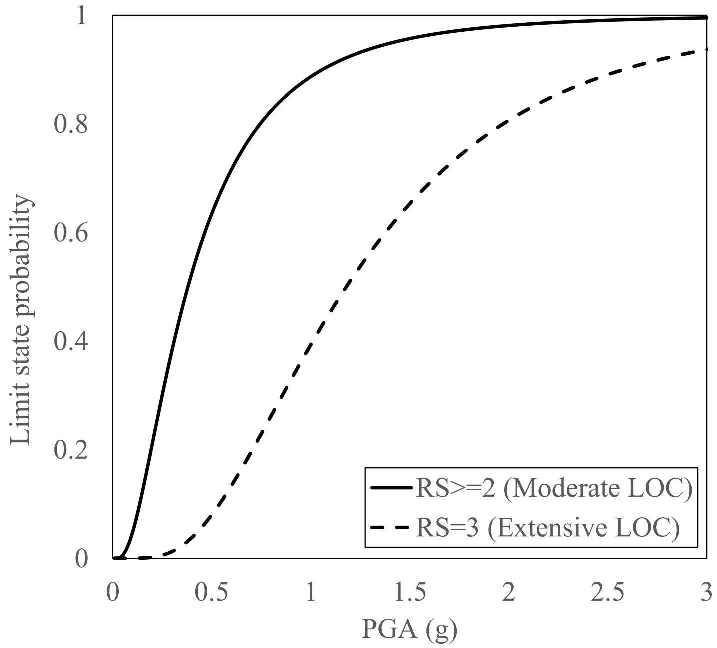


Figure 2.2. 2: Fragility curves for atmospheric storage tanks during earthquakes. The probability of reaching a defined limit state is a function of the PGA. Adapted from (Salzano et al., 2003).*RS=Risk State, LOC=Loss of Containment;*

For the specific case of lightning strikes instead, as can be noticed from Table 2.2. 3, two separate models are required to accomplish this step of the procedure. A first model is required to assess the likelihood that a lightning strike will be captured by the equipment in case it falls in the site area (Necci et al., 2014a). This model has been specifically developed through Monte Carlo simulation applying the established Electro-Geometrical Model (EGM) (Cooray and Becerra, 2010). A second model is then required to assess the probability that a lightning strike will have enough energy to cause a hole in the metal of the containment (Necci et al., 2013). For the sake of brevity, further details on these models are not provided here, although their application will be exemplified in the case study developed in Section 6.2.3.

Once the quantification of the likelihood of a release is performed, the set of credible technological scenarios needs to be defined and their frequencies should be calculated (i.e., step 4 in Figure 2.2. 1). The procedure requires the application of event tree analysis to consider the hazardous properties of the substance in the identification of the final outcomes following a LOC. In many situations (e.g., see (Antonioni et al., 2015)), conventional event tree analysis might be suitable for the application also in the context of Natech (CCPS, 2000; Mannan, 2005; Uijt de Haag and Ale, 2005; Van Den Bosh and Weterings, 2005). Nevertheless, research effort has been made in developing specific event trees for the case of Natech scenarios, in order to catch the main differences with scenarios caused by internal failures (Antonioni et al., 2009a; Campedel, 2008; Cozzani et al., 2010; Necci et al., 2014b; Ricci et al., 2021).

For instance, the analysis of the records available in major accident databases allowed the preliminary estimation of an ad-hoc ignition probability value in the case of earthquakes (Campedel, 2008).

Recently, a thorough analysis of more than 6400 Natech accident records extracted from various database sources led to the development of quantified post-release event trees for geological, hydrological, and meteorological natural hazards, providing also reference ignition probabilities inferred directly from past accidents (Ricci et al., 2021).

In (Cozzani et al., 2010), a comprehensive set of post-release event trees for the case of flood-induced Natech events has been proposed starting from the analysis of the records available in major accident databases. The authors evidenced also the possibility of flood-specific technological scenarios when substances that can react with water are involved, as shown in Figure 2.2. 3.

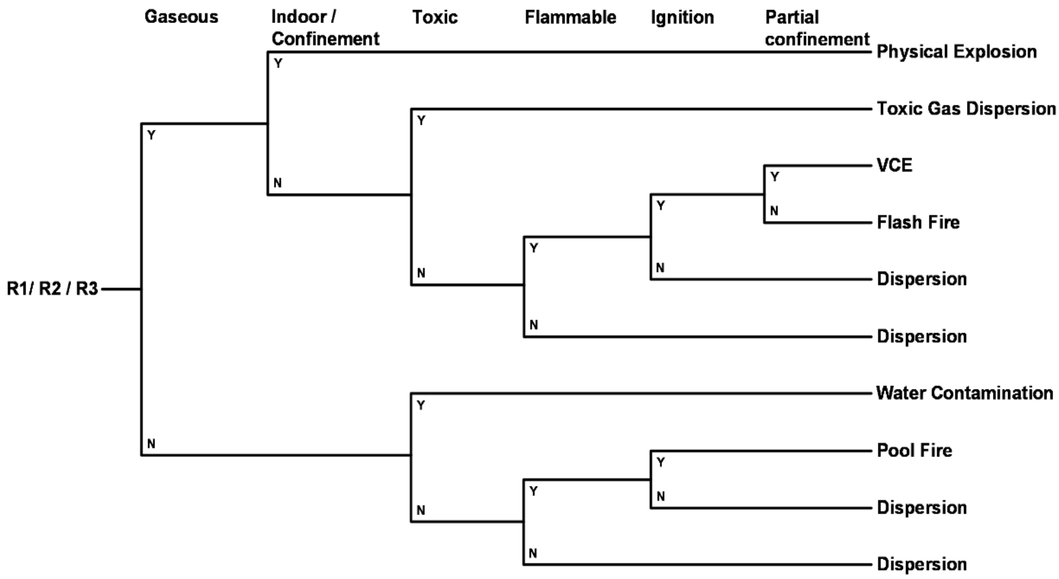


Figure 2.2. 3: Post-release event trees for substances reacting with water in NaTech accidents triggered by floods, according to the analysis of the records reported in major accident databases (Cozzani et al., 2010).

In (Necci et al., 2014b), a set of event trees was developed and validated against past accidents for the specific case of lightning impact on atmospheric storage tanks. For this peculiar case, the typology of atmospheric storage and the protection systems implemented on it (e.g., rim-seal fire extinguishers) determine the final outcomes that can be expected after a lightning strike is captured by the item. Indeed, severe technological scenarios might arise also in case the lightning strike does not puncture the metal containment. Once again, for the sake of brevity, this aspect is not described in detail in this section, since the set of event trees for lightning-triggered Natech will be applied in Section 6.2.3.

Following the identification and frequency assessment of the technological events related to the impact of natural hazards on each critical item, the consequence assessment for each scenario should be carried out (step 5 in Figure 2.2. 1). This step is intended to evaluate the physical effects from the scenarios following the LOCs and then to the application of vulnerability models to assess the impact of such physical effects on defined targets. The former task is usually performed by well-established literature models, aimed at the evaluation of heat radiation from fires, concentrations of flammable or toxic substances during dispersions, and overpressure during explosions (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005). This choice clearly represents a simplification dictated by the absence of specific physical effect evaluation approaches for the case of Natech events, and ad-hoc models able to catch the presence of natural hazards should be opted for in case they were available. This problem has been partially recognized in (Antonioni et al., 2015), where the authors suggest implementing values of roughness length typical of sea surface in the gas dispersion models to mimic the presence of floodwaters during Natech scenarios, and to consider unconfined pools of liquids floating over water in case of their release (e.g., light hydrocarbons). For what concerns the vulnerability models, it should be kept in mind that the chemical and process QRA usually considers human targets as the risk receptors, thus these tools are aimed at estimating the probability that humans show adverse symptoms (i.e., usually death) after the exposure to a given physical effect of a certain intensity (Van Den Bosh, 1992). Threshold-based approaches or probit functions are adopted as human vulnerability models in QRA studies (CCPS, 2000; Finney, 1971; Uijt de Haag and Ale, 2005). As a necessary simplification, the same models applied in conventional QRA are adopted also in Natech QRA, practically assuming that the possibility of synergies between physical effects and natural hazards can be neglected (Krausmann et al., 2017).

The following part of the procedure has been conceptualized to model the possibility of multiple simultaneous outcomes during a Natech scenario (steps 6 to 8 in Figure 2.2. 1). Assessing this peculiar aspect of Natech accidents is particularly important since some categories of natural hazards, as earthquakes and floods, for instance, have an impact on the whole process site. On the other hand, for the case of lightning, this aspect is not considered in the QRA procedure developed in (Necci et al., 2016), where it is assumed that only a single element might be hit by a lightning strike at a time.

In order to assess the identification and the characterization of outcome combinations, a well-established methodology defined in the context of domino effect QRA has been tailored to the case of Natech (Antonioni et al., 2009b; Cozzani et al., 2005). The methodology is based on the assumption that the damage of any of the *n* critical targets identified in Step 2 is probabilistically independent of the contemporary damage of any of the other *n* - 1 elements (Antonioni et al., 2015, 2007; Cozzani et al., 2014). It should be noted that the procedure considers only one reference technological scenario per equipment involved, thus a selection from the event trees developed in the previous steps might be done considering the worst-case outcome before computing scenario combinations.

A single Natech scenario can involve the contemporary damage of *k* out of *n* units resulting in *k* final outcomes, with *k* comprised between 1 and *n*. The number of different Natech scenarios involving exactly *k* out of *n* units N_k can be assessed as:

$$N_k = \binom{n}{k} = \frac{n!}{(n-k)!\,k!} \tag{2.2. 1}$$

Assuming only binary targets (i.e., a generic target is assumed to be safe or to fail featuring the worst-case outcome as explained above), the total number of overall Natech scenarios N_{Natech} (excluding the case when all the items are in a safe state) can be calculated as:

$$N_{Natech} = \sum_{k=1}^{n} \binom{n}{k} = 2^n - 1 \tag{2.2. 2}$$

Assigning an index *m* to each of the possible combinations of *k* out of *n* units ($m = 1, \ldots, N_k$), a single overall Natech scenario may thus be identified as a vector ($\boldsymbol{J}_m^k = [\gamma_1, \gamma_k]$), whose elements ($\gamma_j(j = 1, \ldots, k)$) are the indexes of the *k* rupture events involved. Therefore, the probability of a single overall Natech scenario involving *k* targets $P_{Natech}^{(k,m)}$ can be assessed as:

$$P_{Natech}^{(k,m)} = \prod_{l=1}^{n} \left[1 - P_l + \delta(l, \mathbf{J}_m^k)(2P_l - 1)\right] \tag{2.2. 3}$$

where $\delta(l, \boldsymbol{J}_m^k)$ shows a value of 1 if the *l*-th unit is comprised in the vector $\boldsymbol{J}_m^k$, and the value of 0 in the case is it not. P_l is the probability of the worst-case final outcome considered for the *l*-th target, and its value depends on the specific event tree applied in step 4 of Figure 2.2. 1. For instance, if the identified worst-case scenario for the release of a flammable liquid from the *l*-th target is a pool fire, then the P_l might be the product between a probability of ignition and the damage probability $P_{nhd,l}$ assessed by the application of fragility curves or vulnerability models adopted in step 3 of Figure 2.2. 1. In some publications, as a conservative assumption, $P_{nhd,l}$ is used in the calculation of $P_{Natech}^{(k,m)}$ (e.g., see (Antonioni et al., 2015)).

The frequency of the *m*-th Natech scenario originating involving *k* units $f_{Natech}^{(k,m)}$ can be calculated according to:

$$f_{Natech}^{(k,m)} = f_{nh} \times P_{Natech}^{(k,m)} \tag{2.2. 4}$$

where f_{nh} is the frequency of the natural hazard obtained from the characterization performed in step 1 of Figure 2.2. 1.

Regarding the evaluation of the consequences of overall Natech scenarios (step 8 of Figure 2.2. 1), conventional models cannot be directly used for the assessment of the consequences of a generic combination of k possibly heterogeneous outcomes. Indeed, the well-established consequence assessment models assume single point-source scenarios (Van Den Bosh and Weterings, 2005). Also in performing this task, a procedure proposed in the context of domino effect QRA has been proposed for the case of Natech (Cozzani et al., 2005). The consequences of the overall scenario are expressed as the normalized sum of the death probabilities related to each of the outcomes taking part in the overall Natech scenario (i.e., an upper limit of 1 is considered). Therefore, the death probability in a generic position considering k events involved in the m-th Natech scenario $V_{Natech}^{(k,m)}$ can be assessed as:

$$V_{Natech}^{(k,m)} = \min\left(\sum_{l=1}^{n} \delta(l, \mathbf{J}_m^k)\, V_l\,, 1\right) \tag{2.2. 5}$$

where V_l is the death probability related to the l-th event and $\delta(l, \boldsymbol{J}_m^k)$ is equal to 1 if it is involved in the $\boldsymbol{J}_m^k$ Natech scenario.

Lastly, risk indexes can be computed to summarize the results of the Natech QRA (step 9 in Figure 2.2. 1). The two indices mostly used in the literature are the individual and the societal risk, which can be computed following standardized approaches (CCPS, 2000; Uijt de Haag and Ale, 2005). The former is usually represented by mapping the risk contours over the layout of interest, while the latter is commonly expressed through F/N curves, that is, plots showing the cumulative frequency F of scenarios causing at least N fatalities. In some works, the application of additional risk indexes has been also suggested to summarize the results obtained in terms of societal risk. In particular, in (Campedel et al., 2008) it is advised to evaluate the Potential Life Loss (PLL) index, that is the average expected frequency of fatalities due to accidental events, according to the following expression:

$$PLL = \int_0^{\infty} F(N)\, dN = \sum_N F(N) \tag{2.2. 6}$$

where $F(N)$ is the cumulated frequency of having at least N fatalities. All the steps involved in the calculation of risk figures and indices can be accomplished using well-established tools as the ARIPAR methodology (Antonioni et al., 2007; Cozzani et al., 2014; Egidi et al., 1995; Spadoni et al., 2000).

2.2.3 Similarities with other types of cascading events

Natech events are cascading scenarios triggered by primary natural events. Following this definition, it is thus clear that Natech events share several similarities with other types of cascading events as domino effects (Reniers and Cozzani, 2013a).

Broadly speaking, Natech events might also be seen as particular types of domino effects where the initiating event is actually a natural hazard (Cozzani et al., 2013a).

Indeed, past accident analysis demonstrated that event chains initiated by natural hazards do not always stop at primary technological scenarios, and in some cases, Natech events further escalated leading to disastrous accidents involving multiple secondary targets simultaneously. For instance, during the aforementioned Kocaeli earthquake (see Section 2.1), four tanks storing naphtha ignited due to the sparks caused by floating roof vibrations, and the fire spread through drainage systems to two other tanks located in the same catch basin (Steinberg and Cruz, 2004).

In 1998, in a storage site in Ras Gharib (Egypt) a tank containing petroleum products was hit by a lightning strike during a thunderstorm. The tank caught fire and the accident propagated within all the storage farm, and eventually involved 16 tanks storing more than 2000 t of oil each, causing huge economic losses (Marsh's Risk Consulting Practice, 2001).

Also the fires caused by GEJET at Cosmo Oil Co. refinery in Chiba can be seen as a remarkable example of domino effect from natural hazards (Cosmo Oil Co., 2011; Krausmann and Cruz, 2013). As already described in Section 2.1, the intense seismic load damaged the support braces of one LPG spherical tank in the storage area of the refinery, which collapsed leading to a fire. Exposed to the intense radiation, all the 17 LPG tanks in the area were damaged and fire propagated to nearby tanks and neighbouring petrochemical sites (Cosmo Oil Co., 2011).

As clear from these examples, the overall sequence of events, from the impact of natural hazards to the final technological scenarios can be conceptualized as shown in Figure 2.2. 4.

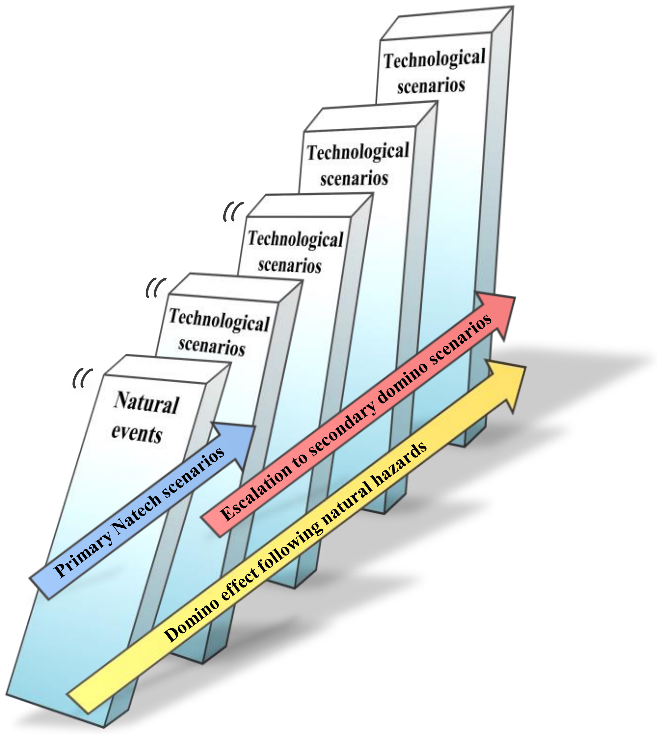


Figure 2.2. 4: Conceptualization of cascading scenarios driven by natural events. Adapted from (Misuri and Cozzani, 2021a).

As can be noticed from the figure, in Natech events (i.e., the yellow arrow in Figure 2.2. 4), the primary accident is triggered by external causes (e.g., by the impact of effects as wind loads, seismic loads, or forces exerted by floodwaters). Following the impact of these events, in some cases, Natech events stop to the primary technological scenarios generated, leading to accident dynamics treated in established Natech risk assessment methodologies (i.e., the blue arrow in Figure 2.2. 4). In some other cases (e.g., as the Ras Gharib and Chiba refinery accidents described above), the accident sequence progresses and a further escalation may occur, leading to catastrophic secondary scenarios triggered by the primary Natech events (i.e., the red arrow in Figure 2.2. 4). These cases are particularly relevant, not only due to the more severe consequences of the accident when additional equipment is involved. Indeed, the likelihood of the escalation might be also heavily increased by the concurrent impact of natural hazards on technical measures implemented in the plant to prevent accidents.

Recently, the analogies between Natech events and domino effects were also recognized from a risk assessment standpoint (Cozzani et al., 2014). The authors discuss the QRA of domino and Natech events evidencing the common points and the need to catch the cascading nature of both phenomena.

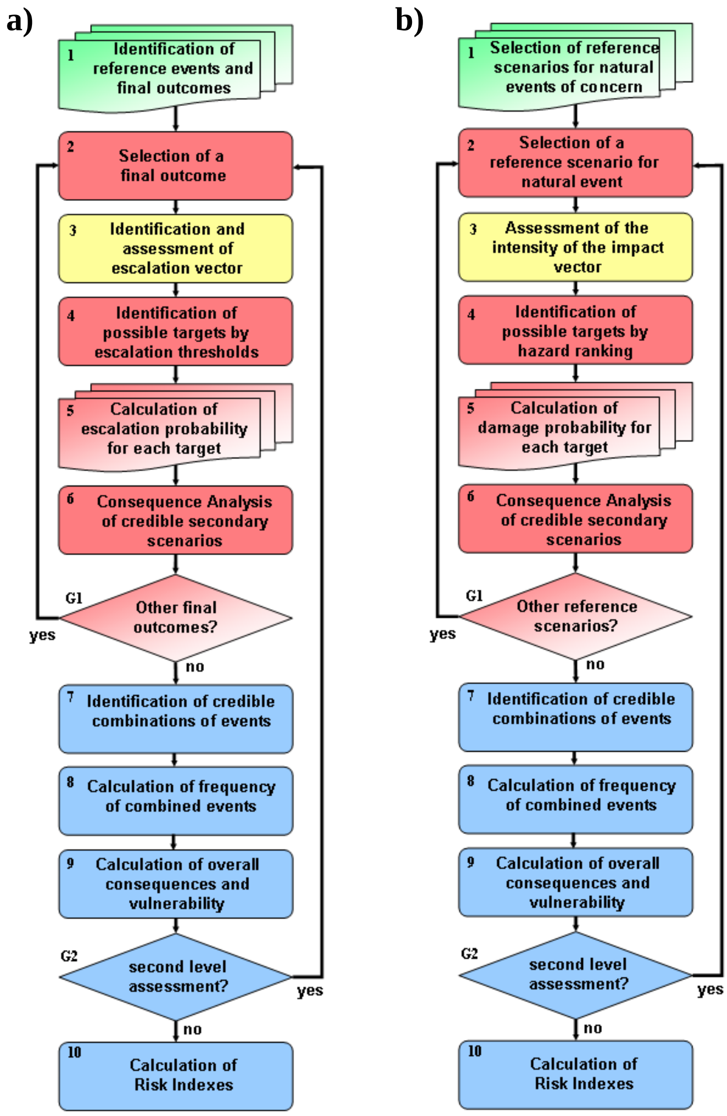


Figure 2.2. 5: Comparison between the methodologies for the quantitative risk assessment of domino effect (panel a) and Natech accidents (panel b). Adapted from (Cozzani et al., 2014).

In particular, a comparison of the two QRA procedures proposed is reported in Figure 2.2. 5 (Cozzani et al., 2014). As can be noticed from the figure, the second level assessment (i.e., aimed at modeling Natech escalation in secondary scenarios) is conceptualized also for the case of Natech QRA. Nevertheless, the assessment of such level is not considered in established QRA approaches reported in Section 2.2.2, and with just a few exceptions addressing specific types of natural hazards (e.g., see (Alessandri et al., 2018; Naderpour and Khakzad, 2018), Natech risk assessment so far is mostly limited to primary technological scenarios (e.g., see (Antonioni et al., 2015, 2009a, 2007; Campedel et al., 2008; Fabbrocino et al., 2005)).

Chapter 3. Research questions

The analysis of relevant past accidents and information retrieved from accident databases was the first step in the identification of possible limitations of the tools available in the literature to assess the risk related to Natech events. The research activity carried out within the present Ph.D. project focused on providing answers to three main research questions identified by the comparison between the capabilities of current Natech risk assessment approaches and the actual features of past accidents. The three main research questions may be summarized as follows:

1) Are the current paradigms applied to the quantitative assessment of Natech scenarios adequate to capture the features and the complexity of such accidents?
2) What is the actual performance of safety barriers in Natech events? Is the performance of the safety barriers and safety systems significantly affected by the natural event?
3) How can the degradation or impairment of safety barriers be considered in the quantitative risk assessment of Natech events?

The first research issue was identified analyzing two recent severe Natech accidents as the Fukushima (2011) Daiichi NPP nuclear disaster and the Arkema accident (2017) (see Section 2.1.1 for concise accident descriptions). These two events indeed showed a degree of complexity that seems to exceed the capabilities of current approaches to the quantification of Natech risk. Recalling the description of the current risk assessment methodologies provided in Section 2.2.2, it might be clear that these are focused solely on the possibility of hazardous material releases following the damage of process and storage equipment (e.g., from a breach caused by floodwater impact) and take the advantage of vulnerability models to quantify the likelihood of such ruptures. On the contrary, in these two milestone incidents, the primary phases of the accident progression did not involve the structural failure of process equipment. In fact, the development of severe technological scenarios was caused by the systemic failure of the plant, that is, by the loss of auxiliary systems, utilities and safety systems. Therefore, Natech accidents caused by auxiliary system failures are automatically overlooked applying the methodologies presented in Section 2.2.2, and consequently the related contribution to risk figures cannot be currently quantified. Hence, the first task of the research activity was aimed at investigating whether the current risk assessment paradigm is outdated, and at conceptualizing a novel holistic approach to the quantification of Natech risk capable of effectively catching the inherent complexity of cascading scenarios both from the direct equipment failure and from the loss of auxiliary systems. This topic will be the core of Chapter 4.

As mentioned above, an important effect of the systemic impact of natural hazards on chemical and process installations evidenced in past Natech events is that safety barriers to prevent or mitigate hazardous scenarios might undergo significant damages up to the point of losing their functionality. Some of these cases have been mentioned in Section 2.1.1. For instance, during the San Jacinto River floods, several manual interruption valves could not be operated being submerged by floodwaters, preventing the possibility of interrupting the release of petrochemical products from breached pipelines. Considering the case of the Kocaeli Earthquake, firefighting means could not be relied on due to water shortage and loss of power connection at the sites involved, and containment basins to limit the spread of toxic liquids were fractured and could not be effective in retaining the spilled substances. Damages to secondary containments and outdoor firefighting systems were reported also in many petrochemical facilities damaged during the Japanese GEJET. Therefore, the second objective of this thesis is to provide a methodology to assess the depletion of safety barriers during Natech events. The shortage of detailed information on safety barrier failure in past accident records found in databases prevented to perform a statistical analysis on barrier failure occurrence, thus the task has been performed leveraging an expert elicitation procedure. Figures obtained from the study confirmed the criticality of the issue and helped to individuate specific factors that can be employed to modify barrier performances in quantitative risk assessment studies. Indeed, the pilot application of the results in the frequency assessment of Natech accident escalation confirmed that barrier depletion enhances the likelihood of domino propagation, producing a more realistic evaluation of the possibility of severe secondary scenarios. This part of the activity will be extensively described in Chapter 5.

Moving from the obtained data and the methodologies developed in Chapter 5, the following question is related to how barrier depletion can be considered in complete QRA studies, including the possibilities of escalation of primary Natech events and of accident propagation through domino effects. Indeed, none of the QRA methodologies described in Section 2.2.2 is capable of including the presence (and thus the depletion) of safety barriers in the analysis. Hence, the natural direction of the research was to investigate the possibility of extending Natech QRA methodologies in order to embed the necessary modifications to model the action and the performance of safety barriers, considering also the possibility of cascading scenarios.This task will be the focus of Chapter 6. First, a risk assessment methodology addressing the role of safety barriers in the possibility of escalation of primary Natech scenarios has been discussed and tested against case studies. This methodology will be detailed in see Section 6.1. Therein, a dedicated barrier assessment step will be described to include the possible specificities of implemented safeguards leveraging a three-level approach partly based on the results obtained from the expert elicitation presented in Section 5.2 and partly based on a fault-tree-analysis approach aimed at the detailed evaluation of complex systems.

Secondly, Section 6.2 will be dedicated to the description of a general Natech QRA methodology addressing the possibility of domino effects following primary scenarios. The application of the approach will be exemplified considering the case of Natech accidents triggered by lightning strikes. This specific natural hazard has been selected since, as shown in Section 6.2, the risk related to lightning strikes can be severely underestimated in case the cascading nature of the accident is not considered. Finally, a comprehensive methodology for Natech QRA including the role of safety barriers in accident escalation through domino effect will be discussed in Section 6.3.

Chapter 4. A novel paradigm to support Natech risk assessment and management

In this chapter, the conceptual framework shared by most of the Natech risk assessment approaches developed to date will be discussed in light of two milestone accidents featuring a peculiar dynamic. A novel paradigm will be then proposed, with the objective of addressing the possibility of utilities and safety barrier failure as a consequence of natural hazards.

4.1 Current paradigm for Natech risk assessment

As clear from the examples provided in Section 2.1, Natech accidents are inherently complex scenarios, and their assessment required the development of ad-hoc methodologies. The need to investigate specifically the features of the hazard posed by Natech scenarios was recognized since the late ‘90s (Lindell and Perry, 1997, 1996; Showalter and Myers, 1994). As described in Section 2.2, to date several approaches are available for the identification of Natech hazard (Krausmann et al., 2017; Suarez-Paba et al., 2019) and the quantitative assessment of risk due to Natech scenarios (Mesa-Gómez et al., 2020b). An important example of such methodologies is the RAPID-N online tool, developed by the European Commission’s Joint Research Centre for the rapid assessment of Natech risk, which focuses on large storage tanks and has the primary aim of supporting competent authorities in land-use and emergency planning (Girgin, 2012; Girgin and Krausmann, 2013). Another example of simplified methodologies is the RNRA approach, which has been proposed with the intent of providing authorities with a flexible tool to assess Natech risk in urban areas (Cruz and Okada, 2008). More recently, some authors proposed the application of Monte Carlo simulations to perform the quantitative assessment of Natech risk for the specific case of earthquakes and implemented it in a software tool named PRIAMUS (Alessandri et al., 2018). Cozzani and coworkers proposed the extension of the Quantitative Risk Assessment (QRA) procedure to include Natech events, specifically including the risk caused by the possibility that natural hazards will impact multiple items at a time, generating simultaneous scenarios (Antonioni et al., 2015, 2009a, 2007; Cozzani et al., 2014). Other studies proposed the application of Bayesian networks to perform the probabilistic vulnerability assessment of storage tanks subjected to floods (Khakzad and Van Gelder, 2018, 2017).

All the above methodologies and, more in general, most of the methodologies proposed in the literature for the risk management and quantitative assessment of Natech scenarios to date are based on the common framework outlined in Figure 4. 1. The framework only takes into account what may be defined as a “direct” path causing the loss of containment (LOC) of hazardous substances, triggered by the structural damage of process or storage equipment directly caused by the impact of the natural event ("Direct accident path" arrow in Figure 4. 1). The possibility of accident escalation through domino effect has been recently recognized as well ("Domino effect" arrow in Figure 4. 1), as a consequence of the structural damage of secondary[1] equipment items (Misuri et al., 2020a; Naderpour and Khakzad, 2018; Yang et al., 2018; Zeng et al., 2021). However, no other pathway than that involving the direct structural damage of equipment items caused by the natural event is currently considered.

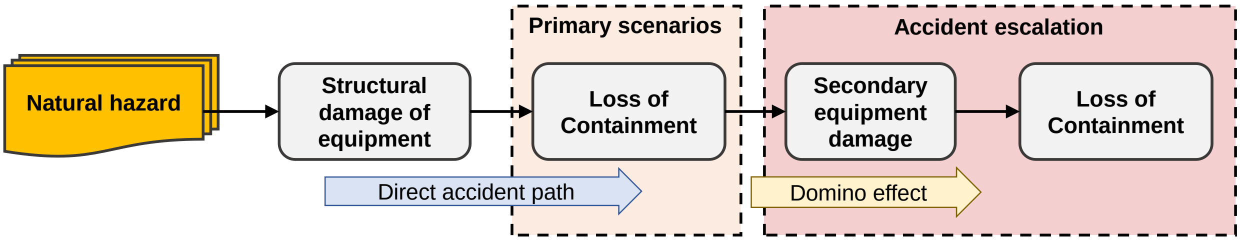


Figure 4. 1: Conventional accident model currently considered in Natech risk assessment.

Actually, to date, Natech risk assessment methodologies focus mostly on the severe scenarios related to the LOCs following the structural damages caused by natural hazards to process equipment or storage tanks. Indeed, relevant studies on past accident analysis showed that this is the more recurrent event sequence in previous Natech events (e.g., see (Krausmann and Salzano, 2017)). Whereas the results of these studies indirectly validate the event sequence shown in Figure 4. 1, when a more comprehensive analysis of past Natech events is carried out, the assumption that technological scenarios are only possible due to the "direct" structural damage of equipment caused by natural hazards becomes questionable. In particular, two severe accidents which received high attention as those that affected the Arkema facility in Crosby (Texas) during Hurricane Harvey in 2017 (U.S. CSB, 2018), and the Dai-ichi nuclear power station in Fukushima (Japan) following Great East Japan Earthquake and Tsunami in 2011 (Tokyo Electric Power Company Inc., 2012), call for a revision of the framework shown in Figure 4. 1 and for an extension of the approach to the hazard identification and risk assessment of Natech accidents. Indeed, despite these two accidents involved two very different technological facilities (i.e., a chemical manufacturing site and a nuclear power station), they share common elements, as the key role played by the failure of auxiliary systems, plant utilities,

[1] Conceptually there is no difference between secondary scenarios and those deriving from further escalation (e.g., tertiary, quaternary) from a risk assessment standpoint. Hence, each scenario following the primary LOC will be defined as "secondary" in the rest of Chapter 4. It should be noted that this is also consistent with domino effect QRA methodologies where further escalation levels are recursively assessed without relevant methodological variations (Antonioni et al., 2015; Cozzani et al., 2014; Landucci et al., 2017b). Nevertheless, in Chapter 6 that is focused on QRA, the terminology will be more specific in order to ease the reader in understanding the main methodological steps described.

and safety barriers in accident evolution, that are not captured by the current Natech risk assessment framework. Such shortcomings may become critical within a risk management system, since they may induce the analysts to overlook severe scenarios specific to Natech events. Therefore, a more comprehensive framework is needed to support the analysis of Natech accidents.

4.2 Lessons from milestone accidents

In the following, lessons learnt from two milestone accidents caused by natural events at the Arkema facility in Crosby (Texas, U.S.) and at the Dai-Chi nuclear power station (NPS) in Fukushima (Japan) are analyzed. It should be noted that, while extremely detailed reports on such accidents are available in the literature (e.g., see (U.S. CSB, 2018) for the Arkema accident and (Tokyo Electric Power Company Inc., 2012; Weightman, 2011) for the Fukushima disaster), a comprehensive discussion of such events is out of scope of this chapter, and only a general outline of the events is reported.

The discussion on the main lessons learned is supported also by the use of the results of a simplified Man, Technology, and Organization (MTO) analysis, focusing on the role of auxiliary systems, plant utilities, and safety barriers in accident evolution. MTO analysis is a well-known accident investigation method, which has been originally developed in the Swedish nuclear sector (Rollenhagen, 1995; Sklet, 2004). The methodology had been also applied in previous research to investigate the JX refinery accident during the Great East Japan Earthquake and Tsunami (2011) (Chakraborty et al., 2018). Representing the accident through an MTO analysis worksheet allows highlighting how human, technical, and organizational factors contribute to accident progression (Sklet, 2004). The analysis was carried out with the specific aim of drawing useful lessons concerning accident evolution. The results are then discussed also in the light of other past accidents, to identify the limitations of the paradigm currently applied to the Natech risk assessment framework represented in Figure 4. 1.

4.2.1 Arkema accident, Crosby, Texas, U.S. (2017)

In the Arkema plant, located in Crosby (Texas) about 30 different types of organic peroxides used as initiators in polymer manufacturing processes are produced (U.S. CSB, 2018). Organic peroxides are inherently unstable due to the presence of the peroxide functional group (-O-O-) (HSE, 1998). In many cases, safe storage of these substances requires very low storage temperatures (e.g., as low as -30°C (Arkema, 2007)) to prevent unwanted exothermal decomposition that may occur at temperatures above a substance-specific threshold, commonly referred to as Self-Accelerating Decomposition Temperature (SADT) (HSE, 1998; PGS, 2011; Sun et al., 2001).

The accident was triggered by Hurricane Harvey that hit Texas in 2017 (Misuri et al., 2019a; U.S. CSB, 2018). Further details on the severity of this natural disaster have already been given in Section 2.1, thus will not be repeated here.
Two days before hurricane landfall, preventive measures were implemented by plant managers, including production shutdown, securing of loose materials, establishing a ride-out crew to ensure surveillance, and checking fuel level in emergency power supply generators and liquid N_2 level in the emergency cooling system.
On August 27th 2017 some areas of the site were flooded by more than 1.2m of water. Rising floodwaters were approaching the refrigeration units of six out of seven low-temperature warehouses, which had to be shut down. Chemicals were thus moved to refrigerated trailers. During the following day, the electric transformers of the site were flooded and backup diesel generators had to be started. Nonetheless, the further rise of flood water forced the actuation of a preventive shutdown of backup generators, leading to the stoppage of the refrigeration unit of the last operating warehouse.
A further emergency cooling system was foreseen, based on liquid N_2 injection. The exploitation of this system would have required manually connecting a pipe to dedicated junctions near the cryogenic N_2 storage tank. Being the junctions located close to ground level, one of the plant managers installed a 0.3m long pipe extension to reduce the likelihood it would have been submerged by floodwater (U.S. CSB, 2018). However, this additional piping was not sufficient and soon the connection was submerged, rendering this barrier unavailable.
In the meantime, also the forklifts used to move the peroxides became inoperable due to high floodwater height (approaching chest-level in the warehouse area), thus, workers were forced to move manually the remaining peroxide pallets to the refrigerated trailers. In total, 10500 containers (about 1.6e+05 kg of peroxides) were moved into nine refrigerated trailers. However, floodwater approached three out of nine trailers which were located in the low ground area and the conditions of the site did not allow workers to move them to a higher location. Foreseeing the risk of explosion, on August 29th the ride-out crew was evacuated and a 2.4 km emergency evacuation radius was implemented by authorities around the facility. By September 1st, the three trailers reached by floodwater caught fire due to peroxide decomposition. Since the conditions of peroxides inside the six remaining trailers could not be monitored, on September 3rd authorities decided to carry out their controlled combustion.

The MTO worksheet has been realized according to the information made available by the CSB investigation report (U.S. CSB, 2018), and is shown in Figure 4. 2. The MTO worksheet includes the event and causal factors chart (ECFC) showing the nodes describing the accident progression sequence.

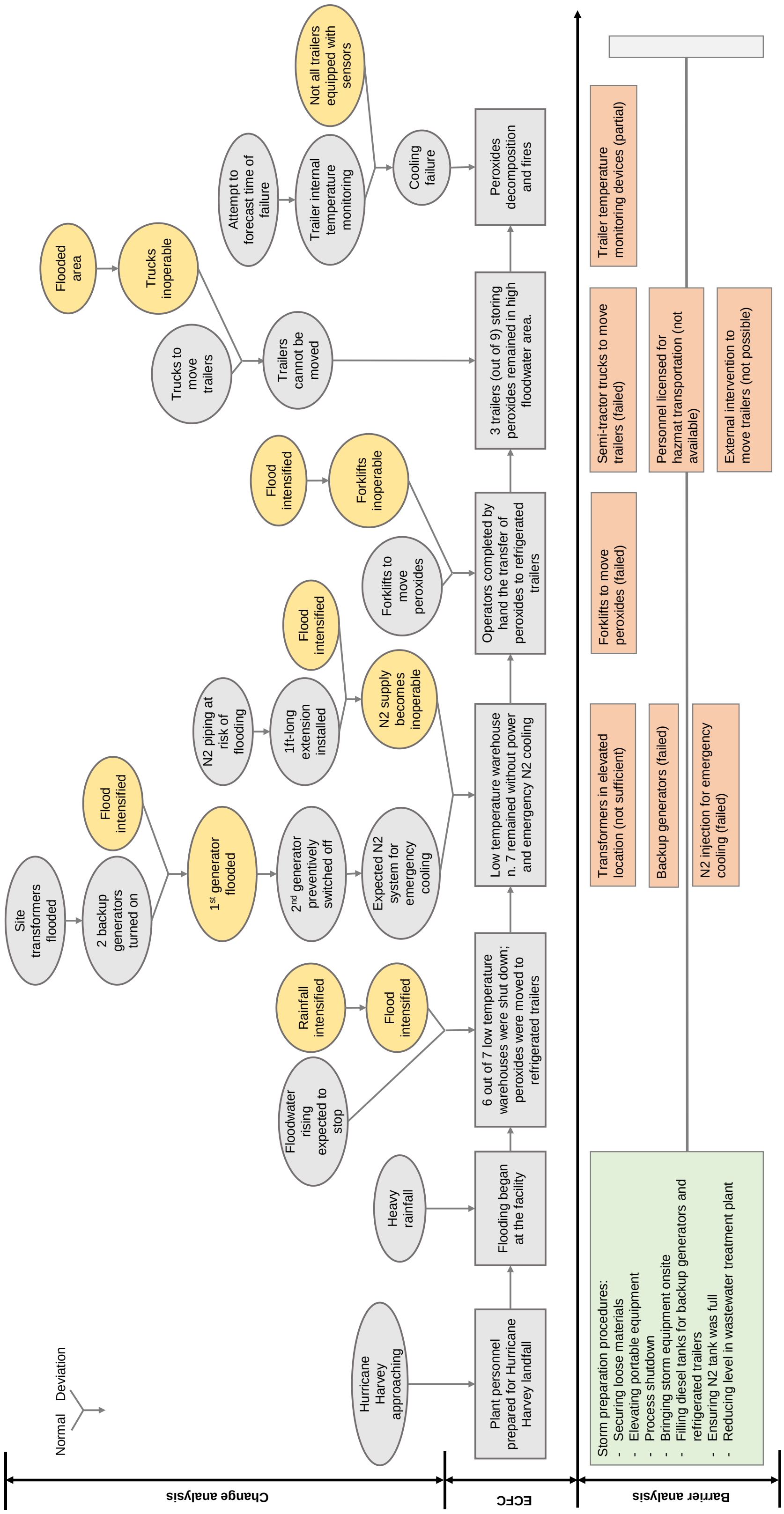


Figure 4. 2: Simplified MTO worksheet obtained for the Arkema accident (2017). ECFC=Event and causal factors chart

The worksheet also shows the results of the change analysis applied to each node, reporting the expected events and the deviations experienced in the actual event sequence. The bottom part of the MTO worksheet in Figure 4. 2 shows the results of barrier analysis. In this part of the diagram, the failure of utility systems, safety systems, and procedures that played a role in the accident evolution is reported.

The event progression toward the final accidental scenario started after the implementation of the preventive procedural measures defined in the case of tropical storms. The underestimation of the actual flood severity caused the loss of the main cooling system and of all the backup systems. This was the result of a number of events (i.e., flooding of transformers, flooding of emergency generators, unavailability of liquid N_2 emergency cooling systems, impossibility to move away trailers, flooding of trailers) all caused by the flood. Actually, all the layers of protections implemented to avoid a prolonged loss of cooling to peroxides were made unavailable by floodwater.
Three important lessons may be learnt from the Arkema accident, based on the evidence provided by the MTO worksheet shown in Figure 4. 2.

The first lesson is that the accident was not caused by structural damage of process of storage systems by the floodwater. The fires and explosions were the results of the failure of the utilities (main and back-up power systems feeding the cooling system of warehouses) and of the safety barriers, both technical (back-up generators and emergency N_2 cooling system) and procedural (procedures to move the chemicals to the trailers and to move the trailers away from the flooded areas). Thus, the framework provided in Figure 4. 1 is not representing the accident sequence that occurred.

The second lesson concerns the specific hazardous properties of the chemicals involved in the accident. Even if the accident was caused by the failure of the cooling system, it should be remarked that such event may lead to a LOC and a hazardous scenario only in specific processes where substances showing a self-decomposition behaviour at ambient temperature are present in relevant quantities. Thus, when considering deviations from the framework shown in Figure 4. 1, the specific properties of substances need to be screened in order to understand if specific scenarios are possible in case utilities or safety barriers become unavailable.

Finally, the third lesson provided by the event is that the chain of failures that affected the utilities and the safety barriers in the accident could have hardly occurred simultaneously for causes different from a flood. Thus, it should be recognized that natural hazards impacting an industrial site can generate specific conditions that modify the performance of utilities and safety barriers and that are not expected in the absence of such external events. Overlooking this feature of Natech scenarios might lead, as in the case of the Arkema accident, to the design of safety barriers whose action might be impaired by natural events, resulting in the escalation of the accident consequences.

4.2.2 Dai-Ichi NPS accident, Fukushima, Japan (2011)

The facility involved in the accident is the Fukushima Dai-Ichi NPS operated by Tokyo Electric Power Company (TEPCO) (Tokyo Electric Power Company Inc., 2012). The plant consisted of six boiling water reactors (BWRs) for an overall power generation of about 4.7GW (Weightman, 2011). Also in this case exhaustive reports on the accident are available, reporting the full details of the event (e.g., see (The National Diet of Japan, 2012; Tokyo Electric Power Company Inc., 2012; Weightman, 2011)). Thus, in the following, only an outline of the events is provided, to support the MTO analysis focused on the specific issues related to the failure of the cooling system of the reactors.

On March 11th 2011 at 2:46 pm JST, the main shock of the Great East Japan Earthquake affected the site and was followed by many severe aftershocks in the days after (Weightman, 2011). The maximum peak ground acceleration registered on the site has been assessed at 0.56g (~5.5 m/s^2) in the basement of reactor buildings (Weightman, 2011). Three reactors (Units 1-3) were in operation, while the other three units were in cold shutdown or under periodic inspection. The earthquake led to the activation of the automatic shutdown procedure (SCRAM) (Bozzola, 1982) and to the isolation of the plant from the national power grid, also due to the severe damage of an electrical substation to which six of the seven transmission lines were connected (The National Diet of Japan, 2012; Watanabe et al., 2015). The latter scenario is commonly referred to as loss of off-site power (LOOP) (Watanabe et al., 2015). The LOOP caused the closure of the main steam isolation valves (MSIVs), the automatic start of emergency diesel generators (EDGs), and the activation of the main systems for handling core thermal transients to bring the reactor in cold shutdown conditions. Around 3:40 pm a 14m tsunami wave generated by the earthquake overtopped the protection barriers implemented on the shoreline, and flooded the area of the reactor buildings, with an estimated water depth between 4 and 6m (Labib and Harris, 2015). Floodwaters entered the area of the buildings where EDGs were located, causing their immediate failure and the complete loss of AC power in the plant. Electrical switchgears were severely damaged by seawater and DC power panels in Units 1, 2, and 4 were impacted as well, since they were located in the basement of the buildings, causing all the instrumentation to fail and preventing the possibility of monitoring plant conditions (Tokyo Electric Power Company Inc., 2012). In Unit 3, DC power was available, since power panels were located in the semi-basement of the building, although only relying on batteries. However, the switchgears were severely damaged, preventing the possibility to connect other power sources, and the panels run out of power one day later (The National Diet of Japan, 2012).

The complete loss of both AC and DC power led to the interruption of all the cooling functions in Units 1-3. Eventually, the water level inside the core of Units 1-3 dropped below fuel level due to uncontrolled boiling, exposing the overheated fuel rods to steam. A relevant quantity of hydrogen was produced by the reaction of Zirconium, present in the cladding of the fuel rods, with steam at high temperatures. Hydrogen mixed with air in the upper part of the reactor buildings, forming a flammable cloud that finally ignited, leading to two severe explosions in Units 1 and Unit 3. The explosion in Unit 3 caused damages also in Unit 4 due to back-flow propagation from venting channels (Tokyo Electric Power Company Inc., 2012). Core meltdown was experienced in Units 1-3, resulting in a major nuclear accident (BBC, 2011; IAEA, 2013, 2011).

A simplified MTO worksheet is reported in Figure 4. 3. It should be remarked that accident progression in each reactor had some specificities which are not considered in the figure since the MTO analysis focused on the role of auxiliary systems failure in the evolution of the accident.
Despite the plant involved in the accident is an NPS, with several specificities in auxiliary and safety systems different from those of chemical and process plants which are the main focus of the Natech framework discussed in Section 4.1, useful lessons can still be learnt from the analysis of the MTO worksheet reported in Figure 4. 3.

A first lesson is that the main cause of the accident was the loss of electric power supply to the cooling system, a key utility of the NPS, following the LOOP and the simultaneous flooding of the EDGs. No structural damage to the reactor containment was reported before the hydrogen explosions. Thus, again, the framework in Figure 4. 1 seems inadequate to capture the chain of events that occurred in Fukushima: the LOC of a hazardous substance (hydrogen in this case) was not caused by the structural damage of an equipment item, but rather by the loss of control of the process caused by the failure of a critical utility (the reactor cooling system).

A second lesson is that similarly to what happened in the Arkema accident, the simultaneous failure of the utilities and of the safety barriers (i.e., the occurrence of a LOOP and the failure of all the EDGs) would have been hardly credible in the absence of the particularly severe circumstances occurred during a seismogenic tsunami. Thus, again, overlooking the specific conditions created by the impact of a natural event on an industrial site may cause the inappropriate design of the process utilities, and the implementation of safety barriers not capable of preventing the accident or at least the escalation of the accident consequences.

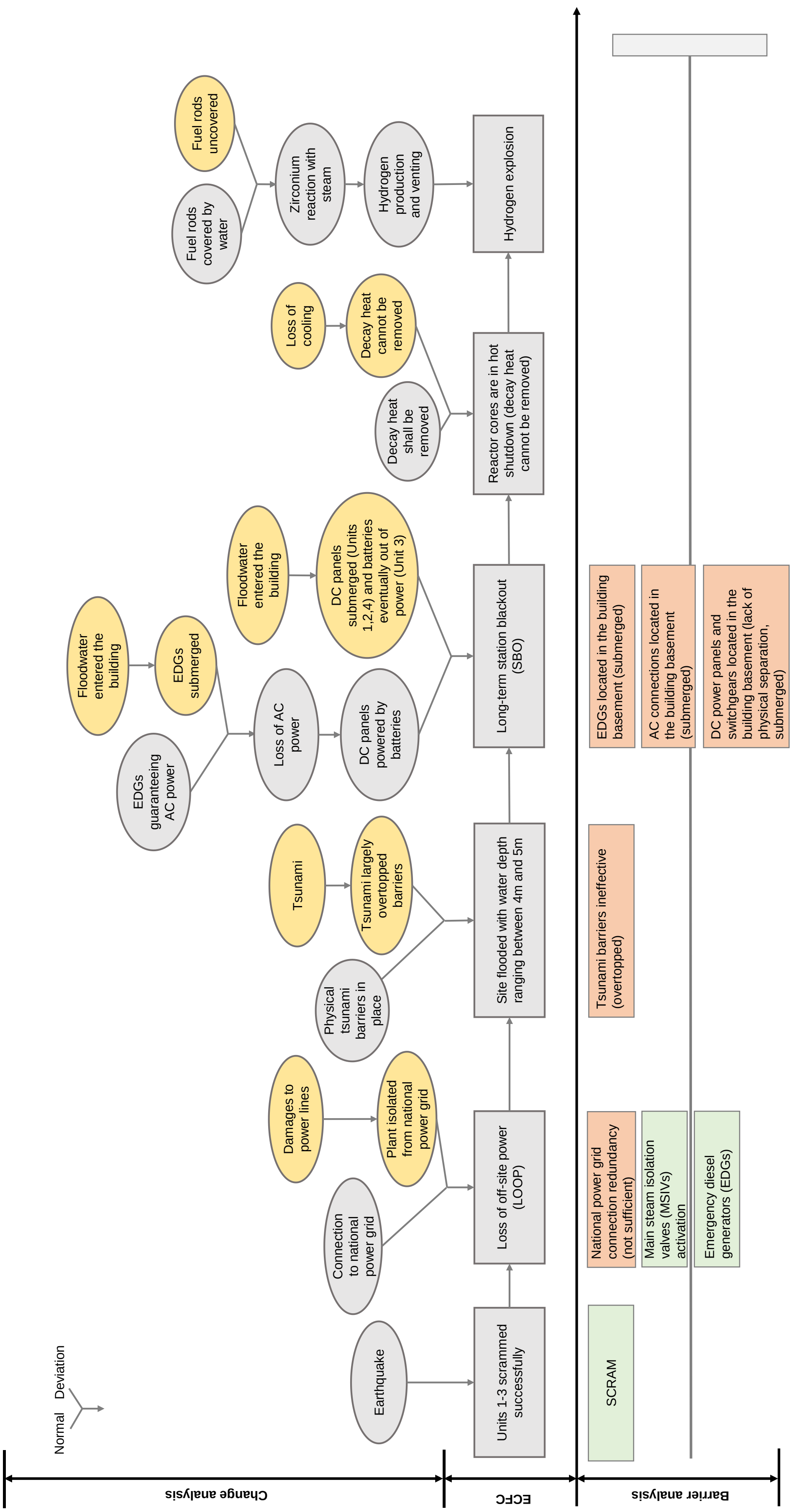


Figure 4. 3: Simplified MTO worksheet for Fukushima Dai-ichi NPS accident (2011). ECFC=Event and causal factors chart.

4.2.3 Implications for the Natech assessment framework

Both in case of Arkema and Fukushima Natech events, the MTO analysis shows that the accidents were initiated by the impact of natural hazards on auxiliary systems, which started the cascade of events, that progressed and escalated due to the impairment or to the depleted performance of safety barriers, also caused by the natural event.

As discussed above, the accident progression experienced in these two milestone accidents is not captured by the current Natech risk assessment framework summarized in Figure 1. Well-established Natech risk assessment methodologies only address technological scenarios following the direct failure of equipment due to natural hazards (e.g., buckling of storage tanks due to seismic load, displacement or floating of equipment items due to floodwater, etc.) (Alessandri et al., 2018; Antonioni et al., 2015; Cozzani et al., 2014; Girgin and Krausmann, 2013), while possible scenarios arising from the failure of auxiliary systems and utility networks, cooling water, power connection, and inert gas blanketing, as well as the role of safety barrier impairment due to the action of the natural event, are important aspects currently not considered. Only two early studies, addressing specific scenarios, mention the importance of auxiliary systems and safety barrier integrity (Cruz et al., 2001; Seligson et al., 1996). In the work of Seligson et al. (1996), power outages and damage to control systems due to seismic load are listed among the possible causes of post-earthquake releases of chlorine and ammonia. In the study of Cruz et al. (2001), the same causes are listed among the possible events capable of leading to technological scenarios following hurricane impact.

Remarkably, while on the one hand the current framework for Natech risk assessment lacks in explicitly considering the risk associated with scenarios related to the failure of safety systems and auxiliary systems, the Arkema and Fukushima milestone accidents are far from being exceptions or black swans. When going through past Natech events reported in the literature, a number of near misses or similar chain of events could be recognized. For instance, the analysis of the severe meteorological events which hit France in 2018 raised concern about the vulnerability of utility networks (The French Bureau for Analysis of Industrial Risks and Pollutions (BARPI), 2018). Also during the Kocaeli Earthquake, which hit one of the most industrialized regions of Turkey in 1999, major damages to utility lines were experienced in petrochemical and process facilities (Girgin, 2011). During the severe storm surge hitting England in December 2013, many industrial sites were impacted and severe damages to the electricity infrastructure, instrumentation, and control systems were experienced besides the structural damages to physical barriers (The French Ministry of Ecology Sustainable Development and Energy, 2015). Evidence of the high vulnerability of auxiliary systems and protection systems dependent on lifelines has been confirmed also during Hurricane Harvey, in a recent study which integrated information retrieved from database analysis with a survey administered to facilities located in areas exposed to the tropical storm (Misuri et al., 2019a). In an inorganic chemical manufacturing site in France, a severe thunderstorm led to a power outage which in turn caused a release of chlorine (The French Bureau for Analysis of Industrial Risks and Pollutions (BARPI), 2019). The damage to the inverter led to the failure of the pumps feeding the water curtains activated to disperse the toxic cloud and to a partial power outage in the control room.

All these events evidence again the limitations of the current Natech risk assessment methodologies. Indeed, even if not always the failure of auxiliary systems and utilities has led to major accidents, it may be considered a precursor incident (Skogdalen and Vinnem, 2012), but the possibility of subsequent technological scenarios is still overlooked in the available approaches to Natech quantitative risk assessment and management. Therefore, a paradigm shift is needed, introducing a more robust and comprehensive framework to support the assessment and management of risk related to Natech scenarios.

4.3 Paradigm shift in Natech accident modeling

4.3.1 Innovative paradigm for Natech risk assessment

Figure 4. 4 presents an innovative paradigm for the identification and assessment of Natech scenarios based on lessons learnt from the Arkema and Fukushima milestone accidents. As can be noticed, the framework is realized from (and also embeds) the current paradigm represented in Figure 4. 1 and extends it to include also the role of utilities, auxiliary systems, and safety barriers.

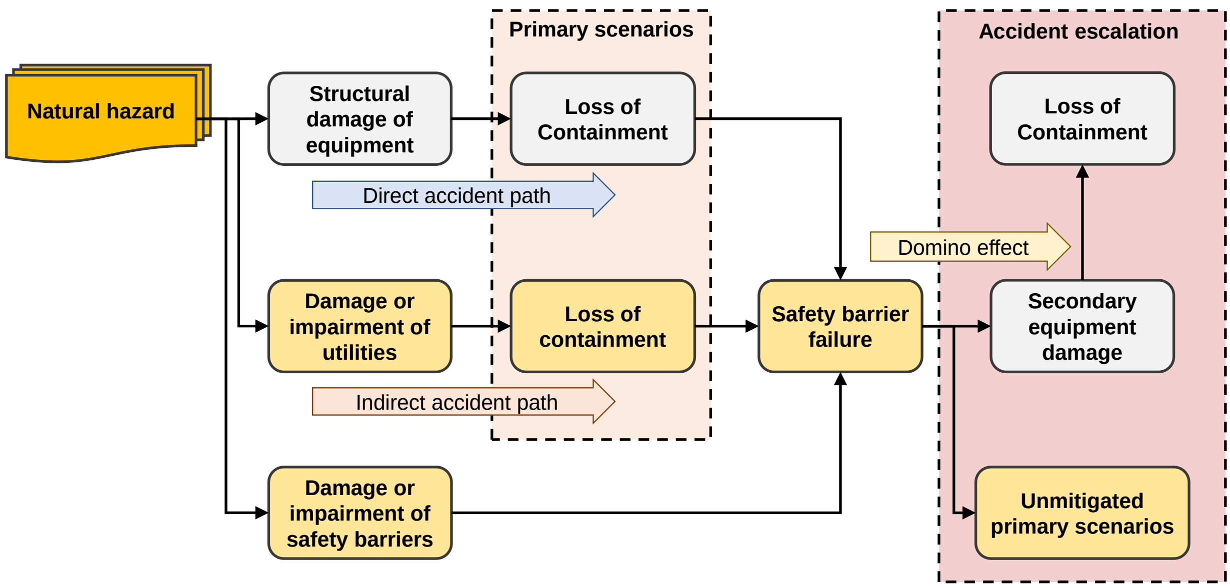


Figure 4. 4: Holistic framework proposed for the assessment of Natech events based on lessons learnt from past Natech events concerning the failure of auxiliary systems and safety barriers (Misuri and Cozzani, 2021b).

As evident in Figure 4. 4, the novel paradigm is characterized by the presence of two distinct paths leading to primary Natech scenarios. Besides the "direct accident path" considered in the current approaches (see Figure 4. 1), a second path involving the failure of utilities and auxiliary systems is introduced (the "indirect accident path" in Figure 4. 4). Clearly enough, the relevance of the latter depends on the specific features of the substances stored or handled on the site. The indirect path is the one that took place in both the Arkema and the Fukushima accidents.

A further novel element introduced in the extended paradigm is the explicit indication of the role of safety barriers. Actually, the impact of the natural event on safety systems is indicated as a possible cause of the failure or depleted performance of safety barriers. Although the failure of safety barriers may be possible also in conventional accidents, both the Arkema and the Fukushima accidents show how the specific conditions created by the natural event may be responsible for common cause failures or for specific damage modes, not credible in normal conditions.

The impairment or depleted performance of safety barriers has a twofold effect on possible accident escalation, as shown in Figure 4. 4. On the one hand, impaired or depleted safety barriers are less effective in mitigating the consequences of the primary technological scenarios, leading to a higher likelihood of unmitigated scenarios (e.g., impaired shutdown systems may lead to the release of higher quantities of hazardous substances, pool fires may spread outside the confined area limited by the catch basins). On the other hand, accident escalation may be caused by the failure or performance depletion of safety barriers aimed at preventing domino effect, leading to the damage of secondary units caused by the primary technological scenarios and to secondary technological scenarios (see Section 4.1 for the meaning of "secondary" scenarios). For instance, the performance of safety systems as fire deluges, fire monitors, blow-down systems, may be affected by the natural event, causing a higher probability of domino effect leading to escalation.

Therefore, the adoption of the framework shown in Figure 4. 4 is crucial to address a correct and comprehensive hazard identification procedure, leading to a complete description of possible Natech scenarios, as well as to support an extended approach to their quantitative assessment, introducing an improved approach for the risk management of cascading accidents triggered by natural hazards.
Clearly enough, the implementation of procedures for the qualitative and quantitative assessment of Natech events based on the framework shown in Figure 4. 4 requires the introduction of specific methods and tools, as discussed in the following.

4.3.2 *Extending Natech risk assessment: a roadmap for the implementation of the innovative paradigm*

Starting from the novel paradigm presented in Figure 4. 4, a roadmap for the comprehensive quantitative assessment of risk due to Natech scenarios is outlined in Figure 4. 5.

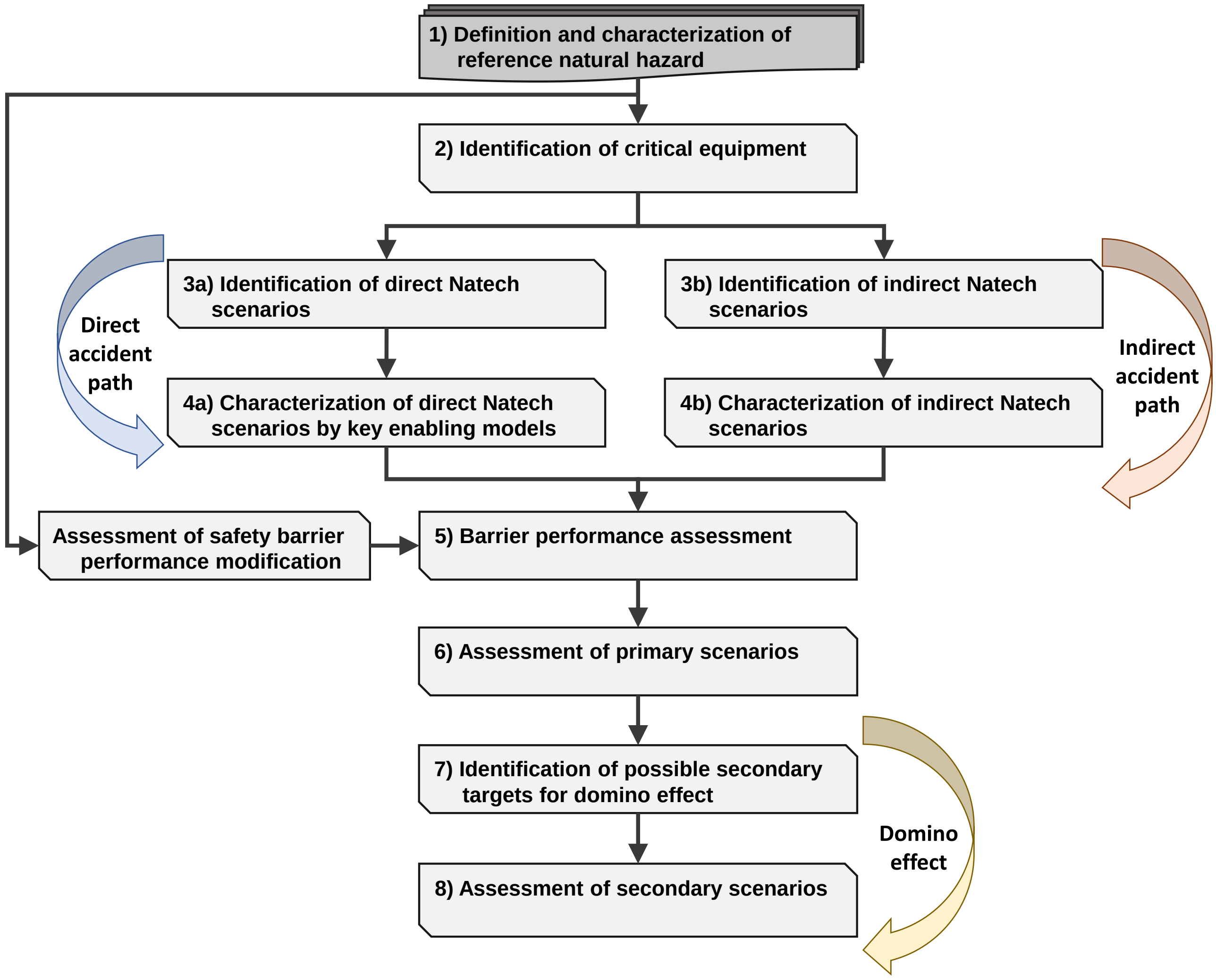


Figure 4. 5: Roadmap for the assessment of Natech scenarios based on the implementation of the framework shown in Figure 4. 4.

The direct accident path indicated in Figure 4. 5 is usually considered in the current approach to Natech quantitative assessment (Antonioni et al., 2015, 2009a; Cozzani et al., 2014). Thus, structured tools, as specific event trees (Cozzani et al., 2010), and key enabling models as fragility models for equipment failure (Kameshwar and Padgett, 2018a; Landucci et al., 2014, 2012; Salzano et al., 2003; Zuluaga Mayorga et al., 2019) are available to carry out these steps.

The indirect accident path is introduced to take into account the possible scenarios caused by the failure of utilities and of auxiliary systems. Although guidance documents providing specific recommendations are available (MAHB, 2020), to the knowledge of the authors no specific quantitative assessment method or structured approach is present in the literature to support the identification and assessment of these scenarios.

Figure 4. 5 also shows that specific steps addressing safety barrier performance assessment need to be introduced, both to support the consequence assessment of primary technological scenarios and to assess the possibility of escalation triggered by domino effect.

The specific methods and tools proposed to implement the roadmap shown in Figure 4. 5 will be discussed in the following subsections. First of all, a brief outline of the tools available for direct accident scenario definition will be provided, recalling the methodologies already discussed in Section 2.2. Then, a specific approach to support the identification of indirect accident scenarios in the chemical and process industry will be introduced. Lastly, the approach to safety barrier performance assessment will be also touched on for the sake of completeness. It should be noted that just a brief outline of the topic will be given herein since it will be extensively discussed in Chapters 5 and 6.

Finally, it is worth noting that the specific approaches that may be implemented for the characterization of the natural hazards in the framework of Natech risk assessment are not affected by the new paradigm introduced, thus the discussion on this point is out of the scope of this chapter. The reader might refer to the publications listed in Section 2.2 for further information on the available approaches to natural hazard characterization suitable for Natech risk assessment (e.g., see (Antonioni et al., 2015; Fabbrocino et al., 2005; Krausmann et al., 2017)).

Direct accident path

The direct accident path (steps 3a and 4a in Figure 4. 5) is aimed at modeling the conventional accident sequence considered in all current approaches to Natech quantitative assessment. In the direct path, possible Natech scenarios are caused by the structural damage of equipment items where hazardous substances are present, as a direct consequence of the natural hazards considered (Step 3a in Figure 4. 5). For instance, during earthquakes, atmospheric storage tanks might experience different damage states (e.g., elephant foot buckling) due to seismic load (Alessandri et al., 2018), leading to LOC generating technological scenarios. During floods, equipment might be damaged due to flotation or floodwater impact, leading to displacement or connection failure resulting in LOCs (Krausmann et al., 2011).

The characterization of direct scenarios requires the application of key enabling models capable to assess the likelihood of LOC of hazardous substances, as well as the magnitude of the expected substance release, due to equipment structural damage caused by the direct impact of the natural hazard (step 4a in Figure 4. 5). In general, simplified probabilistic models are applied. For instance, in the case of earthquakes, equipment fragility models have been applied in Natech assessment for the damage of atmospheric storage tanks (Salzano et al., 2003; Zuluaga Mayorga et al., 2019), of pressurized equipment (Moschonas et al., 2014; Salzano et al., 2009), of pipelines (Lanzano et al., 2015, 2014, 2013) and of other relevant elements of process installations as pumps and reactors (Salzano et al., 2009). In the case of floods, models to assess the damage probability of atmospheric storage tanks (Khakzad and Van Gelder, 2018, 2017; Landucci et al., 2012; Yang et al., 2020) and horizontal vessels (Landucci et al., 2014) are available. Models for fragility assessment of atmospheric storage tanks to storm surge have been also developed in recent research (Kameshwar and Padgett, 2018a, 2018b), as well as models for storage tank damage probability due to strong wind loads (Olivar et al., 2020; Zuluaga Mayorga et al., 2019). Specific models are also available to assess the probability of lightning capture and damage (Necci et al., 2014a, 2013). The use of these tools in the quantitative assessment of the "direct path" to Natech scenarios is exemplified in several previous studies (Alessandri et al., 2018; Antonioni et al., 2015; Campedel et al., 2008; Fabbrocino et al., 2005; Girgin and Krausmann, 2013).

Indirect accident path

The "indirect path" to Natech accidents addresses the identification of technological scenarios deriving from causes different from the direct structural damage of equipment items. As shown in the analysis of the Arkema and Fukushima accidents, the failure of utilities or of auxiliary supporting systems can lead to technological scenarios. It should be noted that redundant safety systems are usually applied to facilities exposed to major accident hazards, and process shutdown is expected immediately after (or even before, when an early warning is given) the impact of the natural hazard. Actually, process shutdown was successful in both the Arkema and Fukushima accidents.

However, depending on the specific properties of the substances present in the process, the availability of auxiliary supporting systems may be required to maintain the system in a safe condition after process shutdown.

Therefore, indirect paths to Natech accidents require at least one of the two following conditions to take place (although frequently both conditions are required to occur simultaneously):

i. the failure of an auxiliary system or of a utility system
ii. the presence of specific categories of hazardous substances, not stable in the conditions occurring after process shutdown

Tailoring the definition the IAEA proposed for nuclear plants (IAEA, 2020), in the broader context of technological installations, all the systems implemented in plants to guarantee the functioning of the main systems can be defined as auxiliary systems. Among these auxiliary systems, those which provide supplies to safety systems are also referred to as “supporting systems” in the nuclear sector (IAEA, 2020). In the chemical and process industry, auxiliary systems and supporting systems are usually defined as “utility systems” (CCPS, 2000; Mannan, 2005). In the following, a reference list of the utilities more widely used in the chemical and process industry and relevant to the present framework is provided:

- Electricity
- Cooling water
- Cooling fluids (e.g., brine, glycol-water solutions, refrigerants)
- Steam (energy vector for heat supply)
- Heating oil
- Nitrogen gas (for purging and blanketing)
- Instrument air (compressed air for pneumatic actuators)

Analysis of past accidents evidences that, among others, the failure of power supply (even in the presence of high redundancy and of emergency power supply systems) was reported in a high number of Natech events and near misses, in particular in the case of flooding (The French Bureau for Analysis of Industrial Risks and Pollutions (BARPI), 2018; The French Ministry of Ecology Sustainable Development, 2013). Failure of cooling systems, heating systems, instrument air, and nitrogen supply was also reported in several Natech accidents. Although the common-cause failure of these systems is usually taken into account in conventional safety assessment procedures (e.g., see (CCPS, 2001a, 2000)), natural events, on the one hand, increase the likelihood of such failures, while on the other hand may affect simultaneously the safety systems and may delay the operations needed to restart the utilities. Thus, the specific conditions occurring during Natech events need to be considered when assessing the availability of auxiliary and utility systems before, during, and after process shutdown.

Indirect accident paths are of particular concern when specific categories of substances, featuring critical properties, are stored or processed on the site. Substances that are stable only in specific conditions (e.g., below a threshold temperature, in the absence of oxygen or humidity) require the availability of one or more of the utility systems for their safe storage even after process shutdown, thus creating an inherent hazard during natural events. For instance, as evidenced by the Arkema accident, substances that may undergo decomposition can generate major accident scenarios in case of loss of cooling (U.S. CSB, 2018).
Table 4. 1 shows a list of specific categories of hazardous substances featuring critical properties which might lead to accident scenarios in the case of failure of utility systems.

Table 4. 1: Categories of hazardous substances showing critical properties in the framework of indirect Natech scenarios. Substance categories identified by a code starting by H are defined in the GHS classification system, while those with a code starting by EUH are defined in the CLP European classification system.

ID	Description	GHS (H) or CLP (EUH) Hazard statements and codes (European Commission, 2008; UN, 2019)	Examples of substances
1	Substances that in contact with water produce flammable gases (even self-ignitable)	In contact with water releases flammable gases which may ignite spontaneously (H260) In contact with water releases flammable gas (H261)	n-Butyllithium Diethylaluminum chloride Diisobuthylaluminum chloride Ethylalyminum sesquichloride Diisobutylaluminum hydride
2	Self-heating substances	Self-heating; may catch fire (H251) Self-heating in large quantities; may catch fire (H252)	Sodium methoxide Sodium ethoxide Potassium ethoxide
3	Pyrophoric substances (igniting spontaneously in contact with air)	Catches fire spontaneously if exposed to air (H250)	Aluminum alkyl n-Butyllithium Diethylaluminum chloride Diisobuthylaluminum chloride Ethylalyminum sesquichloride Diisobutylaluminum hydride
4	Substances that can explode or burn in case of heating	Heating may cause an explosion (H240) Heating may cause a fire or explosion (H241) Heating may cause a fire (H242) Risk of explosion if heated under confinement (EUH044)	p-Methane Hydroperoxide t-butyl peroxypivalate t-amyl peroxypivalate
5	Substances that can explode even in absence of air	May react explosively even in the absence of air (H230) May react explosively even in absence of air at elevated temperature and/or pressure (H231)	1,2-propadiene
6	Substances that can lead to violent reaction in contact with water	Reacts violently with water (EUH014)	n-Butyllithium Chlorosilane Diethylaluminum chloride Diisobuthylaluminum chloride Ethylalyminum sesquichloride Diisobutylaluminum hydride Potassium ethoxide
7	Substances that may produce explosive peroxides in contact with air or light.	May form explosive peroxides (EUH019)	Diethyl ether 1,4-dioxane
8	Substances that in contact with water/acids produce toxic gases	Contact with water liberates toxic gas (EUH029) Contact with acids liberates toxic gas (EUH031) Contact with acids liberates very toxic gas (EUH032)	Trichloroisocyanuric acid Sodium thiocyanate Aluminium phosphide Phosphorus pentasulphide Sodium azide

The list is aimed at supporting the identification of indirect Natech scenarios (step 3b in Figure 4. 5) and was derived from the classification introduced by the Global Harmonized System (GHS) Directive, which constitutes a shared framework accepted worldwide to define substance hazards (UN, 2019). In the GHS, the hazardous properties of the substances are expressed by hazard statements, associated with specific codes (e.g., the hazard statement "In contact with water releases flammable gas" is associated with the code "H260" (UN, 2019)).

Besides GHS classification, the European CLP regulation (European Commission, 2008) was also considered to identify further relevant categories of hazardous substances, not considered in the GHS. These substance categories are identified by codes starting by "EUH" (e.g., the hazard statement "Reacts violently with water" is associated with code "EUH014" in the CLP regulation (European Commission, 2008) and has does not find any direct correspondence in the GHS Directive (UN, 2019)).

As shown in Table 4. 1, eight groups of substances possibly leading to indirect Natech scenarios were identified. Substances belonging to categories 1, 6, and 8 might develop hazardous scenarios in case of contact with water (or ambient moisture). Substances belonging to categories 2, 4, 5 are heat sensitive, therefore may lead to hazardous scenarios in case temperature-controlled conditions cannot be guaranteed. Substances belonging to categories 3 and 7 may lead to an explosion in case of exposure to air (e.g., in case of the loss of blanketing inert gas supply system).

For the sake of clarity, the categories of hazardous substances identified in Table 4. 1 are rearranged in Table 4. 2 according to the three hazard factors more likely to trigger accidents in Natech events: temperature, contact with water, or contact with air.

Table 4. 2: Specific hazard factors that may generate technological scenarios in Natech events based on the features of the categories of sensitive hazardous substances identified in Table 4. 1.

ID	Description	**Hazard statements and relative coding** (European Commission, 2008; UN, 2019)	**Reference scenarios**
R01	Heat sensitive substances	Self-heating; may catch fire (H251) Self-heating in large quantities; may catch fire (H252)	Fire
		Heating may cause an explosion (H240) Heating may cause a fire or explosion (H241) Heating may cause a fire (H242) Risk of explosion if heated under confinement (EUH044)	Explosion/Fire
		May react explosively even in the absence of air (H230) May react explosively even in absence of air at elevated temperature and/or pressure (H231)	Explosion/Fire
R02	Substances reacting with water	In contact with water releases flammable gases which may ignite spontaneously (H260) In contact with water releases flammable gas (H261)	Flash Fire
		Reacts violently with water (EUH014)	Toxic dispersion/Fire
		Contact with water liberates toxic gas (EUH029) Contact with acids liberates toxic gas (EUH031) Contact with acids liberates very toxic gas (EUH032)	Toxic dispersion
R03	Substances reacting with air	Catches fire spontaneously if exposed to air (H250)	Fire
		May form explosive peroxides (EUH019)	Fire

The first group (R01) in Table 4. 2 includes all the substance categories whose hazard is related to heat sensitivity. The second group (R02) includes the substances which react in contact with water releasing energy, or forming hazardous gaseous compounds (flammable or toxic). Clearly enough, R02 substances have properties that are particularly critical in Natech events triggered by floods, since the presence of floodwater raises the probability that the substances come in contact with water or moisture. The third group (R03 in Table 4. 2) includes hazardous substances reacting spontaneously with air, either by oxidation processes (i.e., pyrophoric substances) or producing peroxides which may, in turn, decompose releasing high amounts of energy.

Whereas Table 4. 2 can provide valid support in the identification of indirect scenarios (Step 3b in Figure 4. 5), to date no specific tools are available in the literature for their characterization and quantitative assessment (Step 4b in Figure 4. 5). Moreover, unless extremely conservative assumptions are introduced, the quantitative assessment of several scenarios involving the decomposition or self-reaction of the categories of substances listed in Table 4. 2 needs kinetic data to assess the heat or the amount of decomposition products released, which are seldom available.

A recent guideline on Natech risk management developed by the Major Accident Hazard Bureau (MAHB) suggests that the likelihood of top events led by uncontrolled process upsets might be estimated by applying conventional reliability techniques considering that the performance of some system components can significantly change following natural hazards (MAHB, 2020). In perspective, specific event trees or innovative tools as Bayesian Networks have the potential to support such analysis but have not been applied to date.

Safety barriers and accident escalation

As shown in Figure 4. 4, the impairment of safety barriers during Natech events might play a relevant role in determining the escalation of consequences and the possible domino effects generated by primary technological scenarios thus a step dedicated to barrier performance assessment is required also in the roadmap (step 5 in Figure 4. 5). The broad definition of safety barriers is used to gather a variety of measures applied to prevent/mitigate accidents (Liu, 2020; Sklet, 2006). Common examples of safety barriers usually implemented in process plants are sprinklers, water deluge systems, catch basins, pressure relief valves, and so on (CCPS, 2001b; De Dianous and Fiévez, 2006; PSA, 2013).

Clearly enough, the impact of natural hazards on these systems is inherently connected to their features (e.g., system architecture, dependencies) and to the characteristics of the reference natural events themselves. Thus, including performance modification of safety systems in Natech risk assessment is a complex task. As it will be extensively presented in Chapter 5, current research is addressing the quantification of barrier performance reduction during natural hazards employing performance modification factors (Misuri et al., 2020b). These values can be used for the twofold purpose of assessing the likelihood and severity of primary technological scenarios (step 6 in Figure 4. 5) and of escalation through domino effect (step 8 in Figure 4. 5). Indeed, on the one hand, the depletion of safety barriers might lead to more severe and/or more probable severe outcomes (e.g., failure of secondary containments that can lead to unconfined spreading of spilled liquids or failure of foam systems for fire extinguishment) which should be considered in the assessment of primary Natech scenarios (step 6 in Figure 4. 5). A methodology to address this aspect will be described in Section 6.1.

On the other hand, the likelihood of domino effects from primary scenarios may increase and needs to be assessed considering the specific role and the possible depleted performance of safety barriers. As in well-established domino QRA methodologies, a dedicated step relying on threshold-based approaches might be performed to assess the specific plausibility of domino effect and to identify possible targets (step 7 in Figure 4. 5) (Alileche et al., 2015; Cozzani et al., 2006b). After the target identification, safety barrier depletion (evaluated in step 5 of Figure 4. 5) should be considered in assessing escalation likelihood. The importance of this step has been demonstrated by Misuri et al. (2021a) that reported an increase of unmitigated domino scenario frequencies well above cut-off values normally considered in domino risk assessment when considering barrier depletion in Natech events, as will be discussed in Section 5.3.

Only few publications available in the literature presented structured approaches to perform the quantitative assessment of domino effect from primary technological scenarios in Natech accidents, applicable to carry out Steps 7 and 8 in Figure 4. 5, and reliable methodologies to accomplish this task were mostly lacking. Just recently a few works proposed the application of advanced tools as Bayesian networks to model domino effect in specific Natech scenarios (e.g., see (Naderpour and Khakzad, 2018; Yang et al., 2018)). As explained in Chapter 3, given this gap, in the context of this Ph.D. project a general QRA-based procedure has been developed to accomplish Steps 7 and 8 in Figure 4. 5. This will be the focus of Section 6.2, where the specific case of domino effects generated in Natech events triggered by lightning strikes will be used as an example of effective application of such methodology (Misuri et al., 2020a). Starting from that general procedure, a comprehensive methodology merging a multi-level approach to the assessment of barrier performance depletion and the quantitative assessment of escalation scenarios generated by primary Natech events was proposed by Misuri et al. (2021b). This advancement will be the core of Section 6.3.

4.4 Discussion

The new framework presented in Figure 4 and the roadmap for its implementation shown in Figure 4. 5 provide a breakthrough towards a more consistent and holistic Natech risk assessment. It is aimed at supporting the identification and characterization of specific scenarios as those experienced in the Arkema and Fukushima accidents, not considered in the current approaches to Natech risk assessment. Thus, their implementation is pivotal to foster the preparedness of industry towards

Natech accidents. This is crucial to support the development of proper climate change adaptation strategies for industrial facilities where hazardous substances are handled or stored, also considering the expected increase in the frequency and intensity of climate-related natural events.

The new framework points the attention of company managers and regulators to indirect scenarios, explicitly addressing the cascading and systemic nature of Natech accidents. Indeed, the proposed framework calls for the introduction of a systemic approach looking at the impact of natural hazards not only on equipment storing hazardous materials but also on auxiliary systems, utilities, and safety barriers that might be concurrently affected.

Nevertheless, the roadmap shown in Figure 4. 5 still needs to bridge some gaps in the methods and tools needed for its implementation, in particular for the quantitative risk assessment of indirect Natech scenarios. Indeed, whereas some recent Natech risk management guidelines suggest that the identification of the hazards related to the failure of utility systems or to process upsets might be treated with the same methods applied in the framework for conventional industrial risks, particular attention should be paid to possible depletion of subsystems due to natural hazards which might influence the reliability of auxiliary and utility systems (MAHB, 2020). To the knowledge of the authors, specific vulnerability models for auxiliary system failure during natural hazards are not available to date, and their development still requires a specific research effort.

A further element that should deserve more attention in future research is the consequence assessment of Natech-specific scenarios (step 6 in Figure 4. 5), in particular when considering the effect of the degradation of the safety systems in place. Indeed, in the current practice conventional consequence assessment approaches are directly tailored to the case of Natech risk assessment (Alessandri et al., 2018; Antonioni et al., 2015; Girgin and Krausmann, 2013). However, some specific scenarios might require the development of ad-hoc models. For instance, in the case of floods, the consequences of a release might be highly influenced by floatation, dispersion, and dissolution in floodwater as well as by the possible overtopping of containment dikes and catch basins.

A further gap concerns the performance of procedural barriers (e.g., emergency intervention) during Natech events. Indeed, methodologies to assess their performance modification due to natural hazards are still not available in the literature, while past accidents suggest that complex scenarios might even drive operators and plant personnel to panic, creating confusion and reducing the effectiveness of emergency management strategies (Steinberg and Cruz, 2004). Recent studies proposed to tailor methodologies developed in the context of risk assessment for operations carried out in a harsh environment, obtaining worst-case reference values for time for emergency intervention (Misuri et al., 2021b). Nevertheless, research on models for procedural barriers and emergency intervention performance in the specific context of Natech accidents is still needed, in particular, to provide a more robust assessment of the possibility of accident escalation.

4.5 Conclusions

In this chapter, a new framework for Natech risk assessment and management is outlined, starting from the analysis of lessons learnt in the two milestone accidents that occurred at the Arkema site (2017) and in the Fukushima Dai-ichi NPS (2011). The proposed framework recognizes the systemic and cascading nature of Natech events, addressing the inclusion of specific scenarios deriving from the failure of auxiliary and utility systems which played an important role in past accidents. Indeed, along with primary scenarios triggered by the damage of equipment storing hazardous materials, the possibility of indirect accidents arising from the unavailability of auxiliary systems and plant utilities needs to be considered in the management of Natech risk. Specific categories of hazardous substances showing critical properties towards the development of indirect Natech accidents were identified, based on GHS and CLP classification systems. Moreover, within the novel paradigm, considerable importance has been associated with the role of safety barriers both in the escalation of the consequences of the primary technological scenario and in influencing the possibility of domino effect. The framework proposed represents a further step towards a comprehensive assessment of Natech scenarios, supporting a holistic approach to their identification and assessment. The roadmap provided shows the available methods and tools, as well as the knowledge gaps which need to be filled for the successful application of the new framework, in the perspective of a holistic quantitative assessment and effective management of the risk generated by Natech scenarios.

Chapter 5. Assessment of the performance of safety barriers in Natech events

This chapter will be dedicated to the issue of addressing the quantification of safety barrier performance during Natech events. As pointed out by analyzing the available literature, the established methodologies for Natech risk assessment do not actually include the role of safety barriers. Moreover, the methodologies available for the quantification of barrier performance do not explicitly consider the effects of natural events impacting on the barrier before or during the technological accidents that these systems are intended to prevent or mitigate. Thus, including barriers in Natech risk assessment requires the preliminary availability of an approach to the evaluation of the expected extent of their degradation during natural hazards. Starting from a literature review on the topic of safety barriers, to which Section 5.1 will be dedicated, an approach to the assessment of safety barrier performance during Natech events will be described in detail in Section 5.2 (Misuri et al., 2020b). In this section, qualitative lessons on the systems most likely to be impacted during earthquakes and floods will be provided along with distributions of failure probabilities directly elicited from expert judgment. Performance modification factors were retrieved from such distributions, as indicators of the contribution to failure probability of barriers during Natech events. In Section 5.3, these factors are implemented in a complete frequency assessment procedure aimed at addressing the quantification of the domino effect likelihood following primary Natech scenarios, showing that barrier degradation has an important influence on the likelihood of accident escalation (Misuri et al., 2021b).

5.1 Safety barriers in chemical and process industries

In this section, the main concepts and definitions about safety barriers adopted in the chemical and process industries will be given. Then, the most widely employed classifications will be described, and relevant methodologies to assess safety barrier performance to enable their integration in risk assessment will be commented.

5.1.1 Concepts and definitions

There is a considerable amount of technical literature dedicated to barriers and barrier management (Hollnagel, 2004; Liu, 2020; Reason, 1997; Sklet, 2006) spanning a variety of fields from nuclear industries to aerospace and healthcare. Within the process industry, the concept of safety barriers is used referring to measures to protect vulnerable assets (e.g., people, environment, and so on) against harm possibly posed by failures or dangerous deviations of systems (Rausand, 2011).

Several definitions of safety barriers have been proposed, but probably the more general one can be that of physical and non-physical means planned to prevent, mitigate or control undesired events or accidents (Sklet, 2006).

More specific interpretations are also available. For instance, according to Norwegian Petroleum Safety Authority, in the oil & gas sector the safety barriers are defined as "*systems of technical, operational and organizational elements, which are intended individually or collectively to reduce the possibility for a specific error, hazard or accident to occur, or which limit its harm/disadvantages*" (PSA, 2013).

Recently, the United Kingdom Offshore Safety Directive Regulator coined the definition of Safety and Environmental-Critical Elements (SECEs) to indicate "*parts of an installation and such of its plants […], or any part of those – the failure of which could cause or contribute substantially to a major accident; or a purpose of which is to prevent, or limit the effect of, a major accident*" (HSE, 2015).

Similarly, within the ARAMIS framework, safety barriers are defined as technical and organizational solutions provided to directly serve safety functions, that is, to achieve technical or organizational actions intended to prevent, avoid or control the occurrence of hazardous events, or to mitigate their consequences (Andersen et al., 2004; De Dianous and Fiévez, 2006; Salvi and Debray, 2006). The concept of barrier function (i.e., the barrier design purpose) is shared also by several other literature sources (e.g., see (Svenson, 1991)), and it is necessary to distinguish without ambiguity between the functions and how they are practically accomplished through the implementation of barrier systems.

Despite these definitions pertain to chemical and process industries, they are still general and were applied in adjacent technical fields. For instance, in (Casson Moreno et al., 2018) these conceptualizations are applied for the identification of emerging hazards linked to biogas production.

5.1.2 Safety barrier characterization

Whereas the definitions given in the previous section might shed some light on the main concepts, these still remain quite theoretical, possibly embracing a wide set of heterogeneous measures. It is thus clear that characterizing and classifying safety barriers is particularly important. Given the definition of barriers and the number of sectors adopting these concepts, many different classification criteria are suggested in the literature (Reason, 1997, 1990; Sklet, 2006). Some of these classifications might be hardly applicable within the context of cascading technological accidents prevention and mitigation, thus only the ones relevant for the scope of this thesis will be presented in the following.

One of the earliest classification criteria proposed in the literature was based on the type of functions of the barriers and moves from the defense-in-depth philosophy (Reason, 1997). Following this rationale, safety barriers (i.e., defined as “defenses” by Reason) can be classified according to whether they are designed:

- to create understanding and awareness of the local hazards
- to give clear guidance on how to operate safely
- to provide alarms and warnings when danger is imminent
- to restore the system to a safe in an off-normal situation
- to interpose safety barriers between the hazards and potential losses
- to contain and eliminate the hazards (in case it escapes a given barrier)
- to provide the means of escape and rescue should hazard containment fail

As can be noticed, this classification is still rather general and can be tailored to various organizations, regardless of their operating hazards.

According to another line of research, barrier systems can be categorized into four main groups (Hollnagel, 2008, 2004):

- Physical and material barrier systems, that prevent events or mitigate their effects by interrupting the transportation of mass, energy, or information (e.g., walls, fences, fire curtains);
- Functional barrier systems, which are used to create pre-conditions to be met before events can take place, or actions can be performed (e.g., passwords, interlocks);
- Symbolic barrier systems, that need to be interpreted by someone since they work indirectly through their meaning (e.g., signs, signals, warnings, alarms); and
- Incorporeal barrier systems, that are not present in the situation where they are applied and in industrial facilities can be interpreted as organizational measures as for instance rules, standards, restrictions.

Another more intuitive rationale to classify safety barriers might be based on whether they are aimed at reducing the frequency of hazardous events or lessening their consequences (Rausand, 2011). The former ones can be defined as proactive barriers and are installed to prevent events or reduce their probability (i.e., might be defined also frequency-reducing barriers), while the latter ones are called reactive barriers and are installed to mitigate event outcomes (i.e., might be defined also consequence-reducing barriers).

Differently, one of the classifications most widely applied in the literature is based on barrier working principle, leading to three main barrier categories (CCPS, 2001b; Landucci et al., 2015):

- *Passive barriers*, that is, technical systems not requiring external activation and so featuring a permanently available protective action;

- *Active barriers*, that is, complex technical systems that can exert their safety function only by an activation, whether by operators or by automatic systems triggered by sensors and detectors; and
- *Procedural barriers*, which are in fact operational barriers whose action is based on the activation of specific procedures by plant operators or emergency teams.

This classification shares several similarities with that proposed within the ARAMIS project, although therein also symbolic barriers are considered (Andersen et al., 2004; De Dianous and Fiévez, 2006; Delvosalle et al., 2006).

According to the classification based on working principles, it is clear that all the systems as relief devices, containment measures, catch basins, and fireproofing are generally classified as passive barriers. On the contrary, fire protection systems such as sprinklers and water deluge systems (WDS), being complex systems made up of subsystems for detection, signal processing, and actuation (Hauptmanns et al., 2008; NFPA, 2009, 2003), are clear examples of active barriers. Finally, contingency plans, fire brigade interventions, emergency evacuation are all examples of procedural barriers (Mannan, 2005). It is worth noting that this classification based on working principles has been applied in previous studies on cascading technological scenarios (Landucci et al., 2016, 2015). Hence, it seems the most appropriate in the context of Natech accidents and will be applied in the following sections.

5.1.3 Integration of safety barriers in risk assessment

After having introduced some relevant approaches to classification, it is worth outlining some of the methodologies available to integrate safety barriers in risk assessment. Clearly, these methods require the preliminary evaluation of barrier performance and might require taking into consideration several barrier properties that can determine their quality. For instance, according to the PSA, the definition of the performance requirements for technical barriers should be based on several factors as their reliability, availability, integrity, robustness, capacity, effectiveness, and load resistance (PSA, 2013). These criteria are similar to the ones suggested in other relevant publications (e.g., conditions as efficiency, robustness, resource needs, and availability are specific among the most relevant factors in (Hollnagel, 2008, 2004)).

Analyzing such factors might be too complex in the context of risk assessment of technological scenarios, and a more concise approach to performance quantification is required. In the following, three relevant (yet simplified) approaches to implement the performance of safety barriers in structured risk assessment processes will be briefly presented, in order to give an idea of how systems for accidents prevention and mitigation can be effectively included in process safety management.

The first approach that is worth to be reported is the LOPA methodology (CCPS, 2001b; Dowell et al., 2002; Summers, 2003). This methodology can be considered a semi-quantitative process risk assessment tool intended to be applied following a hazard identification approach (Dowell et al., 2002). The LOPA framework is based on the concept of Independent Protection Layers (IPLs) (CCPS, 2001b; Dowell et al., 2002; Summers, 2003). IPLs can be defined as those barriers that are effective in preventing a scenario from proceeding to its undesired consequence, being also independent of the initiating event or of the action of any other devices, systems, or safeguards associated with that scenario (CCPS, 2001b).

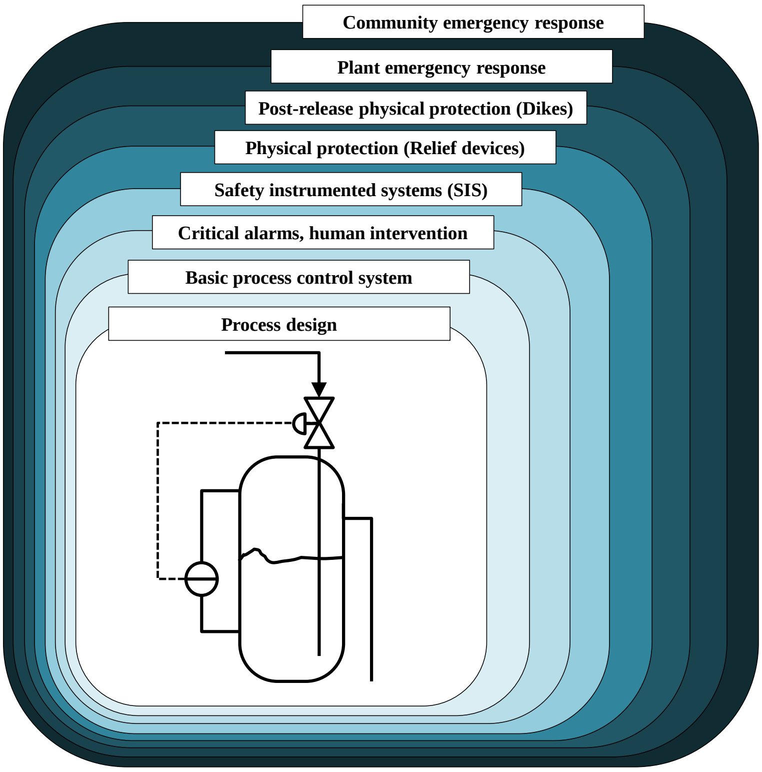


Figure 5.1. 1: The concept of Layers of Protection (CCPS, 2001b).

Safety barriers commonly employed in chemical and process industries can be credited as IPLs, although this requires the fulfilment of several criteria as specificity, independence from other IPLs (to exclude common cause failures), dependability, and auditability (Summers, 2003). As can be inferred from Figure 5.1. 1, according to the IPLs rationale, safety barriers can thus be seen as concentric layers, and a hazardous outcome is deemed to occur if and only if an initiating event evolves with the independent failure of each IPL. This concept is a clear reminder of the defense-in-depth concept widely employed in nuclear safety (Fleming and Silady, 2002; IAEA, 1996).

Reference values are usually used in LOPA for initiating event frequency, consequence severity, and the failure likelihood of the IPLs to approximate the risk of a scenario (CCPS, 2001b). The likelihood of failure for each IPLs is expressed through a Probability of Failure on Demand (*PFD*), that is, the likelihood that a barrier will not be able to perform the safety function when required. The frequency of the identified consequences is thus estimated as the frequency of the selected initiating event times the *PFD*s of each IPL is required to fail to lead to that specific outcome, as can be seen in Figure 5.1. 2. It is worth noting that LOPA is limited to evaluating a single pair initiating event – consequence, thus, usually the path leading to the worst-case scenario is selected (i.e., the lowermost branch of the event tree represented in Figure 5.1. 2) (CCPS, 2001b).

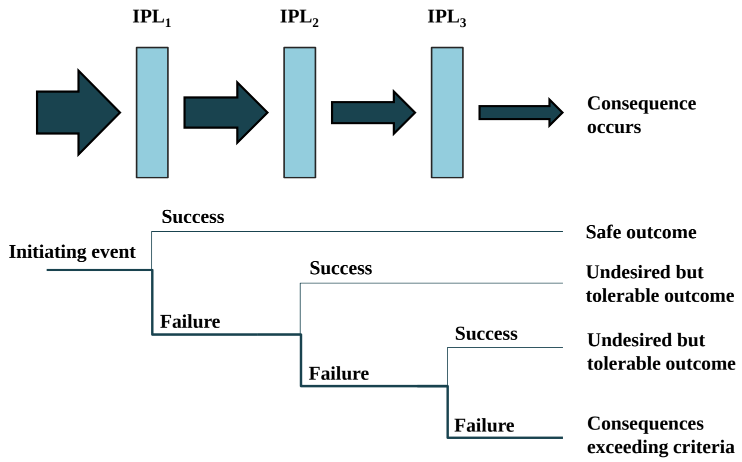


Figure 5.1. 2: Independent Protection Layers (IPLs) used in the LOPA can be interpreted considering barriers in an event tree starting from an initiating event to the identified outcomes. The worst-case scenario is usually selected (lowermost branch). Adapted from (CCPS, 2001b).

The second approach that is worth discussing is the methodology developed during ARAMIS project for the control of major accident hazard in the European Union (Andersen et al., 2004; De Dianous and Fiévez, 2006; Delvosalle et al., 2006; Salvi and Debray, 2006). The ARAMIS methodology is composed of two separate and consecutive steps, the MIMAH (Methodology for the Identification of Major Accident Hazards) and the MIRAS (Methodology for the Identification of Reference Accident Scenarios). The MIMAH is aimed at assessing the maximum hazardous potential for a chemical installation and takes the advantage of a bow-tie approach to identify critical events associated with each piece of equipment, their causes, and their consequences, assuming that no safety barriers are implemented. The outputs of this step are the identified "Major Accident Hazards" and the set of bow-ties for each analyzed equipment. The MIRAS can be then applied to include safety barriers into the bow-tie diagrams of each critical event, both on the fault-tree side (i.e., assess how safety barriers influence the progression from basic causes toward each critical event) and on the event-tree side (i.e., assess how safety barriers influence the progression from the critical event to the final events), and obtain the accident scenarios representing the real hazardous potential of the installation (Andersen et al., 2004). The advantages compared with the LOPA are manifold. Firstly, technical guidelines to support the development of bow-ties are available, enabling the application of the method to a variety of cases (e.g., see (CCPS, 2008; Delvosalle et al., 2006)). Secondly, the analysis based on bow-tie diagrams enables visualization of the paths leading to accident development and the relative position of safety barriers (see Figure 5.1. 3) and the quantification of the likelihood of final events according to both to the frequency of the identified causes, and to the performance of the implemented safeguards.

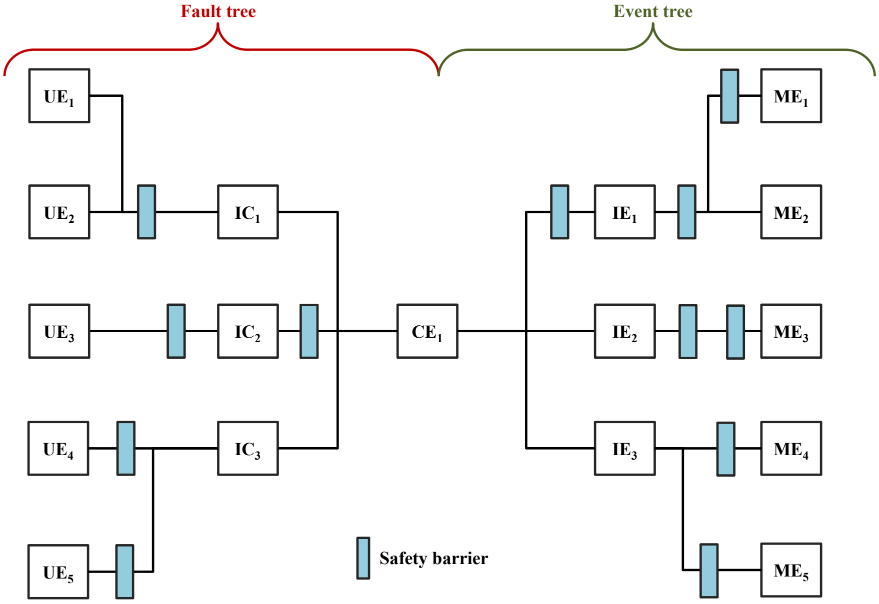


Figure 5.1. 3: Bow-tie diagram with safety barriers (in blue). UE=Undesirable events, IC=Intermediate causes, CE=Critical event, IE=Intermediate events, ME=Major events. The event terminology adopted in the figure is simplified compared to the ARAMIS methodology (i.e., ICs are further specified as detailed direct causes, direct causes, and necessary and sufficient conditions, and IEs comprise secondary critical events, tertiary critical events, and dangerous phenomena)(Andersen et al., 2004)

Clearly, the evaluation of barrier performance is required also in this case to provide data for the frequency quantification of the accident scenarios. Within the MIRAS, the performance of the safety barrier is assessed using three parameters, a Level of Confidence (*LC*), an effectiveness value, and a response time. The *LC* is an expression of the availability of the barrier and is directly linked to the *PFD* (Andersen et al., 2004). The *LC* is similar to the concept of Safety Integrity Level (*SIL*) defined in the IEC 61508 and IEC 61511 to express the performance requirements of Safety Instrumented Systems (SIS) (IEC, 2003, 1998), although within the ARAMIS its application has been extended to a broader set of safety barriers. The effectiveness and the response time are herein defined respectively as the ability of a barrier to performing a safety function, and the time required for the completion of its completion(Andersen et al., 2004). Indications on a general methodology to assess the LC have been defined in the ARAMIS deliverables, while the effectiveness and the response time of barriers cannot be calculated by a generic approach (Andersen et al., 2004).

The last approach that will be presented herein has been specifically developed to perform the QRA of mitigated domino effects in technological accidents. As already explained in Section 2.2.3, domino effects and Natech accidents are two typologies of cascading technological scenarios sharing several similarities from a risk assessment standpoint, thus the methodology presented hereafter is of particular relevance for the rest of this thesis. The flowchart of the methodology is shown in Figure 5.1. 4 (Landucci et al., 2017b).

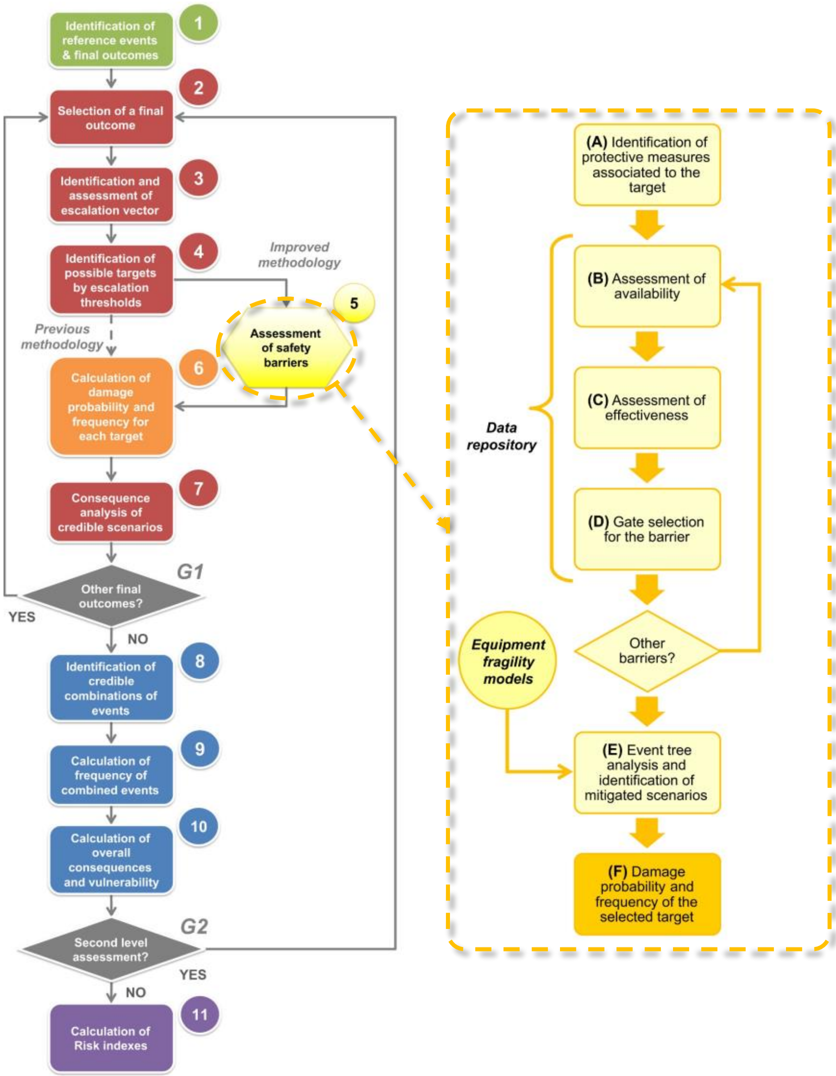


Figure 5.1. 4: Methodology for domino effect QRA including a specific step for safety barrier performance assessment (Step 5, details in the right-hand part of the flowchart). Adapted from (Landucci et al., 2017b).

As can be seen from the figure, the overall domino QRA methodology is similar to the original approach conceptualized in earlier works (Cozzani et al., 2014, 2005), although it leverages an additional key step to accomplish the quantification of safety barrier performance and includes the results in the probabilistic assessment of domino scenarios. The details of this step are shown on the right-hand side of Figure 5.1. 4. The barrier performance metrics adopted herein is based on the concepts of availability (expressed through the *PFD*, as in the LOPA approach) and effectiveness (η), defined in this context as the probability that the barrier, once successfully activated, will be able to prevent the escalation (Landucci et al., 2015). To include the two-parameter performance metrics into the frequency assessment of domino scenarios and to identify the secondary scenarios following the failure/success in the escalation prevention of the barriers involved, a specific event tree analysis (ETA) has been also developed (Landucci et al., 2016, 2015). This approach is capable of modeling the case of barriers that might be effective in preventing the escalation (i.e., once the barrier is activated or is available, no escalation will be possible) as well as the case of barriers only able to mitigate escalation scenarios (i.e., reducing the likelihood of "unmitigated" domino scenarios, but generating one or more "mitigated" scenarios). The ETA is required in Step 6 of the procedure shown in Figure 5.1. 4 and is based on ad-hoc gates associated to logical operators, as shown in Figure 5.1. 5 (Landucci et al., 2015).

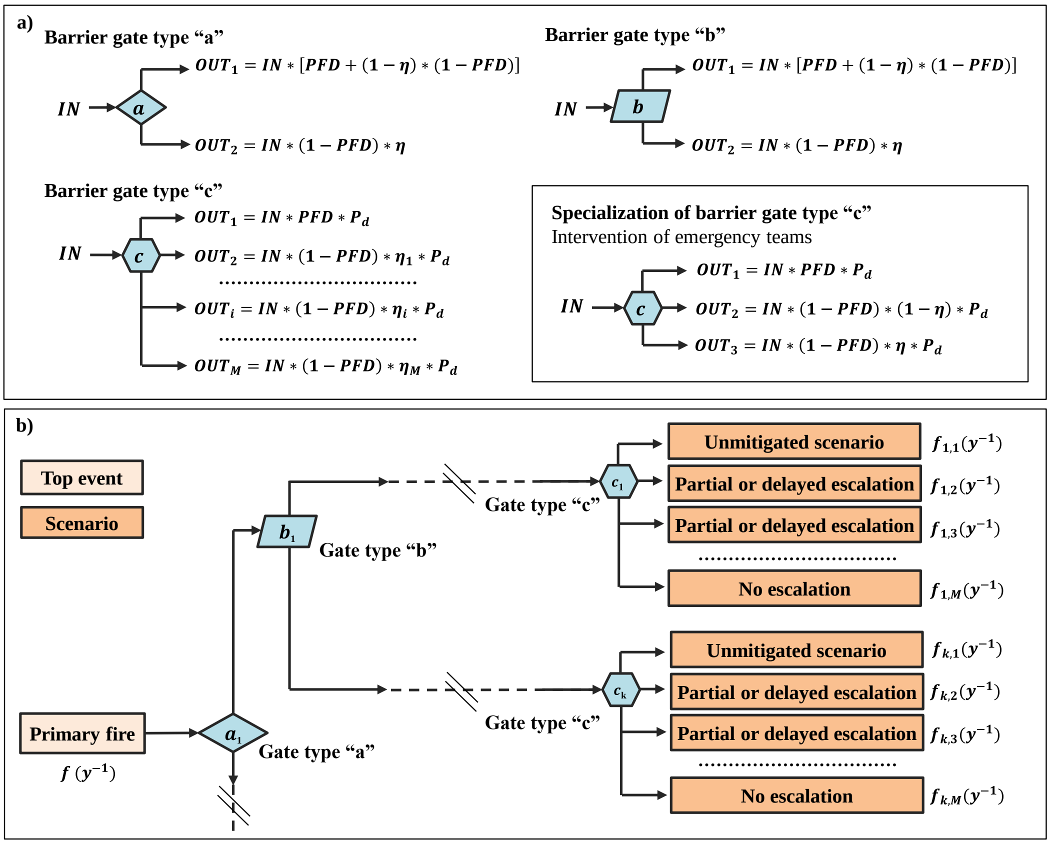


Figure 5.1. 5: a) Definition of barrier gate types and operators. b) Example of event tree used for the probabilistic assessment of safety barriers (Step 6 in Figure 5.1. 4); PFD: probability of failure on demand; η: effectiveness; f: frequency or annual probability (y^{-1}); P_d: equipment failure probability; M: number of possible final scenarios for type "c" gate; Adapted from (Landucci et al., 2015).

The specific three barrier operators introduced, shown in Figure 5.1. 5, can be described as follows:

- *Simple composite probability operator* (barrier gate type "a"): availability, expressed through the *PFD*, is combined with a single probability value expressing barrier effectiveness, that is, the probability of barrier success in the prevention of the escalation;

- *Composite probability distribution operator* (barrier gate type "b"): availability, expressed through the PFD, is combined with a probability distribution expressing barrier effectiveness (the probability of barrier success in the prevention of escalation), thus obtaining a composite probability of barrier failure on demand. It is possible to use an integrated effectiveness value to obtain the quantification rule reported in Figure 5.1. 5;

- *Discrete probability distribution operator* (barrier gate type "c"): depending on barrier effectiveness η, three or more events may originate from the gate describing barrier performance: barrier success (no escalation), barrier failure (unmitigated escalation), and one or more partially mitigated scenarios (partial or delayed escalation). To quantify the gate "c" output, the estimation of equipment damage probability (P_d) is needed: specific methodologies are available for this purpose (e.g., see (Landucci et al., 2009)).

Additionally, the modified ETA enables the assessment of mitigated escalation alternatives to the unmitigated scenario that is expected to take place considering the absence of, or the complete failure of, the safety barrier set (see Figure 5.1. 5). Clearly, the introduction of a set of mitigated scenarios demanded a substantial modification of the QRA procedure compared to the baseline approach (Antonioni et al., 2009b; Cozzani et al., 2014, 2005). Indeed, in earlier studies, only the possibility of unmitigated secondary scenarios was accounted for in the evaluation of overall domino scenarios due to the multiple simultaneous secondary events (Cozzani et al., 2006a, 2005; Khakzad et al., 2013). The most appropriate choice for modeling mitigated scenarios depends on several factors such as target type and the implemented emergency strategy, and is discussed in detail elsewhere (Landucci et al., 2017b).

5.2 Expert survey addressing safety barrier performances during intense natural events

An approach to the characterization of safety barrier depletion and to the quantification of the related performance modification due to the impact of intense natural events will be described in this section. The approach leverages the results elicited from an expert survey, and was applied within the present study to assess the effects of floods and earthquakes on safety barriers.

5.2.1 Overview of the methodology

In order to investigate the performance of safety barriers in Natech scenarios by expert elicitation, a specifically developed approach was applied. The steps of the study carried out are summarized in Figure 5.2. 1. Each step is discussed in the following.

In step 1, the boundaries of the study were set to define the detail of the activity and to make affordable the elicitation process. In particular, it was decided to limit the study to the impact of earthquakes and floods. These were selected since they are the natural events that more frequently triggered severe Natech accidents (Krausmann et al., 2017). In perspective, the approach developed may be applied to assess barrier performance in the case of other types of natural events (e.g., tsunamis, lightning, tornados). However, in order to ensure the focus of the elicited group of experts and to limit the complexity of the survey, the decision was taken to limit this study to the analysis of these two significant categories of events.

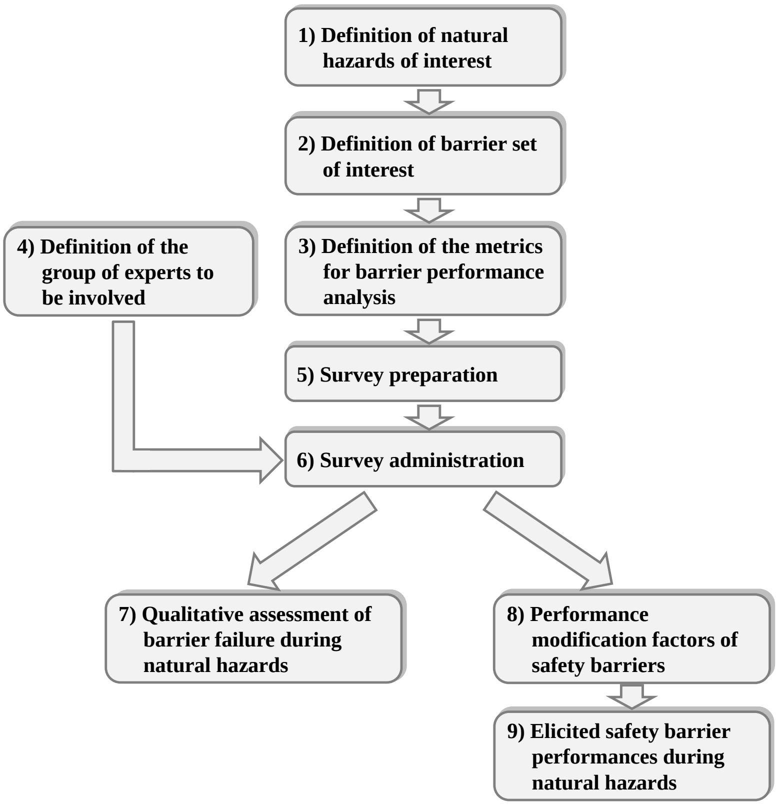


Figure 5.2. 1: Flowchart of the approach based on expert elicitation for barrier performance assessment in Natech events.

The second starting point of the study was the definition of a set of safety barriers to be analyzed (step 2 in Figure 5.2. 1). This is needed both to limit the extension of the study and to allow the preparation of a reference scheme and a description of the function of each safety barrier considered, to support the expert elicitation. Only technical active and passive safety barriers were considered: the choice to exclude organizational and procedural barriers is motivated both by the need to limit the complexity of the study and to the high site-specificity of their performances (e.g., presence of internal emergency teams, distance of the plant from closest firefighter station, presence of specific plans for natural disaster), that undermines the general validity of the performance parameters obtained. On the contrary, baseline values for active and passive technical barriers are mostly related to system architecture, thus are linked to the inherent structure of the safety system.

The definition of the set of barriers to consider was based on a preliminary evaluation of equipment items and substances most frequently involved in earthquake-triggered and flood-triggered accidents based on past accident events. Indeed, it has been highlighted that atmospheric tanks storing an elevated inventory of flammable liquids (e.g., petroleum products) are particularly vulnerable during earthquakes and floods (Campedel, 2008; Cozzani et al., 2010), and escalation due to fire may be critical during such Natech incidents, as confirmed by relevant case histories (see Section 2.1). These findings constituted the drivers for the selection of the set of safety barriers considered. Indeed, since one of the main criticalities of Natech events triggered by floods and earthquakes is the high possibility of accident escalation through domino effect, the investigated barrier set is mainly composed of escalation prevention systems. Moreover, fire protection systems constitute a significant part of the set also because these systems are required in accepted standards on fire protection of petroleum storages (e.g., see (OISD, 2007)).

It is worth specifying that the analyzed set of barriers is not aimed at providing an exhaustive and complete list of possible technological solutions for escalation prevention, rather it is composed of barriers that, based on past accident analysis, may be prone to fail following the impact of natural events. For example, PSVs, despite being the most common passive safety barrier to prevent vessel overpressure, have not been included in the analysis since, due to their features, their failure was never reported in available data on Natech scenarios.

The final set of selected safety barriers considered in the analysis is composed of the 16 items listed in Table 5.2. 1, which also reports a short description and an identification code (i.e., *SB.k*, with k=1,…, 16).

Table 5.2. 1: Safety barriers considered in the survey prepared for the expert elicitation. Barrier ID is used in the following figures of Section 5.2. The classification adopted is based on barrier working principle, as described in Section 5.1.

Safety barrier	ID	Classification	Short description
Inert-gas blanketing system	SB.1	Active	System for inert gas delivery to storage tanks to prevent the possible formation of flammable atmospheres.
Automatic rim-seal fire extinguishers	SB.2	Active	Automatic foam delivery system for prompt extinguishment of rim-seal fires developing in the roof area of atmospheric storage tanks.
Fixed / Semi-fixed foam systems	SB.3	Active	Systems for tank fire extinguishment by means of foam/water delivery.
WDS / Water Curtains / Sprinklers	SB.4	Active	Systems for water delivery during a fire, either for flame extinguishment or critical asset protection (e.g., LPG vessels).
Hydrants	SB.5	Active	Water sources for fire brigades located in multiple areas of the plant.
Fire activated valves	SB.6	Active	Valves activating in case of fire nearby.
Fire and gas detectors	SB.7	Active	Field sensors for detection of flames and gases.
SDVs	SB.8	Active	Isolation valves activating during emergency situations.
BDVs	SB.9	Active	Depressurization valves activating during emergency situations.
Fire walls	SB.10	Passive	Physical barriers for fire protection.
Blast walls	SB.11	Passive	Physical barriers for blast protection.
Fireproofing	SB.12	Passive	Coating materials for fire protection.
Bunds / Catch basins	SB.13	Passive	Physical systems for liquid retaining in case of a spill.
Emergency Blowdown line to flare stack	SB.14	Passive	Line for flaring employed during emergencies.
Mounding tanks	SB.15	Passive	Locating vessels into gravel/ground mounds for fire protection.
Burying tanks	SB.16	Passive	Locating vessels underground for fire protection.

Items *SB.1-SB.9* are active barriers, while *SB.10-SB.16* are passive barriers. It is worth noting that the Emergency Blow-Down (EBD) line was considered passive since it is constituted of pipework (and possibly a KO drum) which is always in place, not needing an activation.

5.2.2 Metrics for barrier performance assessment

The failure modes highlighted by past accident analysis constitute the basis for the definition of the metric for performance parameter adjustment (step 3 in Figure 5.2. 1).

A performance modification factor $\phi_{j,i}$ was defined, expressing the plausibility that, during the *j*-th natural hazard, the *i*-th safety barrier will not be available, due to the direct impact of the natural event on the facility.

Based on the analysis of past accidents and failure modes, natural hazards are supposed to affect the availability of active barriers (and in turn their *PFD*) but to have a negligible effect on the effectiveness of such category of barriers. On the contrary, in the case of passive barriers, the effectiveness is the only parameter that is modified (e.g., the effective capability of catch basins to retain liquid spills), since barriers belonging to this category do not need to be activated and the concept of *PFD* is not applicable.

Thus, in case of active barriers, the modification factor $\phi_{j,i}$ is used to determine a tailored value of $PFD_{j,i}$ starting from a baseline $PFD_{0,i}$ reported by literature sources (DNV, 1997; IEC, 1998; Madonna et al., 2009):

$$PFD_{j,i} = 1 + (\phi_{j,i} - 1)(1 - PFD_{0,i}) \tag{5.2. 1}$$

with $\phi_{j,i} \in [0,1]$. The effectiveness for this category of barriers is assumed to be unmodified:

$$\eta_{j,i} = \eta_{0,i} \tag{5.2. 2}$$

where $\eta_{0,i}$ is the baseline value for barrier effectiveness, independent of the natural event considered. It is worth noting that according to Eq. (5.2. 1), $PFD_{j,i}$ is a linear function of the factor $\phi_{j,i}$.

In the case of passive technical safety barriers, the performance characterization of the *i*-th passive barrier during *j*-th natural hazard may be calculated as follows:

$$\eta_{j,i} = (1 - \phi_{j,i})\, \eta_{0,i} \tag{5.2. 3}$$

with $\phi_{j,i} \in [0,1]$. According to Eq. (5.2. 3), the effectiveness $\eta_{j,i}$ is a linearly decreasing function of $\phi_{j,i}$. In case the natural hazard does not affect the integrity of the barrier (i.e., $\phi_{j,i} = 0$) the performance parameter of the barrier corresponds to its original baseline value $\eta_{0,i}$.

A reference set for the baseline values of the safety barriers considered is proposed in previous studies (e.g., see (Landucci et al., 2015; Necci et al., 2014b) and references cited therein).

5.2.3 *Description of the survey and data elicitation*

An extended group of experts of different nationalities (from Europe, U.S., Canada, and Asia) was invited to participate in a specific online survey in order to obtain information on the expected performance of the reference set of safety barriers defined in the two categories of Natech events selected for the study. Experts of different nature were involved in the survey, involving both academics, i.e., scholars in the field of process safety and industrial design; and practitioners, such as targeting consultancy directors, members of control authorities, facility managers (step 4 in Figure 5.2. 1). Involving experts with heterogeneous backgrounds is useful to cover all relevant aspects of the subject matter, thus enhancing result completeness (Hokstada et al., 1998) (the actual number and the background of experts answering the survey are briefly presented in the result section).

An ad-hoc survey has been prepared (step 5 in Figure 5.2. 1) and administered to the group of experts (step 6 in Figure 5.2. 1) through the Google Form web app. The transcription of the survey form can be found in Appendix A.

Together with the survey, a brief description of each considered barrier was provided to the experts. Given the heterogeneous background of the expert pool, a preliminary section to investigate the background of respondents has been included in the survey. The number of years of experience, together with the belonging institution have been asked. It should be noted that information on the status/background of experts is asked in favor of thorough documentation, and it is deemed a suitable trade-off between anonymity and objectivity in this kind of study (Hokstada et al., 1998).

For both the natural events considered, two questions regarding each safety barrier were asked. Experts were requested to express their opinion on the possibility that the safety barrier could be affected by the specified natural event. A short qualitative answer was required: “YES”, “NO”, “NOT SURE” (e.g., “Do you think in case of floods impacting process facilities, the automatic rim-seal fire extinguisher could be damaged and could be unavailable in case of demand?”). Experts were also given the possibility to leave the question unanswered.

Answers to this part of the survey were firstly analyzed in order to perform a preliminary qualitative assessment of barrier failure (step 7 in Figure 5.2. 1). Since categorical answers were allowed, a simple statistical analysis was deemed sufficient to obtain the percentage of experts agreeing on whether each barrier would fail or not (or being not sure). Results were then compared with those obtained from the quantitative questions in terms of performance modification parameters to check their coherence.

The second question concerned the expert's opinion on the likelihood of the safety barrier failure as an immediate consequence of the natural event considered. Experts were asked to provide an answer through the verbal scale presented in Figure 5.2. 2. The verbal scale was later translated into numerical values according to the association shown in Figure 5.2. 2. The choice of adopting a verbal scale with a background translation to numerical values was preferred to directly requiring to experts a numerical answer since this approach since it was successfully applied in several previous studies, and generally helps respondents providing answers more intuitively (Norrington et al., 2008).

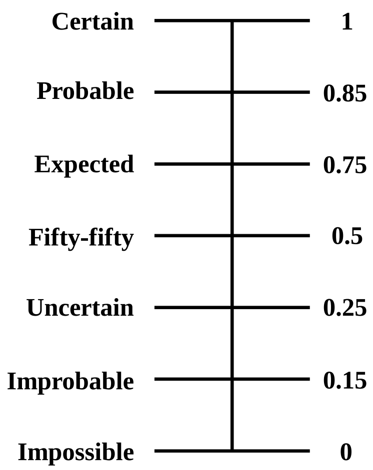


Figure 5.2. 2: Verbal scale adopted in the survey and corresponding quantitative translation adopted in the analysis of the answers.

Modification factors to be used in Eqs. (5.2. 1) and (5.2. 3) in order to update the baseline figures for safety barrier performance in case of Natech accidents caused by floods and earthquakes were obtained from the elaboration of quantitative expert answers (step 8 in Figure 5.2. 1). After the quantitative translation using the verbal scale in Figure 5.2. 2, expert judgments for each barrier were combined to obtain a distribution of values for the modification factor by a linear weighting procedure, associating the same weight to each expert. Even if possibly oversimplified, that applied is the most common and the simplest approach for averaging results obtained from multiple sources. More refined methods, for instance, supra Bayesian combination, have not been applied since they would have required an elevated computational effort (Jacobs, 1995), without providing any added value to results due to the elevated degree of uncertainty of the study.

The results were analyzed by comparing the distributions obtained for different barriers. However, performance parameters need to be expressed concisely to be suitable for risk analysis. Thus, to summarize the information obtained for each barrier, the median value of each distribution has been chosen as a statistical indicator representing the performance modification factor (step 8 in Figure 5.2. 1). Further details on the choice of the median value as a statistical indicator are discussed in Section 5.2.5. The modification factors obtained through this procedure can be then implemented in the proposed metric to assess active and passive safety barrier expected performances during the reference natural hazards (step 9 in Figure 5.2. 1).

5.2.4 *Results of the survey*

Information on respondents

The survey was answered by 41 experts. The final number of answers considered is 38 since 3 respondents declared not to have specific experience within the context of safety barriers and their answers were not further considered. The final number of involved experts was considered satisfactory, in agreement with literature studies (Cooke and Goossens, 1999). Figure 5.2. 3 summarizes the professional background (panel a) and the years of experience of the pool of respondents (panel b).

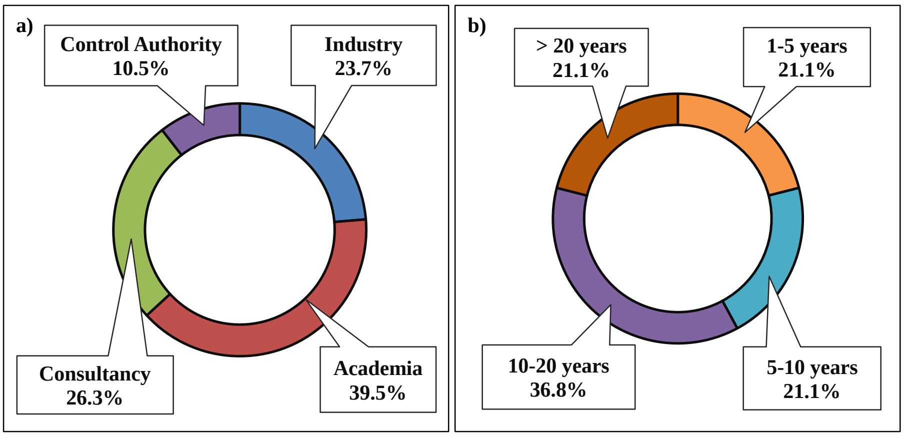


Figure 5.2. 3: Summary of professional background (a) and year of experience (b) of the pool of experts.

As can be seen, experts from different fields were involved. Respondents were mainly from academia with about 40% of the received answers, although a relevant share was provided also by people from consultancy (26.3%) and industry (23.7%). The participation from control authorities was more limited (10.5%) but still significant.

Qualitative results

Qualitative results obtained from the analysis of the answers to the first type of question for each barrier (concerning if the barrier would likely be affected by the impact of the natural event) are reported in Figure 5.2. 4. Missing answers were associated with the "Not sure" category in Figure 5.2. 4, since it was assumed that a missing answer could be interpreted as an uncertainty of the expert in determining an answer.

Qualitative results on the failure of safety barriers in the case of floods are presented in Figure 5.2. 4-a. As it can be noted from the figure, active safety barriers (*SB.1* to *SB.9*) are in general perceived by experts to be more vulnerable to floods compared to passive safety barriers (*SB.10* to *SB.16*). Indeed, more than half of the experts indicated that 5 active barriers out of 9, and 1 passive barrier out of 7 would be damaged and unavailable during flooding scenarios. The active barriers recognized as likely to be unavailable in the case of a flood by most of the experts are mainly complex systems for fire prevention and mitigation, that is, inert gas blanketing systems (*SB.1*), foam systems (*SB.3*), sprinklers, and water deluge systems (*SB.4*), hydrants for fire brigades (*SB.5*), and detection devices as fire & gas detectors (*SB.7*). Automatic rim-seal fire extinguishers (*SB.2*) have been considered unlikely to be affected by most experts, presumably due to their position, above floating roofs of atmospheric storage tanks.

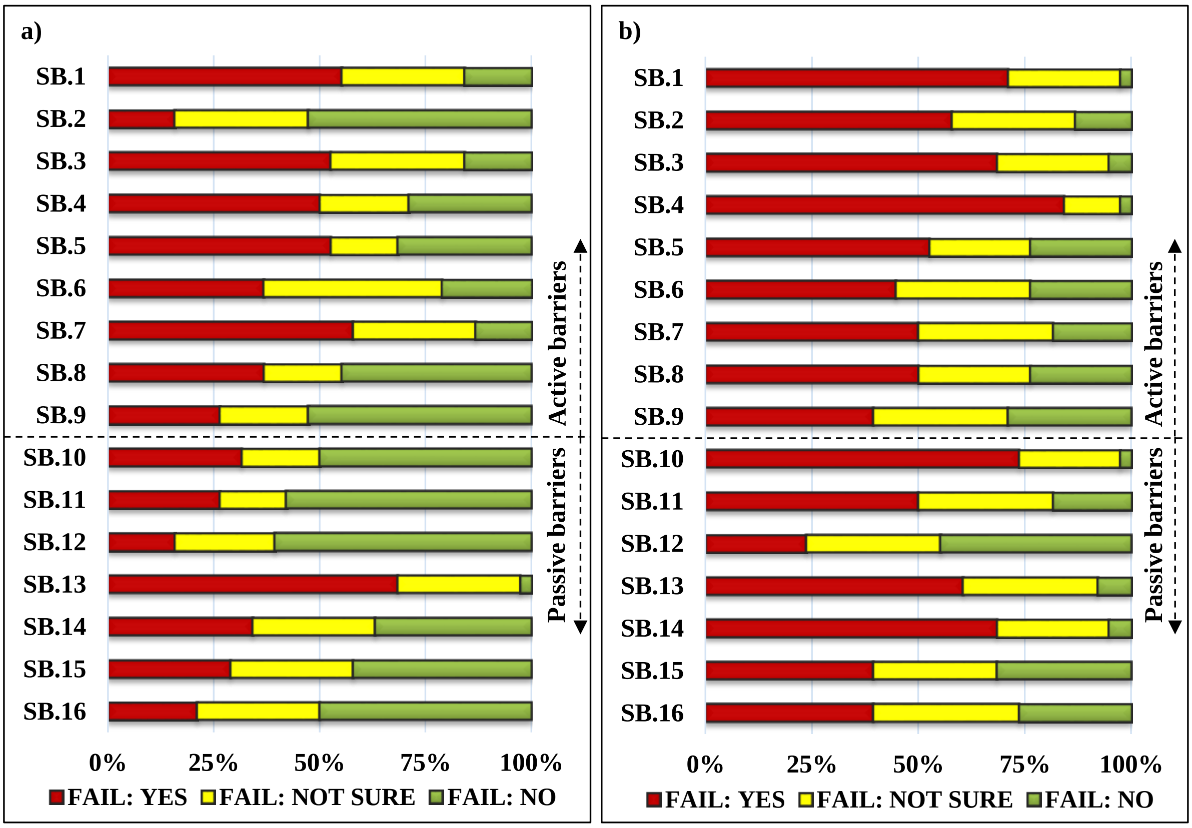


Figure 5.2. 4: Results obtained from the survey concerning the likelihood of barrier failure or unavailability in the case of the impact of (a) flood or (b) earthquake. The key to barrier ID is reported in Table 5.2. 1.

An elevated uncertainty is present concerning the impact of floods on fire-activated valves (*SB.6*), probably due to the high specificity of such safety systems. Both SDVs and BDVs (*SB.7* and *SB.8*, respectively) have been considered to be unaffected by most of the experts, reflecting the fact that these systems are usually designed fail-safe.

For what concerns passive barriers, it is clear that the most critical items perceived by experts are bunds and catch basins (*SB.13*). Experts interviewed seem to have clear in mind the possibility that these systems may be overtopped by floodwaters, annealing the possibility to express their safety function of retaining possible liquid spills, as it was also highlighted by past accident analysis

(Cozzani et al., 2010). The other passive barriers seem not to be significantly affected by floodwaters according to experts' opinions.
Finally, it is worth remarking that if uncertainty is conservatively associated with the likelihood of failure (i.e., considering the sum of "fail" and "not sure" answers) the failure of 12 out of 16 items is deemed plausible by more than 50% of experts.

Qualitative results on the failure of safety barriers in the case of earthquakes are presented in Figure 5.2. 4-b. It is clear from the figure that in most cases the failure of the barriers due to seismic events is expected by the majority of experts.
Among active barriers, the only items which in experts' opinion are unlikely to fail (Fail % lower than 50) are fire activated valves (*SB.6*) and BDVs (*SB.9*). The criticality of active fire protection systems has been strongly highlighted. Indeed, these systems are those considered more vulnerable among the investigated set of active barriers. For instance, WDS and sprinklers (*SB.4*) are expected to be damaged in an earthquake by about 85% of respondents, while the failure of both foam systems (*SB.3*) and inert gas blanketing systems (*SB.1*) is expected by about 70% of experts. These systems are composed of a pipework distribution network (i.e., for delivering firefighting water, foam, or inert gas, respectively), which may be vulnerable during seismic events, as evidenced by past Natech accident analysis (Campedel, 2008).
Among passive barriers, a total of 4 out of the 7 systems present in the selected set of safety barriers were considered likely to fail by more than half of the experts in the pool. The most critical elements resulted to be firewalls (*SB.10*), emergency blowdown lines (EBD line) (*SB.14*), and bunds and catch basins (*SB.13*) whose failure in case of an earthquake is expected respectively by 74%, 68% and 60% of the experts participating in the survey. The criticality of the EBD line evidenced by the survey is probably due to the importance given by experts to the elevated vulnerability of piping during seismic events, emerging from accident analysis (Campedel, 2008). As expected, firewalls, bunds, and catch basins may be particularly prone to structural failures due to seismic loads. The extensive damages to concrete dikes during Kocaeli Earthquake (1999) (see Section 2.1.1) is an example confirming the vulnerability to earthquakes of these safety barriers (Girgin, 2011).

When the results obtained for earthquakes (Figure 5.2. 4-b) are compared to those obtained in the case of floods (Figure 5.2. 4-a), it clearly emerges that the consulted experts consider the failure of the set of technical safety barriers considered more likely in the case of an earthquake than in the case of a flood. Indeed, if only 6 items are considered likely to fail by more than 50% of experts in the case of a flood when an earthquake is considered this number rises to 11. On average, active barriers have been assessed likely to fail by about 43% of experts during floods, and by about 58% of experts

during earthquakes. A similar trend is found for passive barriers, with an average of 33% of experts considering failure likely in case of floods, and 51% in case of earthquakes.
Nevertheless, both in the case of floods and earthquakes, experts agree that passive barriers are generally more robust than active barriers, despite few specific cases (e.g., catch basins are likely to be submerged by floodwaters).

Quantitative results and performance modification factors

The analysis of the answers obtained to the second set of questions, requiring the experts to express verbal graduation of the likelihood of barrier failure during natural hazards, allowed gathering a distribution of the modification factors $\phi_{j,i}$ (see Section 5.2.3). The distributions of the elicited performance modification parameter are reported in Figure 5.2. 5 in the concise form of boxplots. For the sake of brevity, the details of the description of the distributions obtained for each barrier are reported directly in Appendix B.

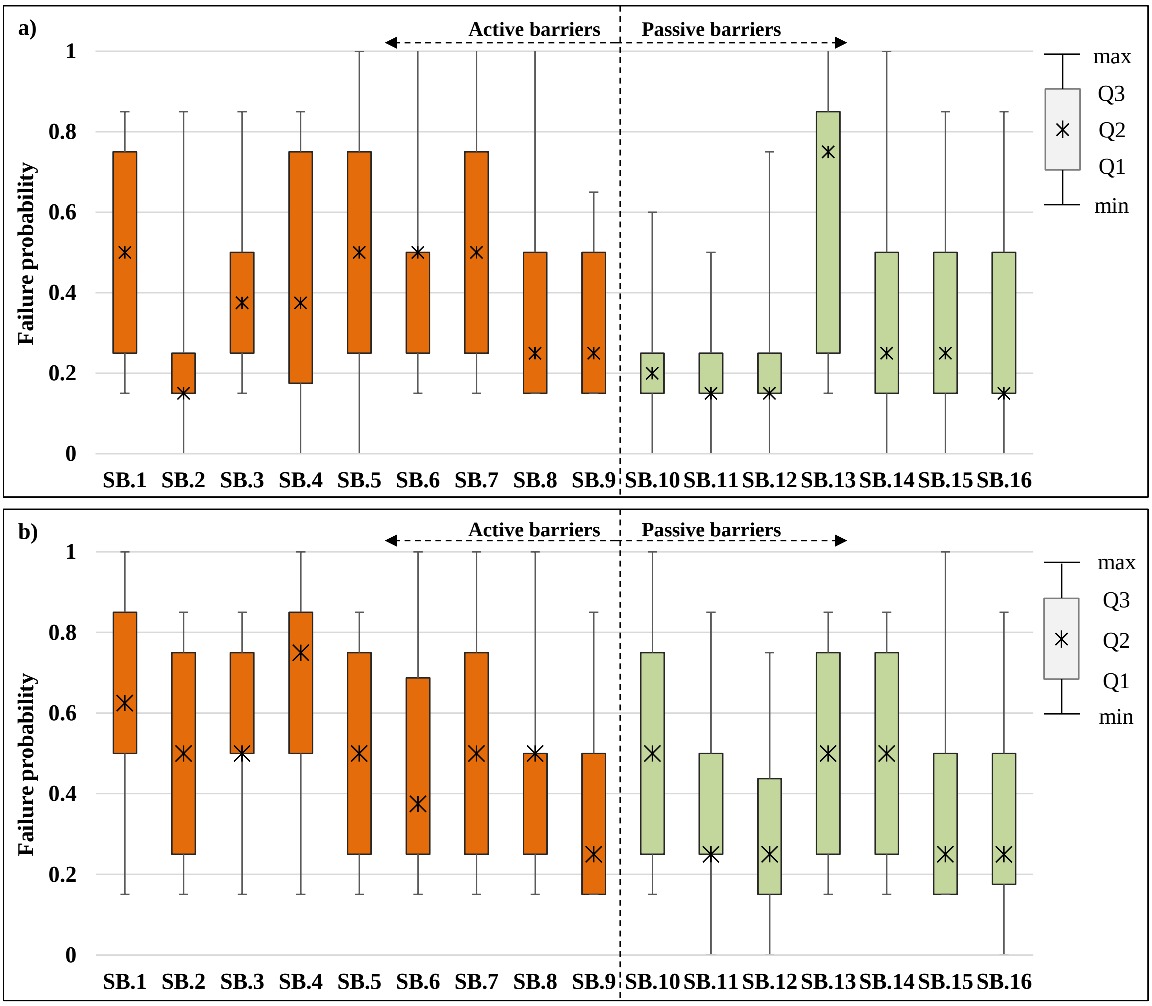


Figure 5.2. 5: Results obtained from the elicitation of performance parameter φ for (a) floods and (b) earthquakes (Q1= higher value for the 1st quartile, Q2= highest value for the 2nd quartile (median value of the dataset), Q3= highest value for the 3rd quartile. Orange = Active barrier, Green = passive barrier. 0: failure impossible; 1: failure certain; see Figure 5.2. 2 for quantitative translation criteria of verbal scales). The key to safety barrier ID is reported in Table 5.2. 1.

In coherence with previous studies (e.g., see (Argenti et al., 2017)), assuming the median value of each distribution as the value for the performance modification factor is suggested. The adoption of the mean value as a statistical indicator, in this case, is not considered the best choice, since it is not fully representative of the distribution in case of disperse judgments: the influence of outliers on the variation of the mean value is rather elevated in the set of data obtained, while the median of the distribution is less affected by outliers, thus better representing the central tendency of data (Manikandan, 2011; O'Hagan et al., 2006).

Distributions of the performance parameters during floods are presented in Figure 5.2. 5-a. The most vulnerable active systems identified by the experts are the inert gas blanketing system (*SB.1*), hydrants (*SB.5*), fire activated valves (*SB.6*), and fire and gas detectors (*SB.7*), with median values of the elicited performance parameter of about 0.5. As evident from Figure 5.2. 4-a, some of these items were recognized as critical by the majority of experts also in the qualitative answers.

It should be remarked that the distributions of answers have a high dispersion for some items. For instance, figures for WDS and sprinkler systems (*SB.4*) show a large disagreement among respondents (i.e., median of 0.375, Q1 and Q3 of 0.175 and 0.75 respectively), despite they had been deemed likely to fail by the majority of experts in the qualitative part of the survey. The same issue affects the set of the most vulnerable items (*SB.1, SB.5,* and *SB.7*). The possible reasons for such distributions are probably due to differences considered by the experts in the layout of complex systems as active barriers.

Automatic rim-seal fire extinguishers (*SB.2*), SDVs (*SB.8*), and BDVs (*SB.9*) show low values of the modification parameter (respectively of 0.15, 0.25, and 0.25), highlighting their expected resilience to floods. It should also be noted that the distribution elicited for *SB.2* is peculiarly narrow, indicating that the majority of experts agree on the scarce vulnerability of this barrier.

Among passive barriers, the catch basins and bunds (*SB.13*) are by far the items showing the highest value of modification factor (0.8). This result was expected since the large majority of experts had already identified the vulnerability of such retaining systems during floods. The other passive barriers investigated have been assessed to be only slightly affected by floodwaters, showing low values of the performance modification parameter (apart from *SB.13*, the average median value is about 0.2).

The distributions of the performance parameter for each barrier considering earthquake are shown in Figure 5.2. 5-b. In this case, the most vulnerable items are by far the gas blanketing system (*SB.1*) and WDS and sprinklers (*SB.4*), with median values of 0.625 and 0.75, respectively. These results are in line with the qualitative answers (see Figure 5.2. 4-b), highlighting that experts are concerned by the vulnerability of these systems to earthquakes. Most of the other active barriers are considered as well likely to be affected by seismic events, showing median values of 0.5 in 5 out of 7 cases. Surprisingly, different figures result for SDVs (*SB.8*) and BDVs (*SB.9*) despite the similarity of such safety systems.

Passive barriers are deemed to be significantly affected by seismic loads in 3 out of 7 cases, with the most critical items being firewalls (*SB.10*), bunds and catch basins (*SB.13*), and emergency blowdown line (*SB.14*): median value is of 0.5 for each of the three distributions. For this subset of barriers, the effectiveness is halved compared to their expected performance during standard operating conditions. Again, the results are in line with those obtained from qualitative answers. The category of passive barriers is associated with an average performance modification parameter equal to 0.36, lower than that corresponding to the set of active systems considered (equal to 0.5), confirming that such category of barriers is considered more resilient to earthquakes.

In order to compare the quantitative performance results obtained for floods and earthquakes, the average distribution of position parameters was calculated for the entire set of barriers investigated, as is reported in Figure 5.2. 6. More specifically, the following parameters were calculated for floods and earthquakes: the average over the entire set of barriers of the minimum and maximum value (i.e., Min and Max in Figure 5.2. 6) and of the highest figure in the 1st, 2nd, and 3rd quartiles of the distributions (i.e., $\overline{Q}_1$, $\overline{Q}_2$, and $\overline{Q}_3$ in Figure 5.2. 6).

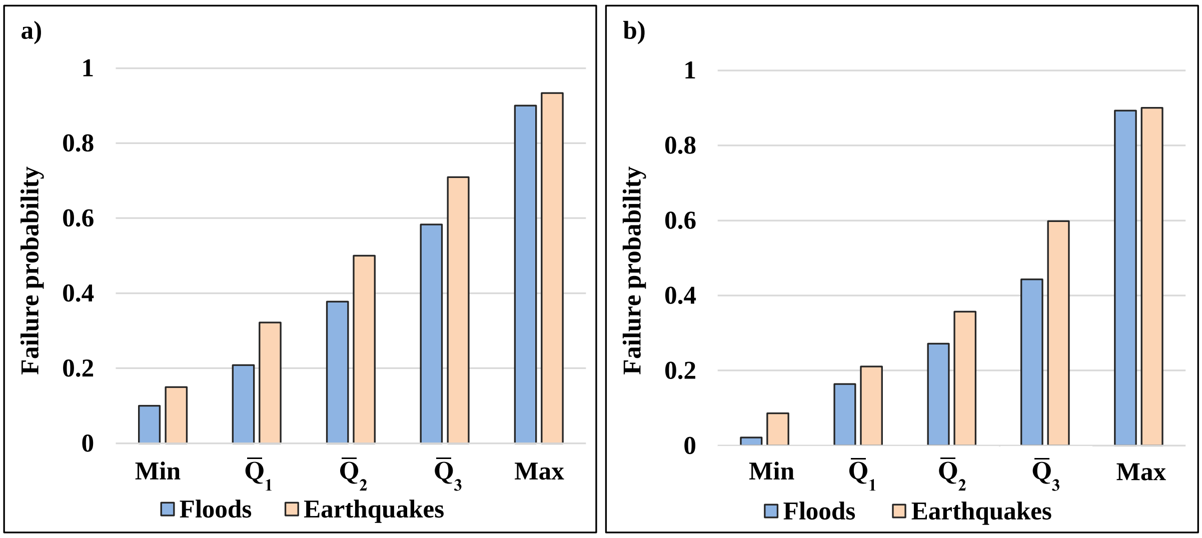


Figure 5.2. 6: Average parameters of the distributions calculated for (a) active barriers and (b) passive barriers. Min = average minimum value, $\overline{Q}_1$ = average higher value in the 1st quartile, $\overline{Q}_2$ = average median value, $\overline{Q}_3$ = average highest value in the 3rd quartile, Max= average maximum value.

From the figure, it clearly emerges that the investigated barriers are deemed in general more vulnerable to earthquakes than to floods. Indeed, considering earthquakes, $\overline{Q}_2$ is of 0.5 for active barriers and 0.375 for passive ones, while the corresponding values for floods are 0.378 and 0.271 respectively. Figure 5.2. 6 further confirms that the investigated active barriers are considered to be more vulnerable to both natural hazards than passive barriers. It should also be noted that the difference among the impact of floods and earthquakes is slightly higher for active barriers than for passive barriers, in general. Indeed, the average difference in performances among $\overline{Q}_1$, $\overline{Q}_2$ and $\overline{Q}_3$ parameters is 0.12 for active barriers and 0.1 for passive barriers.

The differences between the average position of outliers (i.e., Min and Max position parameters) have not been assessed in the comparison since they express the extreme points of each distribution, which in some cases are determined by the judgment of a limited group of experts in disagreement with the majority. For instance, the distribution elicited for the automatic rim-seal fire extinguisher (*SB.2*) in case of floods, shows a maximum value of 0.85, which has been expressed only by 2 experts out of 38 analyzed, while the really narrow distribution confirms general agreement among respondents.

5.2.5 Discussion

The modification parameters elicited from the survey can be considered as a first step to assess safety barrier performance in QRAs of Natech events. However, due to the scarcity of data, this approach represents a first exploration of the topic, and important limitations, in particular when quantitative data are of interest, should be considered. Actually, to maintain a general validity of the assessment, it was decided to ask experts to consider a "plausible" intensity of natural hazards. Indeed, defining the characteristics and the intensity of natural hazards would have restricted the applicability domain of the study. On the one hand, the absence of intensity specification is thus in favor of a more general validity of the results of the survey. On the other hand, it also limits the direct applicability of the results in the quantitative assessment of specific scenarios. The modification parameters obtained should be thus considered as generic baseline values. Site-specific values for quantitative assessment studies might need to be derived from tailoring procedures, based on more detailed data both on the intensity of the natural event and on the specific features of the safety barrier considered.

An additional limitation of the proposed approach is the inherent uncertainty affecting expert elicitation procedures. Experts may be unable to properly express their knowledge within the framework of the prepared survey, or they may be not confident with the verbal scale they were provided of. It is also possible that experts would have preferred to express their opinions on the likelihood of barrier failures through numerical distributions. For instance, some authors suggest employing the Classical Model to better characterize judgment features, thus requiring experts to provide their subjective parameter distributions for each surveyed item in terms of 5^{th}, 50^{th}, and 95^{th} percentiles (Colson and Cooke, 2018). However, this procedure would have made the survey harder to be completed and was considered inappropriate considering the scarcity of data and the explorative nature of the study. Furthermore, the combination of the distributions obtained would have required a proper assessment of the relative weights of expert knowledge, which was not practically feasible.

Another point that is worth to be mentioned is that some analyzed safety systems showed a wide dispersion of the answer distributions, indicating a limited agreement among experts. One of the possible causes may be the technical complexity of some systems analyzed. In particular, for active barriers, a more refined analysis can be required to obtain reliable results. A possibility may be to study these systems through more sophisticated approaches considering the impact of natural hazards in each relevant subsystem. For instance, a failure mode and effect analysis (FMEA) could be used to assess which subsystems are critical during natural hazards, and what is the effect of damages to parts of system architecture (Misuri et al., 2019b).

Finally, it must be remarked that the survey was limited to the analysis of a restricted set of technical barriers particularly relevant in the context of cascading accidents. However, this limitation derived only from the need to limit the number of barriers considered in the survey forms to reduce the time required for the experts to complete them. Moreover, while previous research evidenced that the actions of plant operators and emergency teams may be heavily hindered due to the high stressing environment and the complexity of Natech scenarios (Steinberg and Cruz, 2004), suggesting that procedural barriers and emergency measures may be assessed as well within the proposed framework, various site-specificities might heavily affect their performance and the extension of this exploratory approach to this case might be of extremely limited validity.

5.2.6 Conclusions

In this section, the performances of widely used safety barriers adopted in chemical and process plants during natural hazards have been investigated by expert elicitation. Some safety barriers were identified as having a critical vulnerability to natural hazards. Baseline values to describe how the performance of safety barriers is modified during floods and earthquakes were obtained from the expert elicitation procedure. These parameters can be used to support the probabilistic analysis of Natech scenarios, in order to achieve a better characterization of the final consequences and a more reliable quantification of the possibility of domino effects, laying the basis for an improved risk-informed decision making on proactive strategies enhancing the safety of chemical and process plants against natural disasters.

5.3 Impact of barrier degradation on the likelihood of domino scenarios in Natech events

The figures of performance modification factors obtained in Section 5.2 show the significance of the expected extent of barrier performance reduction during earthquakes and floods, highlighting the need to assess whether this depletion is reflected in the possibility of accident escalation through domino effect. Hence, in this section, a novel approach to frequency assessment of domino scenarios in Natech events considering the degradation of barrier performance is presented. The methodology leverages the data obtained in Section 5.2 to address the quantification of endpoint scenario frequency and probability modification.

5.3.1 Overview of the methodology

The methodology developed for including safety barrier performance in the frequency assessment of domino scenarios in Natech events is outlined in Figure 5.3. 1.

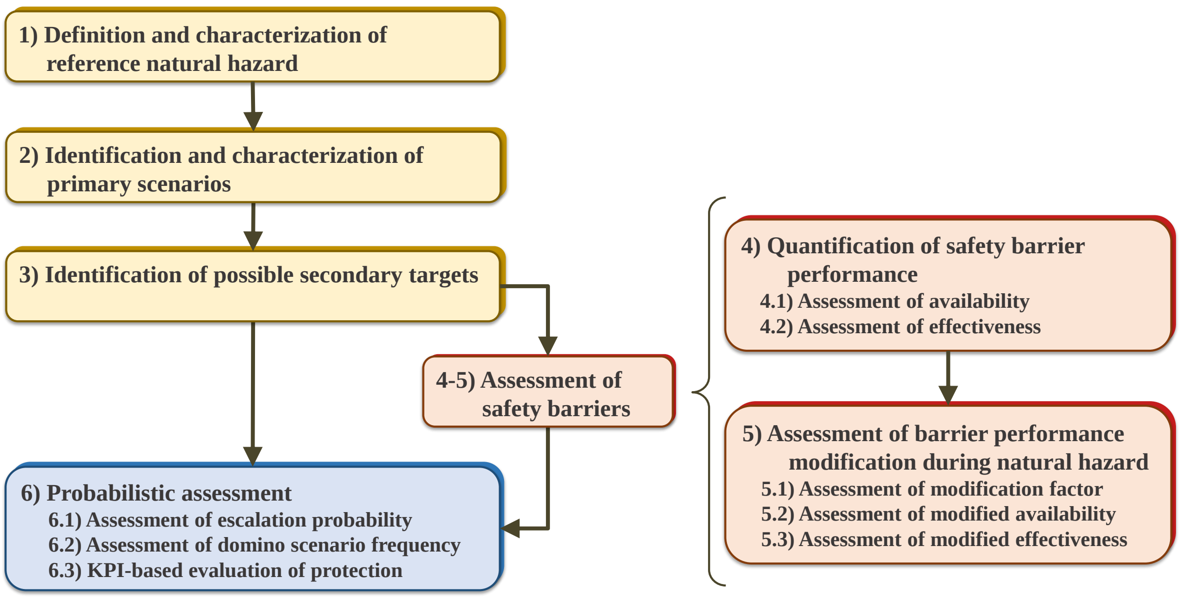


Figure 5.3. 1: Methodology for frequency assessment of mitigated domino scenarios and for the assessment of safety barrier performance in the mitigation of escalation of Natech events (KPI: Key Performance Indicators).

As in most of the quantitative assessment procedures presented in Section 2.2, the first step (step 1 in Figure 5.3. 1) is aimed at defining the reference natural hazards that may affect the industrial site under analysis and at performing a characterization of its main features, with a degree of detail suitable for industrial risk assessment studies. At a minimum, the natural hazard should be defined in terms of a frequency of occurrence, which might be easily calculated also from a time of return, and of quantification of the magnitude of impact at the site of concern. The following discussion focuses on earthquakes and floods since these events were responsible for the most severe Natech events reported in industrial accident databases, as highlighted in the dedicated literature (Krausmann et al., 2017), but it might be extended to other categories of natural hazards.

In the specific framework of Natech, the severity of floods may be characterized in terms of floodwater height and velocity, while the magnitude of earthquakes is usually assessed by estimating the values of the horizontal component of peak ground acceleration (PGA) (Antonioni et al., 2015, 2007; Cozzani et al., 2014). This approach leads to the selection of a limited number of reference scenarios for the natural events, each characterized by a time of return and an intensity, representing the natural hazard present on the site (Antonioni et al., 2015, 2009a; Cozzani et al., 2014).

Coherently with the state of the art of Natech assessment, natural hazards are considered independent (i.e., the assessment considers either the effect of a flood or that of an earthquake, and does not account for any correlation among them or their potential effects). Moreover, barrier degradation due to the effect of previous natural events is not considered (i.e., technical safety barriers are assumed to have undergone regular maintenance).

Primary scenarios caused by Natech are then identified and characterized in terms of frequency and consequences (step 2 in Figure 5.3. 1). The identification of primary events is carried out adopting specific methodologies developed for the framework of Natech scenarios, described in detail elsewhere (Antonioni et al., 2009a; Cozzani et al., 2010). The frequency of primary LOC events can be calculated by multiplying the expected frequency of the natural event of concern by the conditional probability of equipment damage, obtained by applying equipment vulnerability models (Landucci et al., 2014, 2012; Salzano et al., 2003), as explained in Section 2.2.

Specific event trees may be used to define the possible primary scenarios following the LOC events (Antonioni et al., 2009a; Cozzani et al., 2010) and to identify the relevant escalation vectors. Indeed, previous studies (Cozzani et al., 2010; Krausmann et al., 2011) highlighted that most of the Natech events reported in databases collecting data on industrial accidents involved the LOC of petrochemical products (Campedel, 2008; Misuri et al., 2019a), which may lead to fire scenarios.

The possible domino targets may then be identified (step 3 in Figure 5.3. 1) through the application of threshold-based approaches available in the literature (Alileche et al., 2015; Cozzani et al., 2006b; Reniers and Cozzani, 2013a). These methods are based on the comparison between the actual value of the physical effects impacting on equipment items (e.g., heat radiation in case of stationary fires, or peak overpressure in case of explosions) and threshold values below which escalation is considered not credible.

For each identified target, it is then necessary to consider the possible escalation likelihood modification due to the presence of safety barriers for accident prevention and mitigation (steps 4 and 5 in Figure 5.3. 1). However, these systems may be impacted as well by the natural hazard as demonstrated in Section 5.2 (Misuri et al., 2020b), thus a specific evaluation of their performance modification is required (step 5 in Figure 5.3. 1). In analogy with the results obtained in Section 5.2, details on the quantification of barrier performance and on its modification due to the concurrent natural events are discussed respectively in Sections 5.3.2 and 5.3.3.

The assessment of the frequencies of the overall escalation scenarios may then be carried out (Step 6 in Figure 5.3. 1). Probit models based on equipment time to failure (*TTF*) when exposed to heat load may be applied to assess the probability of escalation due to domino effect triggered by fire (Cozzani et al., 2014, 2005; Landucci et al., 2009) (step 6.1 in Figure 5.3. 1). Dedicated methodologies to account for safety barriers are then applied to perform mitigated domino scenario probability and escalation frequency assessment (Landucci et al., 2017b, 2016, 2015) (step 6.2 in Figure 5.3. 1). These two steps are discussed in Section 5.3.3. Finally, a performance analysis of safety barriers and protection systems is carried out through a specific indicator-based methodology (step 6.3 in Figure 5.3. 1), which is presented in Section 5.3.4.

5.3.2 Quantitative performance assessment of safety barriers

Safety barriers are hereby defined as physical and non-physical measures intended to prevent, mitigate or control dangerous deviations of the industrial system under analysis or accidents (Delvosalle et al., 2006; Rausand, 2011; Sklet, 2006). Consistently with the classification adopted in Section 5.2, within the methodology of Figure 5.3. 1 safety barriers are classified according to the classification based on the barrier working principle (CCPS, 2001b; De Dianous and Fiévez, 2006). Briefly recalling the description provided in Section 5.1, according to this rationale safety barriers can be classified in:

- passive barriers, that is, physical protection systems not requiring activation to perform their function, such as fireproofing or containment dikes (Mannan, 2005);
- active barriers, that is, usually complex systems requiring external activation, such as water deluge systems (WDS) and sprinklers (Frank et al., 2013; Hauptmanns et al., 2008; NFPA, 2009, 2003); and
- procedural barriers, that is, procedures and contingency plans performed by internal personnel or external teams to face the occurrence of major accidents (e.g., intervention of firefighters).

As the performance of safety barriers is a critical aspect in evaluating the probability of accident scenarios caused by Natech events, its characterization is needed to support the probabilistic assessment of final scenarios. In analogy with the methodology shown in Section 5.2, the LOPA-based approach developed for the assessment of mitigated escalation scenarios is adopted (Landucci et al., 2015). Thus, Steps 4.1 and 4.2 in Figure 5.3. 1 suggest estimating baseline barrier performance leveraging the concepts of probability of failure on demand (*PFD*) and effectiveness (η). Further details on these concepts and on their application in the assessment of mitigated domino escalation are reported in Section 5.1. A comprehensive catalogue of reliability data sources is also available in previous publications (Necci et al., 2014b).

Once the original performance of safety barriers is quantified, baseline values of *PFD* and η are modified taking into account the effect of the natural event (Step 5 in Figure 5.3. 1), adopting the methodology and the dataset presented in Chapter 5 (Misuri et al., 2020b). Performance modification factors ϕ were elicited from experts through a covariate approach (Cox, 1972; Gao et al., 2010), and implemented for the assessment of the safety barriers (Step 5.1 in Figure 5.3. 1). The 2nd quartile of the obtained failure probability distributions was selected as the value of ϕ to minimize the effect of the outliers (Misuri et al., 2020b). Performance modification factor ϕ can be interpreted as the likelihood that barrier systems are impaired or damaged by natural hazards, hence higher values (i.e., close to 1) indicate a higher probability that the barrier will fail in providing a successful protection action.
A subset of relevant safety barriers along with the specific modification factors in the case of floods (ϕ_f) and earthquakes (ϕ_e) is reported in Table 5.3. 1. In the same table, the uncertainty on the elicited parameters is expressed as the interval comprised between the 1st and the 3rd quartiles of the obtained distributions (i.e., indicated as Q1 and Q3, respectively).

Table 5.3. 1: Performance modification factors for some relevant safety barriers in the case of floods (ϕ_f) and earthquakes (ϕ_f). Q_1=1st quartile of distribution; Q_3=3rd quartile of distribution. Data gathered from (Misuri et al., 2020b). *Further details can be found in Appendix B.*

Safety barrier	ϕ_f	$[Q_1, Q_3]_f$	ϕ_e	$[Q_1, Q_3]_e$
Inert-gas blanketing system	0.5	[0.25, 0.75]	0.625	[0.5, 0.85]
Automatic rim-seal fire extinguishers	0.15	[0.15, 0.25]	0.5	[0.25, 0.75]
Fixed / Semi-fixed foam systems	0.375	[0.25,0.50]	0.5	[0.5, 0.75]
WDS / Water Curtains / Sprinklers	0.375	[0.18, 0.75]	0.75	[0.5, 0.85]
Hydrants	0.5	[0.25, 0.75]	0.5	[0.25, 0.75]
Fire activated valves	0.5	[0.25, 0.50]	0.375	[0.25, 0.69]
Fire and gas detectors	0.5	[0.25, 0.75]	0.5	[0.25, 0.75]
Shut down valves	0.25	[0.15, 0.50]	0.5	[0.25, 0.50]
Blow down valves	0.25	[0.15, 0.50]	0.25	[0.15, 0.50]
Fire walls	0.2	[0.15, 0.25]	0.5	[0.25, 0.75]
Blast walls	0.15	[0.15, 0.75]	0.25	[0.25, 0.50]
Fireproofing	0.15	[0.15, 0.25]	0.25	[0.15, 0.44]

The proposed framework, based on the implementation of the modification factors, thus tailoring baseline barrier performance, derives from considerations and lessons learned from past Natech accidents (Krausmann et al., 2011; Misuri et al., 2019a; Steinberg and Cruz, 2004) (Steps 5.2 and 5.3 in Figure 5.3. 1). In particular, in the case of active barriers, it is assumed that the effect of the natural hazard induces the increment of the *PFD* of active barriers (i.e., reducing their availability), with a negligible effect on effectiveness after successful activation. In the case of passive barriers, the effectiveness is the sole parameter to be reduced by the impact of the natural event, since in this case the barrier does not need any specific activation or action to provide its effect (i.e., failure on demand to provide the protective action does not apply to this barrier category).

Thus, by the proposed approach proposed in Section 5.2, a single modification factor obtained from expert elicitation is applied either to modify the *PFD* (in the case of active barriers) or the effectiveness (in the case of passive barriers). For the sake of clarity, the approach is briefly reported also in the following.

In the case of active barriers, the performance parameters of the *i*-th active barrier are modified according to Eqs. (5.3.1) and (5.3.2):

$$PFD_{j,i} = 1 + (\phi_{j,i} - 1)(1 - PFD_{0,i}) \tag{5.3. 1}$$

$$\eta_{j,i} = \eta_{0,i} \tag{5.3. 2}$$

Where $\phi_{j,i} \in [0,1]$ is the performance modification factor for *j*-th reference natural hazard scenario, and $PFD_{0,i}$ and $\eta_{0,i}$ are the baseline values for the probability of failure on demand and effectiveness, respectively. As discussed above, the impact of natural hazards on the effectiveness of active barriers is neglected, thus the effectiveness value is considered equal to the baseline value $\eta_{0,i}$. In the case of barriers not specifically designed to resist natural events, it is possible that $PFD_{0,i}$ is much lower than $\phi_{j,i}$ (i.e., the probability of their failure in case of natural events is significantly higher than their baseline failure probability).

On the other hand, passive barriers are always available and do not need any activation to provide their action, thus the modification of the performance of the *i*-th barrier may be quantified considering only the effectiveness, as in Eq. 5.3.3:

$$\eta_{j,i} = (1 - \phi_{j,i})\,\eta_{0,i} \tag{5.3. 3}$$

where $\phi_{j,i} \in [0,1]$ is the performance modification factor of the *j*-th reference natural hazard scenario, and $\eta_{0,i}$ is the baseline effectiveness value.

Finally, it must be noted that modification factors for procedural barriers have not been retrieved in the study described in Section 5.2, and a general approach to assess performance degradation during Natech events (as proposed for active and passive barriers) is not advisable. Specific approaches, depending on the procedure foreseen, should be developed. An example is provided for the case of a procedural barrier consisting in the emergency response following a fire, aimed at preventing accident escalation. The characterization of effectiveness leverages a methodology obtained adapting that originally developed by (Landucci et al., 2016) to Natech scenarios. In the original publication, the calculation of the effectiveness η is based on the comparison of the time the equipment is expected to withstand the received heat load, the *TTF*, and the typical time required for the final mitigation of the scenario (*TFM*) (Landucci et al., 2016). However, the *TFM* obtained by the original methodology does not account for the specific conditions that may arise during a Natech scenario, and thus may be interpreted as a “best-case” value. In order to obtain a worst-case estimation of possible delays due to the complex environmental conditions that may be faced during compound disasters as earthquakes and floods, *TFM* was modified applying a methodology accounting for delays in response due to harsh environmental conditions (Landucci et al., 2017a). More details on the evaluation of *PFD* and η for an emergency response to fires are reported in Appendix C.

5.3.3 Frequency assessment of domino scenarios triggered by primary Natech events

The first part of the frequency assessment consists in estimating the frequency of primary LOCs induced by the natural event (as part of Step 2 in Figure 5.3. 1). If a frequency of the reference natural hazard scenario, f_{nh}, is estimated starting from the time of return, it is possible to calculate the frequency of the primary LOC events $f_{I;LOC}$ (where the subscript *I,LOC* indicates a primary LOC scenario) for an item as:

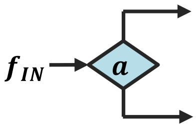
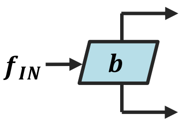
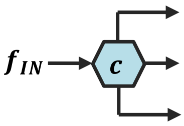
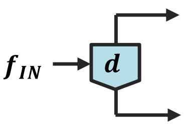
$$f_{I,LOC} = f_{nh} \times P_{nhd} \tag{5.3. 4}$$

where P_{nhd} is the equipment damage probability to the impact of the reference natural hazard scenario. The P_{nhd} damage probability can be estimated using equipment vulnerability models or observational fragility curves available in the literature (Landucci et al., 2014, 2012; Salzano et al., 2003). Models to be adopted can be found in the reference list reported in Section 2.2.

Primary Natech scenarios are identified through dedicated methodologies (Antonioni et al., 2015, 2009a; Campedel et al., 2008; Cozzani et al., 2010) and the evaluation of physical effects is performed through conventional integral models for consequence assessment (CCPS, 2000; Mannan, 2005; Uijt de Haag and Ale, 2005; Van Den Bosh and Weterings, 2005). Subsequently, the tailored ETA proposed in (Landucci et al., 2016, 2015) is applied to include the effect of safety barriers and their performance in escalation probability and frequency assessment (see Section 5.1.3). The methodology is based on the logical operators described as gates in Table 5.3. 2, which are adapted from a previous study (Landucci et al., 2016).

As shown in the table, the uppermost branch Out_1 of each gate represents the failure of the barrier in mitigating escalation. For gates "a" and "b", Out_2 represents the case of successful mitigation. In the specific case of gate "d", which is a target vessel fragility gate rather than a gate expressing barrier performance, Out_1 represents the mechanical failure of the target, while Out_2 indicates that the target withstands the received heat radiation. The probability of failure due to domino propagation P_D to be implemented in gate "d" is identified through the application of probit models based on equipment *TTF* (Landucci et al., 2009). Gate "c" instead has been specifically designed to assess emergency response performance in escalation prevention (Landucci et al., 2016, 2015). Thus, Out_2 represents the case of mitigated domino scenarios due to the successful activation of emergency response, but with a *TFM* higher than *TTF*. On the contrary, Out_3 is the case of successful mitigation due to successful response and *TFM* lower than *TTF*.

Table 5.3. 2: Definition of operators to be used in ETA. f_{IN}: gate input frequency, PFD: Probability of failure on demand, η: effectiveness parameter, P_D: equipment failure probability due to domino escalation. Adapted from (Landucci et al., 2016).

Gate type	Representation and quantification	Description
a	 $Out_1 = f_{IN} * [PFD + (1-\eta) * (1-PFD)]$ $Out_2 = f_{IN} * (1-PFD) * \eta$	Simple composite probability gate (type "a"): unavailability, expressed as a probability of failure on demand, is combined with a single probability value for the effectiveness.
b	 $Out_1 = f_{IN} * [PFD + (1-\eta) * (1-PFD)]$ $Out_2 = f_{IN} * (1-PFD) * \eta$	Composite probability distribution gate (type "b"): unavailability, expressed as a probability of failure on demand, is combined with a probability distribution expressing the effectiveness. It is possible to use an integrated effectiveness value, obtaining the quantification rule reported.
c	 $Out_1 = f_{IN} * PFD$ $Out_2 = f_{IN} * (1-PFD) * (1-\eta)$ $Out_3 = f_{IN} * (1-PFD) * \eta$	Discrete probability distribution gate (type "c"): depending on barrier effectiveness, three or more events may originate.
d	 $Out_1 = f_{IN} * P_D$ $Out_2 = f_{IN} * (1-P_D)$	Vessel fragility gate (type "d"): based on the status of the target equipment (e.g., received heat load, status of protections), the failure probability is calculated through equipment vulnerability models.

It should be noted that the gate set presented in Table 5.3.2 is an upgraded version of the original one shown in Section 5.1.3. Indeed, it should be noted that the gate "d" was not included in the original methodology presented in Landucci et al. (2015), although it is deemed particularly relevant in our approach to probabilistic assessment to account for the capability of the targets to withstand a given primary scenario (e.g., a fire) in possibly avoiding escalation also in the case the protections in place are defective (Landucci et al., 2016). In other words, this gate allows to make the residual vessel resistance explicit in the analysis (e.g., there is the possibility the vessel withstands the heat load from a stationary fire also in the case all the other protections failed).

5.3.4 Monitoring barrier performance

A set of indicators was applied to carry out a simplified quantitative evaluation and monitoring of barrier performance degradation in preventing/mitigating domino effects (Step 6.3 in Figure 5.3. 1). This set of indicators has been developed for passive and active barriers in previous studies on mitigated domino escalation assessment (Landucci et al., 2016). In particular, two Key Performance Indicators (KPIs), namely A and B, are associated with each hardware barrier. The A KPI is defined as:

$$A = \frac{\sigma}{Out_1/f_{IN}} \tag{5.3. 5}$$

where σ is a reference *PFD* indicating a high performance in reduction of escalation probability, f_{IN} is the input frequency to the barrier gate operator and Out_1 is the output frequency of mitigation failure. Therefore, the ratio Out_1/f_{IN} is the probability of barrier failure (i.e., either due to lack of activation or ineffectiveness once activated), which is associated with the uppermost branch of each gate presented in Table 5.3. 2. The A KPI thus summarizes the overall probabilistic performance of each barrier compared to a required safety level. In agreement with previous literature, the application of the risk-based methodology defined in IEC61508 and IEC61511 standards (IEC, 2003, 1998) evidenced that a safety function with Safety Integrity Level (SIL) 3 is required for domino escalation prevention (Landucci et al., 2016). According to the SIL definition, a safety function with SIL3 features a *PFD* between 10^{-4} and 10^{-3}, thus the latter value was conservatively assumed as parameter σ in the case study.

The B KPI is defined as:

$$B = \frac{TTF - TTF_u}{TFM - TTF_u} \tag{5.3. 6}$$

where *TTF* and TTF_u are the values of the time to failure of the equipment item considered respectively in the presence and in the absence of the barrier, while *TFM* is the time required for final mitigation of the fire, which is highly site-specific and may be estimated according to the simplified methodology presented in a previous study (Landucci et al., 2015). Hence, the B KPI specifically quantifies the increase in *TTF* achieved through the implementation of fire protection barriers (e.g., WDS), compared to the time required for emergency intervention at the site.

5.3.5 *Definition of a case study*

A reference case study was defined to assess the modification of risk figures caused by barrier performance degradation during Natech events. The layout considered is shown in Figure 5.3. 2. The layout is composed of two atmospheric tanks storing liquid flammable materials (i.e., T1, T2 in Figure 5.3. 2) and of a pressurized vessel storing LPG (i.e., P1 in Figure 5.3. 2).

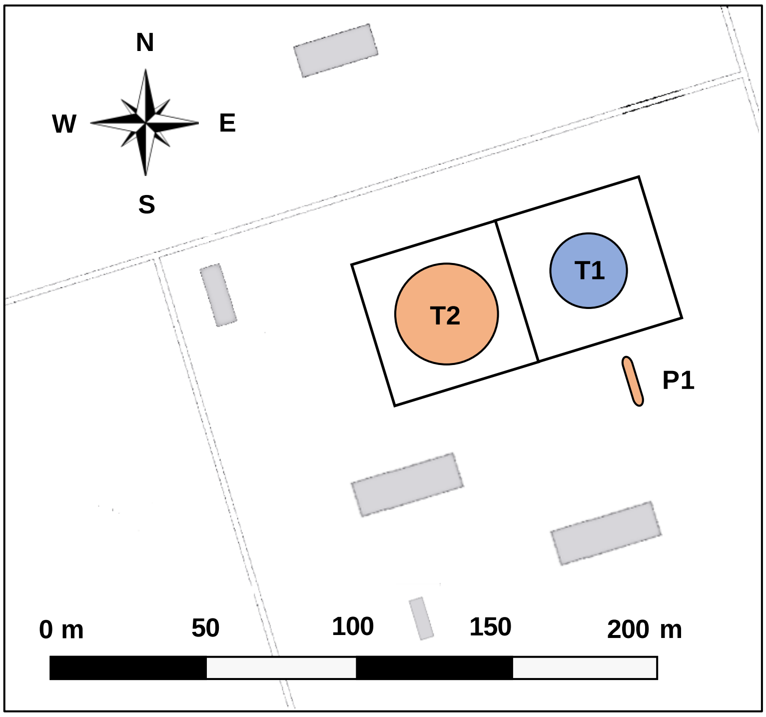


Figure 5.3. 2: Layout considered for the case study.

The main features of the equipment items are summarized in Table 5.3. 3. The facility was assumed to be located in a natural hazard-prone area and to be exposed to the risk of severe floods and earthquakes. The reference natural hazards are described in Table 5.3. 4.

Table 5.3. 3: Equipment items considered in the case study. Tank T1 was considered the source of the LOC causing the primary Natech scenario. V_n = nominal volume; D = Diameter; H = height; L = length; m_t = stored mass; Atm = Atmopsheric storage tank; HV = Horizontal vessel.

ID	Type	V_n [m^3]	D [m]	L or H [m]	Substance	m_t [ton]
T1	*Atm*	*5000*	*24.4*	*10.8*	*Gasoline*	*3000*
T2	Atm	4300	32	5.4	Crude oil	3000
P1	HV	105	2.6	20	LPG	52

As shown in the table, the flood with a return time of 500 years was assumed as the reference scenario for flood hazards. It should be noted that the reference flood scenario associated with this return time is the most severe flood scenario usually considered in flood hazard analysis in the context of Natech risk assessment (Antonioni et al., 2015; Landucci et al., 2014, 2012). In the case of earthquakes, the event with a 10% exceedance probability in 50 years is assumed as a reference case, which roughly corresponds to a 500 years return time, that, for the sake of simplicity, was assumed as the reference value of return time in the analysis of the case-study (Krausmann et al., 2017). Thus, the frequency of both the natural hazards assumed in the case-study results of 2.0×10^{-3} y^{-1}, allowing a straightforward comparison of the results obtained for the two different natural hazards.

Table 5.3. 4: Reference scenarios selected for flood and earthquake in the case study, and consequent LOC and primary scenario probabilities calculated for tank T1 in Table 3. An ignition probability of 0.9 is assumed. t_r = return time; f_{nh} = frequency of the natural hazard; P_{nhd} = Damage probability of T1; $f_{I,LOC}$ = frequency of the primary LOC from T1; $f_{I,PF}$ = frequency of the primary pool fire from T1.

ID	Description	Severity of the natural event	t_r [y]	f_{nh} [y^{-1}]	P_{nhd}	$f_{I,LOC}$ [y^{-1}]	$f_{I,PF}$ [y^{-1}]
W1	High depth flood	$h_w = 2.0\ m$ $v_w = 0.5\ m/s$	500	2.00E-03	2.40E-01	4.79E-04	4.31E-04
E1	Severe earthquake	$PGA = 0.5\ g$	500	2.00E-03	1.74E-01	3.47E-04	3.13E-04

Since this section aims to assess the probability and frequency modification of escalation scenarios due to barrier degradation rather than to perform a complete QRA, for the sake of simplicity a single primary event due to Natech is considered in the analysis of the case study. Therefore, a single primary Natech scenario involving the atmospheric tank T1 only has been assumed, while T2 and P1 are the possible targets for domino effect escalation. Whilst this simplification was required for the sake of simplicity, it should be remarked that the developed methodology is applicable also considering the other primary Natech scenarios generated by tanks T2 and P1 and the following domino effects.

The target items T2 and P1 are equipped with the safety barriers reported in Table 5.3. 5. Both these tanks are assumed to be protected with pressure safety valves (PSV), while tank T2 is equipped with foam-water sprinklers (FWS), and P1 with water deluge system (WDS) and high rating passive fire protection material (PFP). Emergency response plan to a fire involving tank T1 foresees the intervention of external emergency teams (EEI) to further protect both items by using fire monitors.

Table 5.3. 5: Safety barriers considered in the case study. Subscription legend: o= original value; f= in case of flood; e= in case of earthquake. The "X" marks indicate the equipment items for which each safety barrier is considered.

Barrier	Gate	PFD_0	η_0	PFD_f	PFD_e	η_f	η_e	T2	P1
FWS	b	5.42E-03	0.954	3.78E-01	5.03E-01	0.954	0.954	X	
WDS	a	4.33E-02	1	4.02E-01	7.61E-01	1	1		X
PFP	a	0	0.999	0	0	0.849	0.749		X
PSV	a	1.00E-02	1.00	1.00E-02	1.00E-02	1.00	1	X	X
EEI	c	1.00E-01	0;1	1.00E-01	1.00E-01	0;1	0;1	X	X

In Table 5.3. 5 the original *PFD* and effectiveness of each barrier, which have been retrieved from literature sources (DNV, 1997; Landucci et al., 2015; Madonna et al., 2009; Mannan, 2005; Necci et al., 2014b) are reported as PFD_0 and η_0. These values are then modified according to Eqs. 5.3.1 - 3, applying the values of ϕ_f and ϕ_e reported in Table 5.3. 1. The choice of the appropriate gate for each barrier is made according to the specific features of the barrier, the consequence of barrier failure, and the specific functionality of the barrier, which determines how the barrier effectiveness is expressed to model the quality of barrier function (i.e., as a single probability value, or as continuous or discrete probability distributions). For the case of WDS, PFP, and PSV, gate “a” has been selected since their effectiveness can be expressed as a single value. For the specific case of FWS, gate “b” was selected. This choice is made since sprinkler performance is generally expressed as the probability distribution of fire extinguishment in the technical literature (Landucci et al., 2015). Nevertheless, for the sake of simplicity, the minimum value retrieved in the literature is conservatively adopted in this study to assess FWS effectiveness. For the case of emergency intervention, gate “c” has been selected to include partial success in mitigation, as explained in Section 5.3. 3.

The frequencies of the primary Natech scenarios are assessed adopting fragility models available in the literature (see Section 2.2). In the case of floods (W1), the vulnerability model developed in (Landucci et al., 2012), considering buckling as the failure mechanism, has been applied, while in case of an earthquake (E1), the tank is conservatively assumed unanchored and the vulnerability is assessed by the fragility models reported in (Salzano et al., 2003). It should be remarked that any alternative appropriate equipment damage model among those available in the literature could be used for the assessment.
A LOC causing the complete release of the tank content in 10 minutes is conservatively assumed (Antonioni et al., 2015, 2007). An ignition probability of 0.9 is assumed. This choice is in agreement with previous studies, and it is deemed appropriate to highlight the high likelihood of ignition in case of high magnitude compound disasters as earthquakes and floods (Antonioni et al., 2015, 2009a, 2007). Thus, both for flood and for earthquake, the reference primary Natech scenario is a pool fire involving the total inventory of tank T1.

Three possible endpoint scenarios were considered as possible consequences of the primary event, taking into account escalation due to domino effect and the safety barriers considered, involving either tank T2 or P1:

- unmitigated domino scenarios, developing from the escalation of the primary scenario in the absence of activation or with the lack of effectiveness of safety barriers;
- mitigated domino scenarios, that is, scenarios with potentially reduced consequences due to partial activation or reduced effectiveness of safety barriers in the accident sequence;
- no domino scenarios, in which the escalation is prevented due to activation and effective response of the safety barriers.

The consequence assessment of the primary pool fire was carried out using integral models (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005). A single weather condition aggregate has been considered, thus 10°C ambient temperature, 2 m/s wind velocity, and atmospheric stability corresponding to F Pasquill class were assumed. The consequence simulation led to a calculated maximum incident heat radiation on the surface of each target corresponding to $60kW/m^2$.

The *TTF* of targets and the probability of failure as a function of the heat load caused by the primary Natech scenario is evaluated by the approach suggested by (Landucci et al., 2009). Best-case *TFM* values of 65 and 90 min were obtained for P1 and T2 by the simplified approach, based on the features of the fire scenario and on the vessel geometries suggested by (Landucci et al., 2015), not considering the specific conditions of Natech scenarios. A worst-case *TFM* value of 400 min was also estimated, considering the harsh conditions of emergency response in Natech events (see Appendix C).

For the sake of comparison, the possibility of domino effect causing escalation from a pool fire originated by the internal failure of Tank T1 is also considered. A LOC causing the release of the entire inventory of tank T1 in 10 minutes was assumed. A frequency of 2.5×10^{-6} y^{-1} was estimated for the pool fire following the LOC, based on values suggested in the literature for LOC and immediate ignition (Landucci et al., 2016; Uijt de Haag and Ale, 2005). Due to the assumptions introduced, the same heat radiation values calculated for the primary Natech scenarios are associated with this pool fire. In the absence of natural hazards acting on the site, the baseline values for *PDF* and effectiveness of the safety barriers reported in Table 5.3. 5 were assumed in the analysis.

5.3.6 Results obtained for the case study

Probabilities and frequencies of domino scenarios

The methodology described in Sections 5.3.1 - 4 has been applied to the case study defined above. The set of event trees developed to analyze the case study is reported in the following. In order to allow a better comparison of barrier performance, regardless of the initial frequency of the primary scenario, a unitary frequency for the primary event is assumed in Figure 5.3. 3 - Figure 5.3. 6. The actual frequencies can be calculated by multiplying the numbers in the figures by the actual initial frequency. As an example, the frequency of unmitigated escalation scenario from W1 involving P1 (i.e., outcome coded as “FO_P1W1_01” in Figure 5.3. 3) considering barrier degradation, can be calculated as the product of 3.13×10^{-05} (i.e., uppermost outcome in red from gate d_1 in Figure 5.3. 3) by 4.31×10^{-04} y^{-1} (i.e., corresponding to the frequency of pool fire following W1 according to Table 5.3. 4), resulting in 1.35×10^{-08} y^{-1}.

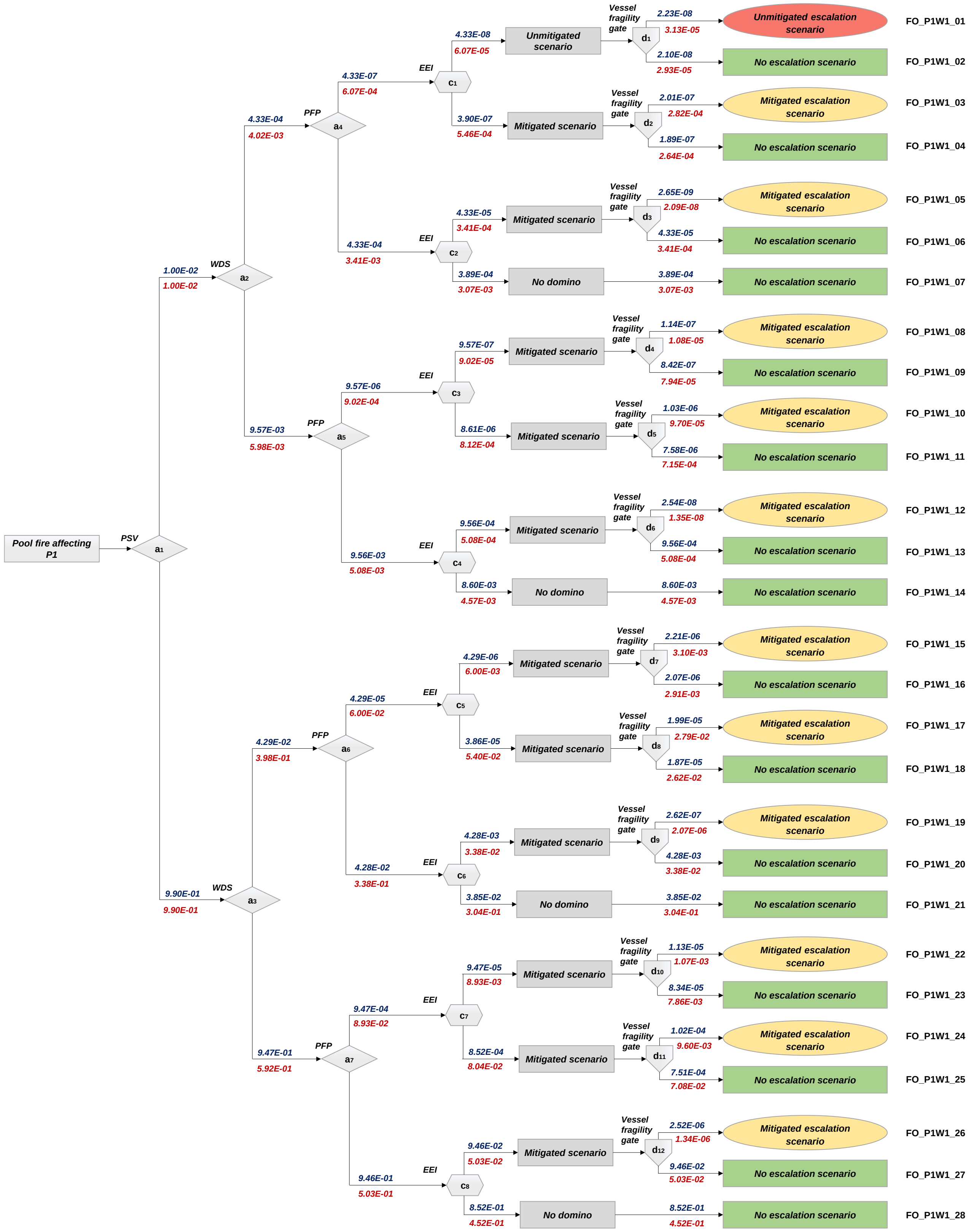


Figure 5.3. 3: Event tree analysis carried out for pressurized vessel P1, in case of W1 flooding conditions (h_w=2.0m, v_w=0.5 m/s). The frequency of the primary event is assumed unitary. Values in blue are calculated with original barrier performances, while values in red are obtained considering performance degradation.

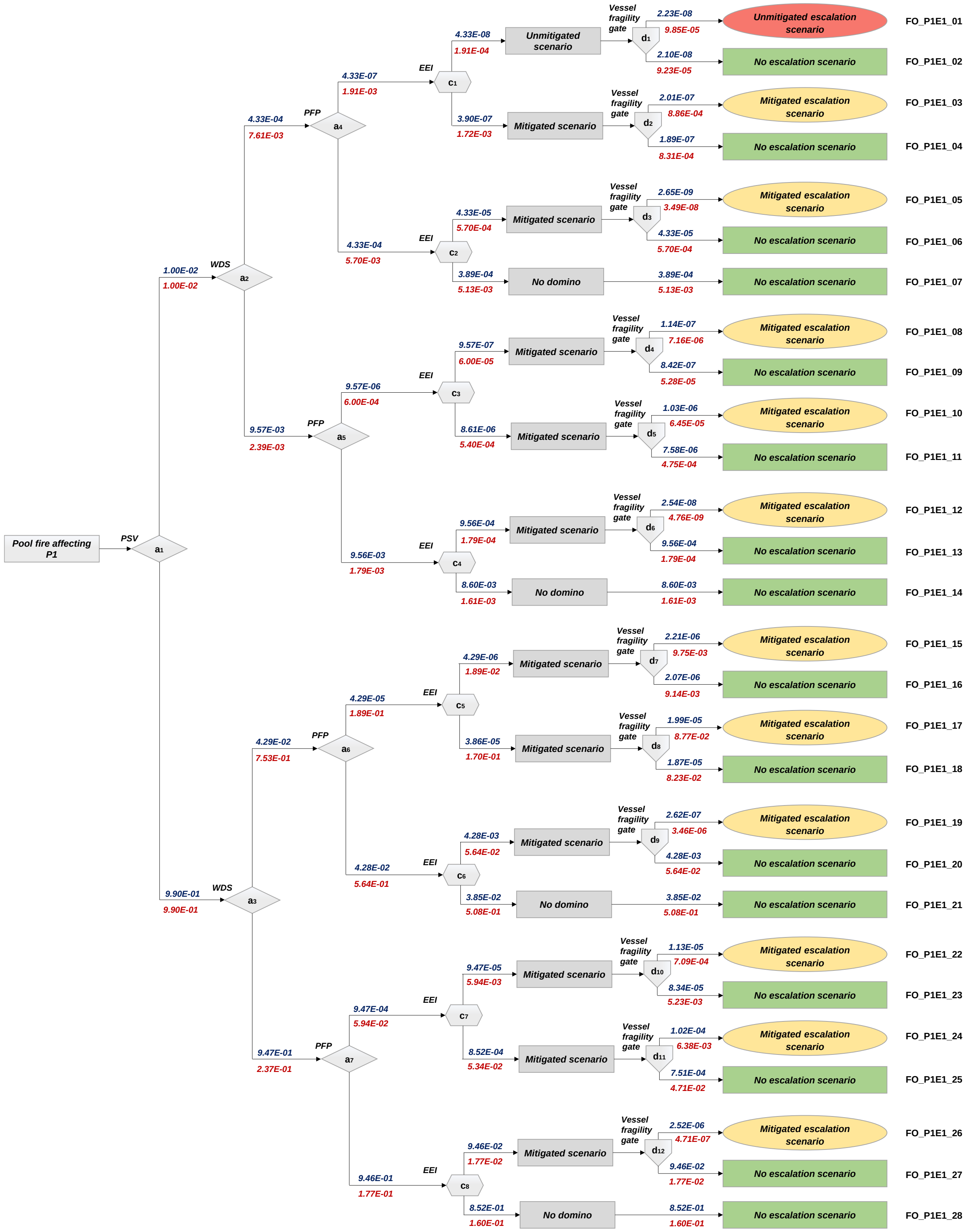


Figure 5.3. 4: Event tree analysis carried out for pressurized vessel P1, in case of E1 earthquake conditions (PGA=0.5g). The frequency of the primary event is assumed unitary. Values in blue are calculated with original barrier performances, while values in red are obtained considering performance degradation.

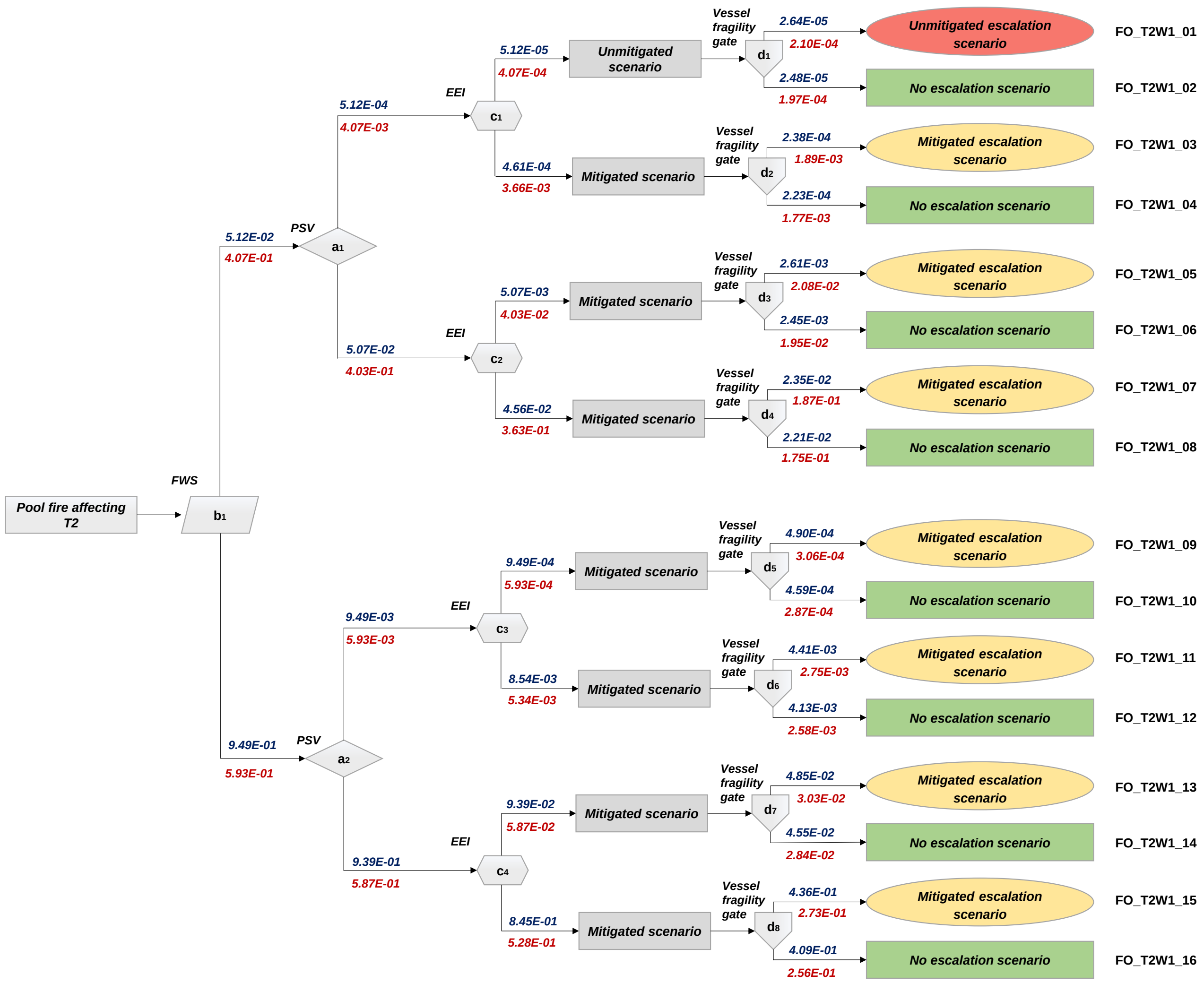


Figure 5.3. 5: Event tree analysis carried out for atmospheric tank T2, in case of W1 flooding conditions (h_w=2.0m, v_w=0.5 m/s). The frequency of the primary event is assumed unitary. Values in blue are calculated with original barrier performances, while values in red are obtained considering performance degradation.

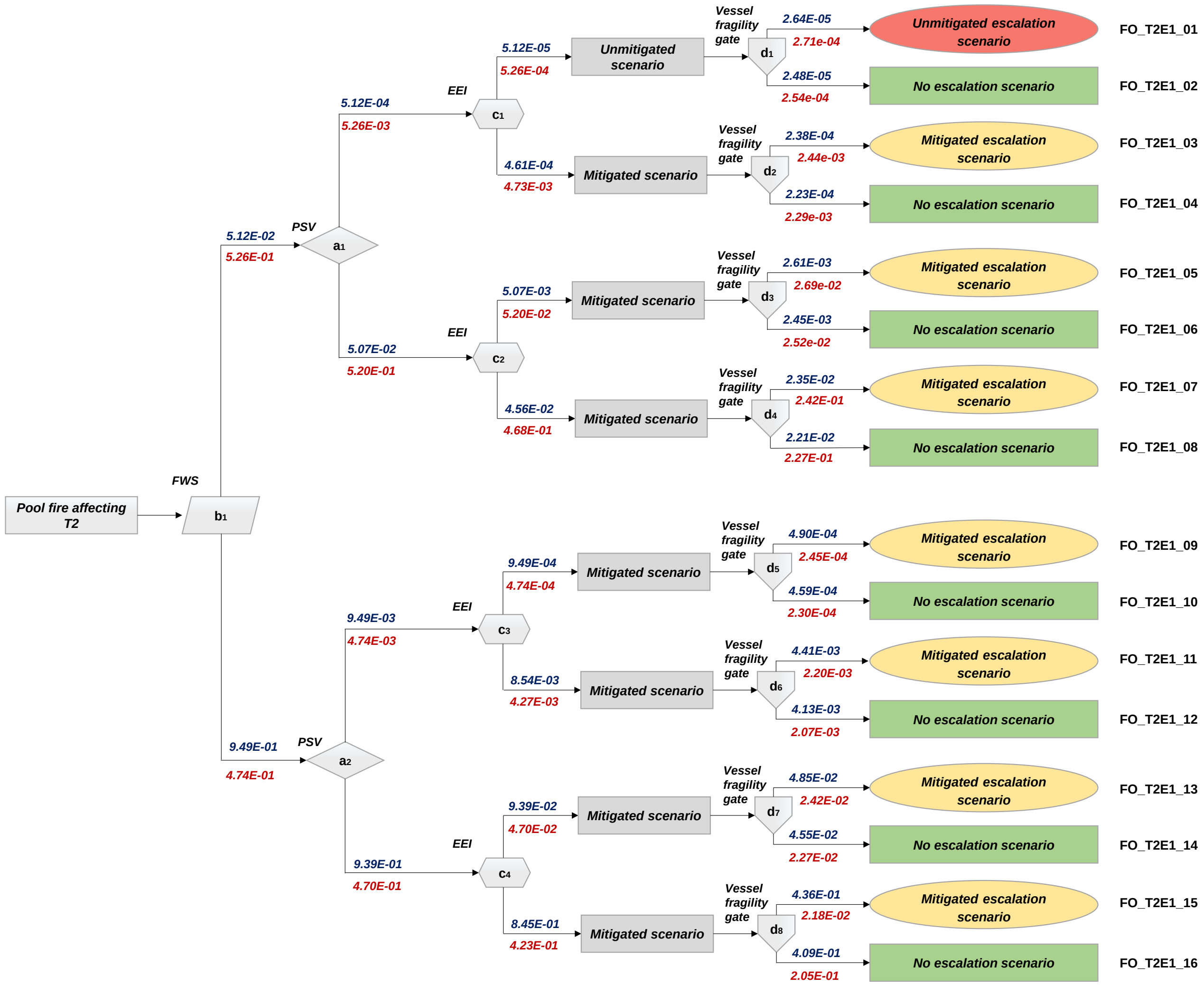


Figure 5.3. 6: Event tree analysis carried out for atmospheric tank T2, in case of E1 earthquake conditions (PGA=0.5g). The frequency of the primary event is assumed unitary. Values in blue are calculated with original barrier performances, while values in red are obtained considering performance degradation.

Since, for the sake of simplicity, the consequences of a single primary event were considered in all the three cases of domino effect analyzed (i.e., due to internal causes, due to flood, or due to earthquake), it is possible to directly compare the probabilities of escalation given the primary event. The results obtained for the conditional probability of the three end-point scenarios considered in the analysis (unmitigated domino scenarios, mitigated domino scenarios, and no domino scenario) calculated considering the possible impact of the natural event on the safety barriers are shown in Figure 5.3. 7. The figure also reports the expected overall frequencies of these final scenarios, considering the frequency estimated for the primary event triggering the domino sequence, either in the presence or in the absence of natural events. Conditional probabilities and frequencies of domino scenarios in case of absence of hardware mitigation (i.e., thus without add-on active and passive barriers) and only accounting for generic data for internal emergency intervention, by the method proposed in (Landucci et al., 2009) are also included in Figure 5.3. 7 as reference values for the sake of comparison.

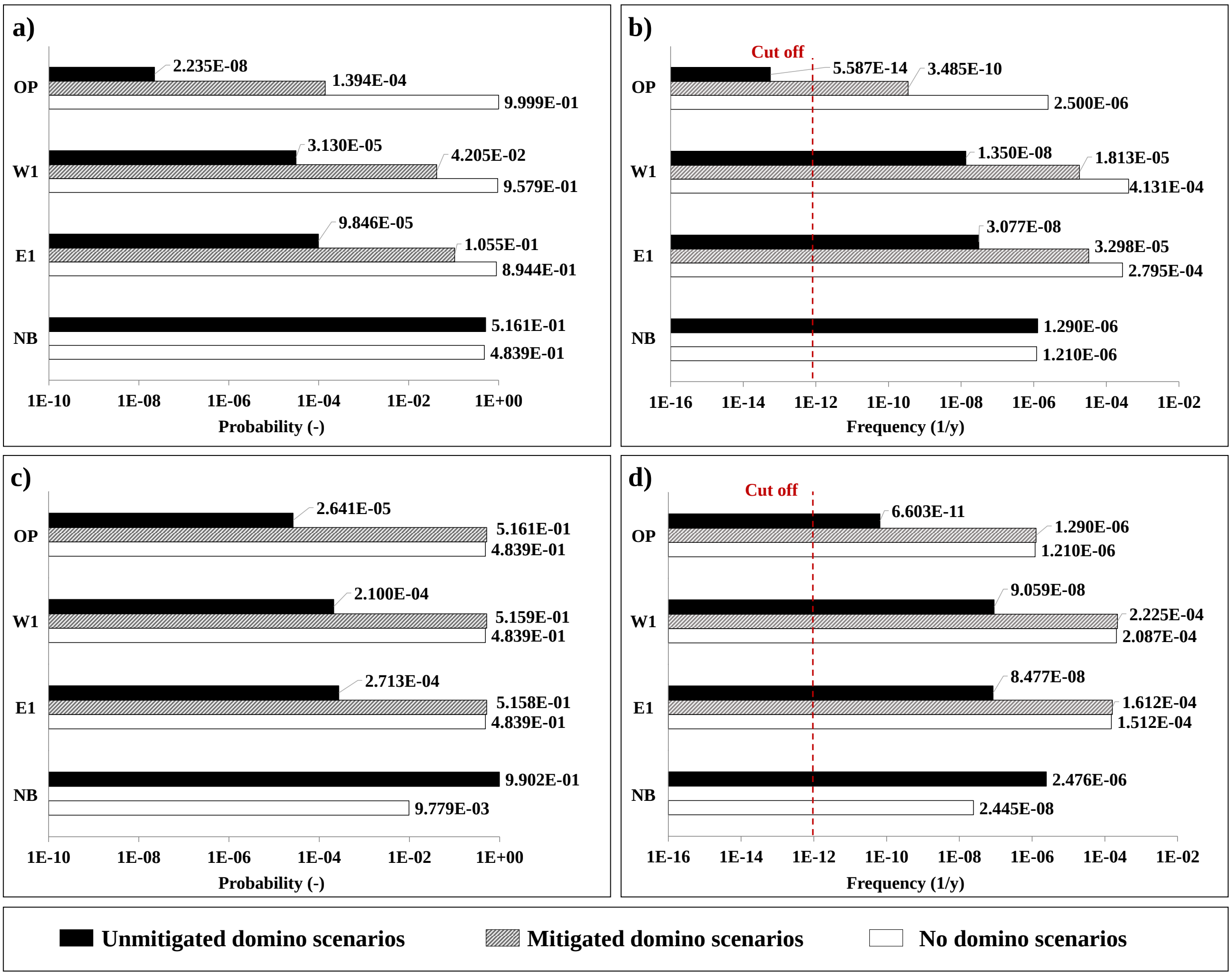


Figure 5.3. 7: Conditional probabilities and overall frequencies of the end-point domino scenarios considered for tanks P1 and T2 following a primary Natech event affecting tank T1, calculated without considering hardware barriers and only generic internal emergency interventions. (a) Conditional probabilities of end-point scenarios calculated for tank P1; (b) Overall frequencies of end-point scenarios calculated for tank P1 considering the frequency of the primary event estimated for tank T1; (c) Conditional probabilities of end-point scenarios calculated for tank T2; (d) Overall frequencies of end-point scenarios calculated for tank T2 considering the frequency of the primary event estimated for tank T1. OP: original performance, i.e. domino effect considered only as a consequence of internal failures and baseline values assumed for safety barrier performance; W1: flood-induced primary Natech scenario; E1: earthquake-induced primary Natech scenario.

As it can be noticed from the figure, the conditional probability associated with unmitigated scenarios exhibits a significant increase due to the impact of flood or earthquake on the barriers considered. For pressurized vessel P1, this increment is of about three orders of magnitude, while in the case of tank T2 it is about five times the original value, suggesting that the degradation of barrier performance might have a greater impact on escalation involving pressurized vessels rather than on atmospheric tanks. Nevertheless, it should be also considered that atmospheric storage tanks are inherently more vulnerable to domino escalation caused by fire (i.e., as shown by the values of probability of unmitigated escalation reported in Figure 5.3. 7), due to their lower mechanical resistance. Thus, the probability of unmitigated escalation scenarios affecting the atmospheric tank T2 is still significantly higher than the value for the pressurized vessel P1, even considering barrier performance degradation.

It is also worth noting that the effect of barrier performance degradation is different for earthquakes and floods, depending on the different effects that such events are expected to have on the degradation of barrier functions, in accordance with the previous findings presented in Section 5.2 (Misuri et al., 2020b).

The overall frequencies of escalation scenarios given primary Natech events are shown in Figure 5.3. 7-b and Figure 5.3. 7-d. The figures also report a baseline cut-off value (1.0×10^{-12} y^{-1}) suggested in the literature (Landucci et al., 2016). As a general remark, it can be observed that the frequencies of unmitigated escalation scenarios triggered by Natech events are at least three orders of magnitude higher than those of unmitigated escalation from conventional primary scenarios due to internal causes. Actually, all escalation scenarios arising from Natech primary scenarios feature higher frequency values compared to those triggered by conventional internal failures. This is a direct consequence both of the higher frequency of natural hazards compared to the frequency of random internal failures (even in case of events having a high time of return, as those considered in the case study), and of the effect of the degradation of safety barriers when impacted by natural events.

As shown in Figure 5.3. 7-b, in the case of vessel P1 the frequency of unmitigated scenarios is negligible in the absence of Natech scenarios. Considering the Natech scenarios and the simultaneous barrier degradation, the frequency of unmitigated scenarios increases by about five orders of magnitude, well above the suggested cut-off value. In Figure 5.3. 7-d a similar trend is present. However, the frequency of unmitigated escalation scenarios is limited but may not be neglected, according to the cut-off criteria selected, also in the case of domino effect due to scenarios caused by internal failures, since the heat load on tank T2 is high and atmospheric tank resistance is lower than that of pressurized vessels.

Thus, starting from the data and assumptions introduced in the case study, the results obtained show that Natech-induced scenarios have frequencies far higher than conventional escalation scenarios. Even if such results should be considered specific for the case study analyzed and derives from the specific assumptions introduced, still some general conclusions may be drawn. In particular, the case study provides evidence that the escalation of Natech scenarios may have an important role in determining the risk figures of a site.

KPI-based monitoring of barrier protection

The approach described in Section 5.3. 4 was applied to monitor the modification of barrier performance during Natech events. The set of KPIs has been calculated both considering baseline barrier performance and the modified performance due to W1 and E1 reference Natech scenarios. Results are shown in the chart reported in Figure 5.3. 8.

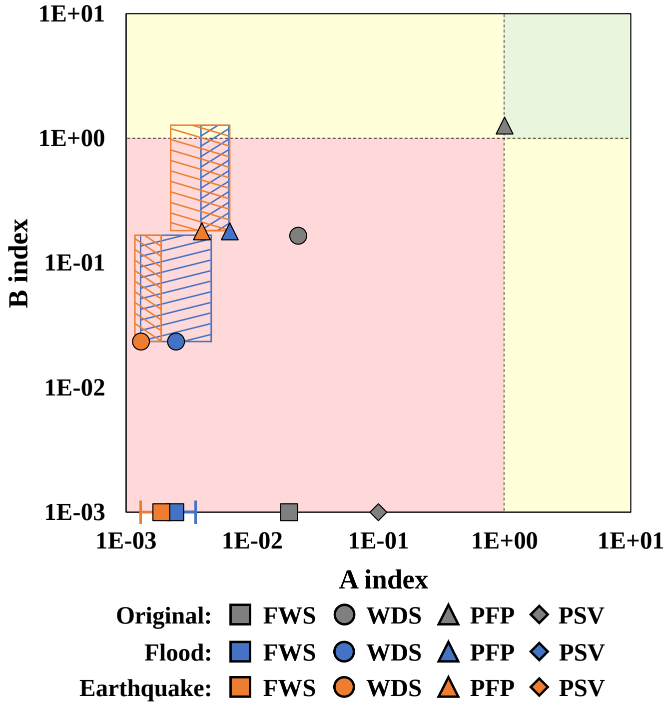


Figure 5.3. 8: Comparison between original and degraded barrier performance as shown by KPI values, A and B, as defined by Eq. 5.3.5 and Eq. 5.3.6 respectively. Legend: FWS = Foam-water sprinkler system, PSV = Pressure safety valve, WDS = Water deluge system, PFP = Passive fire protection. Blue-dashed area = Uncertainty for flood W1, orange-dashed area = Uncertainty for earthquake E1. Uncertainty region for the foam-water sprinkler system is indicated by whiskers.

As can be seen, the chart area is divided into three parts:

- "green area": a region in which both indexes A and B are equal or higher than the reference value of 1. This is the optimal protection region, in which the barrier performance provides an optimal risk reduction;
- "yellow area": intermediate region, in which at least one of the two indexes is below the reference value;
- "red area": region in which both indexes are lower than 1, indicating poor risk-reduction.

Grey markers show the baseline performance of the barriers considered, while blue markers and orange markers show the performance during the natural events W1 and E1, respectively. The performance of barriers aimed at increasing target *TTF* (i.e., WDS and PFP) is represented together with the area of uncertainty on the value (i.e., area covered by pattern in Figure 5.3. 8). The uncertainty on KPI A is expressed calculating the index considering the 1st and the 3rd quartiles of ϕ distributions (see Table 5.3. 1), while KPI B is calculated both considering the original *TFM* (best case) and a *TFM* calculated applying a methodology originally defined for the analysis of cascading scenarios in harsh environment onshore and offshore installations (Landucci et al., 2017a) (worst case). Since the detailed description of such methodology is out of the scope of this chapter, the basics for its application and the resulting *TFM* values for this case study have been directly reported in Appendix C.

For the barriers not significantly providing a direct effect on target *TTF* (i.e., FWS and PSV), a constant minimum value for the B index was set to 10^{-3}. For the FWS, only the uncertainty on KPI A is available. The values of the KPIs are calculated with the same method described above and are represented with whiskers. Both during W1 and E1, in the best case, the PFP falls in the yellow-shadowed area of the KPI plot. However, considering the worst case (i.e., a severely hampered emergency intervention) PFP falls in the red-shadowed area of the plot, indicating that both KPI values are below the reference levels for high protection. PSV is the only barrier that is not affected either by W1 or by E1 in agreement with the outcome of a previous study (Misuri et al., 2020b), as PSV failure was not reported in available data on Natech scenarios.

It is also worth noting that PFP has the best performance in hampering escalation in domino scenarios from internal failures. However, in the case of natural hazards, the performance of PFP in preventing escalation from Natech events is reduced, falling into the red area. Figure 5.3. 8 also shows that in the case study considered the earthquake E1 affects safety systems more severely than flood W1, as it clearly emerges from the more pronounced shift toward lower values of the A index.

5.3.7 Discussion

The results obtained highlight the substantial modification of expected conditional probabilities and overall frequencies of escalation scenarios when considering also primary scenarios induced by Natech events, as in the case of earthquakes and floods affecting a chemical or process facility. The method presented in this chapter provides some key figures needed to develop a comprehensive QRA procedure accounting for Natech events and for the possible domino effects triggered by such scenarios, also considering the action of safety barriers and their degradation during Natech events (i.e., see Section 6.3). As shown in Figure 5.3. 7, both the high expected frequency of Natech primary scenarios in areas exposed to natural hazards (Landucci et al., 2012) and the critical degradation of barrier availability and effectiveness during Natech events (Misuri et al., 2020b) were proven to lead to frequencies of both mitigated and unmitigated escalation scenarios that may be orders of magnitude higher than those corresponding to escalation scenarios from conventional internal failures.

Even if the numerical results of the case study should not be generalized (i.e., the expected frequency of natural events and of Natech accidents may change dramatically depending on the geographical location of the site and on its exposure to natural hazards) still the significance of the escalation scenarios induced by primary Natech is clearly shown by the figures obtained.

It should also be noted that despite the illustrated case study addresses the context of the chemical and process industry, the safety barrier conceptualization is employed in a variety of industrial sectors (Liu, 2020; Saleh and Cummings, 2011; Sklet, 2006). Thus, the approach proposed can be applied to a broad number of industrial systems, also considering that several activities besides those of the chemical and process industry involve the bulk storage and processing of relevant quantities of hazardous substances: Oil & Gas, mining, industrial ports, nuclear, etc. For instance, in the nuclear industry, where there is clear evidence of the potential severity of accidents caused by natural events (Yang, 2014), system safety is traditionally based on the "defense-in-depth" concept (Fleming and Silady, 2002; IAEA, 1996; Saleh et al., 2010). Several studies aim at a more robust safety assessment of these installations, also widening and consolidating the use of probabilistic safety assessment (PSA) in this framework (D'Auria et al., 2017; Mancuso et al., 2017), and specific solutions are proposed to improve the resilience of these installations to natural events (e.g., see (Jabbari et al., 2020)). The specific approach proposed in the present framework is suitable for application within a "defense-in-depth" approach and may contribute to providing a more realistic assessment of the performance of the protection layers when affected by natural events as floods and earthquakes. Indeed, being PSA a reportedly important mean for improving the understanding of system vulnerabilities, as well as a pivotal tool to enhance defence-in-depth principle implementation (Apostolakis, 2004; Yang, 2014), the inclusion within the PSA framework of explicit performance modification of layers of defence during natural hazard might drive better risk-informed decision-making for accident prevention and mitigation.

A further remark concerns the potential importance of the approach in the framework of Safety Integrity Level (SIL) Assessment (Gabriel et al., 2018; Piesik et al., 2016). The use of SIL Assessment to determine and verify the safety performance of safety barriers and protection systems, with particular reference to safety instrumented systems, is a common practice in several industrial sectors, such as the oil&gas, chemical, nuclear, and space industries (Qi et al., 2020). The quantitative approach developed in the present study may be easily complemented with the performance assessment of Safety Instrumented Functions (as several active barriers may be considered), which is needed both in the SIL determination phase based on LOPA, and in the SIL verification phase (Dutuit et al., 2008; Gabriel et al., 2018; Piesik et al., 2016; Qi et al., 2020). Moreover, the outcomes of the present study may be implemented in specific studies dealing with the physical degradation of safety instrumented systems (Srivastav et al., 2020), thus supporting the performance analysis of depleted safety barriers.

5.3.8 Conclusions

A methodology to include the impact of natural hazards on safety barriers in the quantification of the probability and frequency of escalation scenarios caused by domino effect was developed. Specific performance modification factors were implemented and applied to domino effects triggered by Natech primary scenarios. The results highlight that the impact of natural hazards on safety barriers leads to a significant increase in the probability and frequency of unmitigated domino scenarios. As confirmed by the assessment of specific KPIs, safety barrier performance may be significantly depleted during Natech events. In addition, the approach developed may support risk-based decision making addressing the integration of safety barriers and of specific protections aimed at reducing the potential severity of Natech events. Indeed, the results of the case study show that the safety barriers addressing the prevention and mitigation of domino effect from conventional scenarios may not be effective to prevent domino effect from Natech primary scenarios. The development of specific standards to assess the performance of safety barriers during the impact of natural events may contribute to more effective control of risk due to Natech events and to enhance the resilience of chemical and process plants to the impact of natural hazards also in light of their possible modifications due to the effects of climate change.

Chapter 6. Quantitative assessment of Natech risk considering depleted barrier performance and accident escalation

Summarizing the results presented in Chapter 5, it is possible to state that the degradation of safety barriers during floods and earthquakes depends on the type of system considered (i.e., in Section 5.2 it was shown that active barriers are expected to be affected more severely than passive barriers during natural hazards) and on the type of natural hazard (i.e., it was shown that on average earthquakes are deemed to affect more heavily barrier performance in comparison with floods). The degradation of barrier functions in some cases may be critical. This was demonstrated by the use of the performance modification factors elicited from the expert elicitation process that it might have a particularly severe impact on the likelihood of domino effects following primary Natech scenarios (Misuri et al., 2021b). Indeed, the frequency of unmitigated endpoint domino scenarios might reach values well above cut-off reference thresholds used in risk assessment to determine the plausibility of domino effects (see Section 5.3).

Whereas the application of the methodology was performed through a reference case study, these results call for the development of ad-hoc structured procedures to carry out a comprehensive risk assessment of Natech scenarios considering both the inherently cascading nature of the accident and the possible depletion of safety systems in place to prevent and/or mitigate hazardous outcomes from the event chain. Therefore, in this chapter, a set of methodologies to assess the impact of safety barrier depletion on the increase of risk figures related to primary Natech scenarios and with respect to escalation caused by domino effects will be presented, thus addressing the two pathways to escalation of primary events foreseen in the new paradigm for Natech assessment introduced in Section 4 (see Figure 4. 4). The former issue will be addressed in Section 6.1. A formalization of a QRA methodology to approach the assessment of domino effects in Natech accidents (i.e., preliminarily overlooking the issue of safety barrier depletion) will be introduced in Section 6.2. Finally, a refined approach to the assessment of the risk of domino effects in Natech scenarios including barrier depletion will be provided in Section 6.3.

6.1 Escalation of primary Natech scenarios considering safety barrier depletion

In this section, a specific approach to perform the QRA of primary Natech scenarios considering the presence and the depletion of safety barriers during natural hazards will be presented. The approach differs from the baseline methodologies to perform Natech QRA presented in Section 2.2.2 since it includes a detailed characterization of primary scenarios considering all the outcomes from post-release event trees, embedding also the role of implemented safety barriers in modifying their frequencies and consequences.

6.1.1 Overview of the methodology

The methodology developed to perform the QRA of Natech scenarios considering the presence of safety barriers is shown in Figure 6.1. 1.

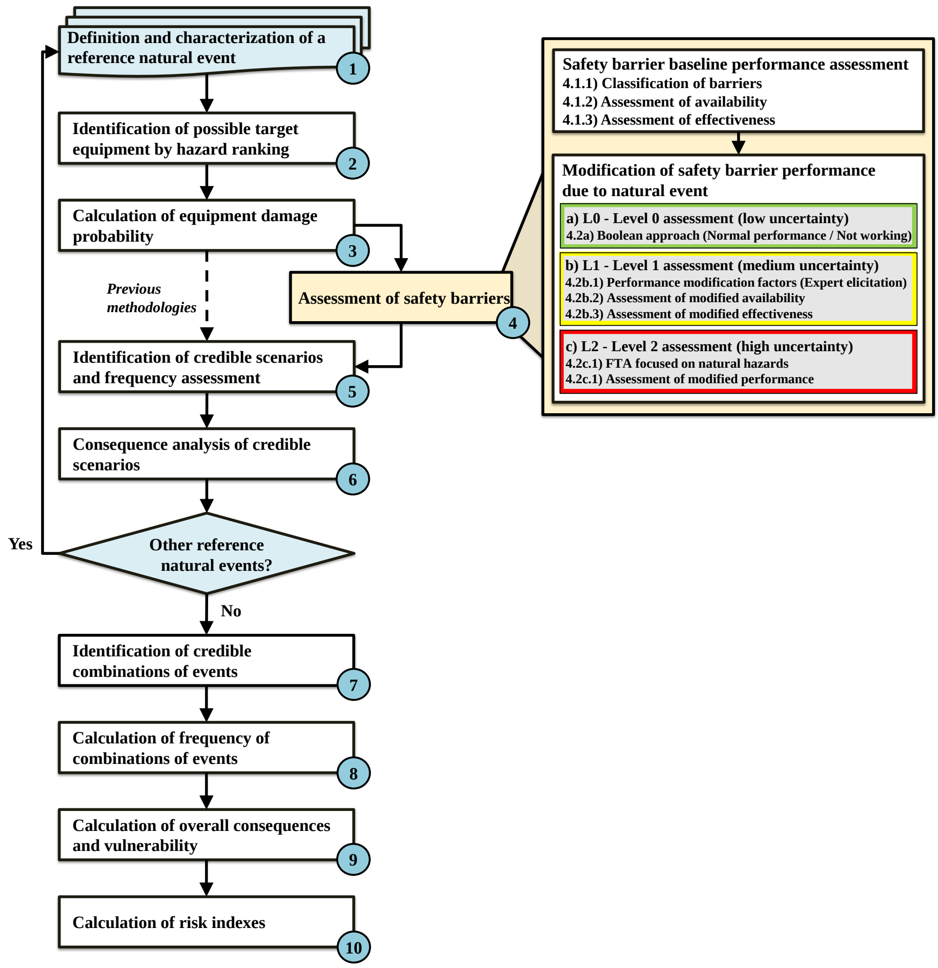


Figure 6.1. 1: Flowchart of the methodology proposed for the risk assessment of primary Natech scenarios integrating a specific step to assess the performance of safety barriers as a consequence of the natural event.

Similarly to the other Natech QRA procedures presented in Section 2.2.2, the methodology starts with the definition and characterization of a reference set of natural hazards (Step 1 in Figure 6.1. 1). Specific approaches are available for this task (see Section 2.2.2). Once the characterization of natural hazards is completed, a preliminary screening procedure might be performed to limit the number of items to be included in the analysis, focusing on the items which are expected to provide the more severe contributions to risk figures (CCPS, 2000; Uijt de Haag and Ale, 2005), as indicated by Step 2 of Figure 6.1. 1. Examples of factors to be considered in this preliminary step are the type of equipment, the amount of stored substances, and their hazardous properties and operating conditions (e.g., equipment operating pressure). The same approaches developed for Natech QRA described in Section 2.2.2 can be applied also within the framework presented in Figure 6.1. 1.

After the identification of the set of equipment which is representative of the layout, the damage probability of each item exposed to the reference natural hazard P_{nhd} has to be evaluated to obtain the likelihood of having a hazmat LOC (Step 3 in Figure 6.1. 1). The set of vulnerability models available in the literature and reported in Table 2.2. 3 allows accomplishing this task within the framework of Figure 6.1. 1.

6.1.2 Metrics for safety barrier performance assessment

The following step of the developed methodology is aimed at addressing the quantification of safety barrier performance during primary Natech scenarios (Step 4 in Figure 6.1. 1).

The conceptualization of safety barriers has been extensively discussed in Chapter 5, to which the reader is referred for the main concepts and definitions related to this topic. Performance of safety barriers is usually assessed leveraging data from reliability databases or through specific methodologies (De Dianous and Fiévez, 2006; Hollnagel, 2008; IEC, 2003). However, such data sources do not consider the possible influence of natural events on the performance of the barriers, as extensively discussed in Chapter 5.

A novel methodology was thus developed to allow the quantitative assessment of barrier performance in Natech QRA, as presented in Figure 6.1. 1. The methodology considers both the results obtained in Section 5.2 and the approaches presented in previous studies to tailor equipment failure frequencies including the effect of environmental factors on their reliability (Misuri et al., 2021c). The barrier assessment starts from the preliminary evaluation of baseline barrier performance, without considering the possible influence of the natural hazards (Step 4.1 in Figure 6.1. 1). In analogy with Sections 5.2 and 5.3, the well-established classification of safety barriers in active, passive, and procedural barriers is suggested also in this case (Misuri et al., 2020b), and the tailored LOPA approach developed in the context of domino escalation assessment is applied also within this QRA framework (Landucci et al., 2016, 2015). The baseline performance of each barrier is thus expressed through *PFD* (i.e., the probability that the barrier will not be available when required to perform its safety function), and the effectiveness η, that is, the conditional probability the barrier is able to perform its safety function once successfully activated.

Once the baseline PFD_0 and η_0 are assessed, a three-level methodology (i.e., Level 0, Level 1, and Level 2 in Step 4.2 of Figure 6.1. 1) is introduced to assess barrier performance modification due to the reference natural event. The three-level approach is introduced to assess the performance of barrier systems with increasing complexity, and requires an increasing amount of information to be applied, from relatively simplified evaluations to detailed system information. The selection of the appropriate level of the analysis should be based on the uncertainty on the possible interaction between the reference natural event and the specific features of the barrier under consideration. Whereas this multi-level approach to barrier assessment has been conceptualized for the case of safety barriers to stop primary Natech scenarios propagation in secondary events from domino effect (Misuri et al., 2021c), it is perfectly applicable also to this case.

The coarsest level, Level 0 (L0), has been conceived to enable a simplified evaluation suitable for simpler barrier systems (Step 4.2a indicated in green in Figure 6.1. 1). The L0 is thus adequate when a low uncertainty is present concerning the quantification of the impact of natural hazards on a barrier. This situation might arise when a feature of the barrier (e.g., the position), on the basis of rules-of-thumb or clear evidence, can justify with sufficient confidence whether the barrier should be considered affected or not during the reference natural event. Conceptually, the L0 can be interpreted as a Boolean approach (Misuri et al., 2021c). Therefore, in the case the *k*-th barrier is considered unaffected, it will retain the baseline performance values $PFD_{0,k}$ and $\eta_{0,k}$ while in case the identified feature indicates that the system would be clearly impacted, the *k*-th barrier should be considered unavailable. In the two-parameter metrics, this is equivalent to setting $PFD_{j,k} = 1$ for active systems and $\eta_{j,k} = 0$ for passive protections.

The intermediate uncertainty level, Level 1 (L1), is based on the performance modification factors obtained for the reference schemes of the safety barriers in Section 5.2 (Misuri et al., 2020b) (Steps 4.2b in Figure 6.1. 1). The L1 level can be interpreted as the application of a proportional hazard model (PHM) (Cox, 1972), where the modification of performance factors ϕ developed in Section 5.2 are the covariates, representing the likelihood that similar reference barriers would fail as a direct consequence of the impact on the site of the reference natural event. This level is suitable for a broad set of barriers, from passive barriers to the simpler active systems, and can be easily implemented in the two-parameter metrics adopted so far.

Indeed, in analogy with the hypothesis made in Sections 5.2 and 5.3, it is assumed that the failure mode of active barriers is the lack of activation. Hence, an increase in the *PFD* is considered for this type of barrier. On the contrary, in the case of passive measures, the possible loss of structural integrity of the barrier is assumed to reduce their effectiveness η.

Thus, as already explained in Section 5.3, the performance parameters related to active barriers are modified according to Eqs. (6.1.1) and (6.1.2) (Misuri et al., 2020b):

$$PFD_{j,k} = 1 + (\phi_{j,k} - 1)(1 - PFD_{0,k}) \tag{6.1. 1}$$

$$\eta_{j,k} = \eta_{0,k} \tag{6.1. 2}$$

where $\phi_{j,k} \in [0,1]$ is the performance modification factor of the *k*-th active barrier for *j*-th reference natural event, and $PFD_{0,k}$ and $\eta_{0,k}$ are the baseline performance parameters of the *k*-th active barrier. Differently, for the case of passive barriers, the modification of performance parameters is addressed through Eq. (6.1.3):

$$\eta_{j,k} = \left(1 - \phi_{j,k}\right) \eta_{0,k} \tag{6.1. 3}$$

where $\phi_{j,k} \in [0,1]$ is the performance modification factor for *j*-th reference natural event, and $\eta_{0,k}$ is the baseline effectiveness value.

Finally, the most detailed level, Level 2 (L2), is based on the analysis of barrier architecture and subsystems, capable of accounting for site-specific conditions and special design provisions (Steps 4.2c in Figure 6.1. 1). The L2 assessment is required when complex active barrier systems are considered, that is when the evaluation of the actual impact of the reference natural event on the system is affected by a high uncertainty. This approach is also suitable for barriers where the specific system architecture differs from reference configurations, and performance modification factors retrieved in Section 5.2 may not be applicable with confidence. The L2 is based on the application of a fault tree analysis (FTA) focused on the possible failure of subsystems due to the impact of the reference natural event. Following the construction of the fault tree based on barrier architecture, the minimal cut sets (MCSs) are identified. Then, basic events are screened to identify which might be influenced by the impact of the natural event, considering detailed information on barrier subsystems, including position, possible fail-safe design, dependence on lifelines, and redundancies. Following the identification of vulnerable barrier subsystems, the probabilities of the related basic events in the fault tree are updated to unitary values (i.e., indicating expected subsystem failure during the reference natural event) (Misuri et al., 2021c). In formulas, the updated probability $Q_j(MCS_{m,k})$ of the *m*-th MCS of the *k*-th barrier during the *j*-th reference natural event can be assessed by Eq. (6.1.4):

$$Q_j\left(MCS_{m,k}\right) = \prod_p \left(q_{p,0} + \delta_{p,j}\left(1 - q_{p,0}\right)\right) \tag{6.1. 4}$$

where $q_{p,0}$ is the probability of the *p*-th basic event comprised in the *m*-th MCS, and the parameter $\delta_{p,j}$ is equal to 1 in case the *p*-th basic event involves one of the vulnerable barrier subsystems identified for the *j*-th reference natural event, and 0 if not. Finally, the updated *PFD* of the *k*-th barrier, $PFD_{j,k}$, can then be conservatively assessed (through an upper bound assumption) according to Eq. (6.1.5):

$$PFD_{j,k} = 1 - \prod_m \left(1 - Q_j\left(MCS_{m,k}\right)\right) \tag{6.1. 5}$$

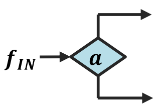
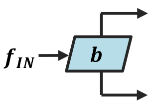
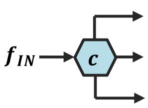
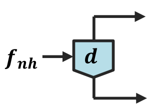
The output of the L2 assessment is thus a scenario-based quantification of barrier updated unavailability given the reference natural event, calculated starting from the impact of such event on each system component (Misuri et al., 2021c).

Due to the high site-specificity of procedural barriers, no generalized methodology was developed for their assessment. An ad-hoc assessment is recommended, analyzing how the reference natural event might influence the key tasks required for implementing the safety function (e.g., the series of actions necessary in emergency intervention).

6.1.3 Characterization and quantitative risk assessment of escalation scenarios

Once the performance of safety barriers is assessed by the methodology described above, an ETA approach analogous to that presented in Section 5.3 can be implemented to assess the identification of expected primary Natech events and for the quantification of their probabilities and frequencies (Step 5 in Figure 6.1. 1). The operators reported in Table 5.3. 2 can be tailored also to this purpose (Landucci et al., 2016), obtaining the rules reported in Table 6.1. 1.

Table 6.1. 1: Modification of the operators presented in Section 5.3.3 to be used in the ETA of primary Natech scenarios. f_{IN}: gate input frequency, f_{nh}: reference natural event frequency, PFD: Probability of failure on demand, η: effectiveness parameter, P_{nhd}: equipment to the reference natural event.

Gate type	Representation and quantification	Description
a	 $Out_1 = f_{IN} * [PFD + (1-\eta) * (1-PFD)]$; $Out_2 = f_{IN} * (1-PFD) * \eta$	Simple composite probability gate (type "a"): unavailability, expressed as *PFD*, is combined with a single probability value for η.
b	 $Out_1 = f_{IN} * [PFD + (1-\eta) * (1-PFD)]$; $Out_2 = f_{IN} * (1-PFD) * \eta$	Composite probability distribution gate (type "b"): unavailability, expressed as *PFD*, is combined with a probability distribution expressing η. It is also possible to use an integrated value for η.
c	 $Out_1 = f_{IN} * PFD$; $Out_2 = f_{IN} * (1-PFD) * (1-\eta)$; $Out_3 = f_{IN} * (1-PFD) * \eta$	Discrete probability distribution gate (type "c"): depending on barrier η, three or more events may originate.
d	 $Out_1 = f_{nh} * P_{nhd}$; $Out_2 = f_{nh} * (1-P_{nhd})$	Vessel fragility gate (type "d"): based on the resistance of the equipment to the reference natural event, P_{nhd} is calculated through equipment vulnerability models.

The definitions of gate types "a", "b", and "c" do not vary, thanks to the generality of the barrier performance metrics which is appropriate also to model the escalation of primary scenarios. The only difference is related to the "d" gate that had been originally developed to include in the ETA the target capability of withstanding a given scenario (e.g., the radiation from a primary fire) and thus to model the residual resistance of the vessel to the escalation (i.e., possibility that the escalation might be avoided also in case all the protections are defective) (Landucci et al., 2016).

In the context of the ETA applied to the identification of primary Natech scenarios escalation due to barrier failures, the gate "d" might be used also to model the possibility that during the reference natural event targets will not undergo any failure leading to a LOC. Thus, the "d" gate is modified to embed the conditional probability of equipment failure due to the reference natural event P_{nhd}, estimated in Step 3 in Figure 6.1. 1 applying equipment vulnerability models (see Table 2.2. 3), instead of the conditional probability of failure when exposed to an escalation vector P_D as in Section 5.3. In perspective, the "d" gate might be also used as a general proxy between different escalation levels (e.g., using P_{nhd} from the natural event to the primary scenarios, and P_D of targets from primary scenarios to further escalation levels).

Clearly enough, the primary Natech events occurring from the failure of the process or storage equipment involved in the accident depend on the expected severity of the LOC: this information is sometimes included in the vulnerability models applied (Salzano et al., 2009), while in other cases assumptions are made considering the typology of mechanical failure that the item is expected to undergo (Antonioni et al., 2015; Landucci et al., 2014), on the type of substance involved, and on the set of barriers implemented on that specific item. Thus, considering a generic *k*-th primary target, the set of m_k possible outcomes is determined, and their likelihood is calculated directly applying the ETA. Further details will be provided in the description of the case study reported in the following.

Once each possible outcome is identified, and its likelihood is calculated through the ETA, it is possible to proceed with the consequence analysis (Step 6 in Figure 6.1. 1). The analysis of the physical effects of each outcome is performed through the application of established literature models in analogy with the previous Natech QRA approaches described in Section 2.2.2. As a difference, it should be noted that the action of some barriers might influence the consequences of outcomes, thus this effect has to be considered in this step of the analysis. For instance, in the case of water curtains aimed at reducing the vapor formation from a pool of toxic liquid, the reduction in evaporation should be accounted for in running appropriate dispersion models. Some examples will be described in the analysis of the case study.

After completing the characterization of each Natech events taken singularly, the methodology proceeds with the evaluation of the possibility of multiple simultaneous scenarios (Steps 7 – 9 in Figure 6.1. 1). It is worth noting that these steps differ substantially from those adopted in the general approach to Natech QRA presented in Figure 2.2. 1. In particular, the inclusion of safety barriers into the problem requires to relax the assumption of binary targets (i.e., the assumption that each piece of equipment can feature two possible states only: being involved in the accident leading to the worst-case scenario or being not involved in the accident) and to account for the possibility of mitigated outcomes. Considering the presence of n items, a single Natech scenario can involve the contemporary damage of k out of n units resulting in k final outcomes. In this situation, relaxing the assumption of binary targets, the total number of hazardous combinations N_{Natech} can be assessed according to Eq. (6.1.6):

$$N_{Natech} = \prod_{k=1}^{n} m_k - 1 \qquad (6.1.6)$$

where m_k is the number of possible outcomes of the k-th primary target impacted (i.e., the safe state is considered as a possible outcome, although the situation of all the elements in the safe state does not count as an overall primary Natech scenario). It might be easily verified that in case all the targets featured only two outcomes, the equation would lead to the same result as the worst-case binary approach shown in Section 2.2.2. In the presence of mitigated scenarios, m_k depends on the type of target, on the set of safety barriers, and on their specific safety functions and might not be defined a priori. It is always possible to identify a set of unmitigated outcomes, a set of mitigated outcomes, and a set of non-hazardous outcomes. Further details on this point will be provided in the analysis of the case study. It should be noted that this approach is similar to that proposed for the characterization of mitigated domino scenarios, although in that case the maximum number of outcomes to be considered for each piece of equipment was assumed at 3 (Landucci et al., 2017b).

Each Natech scenario can be represented as a vector $\boldsymbol{N^n}$ of n elements representing the combination of events involving each of the possible n targets during the reference natural event. Thus, according to what was reported in Eq. (6.1.6), N_{natech} different $\boldsymbol{N^n}$ vectors will be possible during the reference natural event. Each generic k-th element N_k^n of a vector $\boldsymbol{N^n}$ represents the state of the k-th target during the reference natural event. As consequence, the joint probability of a generic Natech scenario $P(\boldsymbol{N^n})$ can be computed by Eq. (6.1.7):

$$P(\boldsymbol{N^n}) = \prod_{k=1}^{n} P(N_k^n) \qquad (6.1.7)$$

where $P(N_k^n)$ is the probability of a given state of the k-th target, assessed using the ETA. It should be noted that the gates as defined in Table 6.1. 1 lead to the calculation of the frequency of each state for a generic k-th target (i.e., useful if each target is considered individually). Thus, to obtain a probability value $P(N_k^n)$ of a generic state of the target to be used in Eq. (6.1.7), a unitary value should be adopted in the gate "d" in place of f_{nh}. The frequency of the natural hazard f_{nh} obtained from the characterization performed in Step 1 of Figure 6.1. 1 is then reintroduced in the analysis by Eq. (6.1.8) to calculate the frequency of a generic overall Natech scenario $f(\boldsymbol{N^n})$:

$$f(\boldsymbol{N^n}) = f_{nh} \times P(\boldsymbol{N^n}) \tag{6.1. 8}$$

Regarding the evaluation of the consequences of overall Natech scenarios (Step 9 of Figure 6.1. 1), as already pointed out in Section 2.2.2, conventional models cannot be directly used for the assessment of the consequences of a generic combination of *k* possibly heterogeneous outcomes (e.g., fires, explosions, toxic releases). Thus, in analogy with the normal Natech QRA approach presented in Section 2.2.2., the death probability $V(\boldsymbol{N^n})$ in a generic position related to a generic overall Natech scenario is computed as the normalized sum of the death probabilities related to each of the outcomes taking part in it:

$$V(\boldsymbol{N^n}) = \min\left(\sum_{k=1}^{n} V(N_k^n)\,, 1\right) \tag{6.1. 9}$$

where $V(N_k^n)$ is the death probability related to the state of the *k*-th target (i.e., the death probability in case the *k*-th target is in state "0" is clearly equal to zero).

Once the overall Natech scenarios are characterized, the calculation of the overall risk level may be performed (Step 10 in Figure 6.1. 1). As for the other QRA methodologies, the risk level is expressed by the individual risk and the societal risk. These two metrics will be here recalled for the sake of completeness. The former can be expressed by mapping local specific individual risk (LSIR) following standardized procedures, while the latter can be expressed with F/N plots, being $F(N)$ is the cumulative frequency of scenarios causing N or more expected fatalities, which is calculated directly from the frequency $f(N)$ of scenarios causing N fatalities (CCPS, 2000; Mannan, 2005; Uijt de Haag and Ale, 2005). Lastly, a summarized quantification of societal risk figures is obtained computing the *PLL* and *EV* indexes according to Eqs. (6.1.10) and (6.1.11) (Carter and Hirst, 2000):

$$PLL = \sum_N f(N)N = \sum_N F(N) \tag{6.1. 10}$$

$$EV = \sum_N f(N)N^a \ with\ a = 2 \tag{6.1. 11}$$

As might be clear from the two equations, the main difference between the two indices is that when assessing the *EV* the exponent associated with the number of fatalities N is higher than one, thus weighting more the number of fatalities that the frequency $f(N)$, while in the *PLL* these two contributions are assumed to have equal importance. Therefore, the indicator *EV* gives more relevance to the severity of scenarios and has been specifically conceived to account for the heavier social perception of high magnitude accidents (Hirst and Carter, 2002).

All the computational procedures required to calculate risk figures and risk indices can be accomplished employing the same tools adopted for the normal Natech QRA, which are consistent with the ARIPAR methodology (Antonioni et al., 2007; Cozzani et al., 2014; Egidi et al., 1995; Spadoni et al., 2000).

6.1.4 Definition of case studies

The layout considered for the development of a case study is depicted in Figure 6.1. 2. As can be noticed, four atmospheric storage tanks (T1 to T4 in Figure 6.1. 2) and three horizontal pressurized vessels (P1 to P3 in Figure 6.1. 2) are included in the analysis.

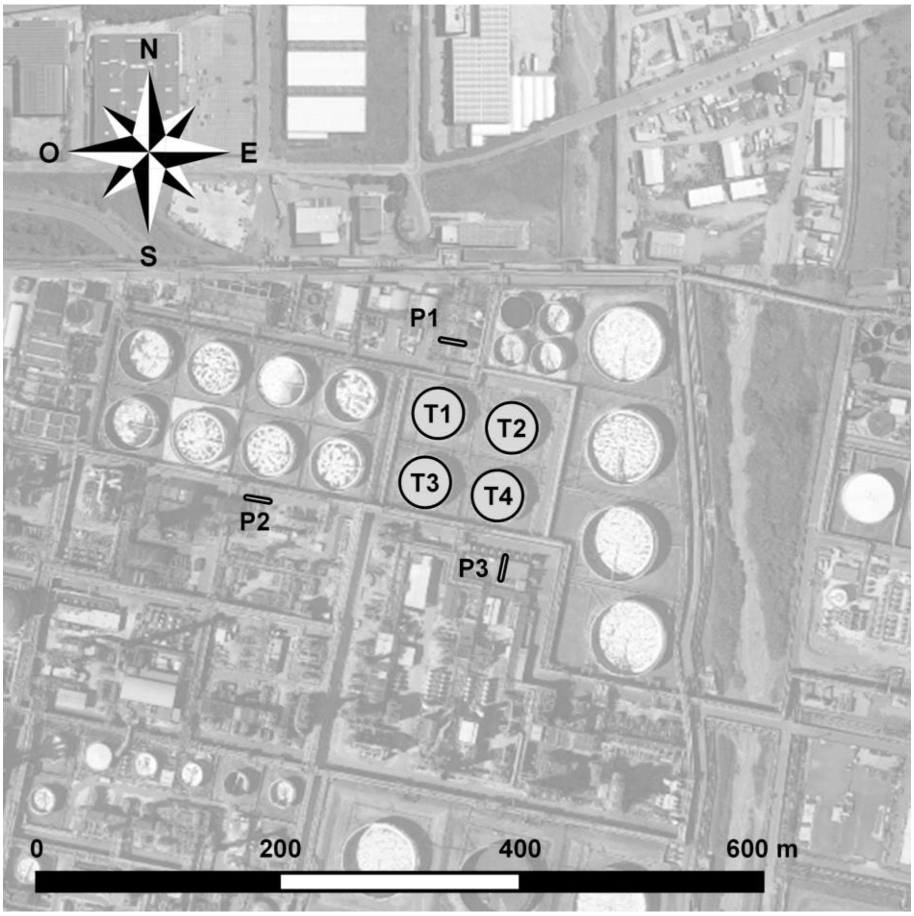


Figure 6.1. 2: Layout considered in the case study. Equipment features are summarized in Table 6.1. 2.

The substances stored and the dimensions of the equipment are presented in Table 6.1. 2. As can be noticed, the four atmospheric storage tanks (T1 – T4) store gasoline, while two out of the three pressurized vessels (P1 – P2) store ammonia, and one (P3) stores propane. Moreover, also the area of the catch basins is reported for the case of atmospheric tanks.

Table 6.1. 2: Equipment items considered in the case study represented in Figure 6.1. 2; D = Diameter; H = height; L = length; m_t = stored mass; p_o = operating pressure; V_n = nominal volume; ρ_L = liquid density; ρ_V = vapour density, Atm = Atmopsheric storage tank; HV = Horizontal vessel.

ID	D [m]	H or L[m]	V_n [m^3]	Substance	ρ_L [kg/m^3]	ρ_V [kg/m^3]	p_o [bar]	m_t [t]	Item typology	Catch basin area [m^2]
T1	42	7.2	9975	Gasoline	750	-	1.01	5610	Atm	3200
T2	42	7.2	9975	Gasoline	750	-	1.01	5610	Atm	3200
T3	42	7.2	9975	Gasoline	750	-	1.01	5610	Atm	3200
T4	42	7.2	9975	Gasoline	750	-	1.01	5610	Atm	3200
P1	3.2	22	170	Ammonia	600	4.9	8.5	91.9	HV	-
P2	3.2	22	170	Ammonia	600	4.9	8.5	91.9	HV	-
P3	2.6	19.2	100	Propane	497	18.9	8.4	44.9	HV	-

To exemplify the application of the methodology, an earthquake has been selected as the reference natural event. In particular, a seismic event with a time of return of 500 years (f_{nh} = 2.00 × 10^{-3} y^{-1}) and an expected PGA value of 0.5g (~4.9 m/s^2) was considered. Clearly enough, the methodology can be applied also to other categories of natural hazards generating Natech events.

Three cases were defined in the following to ease the interpretation and the discussion of the results:

- Case 1: primary Natech scenarios assuming the absence of safety barriers, to define a worst-case situation associated with the impact of the seism on the site;
- Case 2: primary Natech scenarios assuming the presence of safety barriers with baseline performance (i.e., not considering the possibility that the earthquake might impair their operation), to defined a best-case situation;
- Case 3: primary Natech scenarios assuming the presence of safety barriers and accounting for the possibility of their depletion through the methodology presented in Section 6.1.2.

In addition to the above-described cases, a baseline QRA was also developed. This case is termed as case 0 in the following. Case 0 was carried out considering conventional scenarios generated by LOCs from the equipment included in the layout, considering the safety barriers implemented for their mitigation (see Table 6.1. 3 in the following) with their baseline performance (see Table 6.1. 5 in the following) in normal operating conditions (i.e., not affected by the natural event). The description of the procedure applied to carry out the QRA of case 0, based on consolidated guidelines for risk assessment (Uijt de Haag and Ale, 2005) and on specific methodologies for ignition probability estimation (Energy Institute, 2019), is documented in detail in Appendix D.1. The contribution of case 0 is considered in all the cases defined above.

It should be also noted that in case 1 the complete post-release event trees have been considered in primary Natech scenario characterization, relaxing the assumption of a single reference outcome (i.e., a worst-case event) on which most of the methodologies shown in Section 2.2.2 are based. This choice has been made to avoid that the arbitrary reduction in the number of scenarios influences the possible impact of barrier degradation on the overall risk figures. For the sake of completeness, the results obtained for case 1 are validated against the figures obtained following the simplified approach shown in Section 2.2.2 (e.g., the methodologies presented in (Antonioni et al., 2015, 2009a)), showing a nearly-perfect agreement, as discussed in Appendix D.2.

In order to obtain the probabilities and frequencies of the final scenarios related to cases 1, 2, and 3, specific values of ignition probabilities retrieved from the comprehensive database analysis performed in (Ricci et al., 2021) were adopted. Further details on ignition probability values will be given in the discussion of case 1 reported in Appendix D.2.

The consequence analysis of each scenario was performed applying well-established literature models for physical effect modeling (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005). For the sake of simplicity, a uniform wind distribution and a single set of meteorological conditions have been considered, assuming wind speed at 5 m/s and neutral atmospheric stability (i.e., Pasquill class D) (Uijt de Haag and Ale, 2005; Van Den Bosh and Weterings, 2005). In addition, the atmospheric temperature was assumed at 20°C and relative humidity at 70%. Clearly enough, these assumptions have been made only for exemplification purposes and different meteorological conditions might be equivalently considered.

Both probit and threshold-based models available in the literature were applied to assess human vulnerability. Further details on the models adopted are provided in Appendix D.1. In order to obtain societal risk figures, a uniform population density equal to 200 people/ha^2 with a 60% presence probability was assumed (i.e., local-specific effects due to possible areas featuring higher population density are not considered). The methodology presented in (Egidi et al., 1995; Misuri et al., 2020a) was applied to perform risk calculations. Other approaches to accomplish this step are available in the literature and can be applied without conceptually modifying the methodology presented in Figure 6.1. 1 (CCPS, 2000).

For the sake of brevity, only the probabilistic assessment of case 3 will be described in the following, limiting the presentation of case 1 and case 2 to the discussion of the results. Further details on the intermediate results for cases 1 and 2 are reported in Appendix D.2 and Appendix D.3.

The set of safety barriers associated with each piece of equipment considered is shown in Table 6.1. 3. Only technical barriers have been included in the case study to show the application of the barrier assessment methodology. As can be seen, catch basins and foam-water systems (FWS) are considered for atmospheric equipment, while for the case of pressurized vessels the presence of water curtains (WC) to mitigate releases is assumed. In addition, it is assumed that WC are designed to mitigate severe continuous releases (e.g., 10-minute releases). Indeed, in case of catastrophic ruptures, the consequent violent vaporization of liquefied ammonia and LPG is deemed to prevent any possibility of mitigation (Landucci et al., 2017b).

*Table 6.1. 3: Safety barriers considered for each item included in the layout. FWS = Foam-water systems; WC = Water curtains. *The WCs are assumed to be designed considering a 10-min continuous LOC, while the mitigation of instantaneous releases from catastrophic rupture of pressurized vessels is not deemed credible* (Landucci et al., 2017b).

ID	Catch basin	FWS	WC
T01	X	X	
T02	X	X	
T03	X	X	
T04	X	X	
P01			X*
P02			X*
P03			X*

6.1.5 *Results obtained for the case study*

To assess the vulnerability of equipment, the probit models developed in (Salzano et al., 2009) for the specific case of earthquakes were applied to the case study, obtaining the characterization and the P_{nhd} values reported in Table 6.1. 4. For what concerns items T1 to T4, a catastrophic rupture has been considered as a LOC. Indeed, according to (Salzano et al., 2009), if the PGA exceeds a value of 0.118g, a severe release state (RS) (i.e., RS=3 in the original publication) might be expected from unanchored atmospheric steel tanks (i.e., anchoring systems are not considered to have conservative results). On the contrary, for pressurized vessels P1 to P3, a continuous 10-minute release was considered, since the threshold PGA value of 0.526g required for RS = 3, in this case, is not exceeded (Salzano et al., 2009).

Table 6.1. 4: Characterization of the LOCs expected from the equipment considered in the case study. k_1, k_2 = coefficients of the probit equation for fragility assessment (Salzano et al., 2009); RS = Release State (Salzano et al., 2009); P_{nhd} = Probability of LOC given the reference natural event.

ID	k_1	k_2	RS	LOC assumed	P_{nhd}
T1 – T4	5.51	1.34	3	Catastrophic rupture	3.38E-01
P1 – P3	4.50	1.12	≥2	10-min continuous release	1.01E-01

Assessment of safety barrier performance

The main outputs from the barrier performance assessment step are summarized in Table 6.1. 5. For each barrier, the original performance values are reported (these are adopted in case 2) together with their classification according to the discussion in Section 6.1.2. Barrier performance is then modified according to one of the three levels of analysis shown in Step 4 of the methodology of Figure 6.1. 1, as is reported in Table 6.1. 5.

Table 6.1. 5: Safety barriers performance assessed by means of the methodology presented in Section 6.1.2. FWS = Foam-water systems; WC = Water curtains; PFD = Probabilty of failure on demand; η = effectiveness.

Barrier	**Classification**	**Gate**	PFD_0	η_0	**Level of Analysis**[a]	PFD_{eq}	η_{eq}
Catch basin	Passive	a	0	9.99E-01	L1	0	0.5
FWS	Active	b	5.42E-03	9.54E-01	L2	1.00	9.54E-01
WC	Active	a	4.33E-02	1.00	L2	1.44E-01	1.00

[a]Analysis level selected in Step 4 in Figure 6.1. 1.

The L1 analysis is applied to the catch basins to include the possibility that these elements would undergo some structural failures under seismic loads. This barrier features relatively limited complexity, not requiring the application of a more complex assessment procedure. Nevertheless, there is uncertainty on the effects of the impact of the earthquake on it (e.g., catch basins might be constructed with different materials) and the application of L0 was thus considered not appropriate. Therefore, a performance modification factor $\phi_{eq,CatchBasin}$ = 0.5 retrieved from the expert survey presented in Section 5.2 (Misuri et al., 2020b) was adopted to modify barrier effectiveness according to Eq. (6.1.3), obtaining $\eta_{eq,CatchBasin} = 5.0 \times 10^{-1}$ (as reported in Table 6.1. 5).

On the other hand, the L2 level of analysis was applied to both the foam-water system (FWS) equipped on tanks T1 – T4 and on the water curtains equipped on horizontal vessels P1 – P3. Indeed, assessing the performance of these two complex active barrier systems during Natech scenarios related to the reference earthquake event requires a deeper understanding of how the seism impacts the barrier subsystems leading to the modification of their expected availability and probability of failure on demand. The tailored FTA carried out for the FWS is reported in Figure 6.1. 3.

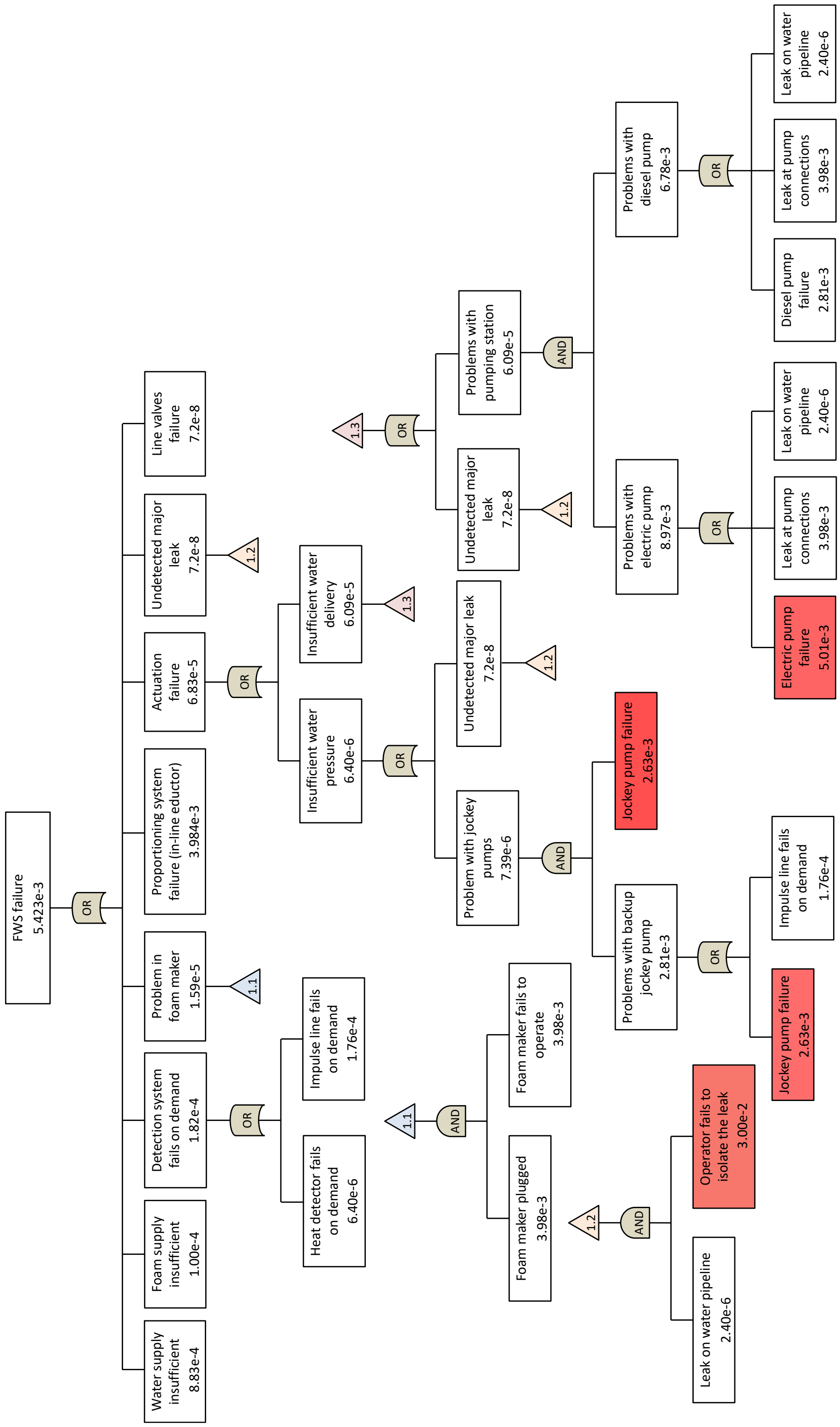


Figure 6.1. 3: Fault tree for the foam-water system (FWS) considered in the case study. Values reported are the baseline unavailability values $q_{p,0}$ which have been used to quantify baseline barrier PFD_0 and updated PFD_{eq}, according to L2 analysis. Basic events involving components/subsystems which are deemed not available during the reference seismic event are highlighted in red.

The values reported in Figure 6.1. 3 represent the probability of events calculated considering baseline component unavailability figures $q_{p,0}$. These values were retrieved from conventional reliability data reported in the literature (API, 2008; Cadwallader, 1995; DNV, 1997; Madonna et al., 2009; Mannan, 2005; New Zealand Fire Service Commission, 2008). Additionally, the contribution of common cause failure is included through a 5% beta factor in PFD_0 (Mannan, 2005). On top of the FTA, the value of PFD_0 is reported, expressing the original barrier performance.

The most vulnerable nodes are then identified considering the impact of the reference earthquake event on subsystems and components (i.e., in red in Figure 6.1. 3) and they are associated with unitary unavailability (i.e., δ_p = 1 for events reported in red in the application of Eq. (6.1.4)). Finally, the updated PFD_{eq} is calculated applying Eq. (6.1.5).

As it might be noticed from Figure 6.1. 3, the main issue that contributes to modify the unavailability of the FWS is related to the expected lack of power connection. Indeed, as reported in (Karagiannis et al., 2017) whereas electricity utility buildings performed generally well during earthquakes with PGA up to 0.97g, a power outage is particularly frequent due to damages to transmission and distribution systems. Therefore, jockey pumps aimed at keeping the pipework at the correct pressure before operations and electric pumps are deemed unavailable. This is consistent with evidence reported during past Natech accidents triggered by severe earthquakes (i.e., during the Kocaeli earthquake, only pumps driven by diesel motors could be operated, while all the electricity-dependent subsystems were not operating (Girgin, 2011)).

In addition, during severe earthquakes the possibility that internal roads are damaged and that some areas of the plant are isolated due to the presence of rubbles and debris might be considered. For instance, several Japanese petrochemical facilities experienced damages to internal roads during the Tohoku earthquake of 2011 (FDMA, 2011; Krausmann and Cruz, 2013). Also during other severe seismic events this pattern was identified (e.g., see (Girgin, 2011; Krausmann et al., 2010)). This in turn might lead to the impossibility for operators to intervene in case of leakages from the hydraulic circuit of the FWS. Thus, the other contribution to barrier unavailability is the expected failure of operators in the isolation of possible leaks from the FWS pipework caused by the earthquake (see Figure 6.1. 3).

Therefore, considering the system reported in Figure 6.1. 3, the PFD_{eq} resulting from the FTA evaluation is unitary and the barrier is thus considered unavailable during the accident.

Analogously, the L2 level was applied to the WC, as shown in the FTA reported in Figure 6.1. 4. Consistently with the case of FWS, the same standard reliability databases and a 5% beta factor have been adopted also for the WC (API, 2008; Cadwallader, 1995; DNV, 1997; Madonna et al., 2009; Mannan, 2005; New Zealand Fire Service Commission, 2008).

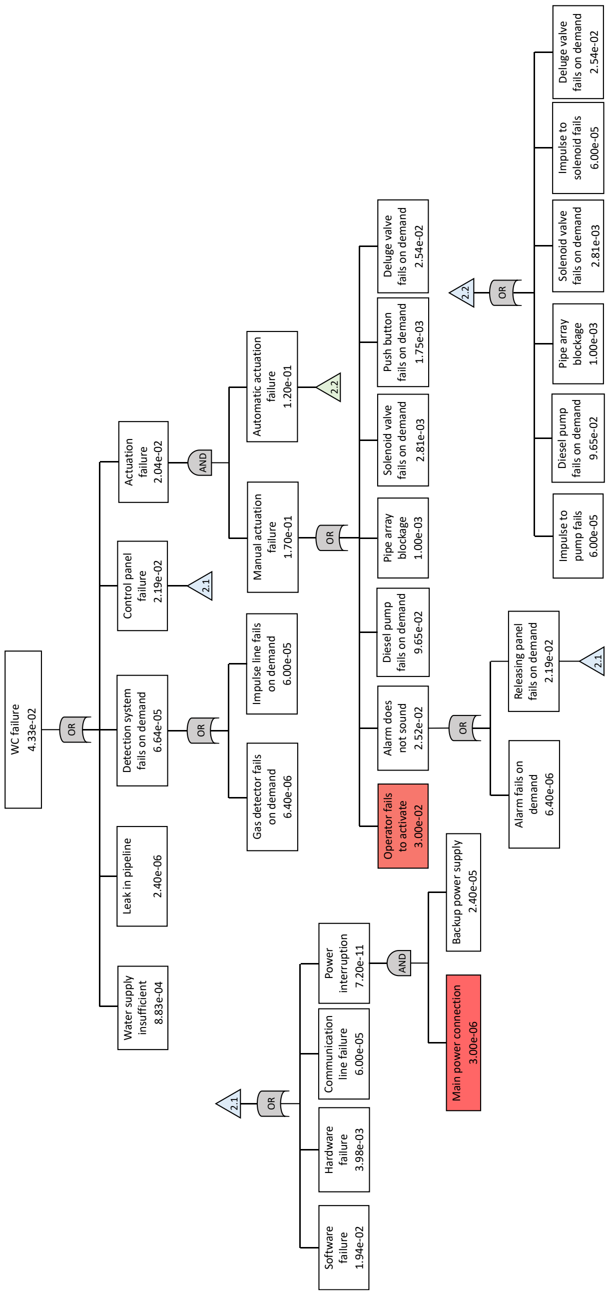


Figure 6.1. 4: Fault tree for the water curtains (WC) considered in the case study. Values reported are the baseline unavailability values $q_{p,0}$ which have been used to quantify baseline barrier PFD_0 and updated PFD_f, according to L2 analysis. Basic events involving components/subsystems which are deemed not available during the reference seismic event are highlighted in red.

The most vulnerable nodes identified for the WC are highlighted in red in Figure 6.1. 4. Also in this case, the main factor influencing barrier unavailability is the power outage. As previously explained indeed, during a severe earthquake power outage is a common event (Karagiannis et al., 2017). Thus, the activation of the barrier can rely only on a backup power supply. In addition, the intervention of operators in manually activating the barrier is deemed not credible considering the possible damages to site passages and the presence of rubbles. Therefore, by the application of the L2 methodology, the PFD_{eq} of the WC is reassessed at 1.44E-01, as shown in Table 6.1. 5.

It should be noted that the FTA realized to apply the L2 analysis to FWS and WC barriers was based on specific assumptions for the architecture of these complex systems. For the sake of brevity, the main assumptions considered in the construction of the FTs are not discussed here, and a description of the main points considered is reported in Appendix F.

Assessment of the final outcomes

The approach based on the modified gates presented in Table 6.1. 1 was applied to the identification and the frequency assessment of primary Natech scenarios, considering the set of safety barriers with depleted performance (see Table 6.1. 5). The ET obtained for atmospheric equipment (i.e., T1 to T4) is shown in Figure 6.1. 5. As can be noticed, compared with the ET obtained considering baseline barrier performance (i.e., used for case 2, see Appendix D.3) some of the branches reported are marked with a red cross, indicating that the expected unavailability of the FWS assessed by means of the FTA developed for the L2 analysis leads to exclude some of the mitigated outcomes (i.e., outcomes with mitigated SEP or reduced evaporation).

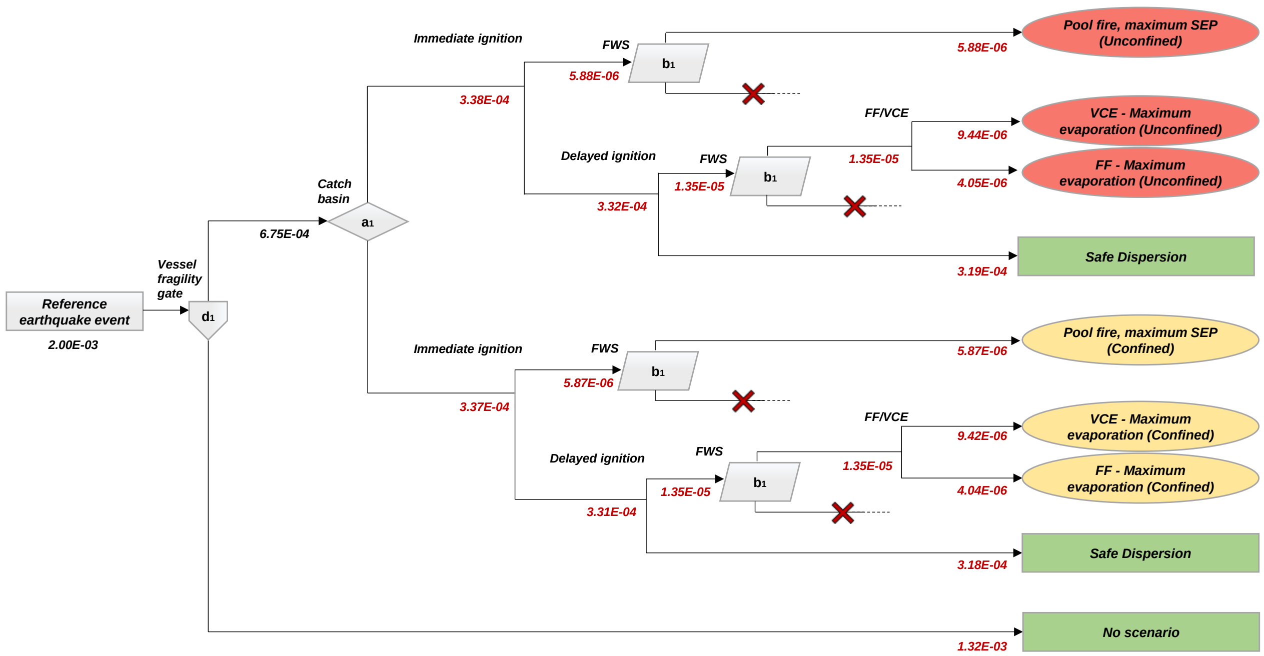


Figure 6.1. 5: Event tree reporting the quantification of the frequencies (in y^{-1}) of primary Natech scenarios involving tanks T1 to T4. Values in red are influences by barrier depletion caused by the reference earthquake event. The branches indicated with a red cross are not further considered, as a consequence of the failure of FWS, as indicated by FTAs in L2 analysis.

On the other hand, the ETs obtained for pressurized vessels containing ammonia (i.e., P1 and P2) and flammable propane (i.e., P3) are represented respectively in Figure 6.1. 6 and Figure 6.1. 7. Compared to the ETs depicted for the same equipment in case of barrier with baseline performance (i.e., case 2, see Appendix D.3), it can be noticed that the frequency of most severe outcomes feature a relevant increase, as it was also expected considering the results obtained in Section 5.3 (Misuri et al., 2021b).

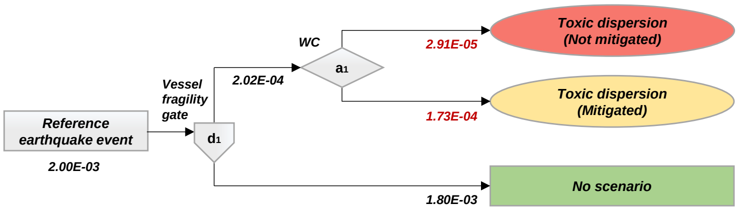


Figure 6.1. 6: Event tree reporting the quantification of the frequencies (in y^{-1}) of primary Natech scenarios involving vessels P1 and P2. Values in red are influences by barrier depletion caused by the reference earthquake event.

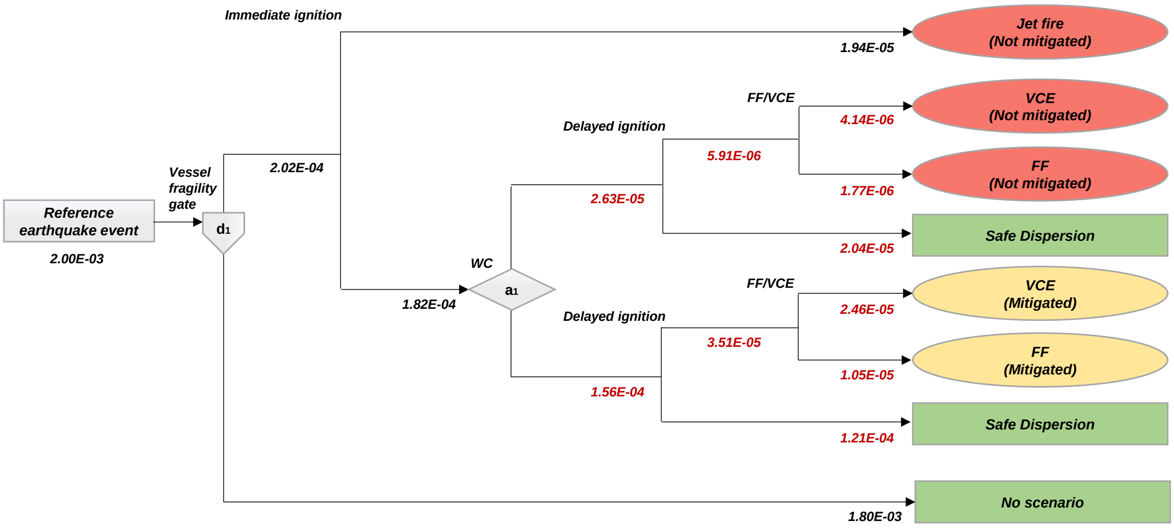


Figure 6.1. 7: Event tree reporting the quantification of the frequencies (in y^{-1}) of primary Natech scenarios involving vessel P3. Values in red are influences by barrier depletion caused by the reference earthquake event.

The frequencies and the probabilities for the set of primary Natech scenarios identified for each item of case 3 are summarized in Table 6.1. 6.

According to the table, each atmospheric tank T1 to T4 is associated with 6 hazardous technological scenarios plus a safe condition (i.e., either the safe dispersion or the absence of LOC during the seism). The pressurized vessels P1 and P2 are assumed to feature only 2 possible technological scenarios plus the safe condition of absence of damage to equipment, while, as for case 2 (see Appendix D.3) the release from vessel P3 can cause 5 different hazardous outcomes plus the safe condition of absence of LOC or safe dispersion. The total number of overall primary Natech scenarios can be assessed at 129653 by the application of Eq. (6.1.6). It might be noticed that the unavailability of FWS reduces significantly the number of possible combinations compared to case 2 (i.e., in this latter case 1542293 different overall scenarios were assessed, as reported in Appendix D.3).

Table 6.1. 6: Details of the frequencies and probabilities of final scenarios considered in case 3 (barriers with depleted performance, as reported in Table 6.1. 5). SEP=surface emissive power; VCE = Vapour cloud explosion; FF = Flash fire; $f(N_k^7)$ = frequency of a final scenario from the k-th equipment involved (out of 7 total elements of the layout); $P(N_k^7)$ = probability of a final scenario from the k-th equipment involved (out of 7 total elements of the layout) (see Section 6.1.3).

Item involved	LOC	*Final scenario*	$f(N_k^7)$ [y^{-1}]	$P(N_k^7)$
T1 – T4	Catastrophic rupture	Pool fire, maximum SEP (Unconfined)	5.88E-06	2.94E-03
		VCE – Maximum evaporation rate (Unconfined)	9.44E-06	4.72E-03
		FF – Maximum evaporation rate (Unconfined)	4.05E-06	2.03E-03
		Pool fire, maximum SEP (Confined)	5.87E-06	2.94E-03
		VCE – Maximum evaporation rate (Confined)	9.42E-06	4.71E-03
		FF – Maximum evaporation rate (Confined)	4.04E-06	2.02E-03
		Safe dispersion / No scenario	1.96E-03	9.79E-01
P1 – P2	Continuous release in 10 min	Toxic dispersion (Not mitigated)	2.91E-05	1.46E-02
		Toxic dispersion (Mitigated)	1.73E-04	8.65E-02
		No scenario	1.80E-03	9.00E-01
P3	Continuous release in 10 min	Jet fire (Not mitigated)	1.94E-05	9.70E-03
		VCE (Not mitigated)	4.14E-06	2.07E-03
		FF (Not mitigated)	1.77E-06	8.85E-04
		VCE (Not mitigated)	2.46E-05	1.23E-02
		FF (Not mitigated)	1.05E-05	5.25E-03
		Safe dispersion / No scenario	1.94E-03	9.71E-01

Then, Eq. (6.1.7) and Eq. (6.1.8) were applied to assess the probability and frequency of overall primary Natech scenarios for case 3. The outcomes of this step will not be explicitly reported here since the number of different combinations is too high to enable an efficient visualization of the results. Nonetheless, as for case 2, the same Matlab implementation of Eq. (6.1.7) and Eq. (6.1.8) previously used in the validation of the results of case 1 shown in Appendix D.2 is applied. Finally, the vulnerability maps related to the 129653 overall primary Natech scenarios of case 3 are computed by Eq. (6.1.9).

Risk figures

The LSIR results obtained for the case study are shown in the following. In particular, the LSIR contours obtained for case 1 (worst-case), case 2 (best-case), and case 3 are respectively shown in Figure 6.1. 8, Figure 6.1. 9, and Figure 6.1. 10. In all the three cases, the baseline contribution of conventional scenarios (case 0) has been included. Further details on LSIR obtained in case 0 can be found in Appendix D.1.

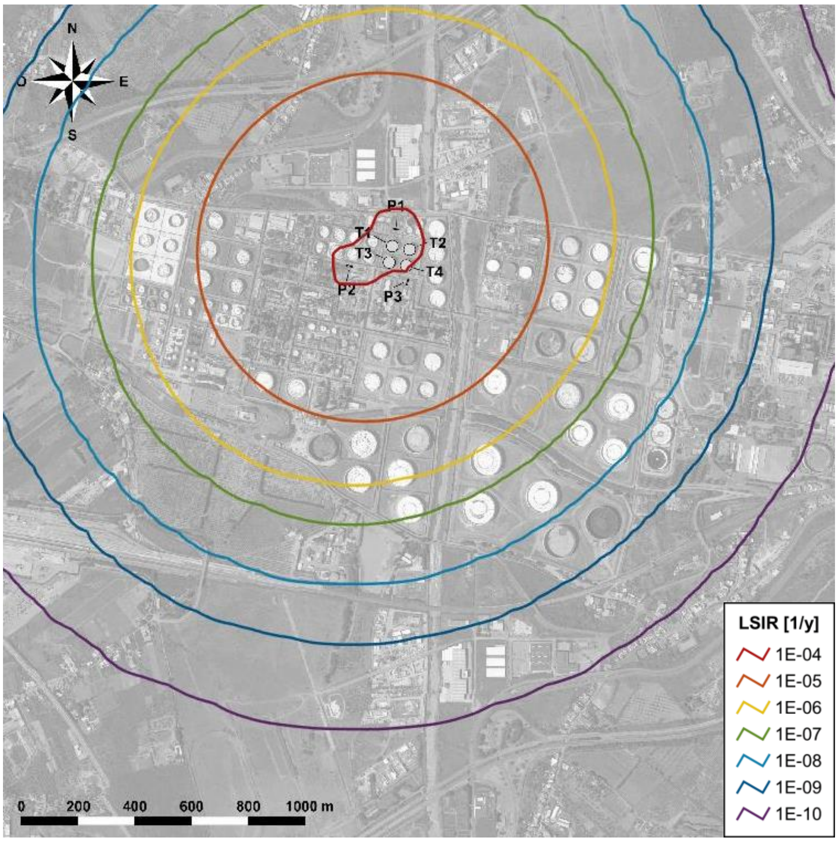


Figure 6.1. 8: LSIR contours obtained for case 1 (worst-case, considering absence of barriers in mitigating primary Natech scenarios).

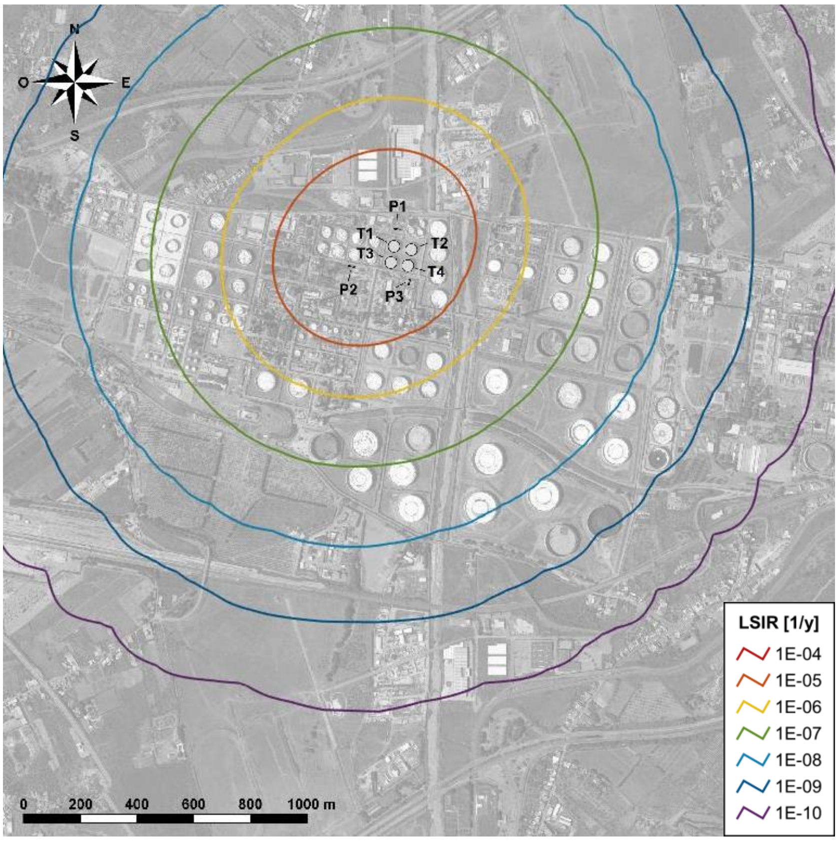


Figure 6.1. 9: LSIR contours obtained for case 2 (best-case, considering barriers with baseline performance).

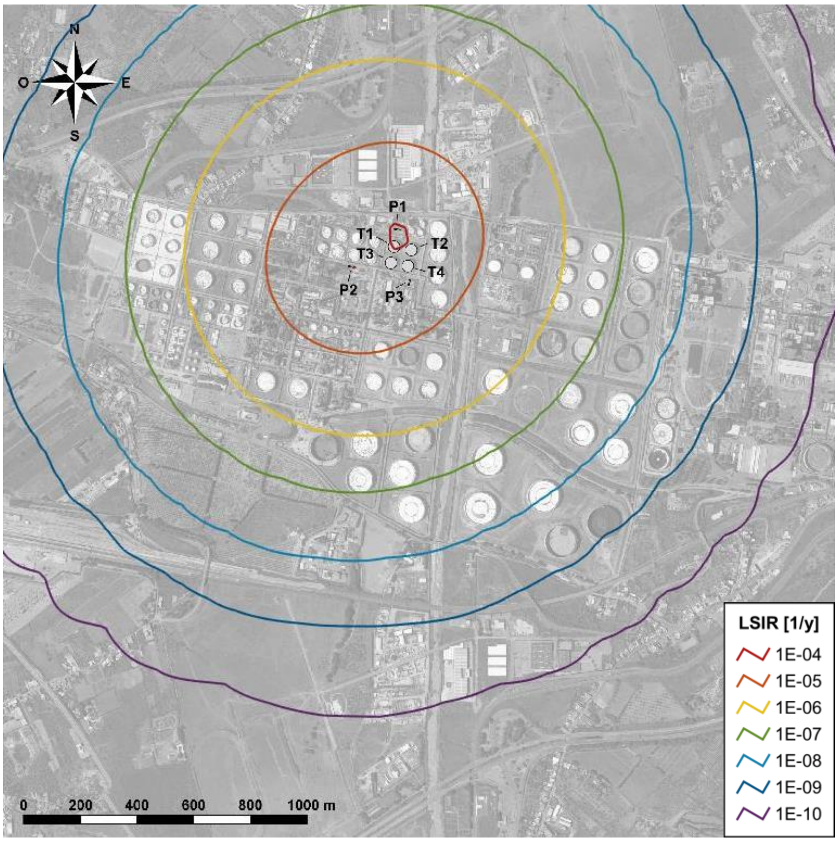


Figure 6.1. 10: LSIR contours obtained for case 3 (accounting for barriers with depleted performance due to the reference earthquake event).

Comparing the results shown in Figure 6.1. 8 with the figures reported in Figure 6.1. 9 and Figure 6.1. 10, it is evident that accounting for the action of safety barriers during primary Natech scenarios leads to lower and more realistic risk figures compared to the worst-case situation of assuming the absence of safety barriers, as done in the current Natech QRA approach (see Section 2.2.2). Nonetheless, a comparison between Figure 6.1. 9 and Figure 6.1. 10 also suggests that barrier depletion during the reference earthquake event leads to a relevant increase in the individual risk figures. Indeed, the areas exposed to LSIR higher than 10^{-6} y^{-1} and than 10^{-7} y^{-1} in Figure 6.1. 10 are respectively about 1.6 and 1.2 times those in Figure 6.1. 9. In addition, the highest LSIR level that is reported in Figure 6.1. 9 is between 10^{-5} y^{-1} and 10^{-4} y^{-1}, while in Figure 6.1. 10 an area of the site is exposed to a LSIR value higher than 10^{-4} y^{-1}.

The results obtained comparing the LSIR contours are reflected also in the societal risk calculated for the three cases considered as can be noticed from Figure 6.1. 11 and Figure 6.1. 12.

In particular, in the F/N plot reported in Figure 6.1. 11 it is clear that the societal risk related to case 3 (i.e., the thick red curve) lies in between the best-case indicated by the black-dashed curve (i.e., case 2) and the worst-case indicated by the red-dashed curve (i.e., case 1).

The intermediate severity of case 3 thus indicates that current QRA methodologies based on the absence of safety barriers in the primary Natech scenarios characterization would lead to possibly over-conservative results (i.e., comparing the thick-red curve with the red-dashed curve), while in the meantime, considering barriers without including the possibility of their depletion during the seism would have led to a substantial underestimation of societal risk figures (i.e., comparing the thick-red curve with the black-dashed curve).

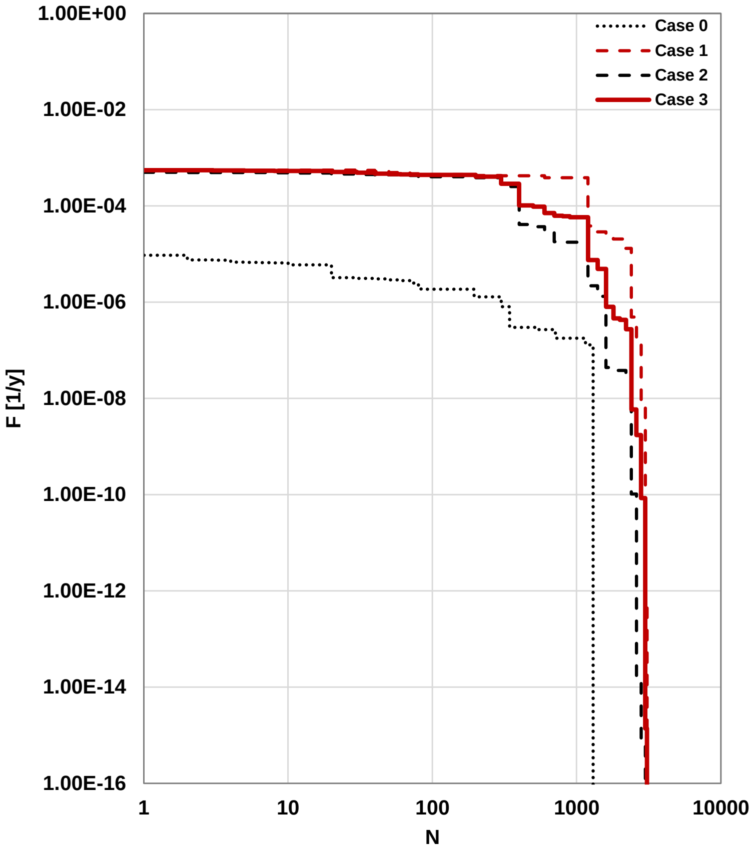


Figure 6.1. 11: Societal risk expressed through F/N curves for case 0 (black-dotted line), case 1 (red dashed line), case 2 (black dashed line), and case 3 (thick-red line).

The results discussed above have a further confirmation considering the PLL and EV figures reported in Figure 6.1. 12. As can be seen, the PLL values obtained for case 1, case 2, and case 3 compared to the PLL resulting from conventional scenarios (i.e, case 0), are respectively 632, 189, and 251 times higher, indicating that the influence of Natech contribution is particularly relevant. The importance of considering Natech scenarios is also evidenced by analyzing the EV. Indeed, compared to case 0, the EV values obtained for case 1, case 2, and case 3 are respectively 1410, 156, and 296 times higher. These figures clearly confirm the interpretation of the intermediate results obtained for case 3 in Figure 6.1. 11. Indeed, on the one side, it is clear that considering the worst-case scenario of the absence of barriers (i.e., case 1) would have led to a severe overestimation of the indicators (i.e., PLL and EV obtained for case 1 are respectively 2.5 and 4.8 times higher than the values obtained for case 3). On the other side, considering the presence of barriers with baseline performance during primary Natech scenarios would have led to lower values of risk indicators (i.e., PLL and EV obtained for case 3 are respectively 1.3 and 1.9 times greater than the values related to case 2).

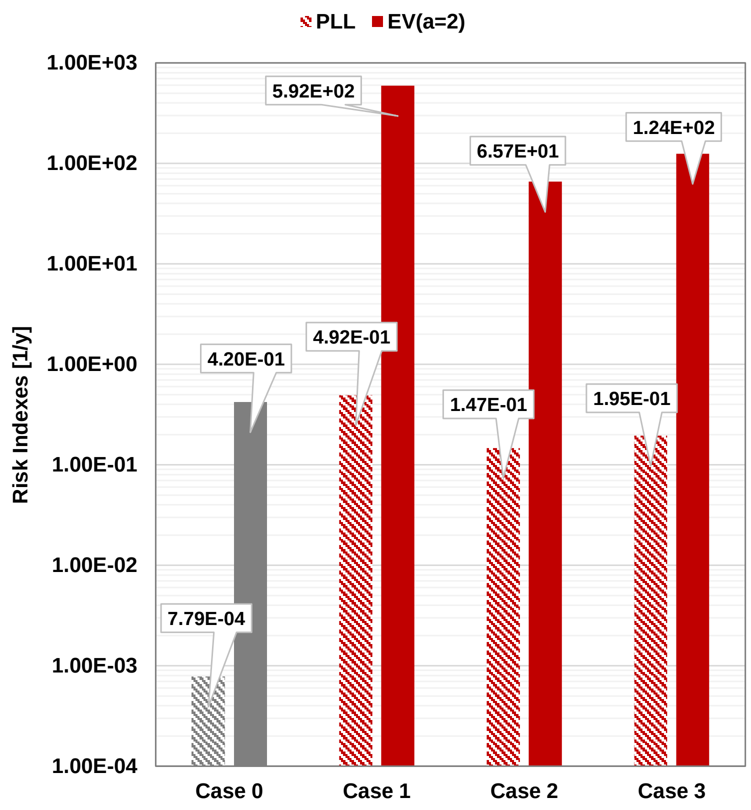


Figure 6.1. 12: Potential Life Loss (PLL) and expectation value (EV) values calculated for the case study. Case 0 is also reported (in grey) to provide baseline PLL and EV values from conventional scenarios.

6.1.6 Discussion

The results shown in the previous section highlight the important role that safety barriers might play in influencing the likelihood and the severity of primary Natech scenarios. As already pointed out in Section 5.2, safety barriers might undergo a significant performance depletion during natural hazards, and in case of a Natech accident, this depletion might influence the technological scenarios following the release of hazardous substances. Thus, assuming that the barrier will retain their baseline performance might lead to an inaccurate evaluation of risk figures. Indeed, as shown in the analysis of the case study, the safety barriers considered are expected to feature a significantly lower performance (e.g., the FWS is found to be not available at all during the seism), thus a reduced level of protection should be considered in the analysis. Nevertheless, a residual level of protection is still present (e.g., the catch basins and the WCs of the case study feature a lowered but not-null likelihood of successful mitigation) and considering the complete absence of safety barriers as done in the established Natech QRA approaches (see Section 2.2.2) might also lead to unrealistic results. Thus, as demonstrated in the case study, the methodology proposed in Section 6.1.3 on the one side enables the inclusion of the expected performance during a specific reference natural events, while on the other side avoids the application of possibly over-conservative approaches based on the worst-case assumption of complete absence of action by safety barriers.

As clear from Section 6.1.3, selecting an appropriate approach for the barrier performance assessment is critical for the application of the methodology, and the choice of the most suitable level of detail to be applied to Step 4 of Figure 6.1. 1 should be made considering the information available for the systems included in the study. As a general rule, the selection of the most information-intensive level of analysis (L2) is suggested for complex systems and in specific situations where particular design features of the barriers are required to be included in the QRA. Nevertheless, it should be noted that assessing the actual behaviour of system components during natural hazards might be difficult and uncertainty may still be present in the results obtained through the L2 level. Levels L1 and L0 instead are deemed suitable for simpler systems that cannot be split into subsystems or whose analysis is not convenient using time-demanding approaches. The modification factors suggested for the use in the L1 level have been retrieved for reference schemes, thus their application might be appropriate for a variety of technical systems (Misuri et al., 2020b). Clearly enough, there is still some arbitrariness concerning the selection of the most appropriate level of safety barrier assessment and this, in turn, might introduce some uncertainty. In any case, as shown in the previous sections, it is still possible to identify a risk region bounded between the best-case situation of barriers retaining their baseline performance (i.e., case 3 in the case study) and the worst-case situation of absence of barriers (i.e., case 1 in the case study) calculated with established Natech QRA approaches (e.g., see (Antonioni et al., 2015)). Therefore, the methodology can be applied to the ranking of the possible strategies to enhance barrier performance, based on the shift of the risk level from the upper-bound (i.e., primary Natech scenarios with the absence of mitigation) to the lower risk bound identified by the procedure (i.e., the situation with baseline barrier performance).

It should be also remarked that the approach to barrier assessment described in Section 6.1.2 can be applied also to assess the role of safety measures in the following part of accident progression, that is, in the escalation through domino effect, as shown in Figure 4. 5 of Chapter 4. This topic will be presented in detail in Section 6.3.

6.1.7 Conclusions

In this section, an updated methodology for the detailed assessment of the risk related to primary Natech scenarios has been developed. In comparison with the previous approaches to Natech QRA shown in Section 2.2.2, the described methodology was specifically conceptualized to account for the role of safety barriers in the characterization of expected scenarios following the LOCs caused by reference natural events. In addition, the methodology embeds a specific multilevel step conceived to enable the inclusion of the possibility of concurrent barrier performance reduction during the natural event. A case study was defined to test the proposed framework. The results obtained are compared with the worst-case outcomes obtained by the application of current QRA approaches considering the absence of safety barriers in the characterization of primary Natech scenarios, showing that the novel approach enables a more realistic quantification of risk figures. In addition, the results were compared also with the outcomes obtained in the best-case of barriers with baseline performance (i.e., as if during the reference natural event barriers will not undergo any kind of depletion), clearly showing that overlooking the possibility of reduced protection/mitigation leads to a significant underestimation of risk figures. Clearly, the methodology might also be used to extract risk-based indications on the most critical subsystems of the technical safety barriers, to quantify the impact of their enhancement in shifting the risk figures related to primary Natech scenarios, and in turn to identify the most effective strategies to reduce the gap between the actual level of protection and the best case of barriers with baseline performance.

6.2 Domino effects in Natech accidents

As shown in Section 2.2.3, Natech events and domino effects share several features from a risk assessment standpoint. Nevertheless, as already discussed, the Natech QRA methodologies proposed to date are mostly focused on primary technological scenarios. Therefore, to fill this gap in this section a general methodology for Natech QRA accounting for the possibility of accident propagation through domino effect will be provided and tested analyzing a notional case study exposed to lightning hazard.

6.2.1 Overview of the methodology

The methodology presented in the following has been developed with the aim of enabling the assessment of the overall risk posed by Natech events, considering also the possibility of accident propagation leading to secondary scenarios. Both the possibility of domino effects from primary Natech scenarios and the possibility of further accident escalation have been considered. The methodology has been inspired by the traditional QRA approaches to Natech and domino risks (Cozzani et al., 2014), and is summarized in the flowchart reported in Figure 6.2. 1.

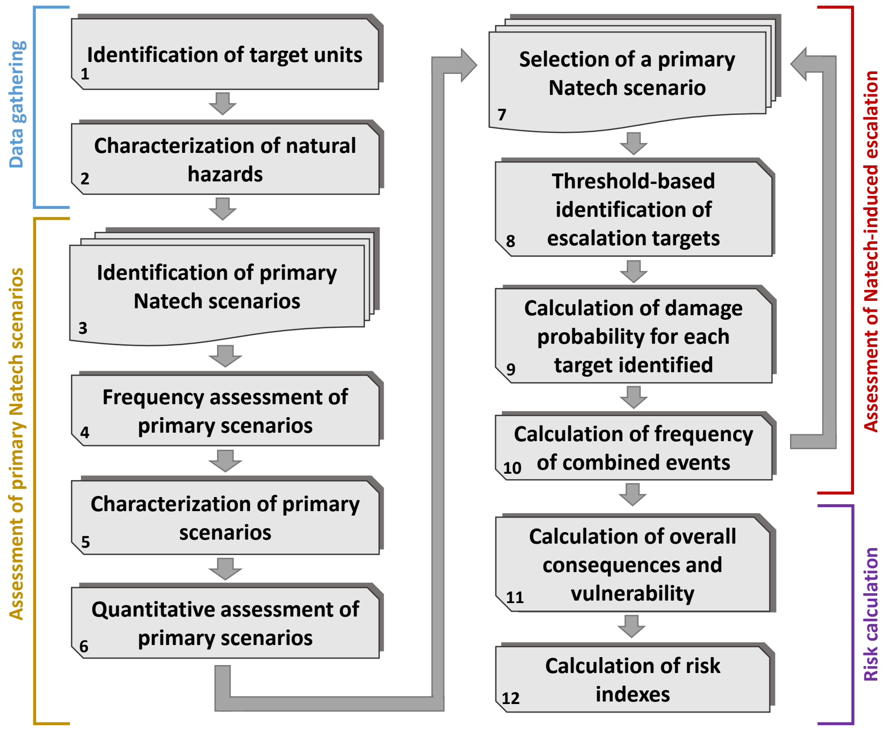


Figure 6.2. 1: Methodology for quantitative risk assessment of domino effects in Natech scenarios. Adapted from (Misuri and Cozzani, 2021a)

As shown in the figure, the procedure presented has a general aim and can be split into four main parts:

I. Preliminary data gathering (i.e., indicated in blue in the figure), aimed at performing the characterization of the site for what concerns the natural hazards which it is possibly exposed to and the identification of the target units to be considered in the successive steps of the analysis;

II. Assessment of primary Natech scenarios (i.e., indicated in yellow in the figure), aimed at the complete characterization of primary technological scenarios led by the impact of the selected reference natural events at the site;

III. Assessment of Natech-induced escalation (i.e., indicated in red in the figure), aimed at assessing the possibility of generation of domino effects from the primary Natech scenarios obtained in the previous phase of the analysis and to the characterization of the expected final outcomes; and

IV. Overall risk calculation (i.e., indicated in purple in the figure), aimed at the quantification of overall risk figures and summarize the results through risk indices valuable to support decision-making processes and the successive definition of risk mitigation strategies.

The developed methodology is general and can be applied to a variety of natural hazards. Moreover, it should be noted that there is a direct correspondence between the steps included in the procedure and the cascading nature of domino effects driven by natural hazards as presented in Section 2.2.3.

Indeed, the left-hand side of the methodology shown in Figure 6.2. 1 is devoted to the assessment of the initial steps of the cascading chain, that is, the ones related to the impact of natural events at the site which causes primary Natech scenarios (i.e., blue arrow represented in Figure 2.2. 4). On the other hand, the right-hand side, and in particular the assessment of Natech-induced escalation, is aimed at evaluating the possibility of further propagation of the accident following the primary scenarios (i.e., corresponding to the orange arrow in Figure 2.2. 4).

In the following, the steps of the methodology of Figure 6.2. 1 are described to clarify how it can be applied to provide an exhaustive assessment of domino effects driven from natural events, starting from their impact on the site to possible secondary technological scenarios linked to accident escalation.

As anticipated, the first step of the methodology, as in conventional QRA applications, is the identification of possible target units. This step is aimed at the definition of a set of items representative of the layout, yet including a limited number of elements not to overburden the calculation procedures. Therefore, a preliminary identification of the most critical items should be carried out according to ranking criteria available in the literature (e.g., see (Antonioni et al., 2009a)).

Subsequently, the natural hazards to which the site of concern is exposed should be characterized. This step is aimed at providing the input parameters relevant for the evaluation of the frequency and severity of reference natural events included in the analysis. Clearly enough, the level of detail in carrying out this task should be defined with the sole objective of providing necessary data to carry out a quantitative risk assessment, rather than of performing a detailed characterization of natural events.

Therefore, the characterization should provide at a minimum the frequency of occurrence (or a time of return, which can be easily converted into a frequency value) of reference natural events, and a set of parameters summarizing their magnitude (Cozzani et al., 2014). For instance, considering the case of floods, the severity is usually expressed in terms of a couple of parameters, namely the floodwater height and velocity (Antonioni et al., 2015, 2009a). On the contrary, the magnitude of seismic events is usually expressed using the horizontal component of peak ground acceleration (PGA) (Campedel et al., 2008; Fabbrocino et al., 2005), and for some specific cases (i.e., for pipelines) of the peak ground velocity (PGV) (Lanzano et al., 2014, 2013).

It should be noted that, in agreement with the current state of the art in Natech QRA, each natural hazard is considered independently, and the possibility of the simultaneous impact of more than one natural event is not considered. Thus, a reference set of natural events is defined, each being characterized in terms of frequency and magnitude. These events are assumed to be representative of the overall natural hazard the site is prone to (Cozzani et al., 2014).

An exception to this approach is related to the case of lightning hazard characterization, which is based on a single parameter expressing the frequency of lightning impact at the ground per surface area (i.e., the ground flash density n_g) (Misuri et al., 2020a; Necci et al., 2016), as exemplified in the case-study discussed in Sections 6.2.3 to 6.2.5.

Once the characterization of natural hazard is completed, primary Natech scenarios following a LOC from equipment comprised in the set of critical items identified in the preliminary steps of the methodology should be defined (Step 3 in Figure 6.2. 1). Specific event trees (ETs) might be used to support the identification of such scenarios. For instance, ETs are available in the literature for the case of flood which can lead to peculiar scenarios following the release of water-reacting substances (Cozzani et al., 2010). Ad-hoc ETs are also available for the case of lightning strikes, which can give rise to technological scenarios according to the kind of equipment impacted, presence of confined vapor space, and protection system implemented (Necci et al., 2014b; Renni et al., 2010). In the other cases, conventional ETs available in reference literature sources might be applied to determine scenarios following LOCs (CCPS, 2000; Uijt de Haag and Ale, 2005). The possible modification of ignition probability during natural hazards compared to scenarios linked to internal causes might be also considered. Indeed, specific ignition probability values for the case of Natech accidents have been proposed in recent research (Ricci et al., 2021).

The characterization and the quantitative assessment of the primary Natech scenarios should then be performed (Steps 4 to 6 in Figure 6.2. 1).

As in the other methodologies for Natech QRA presented in Section 2.2.2, the calculation of the frequency of LOC $f_{I;LOC}$ is performed directly from the frequency of the reference natural event f_{nh} as reported in Eq. (6.2.1):

$$f_{I,LOC} = f_{nh} \times P_{nhd} \tag{6.2. 1}$$

where P_{nhd} is the equipment conditional probability of experiencing damages that can trigger a LOC when the natural event impacts the site. A variety of vulnerability models has been developed in the dedicated research literature to address this task, as already presented in Chapter 2. Once $f_{I,LOC}$ is calculated, the frequency of primary Natech scenarios, $f_{I,Natech}$, can be assessed applying the ETs used for scenario identification presented in Section 2.2.2. Subsequently, the quantitative assessment of primary scenarios should be completed evaluating their expected consequences, as already presented in Section 2.2.2. Subsequently, the possibility of accident escalation has to be evaluated. Clearly, among the primary Natech scenarios, only those producing physical effects that may lead to escalation have to be considered. For instance, stationary fires trigger cause domino effects because the intense heat radiation is a possible vector of escalation by undermining the integrity of neighboring equipment, whereas escalation from toxic dispersions is not deemed possible (Reniers and Cozzani, 2013b).

A the limited set of primary Natech scenarios that lead to escalation is characterized, a preliminary identification of the credible targets (Step 8 in Figure 6.2. 1) can be performed leveraging threshold-based approaches available in the literature (Cozzani et al., 2013b). For instance, for the case of escalation from stationary fires, established threshold values on heat radiation impacting target equipment can be found in the literature (i.e., 15kW/m^2 and 45kW/m^2 respectively for atmospheric and pressurized equipment (Cozzani et al., 2013b)). Specific approaches have been also developed for the cases of escalation from overpressure and due to missile (fragment) projection (Cozzani et al., 2006b).

After the restricted set of plausible escalation targets have been identified, their failure probability as a consequence of their exposure to the specific escalation vector can be assessed by vulnerability models (Step 9 in Figure 6.2. 1).

Considering for instance the case of heat radiation, vulnerability models have been proposed and validated in the literature to enable the calculation of failure probability from equipment time to failure (*TTF*), as already mentioned in Section 5.3. This parameter can be assessed for pressurized storage vessels and atmospheric tanks respectively using Eq. (6.2.2) and Eq. (6.2.3):

$$\ln(TTF) = -1.13 * \ln(I) - 2.67 * 10^{-5} * V + 9.9 \tag{6.2. 2}$$

$$\ln(TTF) = -0.95 * \ln(I) + 8.845 * V^{0.032} \tag{6.2. 3}$$

where I is the heat radiation impacting the target expressed in kW/m^2 and V is its volume in m^3 and *TTF* is obtained in s (Landucci et al., 2009).

On the basis of the *TTF*, the probability of equipment failure is then assessed through the application of a probit function (Finney, 1971). Hence, a probit variable Y and the related damage probability of a target P_D are calculated according to Eq. (6.2.4) and Eq. (6.2.5):

$$Y = 9.25 - 1.85 * \ln(TTF/60) \tag{6.2. 4}$$

$$P_D = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} e^{-\frac{u^2}{2}} du \tag{6.2. 5}$$

Similar approaches have been developed also for the cases of overpressure and fragment projection (Gubinelli and Cozzani, 2009a, 2009b; Mébarki et al., 2009b, 2009a).

The successive part of the methodology is then aimed at the characterization of simultaneous scenarios involved in Natech accident escalation (Step 10 in Figure 6.2. 1).

The well-established approach for assessing domino scenarios involving the contemporary damage of k out of n possible targets can be applied to accomplish this task (Antonioni et al., 2007; Cozzani et al., 2014). As it will be clearer from the following discussion, this is the approach that had been tailored also to the case of primary Natech scenarios involving the contemporary failure of multiple items, assuming a single reference event per target, as explained in Section 2.2.2.

Considering a generic primary Natech scenario, the number N_k of domino scenarios involving exactly k targets can be calculated according to Eq. (6.2.6):

$$N_k = \binom{n}{k} = \frac{n!}{(n-k)!\,k!} \tag{6.2. 6}$$

The probability of an overall domino scenario involving k targets $P_E^{(k,m)}$ resulting from the specific primary Natech event considered might then be assessed applying Eq. (6.2.7):

$$P_E^{(k,m)} = \prod_{l=1}^{n} \left[1 - P_{D,l} + \delta(l, \mathbf{J}_m^k)(2P_{D,l} - 1)\right] \tag{6.2. 7}$$

where, $\boldsymbol{J}_m^k$ is a vector used to identify the scenario, whose elements γ_j (with $j = 1, \ldots, k$) are the indices of the k events taking place during the domino scenario, m indicates that the domino scenario is the m-th ($m = 1, \ldots, N_k$) combination of k secondary events, $\delta(l, \boldsymbol{J}_m^k)$ shows a value of 1 if the l-th secondary event is comprised in the vector $\boldsymbol{J}_m^k$, and the value of 0 in the case is it not, and $P_{D,l}$ is the failure probability of the l-th target (estimated in Step 9).

Finally, defining $f_{I,Natech}$ as the frequency of the primary Natech event originating the escalation, the frequency of the m-th overall scenario originating from it and simultaneously involving k targets in the escalation, $f_E^{(k,m)}$, can be calculated according to Eq. (6.2.8):

$$f_E^{(k,m)} = f_{I,Natech} \times P_E^{(k,m)} \tag{6.2. 8}$$

It might be noticed that the formulation presented herein is based on the assumption of considering only a single primary Natech event at a time. This choice is made for the sake of simplicity, although the procedure can be clearly extended both to the case of multiple primary Natech events simultaneously contributing to trigger a domino effect, and to a further level of escalation, by the recursive application of the methodology proposed in (Cozzani et al., 2014).

After the frequency assessment of domino scenarios is accomplished, the following step might be applied to analyze the expected consequences from such scenarios (Step 11 in Figure 6.2. 1). As explained also in previous sections (see Section 2.2.2 and Section 6.1), the direct application of integral models to consequence assessment is not possible. The methodology applied in established QRA approaches to domino effects (Antonioni et al., 2009b; Cozzani et al., 2005) and Natech accidents (Antonioni et al., 2015, 2009a) is thus suggested for application, as discussed in Section

2.2.2. In the specific case of domino effect following a primary Natech scenario, in each point of the space, the local contributions related to the physical effects both from the primary events and the outcomes belonging to the *m*-th overall domino scenario need to be considered. The death probability in a generic location considering *k* events involved in the *m*-th overall domino scenario $V_D^{(k,m)}$ can be estimated by Eq. (6.2.9):

$$V_D^{(k,m)} = \min[(V_I + \sum_{l=1}^{n} \delta(l, \mathbf{J}_m^k)\, V_{D,l}), 1] \tag{6.2. 9}$$

where V_I is the death probability connected to the primary Natech scenario, $V_{D,l}$ is the death probability related to the *l*-th domino event and $\delta(l, \boldsymbol{J}_m^k)$ is 1 if the *l*-th event is involved in the $\boldsymbol{J}_m^k$ overall domino scenario, and 0 otherwise.

The final step of the methodology consists of the calculation of risk figures (Step 12 in Figure 6.2. 1). Individual risk is usually expressed through location-specific individual risk (LSIR) maps, while societal risk values are obtained by standardized approaches and represented by F/N curves and *PLL* and *EV* indices, as already explained in Section 6.1. For the sake of clarity, the definitions of these two risk indexes are reported also in Eq. (6.2.10) and Eq. (6.2.11):

$$PLL = \sum_{N} f(N)N = \sum_{N} F(N) \tag{6.2. 10}$$

$$EV = \sum_{N} f(N)N^a \ with\, a = 2 \tag{6.2. 11}$$

where *f(N)* is the overall frequency of scenarios causing *N* fatalities, and *F(N)* is the cumulative frequency of scenarios causing at least *N* fatalities. The difference between the two indices has been already discussed in Section 6.1, thus will not be repeated here.

6.2.2 Case study: QRA of domino effects triggered by lightning strikes

To demonstrate the application of the methodology for the QRA of domino effects in Natech accidents, the specific case of keraunic hazard has been selected. It is worth noting that lightning was chosen since it is one of the most frequent natural hazards causing Natech accidents (see Section 2.1.2) and, contrarily to the perception that the consequences of the related primary scenarios might be not as severe as those caused by wide-impact natural events as floods and earthquakes, past accident analysis shows several examples of severe domino effects during Natech events following the impact of lightning strikes (Persson and Lonnermark, 2004). Some examples of domino effects triggered by keraunic phenomena are shown in Table 6.2. 1.

Table 6.2. 1: Relevant examples of domino effects in Natech accidents triggered by lightning strikes on chemical and process installations. Accident descriptions extracted from (Persson and Lonnermark, 2004; The French Bureau for Analysis of Industrial Risks and Pollutions (BARPI), 2020).

Location	Date	Description
Karkateevy, Russia	June 1990	A storage tank with 5000 t of oil ignited after a lightning strike hit it, leading to fire spread by domino effect to other three tanks nearby.
Kucove, Albania	August 1995	A crude oil tank was involved in a major fire as a result of a lightning strike. The accident propagated by domino effect to two other tanks with a loss of more than 1650 f of crude oil. One fatality and four severe injuries resulted from the accident.
Cilacap, Indonesia	October 1995	A lightning struck a petroleum product tank, igniting the flammable chemical and causing the collapse of the roof. Eventually, the fire propagated to six other tanks storing naphtha and jet fuel located in the same dike resulting in a severe domino accident.
Ras Gharib, Egypt	May 1998	During a thunderstorm, a tank in an oil terminal was struck by a lightning and caught fire. The fire led to domino propagation of the accident, which eventually involved all the 16 tanks in the terminal, storing 2000t of oil each.
Florence, Kansas	October 2001	Five tanks caught fire as a result of a lightning strike.
Refugio, Texas	September 2002	A 37 m^3 oil tank was struck by a lightning and caught fire. The accident propagated by domino effect spreading to two other tanks and to two tanker trucks located nearby.
Puertollano, Spain	August 2020	A lightning strike hit and ignited a petrochemical product storage tank. The fire escalated propagating to the nearby tank storing petrochemical products as well.

The notional layout presented in Figure 6.2. 2 has been derived from an existing plant located in Italy and has been considered to perform the pilot application of the approach (Misuri et al., 2020a). As shown in the figure, both atmospheric storage tanks and pressurized vessels containing hazardous substances are included in the case study. Six atmospheric tanks storing gasoline (T1-T6 in Figure 6.2. 2), four pressurized horizontal vessels, three of them storing GPL (P2-P4 in Figure 6.2. 2), and one with ammonia (P1 in Figure 6.2. 2) are considered in the layout.

The main features of each piece of equipment are summarized in Table 6.2. 2. As can be seen in the table, various typologies of atmospheric tanks are considered, leading to different outcomes as a consequence of lightning strikes (Necci et al., 2014b). Indeed, on the one side, items T1 to T4 are external floating roof tanks (EFRT), where the roof floats directly upon the liquid stored and there is no confined vapor space.

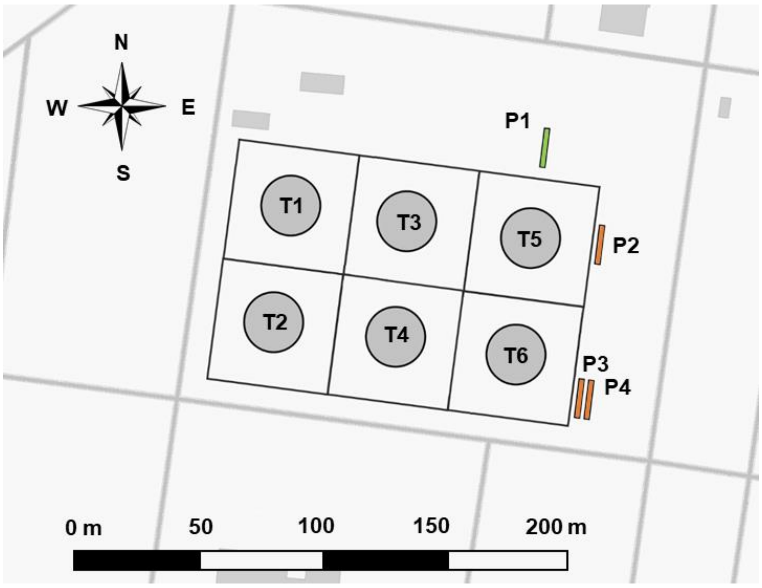


Figure 6.2. 2: Layout considered for the case study (Misuri et al., 2020a).

On the other side, T5 and T6 are cone roof tanks (CRT), where the roof is fixed and there is a confined vapor space above the liquid level. In case CRTs are designed in compliance with API 2000 and API 650, they should be equipped with a weak (frangible) roof-to-shell joint connection, which fails preferentially in case of internal overpressure (API, 2007, 1998). Concerning this technical detail, T5 is supposed not to comply with this design feature (thus it is assumed not to be equipped with a weak joint), while T6 is supposed to feature a weak roof-to-shell joint connection in agreement with the indications of the API standards (see Table 6.2. 2).

Table 6.2. 2: Summary of the features of the equipment considered in this case study. EFRT = External floating-roof tank, CRT = Cone-roof tank. Adapted from (Misuri et al., 2020a; Misuri and Cozzani, 2021a).

ID	**T1-T4**	**T5**	**T6**	**P1**	**P2-P4**
Storage type	Atmospheric tank (EFRT)	Atmospheric tank (CRT)	Atmospheric tank (CRT, weak joint)	Pressurized vessel	Pressurized vessel
Nominal capacity [m^3]	6511	6511	6511	150	110
Diameter [m]	24	24	24	3.2	2.75
Length[a] / Height[b] [m]	14.4	14.4	14.4	19.4	19.2
Shell thickness [mm]	12.5	12.5	12.5	27	24
Filling level	75%	75%	75%	90%	90%
Substance	Gasoline	Gasoline	Gasoline	Ammonia	LPG[c]
Substance state	Liquid	Liquid	Liquid	Liquefied gas	Liquefied gas
Operating pressure [bar]	1.00	1.05[d]	1.05[d]	8.5	2
Inventory [ton]	3656	3656	3656	84	55

a: horizontal vessels (P1-P4), b: vertical vessels (T1-T6), c: assumed as pure butane, d: considering N_2 (nitrogen) gas blanketing.

Moreover, tanks T1 to T4 are supposed to be equipped with rim-seal fire extinguishers (dispensing foam), while T5 and T6 are protected with a N_2 blanketing system to prevent the formation of explosive atmospheres in the confined vapor space, as shown in Table 6.2. 3. In the same table, reference values for the *PFD* for these two protection systems are provided, which were retrieved from (Necci et al., 2016). These systems are specifically included to lower the likelihood of fire scenarios in case of lightning strikes (Necci et al., 2014b).

Table 6.2. 3: Fire protection systems considered in the case study. PFD = Probability of failure on demand. Adapted from (Misuri et al., 2020a; Misuri and Cozzani, 2021a).

ID	Rim-seal fire extinguisher	N_2 blanketing system	*PFD*	Roof-to-shell weak joint connection
T1-T4	Yes	-	8.1E-3	-
T5	-	Yes	5.0E-3	No
T6	-	Yes	5.0E-3	Yes

To have a baseline for the risk level linked to internal failures (i.e., excluding both Natech and escalation scenarios), a QRA was preliminary performed considering only the conventional scenarios summarized in Table 6.2. 4.

Table 6.2. 4: Conventional scenarios considered to assess baseline risk in the case-study. f_{LOC} *= frequency of LOC;* P_{ign} *= immediate ignition probability;* $P_{ign}^{delayed}$ *= delayed ignition probability.* f_{LOC} *= frequency of the conventional scenario;*

ID	LOC	f_{LOC} [y^{-1}]	P_{ign}	$P_{ign}^{delayed}$	Final scenario	f_{SCE} [y^{-1}]
T1-T6	Catastrophic rupture	5.00E-06	6.50E-02	9.00E-01	Pool fire (catch basin)	3.25E-07
					Flash fire	1.26E-06
					VCE	2.95E-06
	Continuous release in 10 min	5.00E-06	6.50E-02	9.00E-01	Pool fire (catch basin)	3.25E-07
					Flash fire	1.26E-06
					VCE	2.95E-06
	Leak from 10mm hole	1.00E-04	6.50E-02	-	Pool fire	6.50E-06
P1	Catastrophic rupture	5.00E-07	-	-	Toxic dispersion	5.00E-07
	Continuous release in 10 min	5.00E-07	-	-	Toxic dispersion	5.00E-07
	Leak from 10mm hole	1.00E-05	-	-	Toxic dispersion	1.00E-05
P2-P4	Catastrophic rupture	5.00E-07	7.00E-01	9.00E-01	Fireball	3.50E-07
					Flash fire	4.05E-08
					VCE	9.45E-08
	Continuous release in 10 min	5.00E-07	5.00E-01	9.00E-01	Jet fire	2.50E-07
					Flash fire	6.75E-08
					VCE	1.58E-07
	Leak from 10mm hole	1.00E-05	2.00E-01	-	Jet fire	2.00E-06

Top event frequencies were retrieved from standardized sources (Uijt de Haag and Ale, 2005), while consequence assessment was performed adopting well-established integral models (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005). The likelihood ratio between flash fire and VCE is assumed equal to 0.3/0.7 (Uijt de Haag and Ale, 2005). The calculation of the risk figures was performed implementing the ARIPAR methodology (Egidi et al., 1995). Probit models used to assess the death probability distributions associated with conventional scenarios are consistent with the ones reported in Appendix D.1. For the sake of simplicity, a uniform population density was assumed (200 people/ha with 60% presence probability).

Whereas the general methodology for the QRA of domino effects in Natech events presented in Figure 6.2. 1 is of general validity, for the sake of clarity it has been explicitly tailored to the case of lightning, obtaining the flowchart reported in Figure 6.2. 3 to better evidence the peculiarities of some of the steps required to perform the equipment vulnerability assessment and the primary Natech scenarios identification.

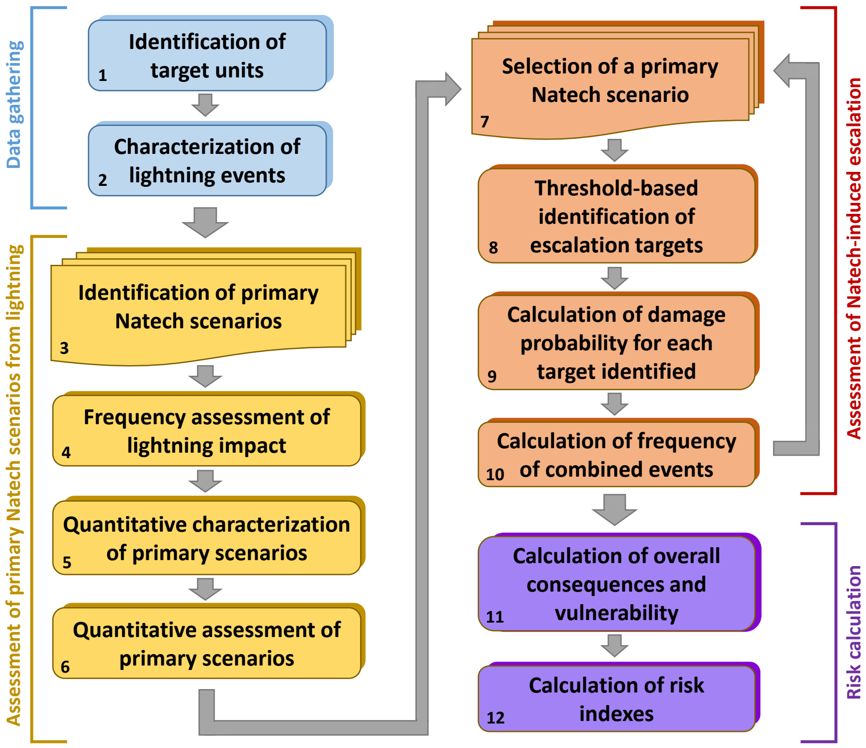


Figure 6.2. 3: Adaptation of the methodology for QRA of domino effects driven by natural hazards to the case of lightning strikes (Misuri et al., 2020a)

Additionally, the case study has been realized as a simplified version of a real plant layout and has been specifically conceived to include only the equipment necessary to show the application of the subsequent calculation steps of the methodology of Figure 6.2. 3. Thus, the application of the first step of the approach (i.e., aimed at reducing the number of items considered in the QRA) was not required and all the pieces of equipment shown in Figure 6.2. 2 were included in the analysis.

Nevertheless, it is worth recalling that in general the items mostly involved in severe past accidents driven by lightning strikes are atmospheric storage tanks with a relevant inventory of petrochemical products, whereas pressurized vessels feature only a limited share in past events (i.e., probably due to their limited size and significant shell thickness) (Renni et al., 2010). Actually, pressurized vessels can be involved in a domino effect from primary Natech events, thus they were included in the case study to enable an exhaustive assessment of secondary scenarios.

The keraunic hazard characterization should be based on the average number of lightning strikes reaching the ground level per year in the area of interest, as explained in Section 2.2.2. This quantity is defined as the flash density at ground level, n_g, and can be retrieved from several sources (e.g., see (Cecil et al., 2014; CEI, 2021; Matsui et al., 2019)).

Correlations to estimate n_g on the basis of the number of thunderstorm hours or days for a given location were also proposed in the literature for cases when direct data is not available (Cigré Working Group, 2013; Huffines and Orville, 1999; IEC, 2010). For instance, n_g, expressed in *flashes/(km²y)*, can be estimated for temperate regions by Eq. (6.2.12):

$$n_g = 0.1\, T_d \tag{6.2. 12}$$

where T_d is the average number of thunderstorm days per year retrieved from isokeraunic maps (IEC, 2010). Clearly, the adoption of these simplified approaches introduces uncertainty in the results.

The facility considered in the case study is supposed to be located in Italy, thus the reference n_g is assumed at 5 *flashes/(km²y)* (Kotroni and Lagouvardos, 2016). It should be noted that other sources available online could have been used to assess the keraunic hazard of the site (Cecil et al., 2014; CEI, 2021).

The following step in the QRA is the assessment of the lightning capture frequency for each item considered (Step 4 in Figure 6.2. 3). The frequency of lightning strike hitting a generic j-th item is proportional to the keraunic hazard of the site and can be evaluated as the product of the parameter n_g and the lightning capture area $A_{c,j}$ (Misuri et al., 2020a; Necci et al., 2016, 2014a), as reported in Eq. (6.2.13):

$$f_{c,j} = n_g A_{c,j} \tag{6.2. 13}$$

As can be noticed, the evaluation of A_c for each item is thus required before the application of Eq. (6.2.13). Sophisticated methodologies are available to calculate this quantity (e.g., see (Necci et al., 2014a) and references cited therein), although in the following only two simplified approaches more suitable in the context of QRA are presented.

According to the more conservative strategy, each item is considered isolated and a standalone capture area (i.e., independent of the neighboring items and structures) can be estimated on the basis of a parameter defined as the average projection at the ground of the lightning capture distance $r_{cm,j}$ (Necci et al., 2014a), quantifiable by applying Eq. (6.2.14):

$$r_{cm,j} = 50.07 + 1.89H_j - 2.33 * 10^{-2}{H_j}^2 \qquad (6.2.\ 14)$$

where H_j is the j-th item height expressed in m (i.e., $r_{cm,j}$ is obtained in m from the correlation). The average standalone capture area can be calculated considering the area included into a distance equal to $r_{cm,j}$ from item perimeter, as graphically depicted in Figure 6.2. 4.

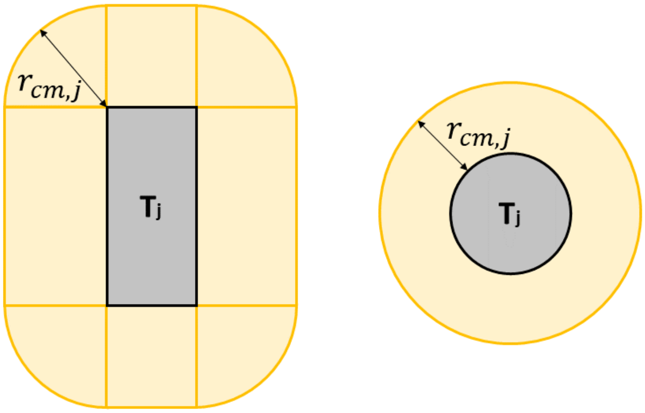


Figure 6.2. 4: Correlation between the standalone lightning capture areas of two generic T_j layout elements with the respective average projection at the ground of the lightning capture distance $r_{cm,j}$ (Misuri and Cozzani, 2021a).

In the case of horizontal vessels (i.e., and of not axisymmetric items in the vertical direction in general), assuming an equivalent diameter as D_j to quantify the projection at the ground is still acceptable (Misuri et al., 2020a).

The second strategy to estimate the capture area is more refined, being based on relaxing the strong assumption of perfectly isolated items. Indeed, when the spatial distribution of items on the layout is relatively dense, they cannot be considered isolated, and the relative lightning capture areas might partially overlap. To consider the effects of the proximity of neighboring equipment and structures on the capture area associated with each item, a specific procedure to associate the overlapping parts of each capture area is required. A validated approach based on layout discretization has been proposed in the literature (Necci et al., 2014b). This procedure has been applied to the case study of this section, considering 250’000 square cells of uniform dimensions (Misuri et al., 2020a).
A generic i-th cell is attributed to j-th item if the distance between the central point and the closest point of the j-th item $d_{cc,j,i}$ is lower than the lightning capture distance $r_{cm,j}$, according to Eq. (6.2.15):

$$d_{cc,j,i} \leq r_{cm,j} \qquad (6.2.\ 15)$$

This relation is graphically depicted in Figure 6.2. 5.

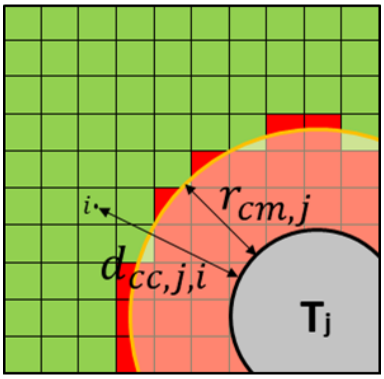


Figure 6.2. 5: Evaluation of the lightning capture area for a generic T_j element considering a layout discretization in square cells (Misuri and Cozzani, 2021a).

Clearly enough, Eq. (6.2.15) can be verified for multiple items in a generic *i*-th cell (i.e., being thus in a position featuring overlapped capture areas). In this case, the cell should be assigned to the item with the highest value of capture height calculated in the central point of that cell $z_{j,i}$, according to the following equation:

$$z_{i,j} = \sqrt{114.3^2 - d_{cc,i,j}^2} + H_j \tag{6.2. 16}$$

The lightning capture area $A_{c,j}$ for the generic *j*-th item can be thus assessed summing the areas of all the cells associated with that item, according to the following equation:

$$A_{c,j} = \sum_{i=1}^{N_c} \delta_{i,j} A_i \tag{6.2. 17}$$

where N_c is the overall number of cells, A_i is the area of the *i*-th cell, and $\delta_{i,j}$ is equal to one when the *i*-th cell is associated with the *j*-th item according to the criteria presented above, and zero otherwise. The areas obtained for the items included in the case study are reported in Figure 6.2. 6. As clear from the figure, the proximity to other items is relevant in the definition of the capture areas of all the pieces of equipment in the layout. Indeed, the shapes of the capture areas are not regular and are clearly significantly less extended than the standalone capture area that would have been obtained following the conservative calculation procedure described above.

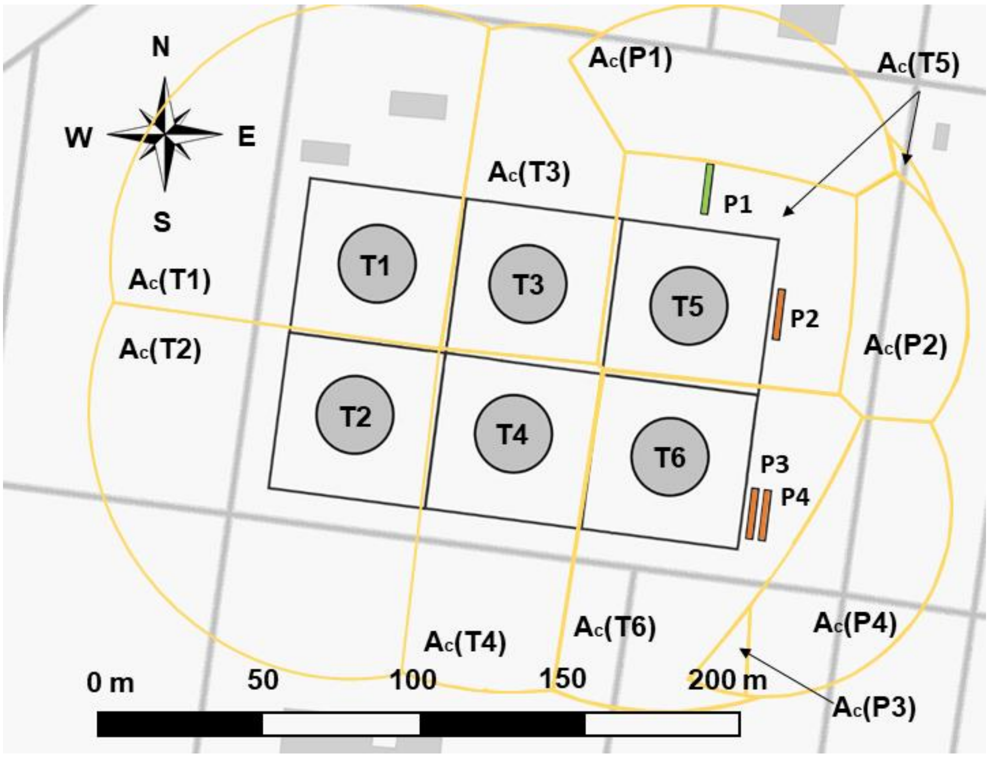


Figure 6.2. 6: Lightning capture areas estimated through the discretization procedure explained above. Adapted from (Misuri et al., 2020a; Misuri and Cozzani, 2021a).

After calculating the lightning capture frequency, f_c, primary Natech scenarios might be identified by applying specific ETs and their related frequencies f_P can be evaluated (Necci et al., 2016). As already explained, different outcomes are possible following a lightning strike on storage tanks depending on the typology of storage. The major factors that determine the expected outcomes are whether the tank is pressurized or atmospheric, and in this latter case also whether the tanks are of EFRT-type or CRT-type. The set of ETs applied to the case study is shown in Figure 6.2. 7. The ET shown in Figure 6.2. 7-a, developed for EFRTs (Necci et al., 2014b), was applied to tanks T1 to T4. The ET reported in Figure 6.2. 7-a, which were specifically developed for CRTs and are capable to consider the possible presence of roof-to-shell weak joint connection (Necci et al., 2014b), have been applied to characterize primary scenarios from tanks T5 and T6. Finally, the ETs shown in Figure 6.2. 7-c and Figure 6.2. 7-d were applied to address the frequency assessment of primary scenarios involving vessel P1 and vessels P2-P4 respectively (Necci et al., 2016).

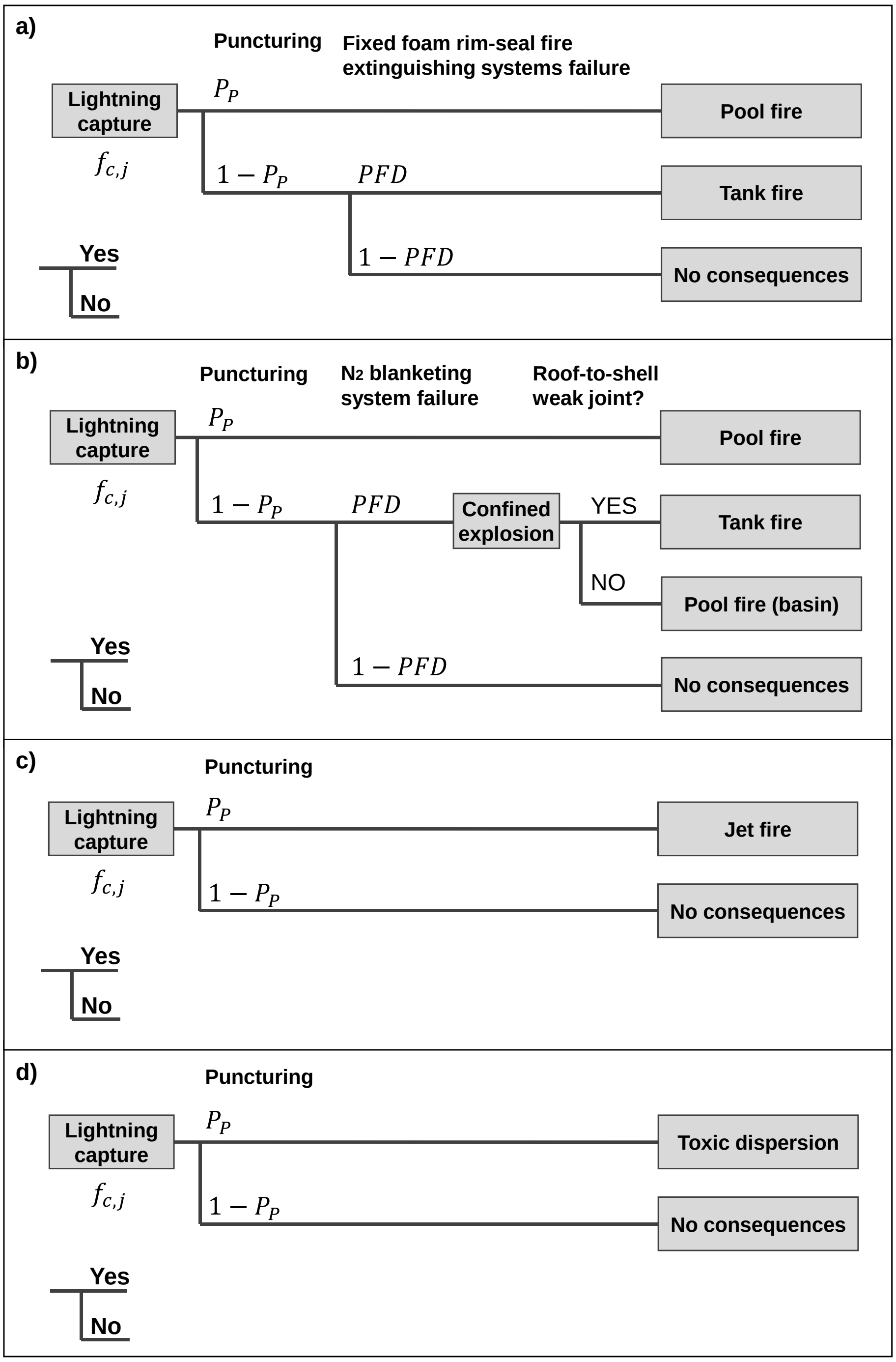


Figure 6.2. 7: Event trees (ETs) for accidental scenarios triggered by the lightning impact on a) external floating roof tanks (EFRT) storing flammable substances; b) cone roof tanks (CRT) and internal floating roof tanks (IFRT) storing flammable substances; c) pressurized storage tanks storing flammable substances; d) CRT and pressurized storage tanks storing toxic substances. $P_{P,j}$ = Lightning puncturing probability for the j-th item, PFD = Probability of failure on demand.

As can be noted from Figure 6.2. 7-a and Figure 6.2. 7-b, in addition to direct scenarios following the puncturing of the containment, in the case of atmospheric storage only, also indirect scenarios might arise. These are caused by the ignition of flammable vapors assumed to be present in the sealing area of the roof of EFRTs and in the confined volume between the liquid surface and the roof of CRTs in the case of blanketing system unavailability. The possibility of unavailability of the protection systems implemented in tanks T1-T6 is included in the ETs by means of the *PFD* values presented in Table 6.2. 3. It should be noted that in this case the possibility of barrier failure due to the current produced by the lightning strike is not considered.

Lastly, the puncturing probability P_P should be estimated to complete the quantification of the ETs and obtained the frequencies of the primary scenarios.

Models based on the quantity of energy required to melt a portion of equipment containment have been proposed in the literature (Necci et al., 2013). A simplified version of those models has been applied in the case study, according to what reported in Eq. (6.2.18):

$$\ln(P_{P,j}) = 0.924 - 0.908t_j \tag{6.2. 18}$$

where t_j is the thickness of the containment of the j-th item (expressed in mm). This approach is particularly flexible and can be also easily tailored to specific cases of items featuring variable thickness (e.g., atmospheric storage tanks can be designed with decreasing thickness at increasing height) (Necci et al., 2016).

Finally, to apply consequence assessment models to direct scenarios, the evaluation of the expected hole diameter generated by the puncturing $D_{h,av,j}$ is required. This parameter can be correlated to t_j according to the following expression (Necci et al., 2013):

$$D_{h,av,j} = 8.5 * 10^{-3}t^2 - 6.6 * 10^{-3}t_j + 5.23 \tag{6.2. 19}$$

The characterization of primary Natech scenarios is thus completed at this point. The main results for each item considered are summarized in Table 6.2. 5.

Table 6.2. 5: Characterization of primary Natech scenarios obtained from the application of the presented procedures. A_c = lightning capture area, f_c = lightning capture frequency, P_P = puncturing probability, $D_{h,av}$ = average hole diameter; f_I = frequency of the primary scenario. Adapted from (Misuri and Cozzani, 2021a).

ID	**A_c [m²]**	**f_c [y⁻¹]**	**P_P**	**Direct scenarios**			**Indirect scenarios**	
				$D_{h,av}$ [mm]	**Type**	**f_I [y⁻¹]**	**Type**	**f_I [y⁻¹]**
T1	1.022E+04	5.11E-02	1.57E-05	6.5	Pool fire	8.022E-07	Tank fire	4.139E-04
T2	1.044E+04	5.22E-02	1.57E-05	6.5	Pool fire	8.192E-07	Tank fire	4.227E-04
T3	4.835E+03	2.42E-02	1.57E-05	6.5	Pool fire	3.796E-07	Tank fire	1.958E-04
T4	5.281E+03	2.64E-02	1.57E-05	6.5	Pool fire	4.146E-07	Tank fire	2.139E-04
T5	5.467E+03	2.73E-02	1.57E-05	6.5	Pool fire	4.291E-07	Catastrophic pool fire (catch basin)	1.367E-04
T6	7.180E+03	3.59E-02	1.57E-05	6.5	Pool fire	5.636E-07	Tank fire	1.795E-04
P1	4.284E+03	2.14E-02	5.68E-11	11.2	Toxic cloud	1.216E-12	-	-
P2	2.397E+03	1.20E-02	8.65E-10	10.0	Jet fire	1.038E-11	-	-
P3	2.632E+02	1.30E-03	8.65E-10	10.0	Jet fire	1.125E-11	-	-
P4	3.633E+03	1.82E-02	8.65E-10	10.0	Jet fire	1.574E-11	-	-

As shown in Table 6.2. 5, the majority of f_c values obtained are of the order of 10^{-2} y^{-1} while there are significant differences in the values obtained for puncturing probability, P_P for atmospheric and pressurized equipment. Indeed, whereas for atmospheric storages (i.e., T1 to T6) P_P is of about 10^{-5}, for pressurized vessels (i.e., P1 to P4) this value is critically lower (i.e., around 10^{-10}) due to greater shell thickness. This relevant difference in puncturing probability explains the lower frequencies obtained for primary scenarios f_I involving vessels P1 to P4. These values turned out to be well-below established cut-off frequencies (i.e., corresponding to 10^{-10} y^{-1}), which was applied in the literature addressing the QRA of domino effect (Cozzani et al., 2014), thus primary Natech scenarios from these items were deemed not credible and were excluded from further analysis.

For what concerns the severity of the LOCs resulting from T1-T6 puncturing, the $D_{h,av}$ is assessed at about 6.5 mm by the application of Eq. (6.2.19), as shown in Table 6.2. 5. This value is lower than 10 mm, which is the smallest diameter suggested in established QRA guidelines for continuous LOCs (Uijt de Haag and Ale, 2005). Therefore, the value of 10mm was conservatively assumed in source models. Consequence assessment has been then performed applying well-known integral models available in the technical literature (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005).

6.2.3 Results obtained for the case study

Characterization of overall domino scenarios

Once the characterization of primary Natech scenarios is completed, the possibility of their escalation due to domino effect is assessed (Step 7 of Figure 6.2. 3). The first step to accomplish this part of the procedure is the application of threshold-based approaches to determine which of the primary Natech scenarios might lead to a credible escalation. For the sake of simplicity, in this case study, it was assumed that heat radiation from primary fires is the only possible escalation vector, practically neglecting the contribution related to possible fragment projection (i.e., this might be generated in case of confined explosions of T5 and T6).

Conservative threshold values for heat radiation suggested in the literature were considered for atmospheric tanks and pressurized vessels, equal respectively to 15 kW/m^2 and 45kW/m^2 (Cozzani et al., 2013b). By their application, primary Natech scenarios were screened and the subset possibly leading to escalation was identified, along with the related targets. The results of this step are described in Table 6.2. 6, along with the associated targets and expected secondary scenarios. As can be seen from the table, in case atmospheric tanks storing flammable chemicals (i.e., T1-T6) are the credible targets of escalation, pool fires following their catastrophic failure were assumed as secondary scenarios.

Table 6.2. 6: The identified subset of primary Natech events possibly generating further escalation, with related targets and expected secondary scenarios. I: heat radiation on targets; P_D: target damage probability due to heat radiation. Adapted from (Misuri et al., 2020a).

Primary scenario	**Target ID**	**Secondary scenario**	***I* [kW/m^2]**	**P_D**
Tank fire from T1	T2	Catastrophic pool fire	17.3	4.17E-01
	T3	Catastrophic pool fire	17.3	4.17E-01
Tank fire from T2	T1	Catastrophic pool fire	16.8	3.93E-01
	T4	Catastrophic pool fire	15.4	3.25E-01
Tank fire from T3	T1	Catastrophic pool fire	16.8	3.93E-01
	T4	Catastrophic pool fire	17.5	4.26E-01
Tank fire from T4	T5	Catastrophic pool fire	15.2	3.16E-01
	T2	Catastrophic pool fire	15.2	3.16E-01
	T3	Catastrophic pool fire	17.1	4.08E-01
	T6	Catastrophic pool fire	15.2	3.16E-01
Catastrophic pool fire (catch basin) from T5	T3	Catastrophic pool fire	40.2	9.40E-01
	T4	Catastrophic pool fire	23.1	6.54E-01
	T6	Catastrophic pool fire	43.2	9.56E-01
	P1	Toxic dispersion	75.2	5.82E-01
	P2	Fireball	75.7	6.59E-01
Tank fire from T6	T4	Catastrophic pool fire	15.5	3.30E-01
	T5	Catastrophic pool fire	16.9	3.98E-01

On the contrary, if the escalation involves pressurized vessels, the toxic dispersion of ammonia is assumed for P1 and a fireball is considered for P2 since it contains LPG (Cozzani et al., 2006a). In the same table, the heat radiation impacting targets from each identified primary Natech scenario and the target damage probability P_D assessed leveraging the equipment vulnerability models based on *TTF* (see Eq. (6.2.2) and Eq. (6.2.3)).

Finally, according to the methodology described in Figure 6.2. 3, starting from each single primary Natech scenario, the characterization of the credible simultaneous secondary outcomes that might arise should be performed applying Eq. (6.2.7) and Eq. (6.2.8). In Table 6.2. 7, the possible overall scenarios with the related frequencies have been reported. As can be noticed from the table, in total 60 different overall scenarios have been identified (i.e., this number can be obtained summing the results obtained from Eq. (6.2.6) over the subset of 6 primary Natech scenarios that can lead to escalation reported in Table 6.2. 6).

Table 6.2. 7: Summary of the identified overall domino scenarios with their frequencies f_E. The item involved in the primary Natech event is reported in bold (Misuri et al., 2020a).

ID	Involved items	f_E [y^{-1}]	ID	Involved items	f_E [y^{-1}]
FO01	**T1**	1.41E-04	FO31	T4, **T5**, T6	7.32E-07
FO02	**T1**, T2	1.01E-04	FO32	T3, T4, **T5**, T6	1.14E-05
FO03	**T1**, T3	1.01E-04	FO33	**T5**, P1	2.50E-08
FO04	**T1**, T2, T3	7.20E-05	FO34	T3, **T5**, P1	3.91E-07
FO05	**T2**	1.73E-04	FO35	T4, **T5**, P1	4.72E-08
FO06	T1, **T2**	1.12E-04	FO36	T3, T4, **T5**, P1	7.38E-07
FO07	**T2**, T4	8.35E-05	FO37	**T5**, T6, P1	5.41E-07
FO08	T1, **T2**, T4	5.41E-05	FO38	T3, **T5**, T6, P1	8.45E-06
FO09	**T3**	4.66E-05	FO39	T4, **T5**, T6, P1	1.02E-06
FO10	T1, **T3**	3.02E-05	FO40	T3, T4, **T5**, T6, P1	1.59E-05
FO11	**T3**, T4	3.47E-05	FO41	**T5**, P2	3.47E-08
FO12	T1, **T3**, T4	2.25E-05	FO42	T3, **T5**, P2	5.42E-07
FO13	**T3**, T5	2.15E-05	FO43	T4, **T5**, P2	6.54E-08
FO14	T1, **T3**, T5	1.39E-05	FO44	T3, T4, **T5**, P2	1.02E-06
FO15	**T3**, T4, T5	1.60E-05	FO45	**T5**, T6, P2	7.50E-07
FO16	T1, **T3**, T4, T5	1.04E-05	FO46	T3, **T5**, T6, P2	1.17E-05
FO17	**T4**	5.94E-05	FO47	T4, **T5**, T6, P2	1.41E-06
FO18	T2, **T4**	2.74E-05	FO48	T3, T4, **T5**, T6, P2	2.21E-05
FO19	T3, **T4**	4.08E-05	FO49	**T5**, P1, P2	4.84E-08
FO20	T2, T3, **T4**	1.88E-05	FO50	T3, **T5**, P1, P2	7.55E-07
FO21	**T4**, T6	2.74E-05	FO51	T4, **T5**, P1, P2	9.13E-08
FO22	T2, **T4**, T6	1.26E-05	FO52	T3, T4, **T5**, P1, P2	1.43E-06
FO23	T3, **T4**, T6	1.88E-05	FO53	**T5**, T6, P1, P2	1.05E-06
FO24	T2, T3, **T4**, T6	8.68E-06	FO54	T3, **T5**, T6, P1, P2	1.63E-05
FO25	**T5**	1.80E-08	FO55	T4, **T5**, T6, P1, P2	1.97E-06
FO26	T3, **T5**	2.80E-07	FO56	T3, T4, **T5**, T6, P1, P2	3.08E-05
FO27	T4, **T5**	3.39E-08	FO57	**T6**	7.24E-05
FO28	T3, T4, **T5**	5.29E-07	FO58	T4, **T6**	3.57E-05
FO29	**T5**, T6	3.88E-07	FO59	T5, **T6**	4.79E-05
FO30	T3, **T5**, T6	6.06E-06	FO60	T4, T5, **T6**	2.36E-05

Risk figures

After the characterization of the overall domino scenarios is completed, risk indices can be calculated. The results obtained for the case study in terms of LSIR are shown in Figure 6.2. 8. In particular, the values obtained for conventional scenarios are shown in Figure 6.2. 8-a. In Figure 6.2. 8-b, the LSIR obtained considering conventional scenarios and the contribution of primary Natech events triggered by lightning are shown. Finally, in Figure 6.2. 8-c, the LSIR obtained considering also the overall escalation scenarios are shown. The results clearly evidence that neglecting the cascading nature of Natech accidents leads to an underestimate of individual risk over significant areas. Indeed, LSIR turns out to be up to two orders of magnitude higher than the value expected considering conventional scenarios only. This is caused by the twofold contribution of the high frequency of scenarios deriving from lightning strikes and to the severity of secondary scenarios triggered by domino effect.

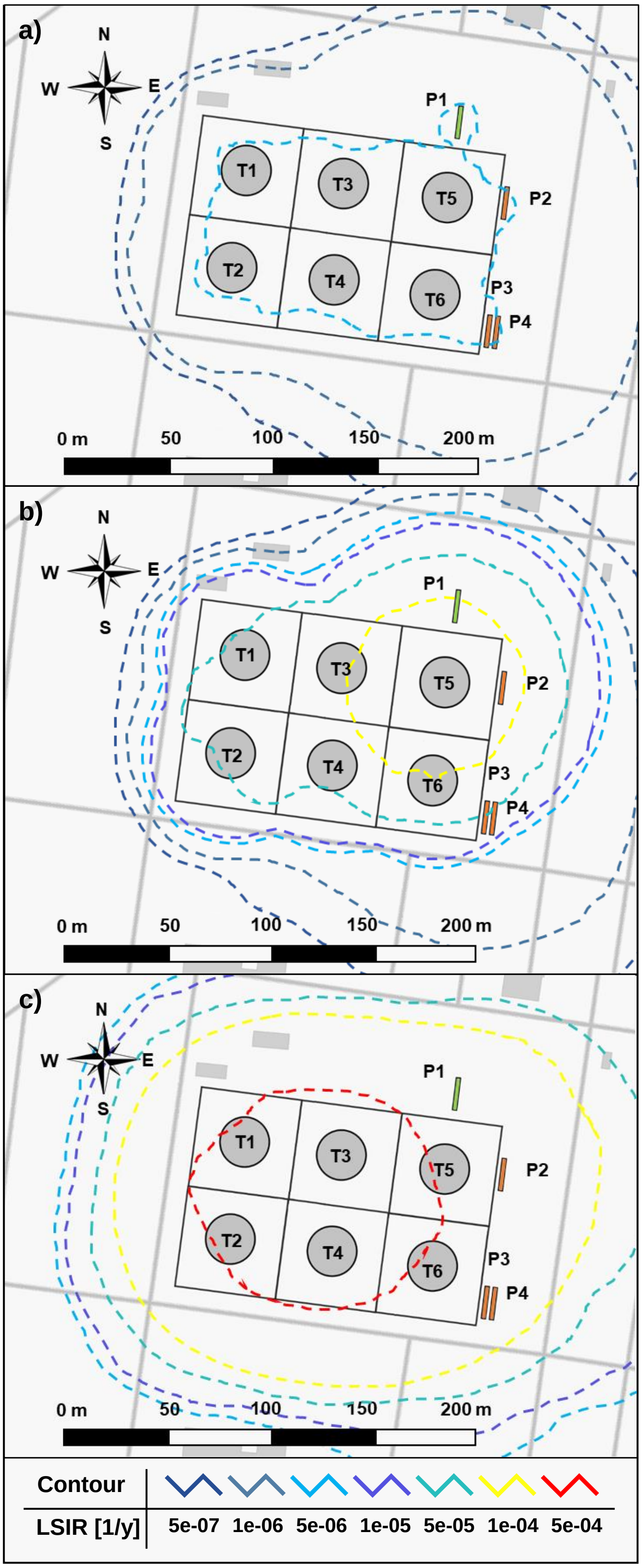


Figure 6.2. 8: Comparison of local-specific individual risk (LSIR) contours obtained: a) considering only conventional scenarios, b) conventional and primary lightning-triggered Natech scenarios, c) and considering also the additional contribution related to the escalation from primary Natech scenarios.

The importance of considering the possibility of domino effect in Natech accidents triggered by lightning strikes is clear also analyzing societal risk results, which are expressed in terms of the F/N curves drawn in the plot of Figure 6.2. 9.

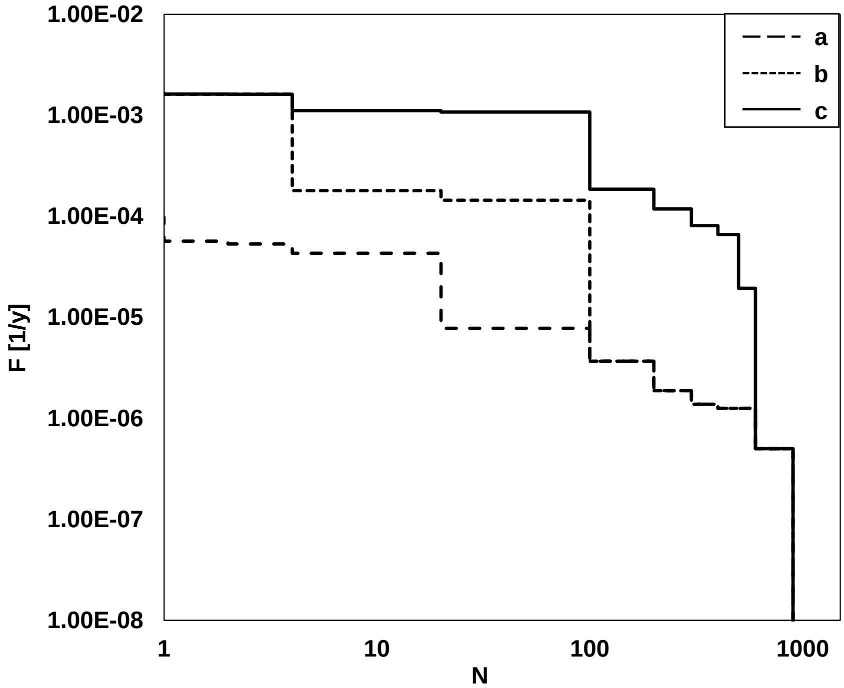


Figure 6.2. 9: Societal risk obtained for the case study, expressed by F/N curves: a) conventional scenarios only; b) conventional and primary lightning-induced Natech scenarios only; c) conventional and Natech scenarios including overall escalation scenarios.

As shown in the figure, the F/N curve obtained considering the possibility of primary scenarios from lightning strikes is significantly shifted towards higher frequency values compared to the curve obtained considering conventional scenarios only (i.e., highlighting the high frequency of hazardous outcomes deriving from lightning strikes). Nonetheless, frequency increase is mostly limited to the region of low-to-medium-severity scenarios produced by lightning strikes (i.e., N < 100).

Differently, when the possibility of escalation to secondary domino scenarios following primary Natech events is considered, higher-severity events become more relevant, and overall scenarios with high magnitude and lower frequencies affect significantly the societal risk figures. This again evidences that overlooking the cascading nature of the accident might lead to a severe underestimation of the risk related to severe scenarios caused by accident escalation.

The same suggestion can be found analyzing the *PLL* and *EV* indices calculated for the three cases, as shown in Figure 6.2. 10. As shown in the figure, there is a clear difference between the values resulting from lightning-driven primary scenarios only, and those calculated including the possibility of escalation through domino effect.

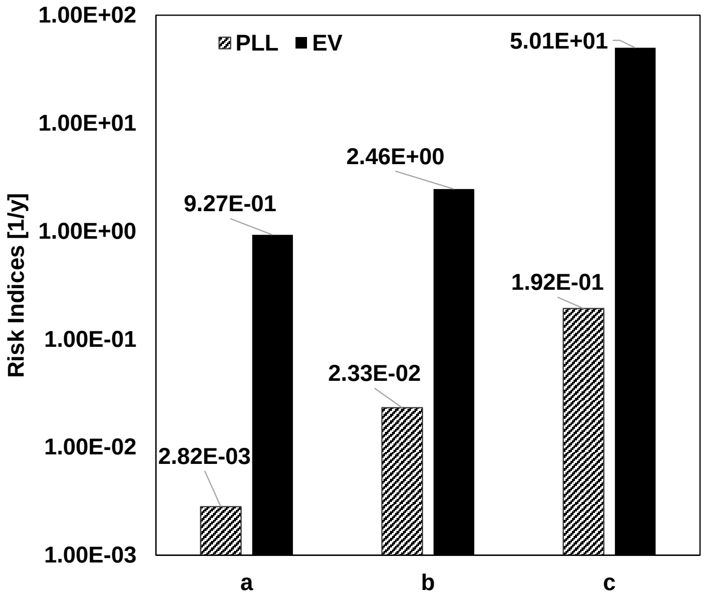


Figure 6.2. 10: Potential Life Loss (PLL) and expectation value (EV) risk indices calculated for the case study: a) considering only conventional scenarios; b) considering both conventional and primary lightning-induced Natech scenarios; c) considering also overall escalation scenarios.

Indeed, compared to the baseline values obtained from conventional scenarios (i.e., series 'a' in Figure 6.2. 10), when only primary Natech scenarios are considered (i.e., series 'b' in Figure 6.2. 10) *PLL* and *EV* increase respectively of about 8 and 3 times, whereas if escalation through domino effect is also included in the assessment (i.e., series 'c' in Figure 6.2. 10) the increases in the two indices jump to 68 and 54 times the values of the case 'a'.

6.2.4 Discussion

The results obtained in the case study are important for several reasons. First of all, the figures obtained highlight the importance of considering domino effect in the risk assessment of lightning-induced Natech accidents. Indeed, previous studies (Necci et al., 2016) reported that Natech scenarios triggered by lightning, while having a high frequency, usually result in relatively low-severity accidents due to the low credibility of direct damages to pressurized equipment. These results were confirmed by the analysis of the present case study, although when considering the possibility of domino effect, such conclusions should be modified. In fact, the escalation of lightning-induced scenarios might cause severe overall scenarios with non-negligible frequencies, as shown by the results of the case study.

Secondly, the results obtained are significant in general for all the typologies of Natech accidents. Indeed, while primary Natech events caused by earthquakes or floods might be particularly severe, assuming the accident progression stops to primary technological scenarios might not produce realistic results. Clearly, severe Natech events can easily trigger an escalation to secondary scenarios. In addition, the possibility of domino effects might be even enhanced by the adverse conditions taking place during severe natural hazards that can play a role in reducing the performance of safety systems designed to stop accidental progression, as shown in Section 5.3 (Misuri et al., 2021b). Related to this point, it should be noted that the methodology discussed in this chapter does not allow to explicitly include barrier depletion in the QRA of Natech accident escalation. Nevertheless, the general framework shown in Section 6.2.1 can be considered a preliminary approach that paves the way for the comprehensive methodology that will be developed in Section 6.3.

6.2.5 Conclusions

In this section, a general framework to perform the QRA of domino effects in Natech events is outlined. The framework can be applied to various categories of natural hazards and enables a better representation of the cascading nature of this typology of accidents. The methodology can be leveraged by decision-makers to estimate risk figures and indices related to Natech scenarios and to their possible propagation to nearby equipment by domino effect. A pilot case has been presented and discussed, considering the specific case of Natech scenarios generated by lightning strikes. As already pointed out, lightning is among the natural hazards most frequently leading to Natech accidents, and the application of the proposed methodology allowed to demonstrate that overlooking their cascading nature (i.e., considering only primary Natech events) would lead to a severe underestimation of risk figures.

6.3 Assessment of Natech risk considering domino effect and concurrent safety barrier depletion

Analyzing the results obtained in the previous sections of this chapter two important lessons can be drawn. First of all, it was clearly demonstrated that barrier depletion influences the risk related to primary technological scenarios (i.e., from Section 6.1). Second of all, the relevance of the contribution to overall risk figures of possible Natech event escalation through domino effects was also highlighted (i.e., from Section 6.2). Nonetheless, as already mentioned in Section 6.2.4, the effect of barrier depletion in the phase of accident escalation through domino effect has not been addressed in the previous sections. Therefore, in the following, a comprehensive methodology to assess Natech risk will be presented, including both the possibility of escalation through domino effect, and the possibility that the safety systems implemented to prevent/mitigate this phase of the accident chain might undergo concurrent depletion of significant extent during natural hazards.

6.3.1 *Overview of the methodology*

An overview of the method is provided in Figure 6.3. 1. Also in this case the starting point of the methodology is the definition and characterization of a reference set of natural hazards that will be considered in the analysis (Step 1 in Figure 6.3. 1).

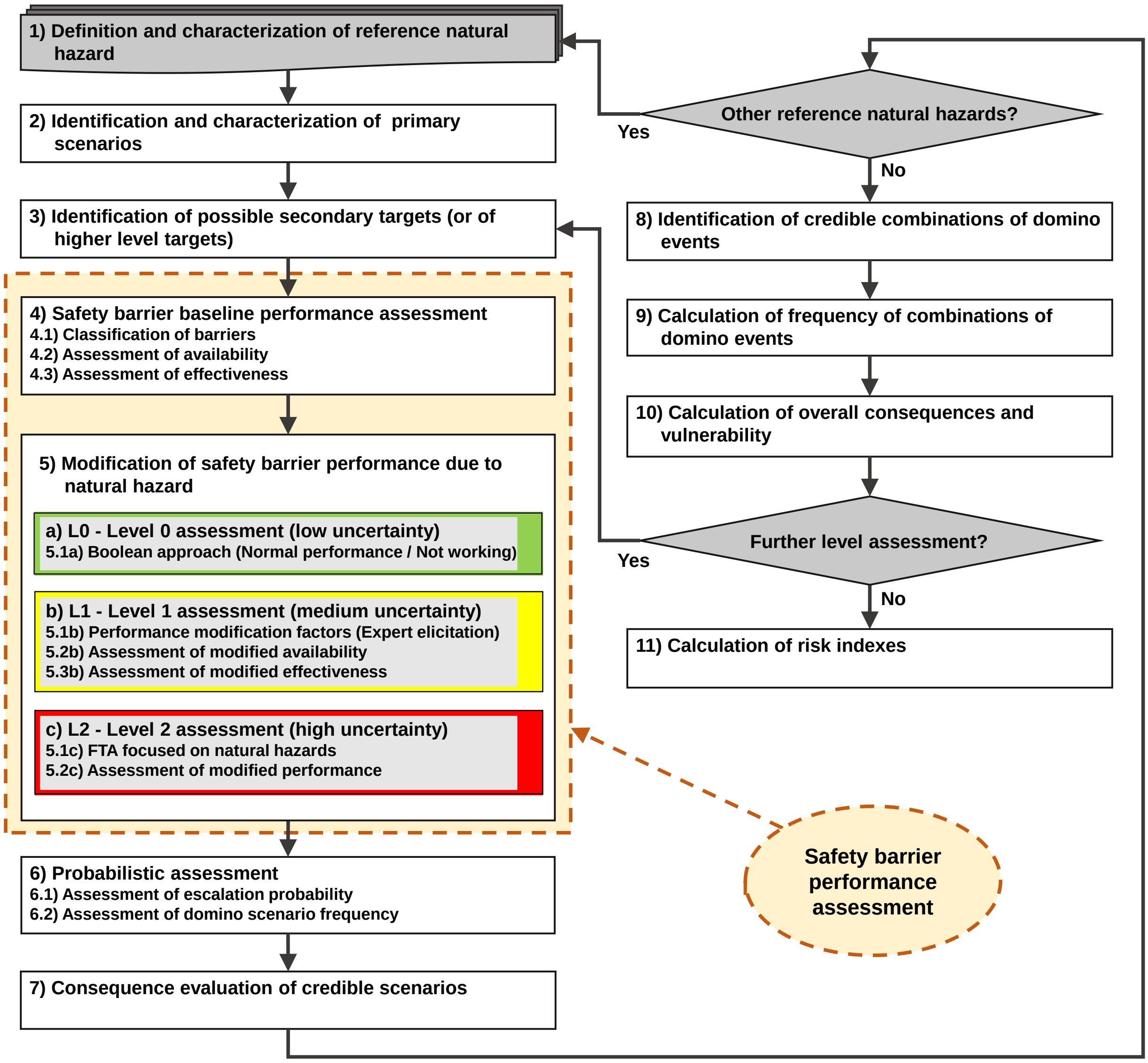


Figure 6.3. 1: Flowchart for the methodology proposed for risk assessment of mitigated domino scenarios during natural events integrating the specific performance assessment of safety barriers considering the impact of the natural event.

Specific indications on the approaches to the quantitative characterization of natural hazards in terms of parameters expressing the frequency and the intensity of the events, with a degree of detail suitable for the assessment of Natech events, are available in the literature (Antonioni et al., 2007; Fabbrocino et al., 2005; Salzano et al., 2009). For instance, floods may be characterized in terms of return time (linked to the frequency of occurrence) and floodwater depth and velocity (Antonioni et al., 2015; Landucci et al., 2014, 2012). Clearly enough, this step is not intended to provide a detailed characterization of natural hazards, but rather to have a concise expression of complex natural phenomena through a limited set of parameters, which is suitable for the framework of QRA (Cozzani et al., 2014). Among the established methodologies available to accomplish this task, it is worth mentioning the Probabilistic Seismic Hazard Analysis for earthquakes (Baker, 2008) or the use of hazard maps developed from data on past events for the case of floods (de Moel et al., 2009). Appropriate methodologies need to be selected with the contribution of sectoral experts, also considering the level of detail and the uncertainty compatible with the aims of the analysis. As an example, for the case of floods, the accuracy of the estimates of scenario return time might be influenced by several factors as the amount of available data (and their related accuracy), the possible effects of climate change, or modifications of the river drainage area (Holmes and Dinicola, 2010).

The impact of the natural hazard on equipment items that may lead to the release of hazardous materials and, consequently, to primary technological scenarios is then assessed. Reference equipment items that may lead to a LOC generating primary technological scenarios are identified (Step 2 in Figure 6.3. 1). Specific criteria developed for the framework of Natech risk assessment for the identification and ranking of equipment to be considered, based on hazardous material inventory, substance features, and storage conditions might be adopted (e.g., see (Antonioni et al., 2009a; Cozzani et al., 2010)).

The frequency of primary LOC events $f_{I,LOC}$ can be assessed as follows (Misuri et al., 2021b):

$$f_{I,LOC} = f_{nh} \times P_{nhd} \tag{6.3. 1}$$

where f_{nh} is the frequency of the reference natural hazard and P_{nhd} is the conditional probability of equipment failure, estimated applying equipment vulnerability models, that is, simplified models based on the intensity of the natural event impacting on it (Cozzani et al., 2014). Further details on such models have been provided in Section 2.2.2.
The primary technological scenarios following the LOC event are then characterized in terms of frequency (f_P) and consequences by the application of specific event trees, conceptually analogous to those obtained in the conventional assessment of technological scenarios following a release (Antonioni et al., 2009a; Campedel et al., 2008). For instance, in the case of floods, water-reacting substances might give rise to specific scenarios after the release, which were the object of previous studies (Cozzani et al., 2010).

The identification of further equipment items that may be the possible secondary targets of domino effects generated by the primary scenarios (Step 3 in Figure 6.3. 1) is then performed using well-established threshold-based screening methodologies applied to the escalation vectors generated by the primary technological scenarios (Alileche et al., 2015; Cozzani et al., 2013b, 2006b). It should be remarked that past accident analysis evidenced that most Natech events reported in the literature and in industrial accident databases involved the release of flammable chemicals (Campedel, 2008; Cozzani et al., 2010; Krausmann et al., 2011), which may lead to domino effect due to fire escalation in case of ignition. Thus, in the following, the methodology was focused on domino effects generated by the escalation of fire scenarios. Nevertheless, the methodology may be applied as well to other escalation vectors, when relevant (e.g., fragment projection or blast waves).

A thorough assessment of the effect of safety barriers on the likelihood of escalation considering the impact of the natural event on these measures is then required (Steps 4-5 in Figure 6.3. 1). A multi-level quantitative methodology specifically addressing the Natech framework is developed to consider the presence and performance of safety barriers in the assessment of escalation likelihood. Considering barrier complexity and uncertainties related to the intensity and impact of natural hazards, three levels of assessment are conceptualized (Steps 5a to 5c in Figure 6.3. 1). The approach proposed will be described in detail in Section 6.3.2.

Probabilistic assessment of domino event frequencies can then be performed (Step 6 in Figure 6.3. 1). The probability of escalation of stationary fires is evaluated utilizing probit models based on the time to failure (*TTF*) of target vessels when impacted by the heat load (Cozzani et al., 2014; Landucci et al., 2009; Reniers and Cozzani, 2013a). Probabilities and frequencies of the final events are then assessed applying a dedicated event tree (ETA) methodology, which was specifically developed in earlier studies to include safety barriers in the modeling of escalation (Landucci et al., 2017b, 2016, 2015). The model allows for the characterization of both unmitigated and mitigated secondary scenarios, based on barrier performance, as already shown in Section 5.3.

The following step of the methodology is the consequence assessment of the secondary domino scenarios (Step 7 in Figure 6.3. 1), which is carried out adopting literature models (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005). In order to obtain a less conservative description of the secondary scenarios, the consequences of mitigated events are modelled considering the mitigation action of the safety barriers, as described in detail in Section 6.3.3.

The final steps of the methodology (Steps 8-10 in Figure 6.3. 1) involve the characterization of the overall domino scenarios and are described in Section 3.3. The analysis can be extended to the identification and assessment of tertiary events and/or higher-level events. In case, the procedure is applied recursively and the selection of possible tertiary/higher-level targets possibly affected by escalation needs to be carried out (Cozzani et al., 2014; Landucci et al., 2017b). Risk index calculation may be carried out (Step 11 in Figure 6.3. 1) using standardized procedures (CCPS, 2000; Uijt de

Haag and Ale, 2005), in analogy also with other approaches to Natech QRA (Antonioni et al., 2015; Cozzani et al., 2014).

6.3.2 Multi-level approach to safety barrier assessment

As already discussed in Section 5.1, the concept of safety barriers is extensively used in the chemical and process industry referring to physical and non-physical means implemented to reduce the possibility of technological accidents or to lessen their impact (PSA, 2013; Rausand, 2011; Sklet, 2006). Performance of safety barriers can be assessed through specific methodologies or retrieving generic data from reliability databases (De Dianous and Fiévez, 2006; Hollnagel, 2008; IEC, 2003). Moreover, methodologies are available in the literature to tailor failure frequencies of equipment items and to include the effect of specificities and environmental factors on reliability figures (Gao et al., 2010; Kumar and Klefsjö, 1994; Pitblado et al., 2011). For instance, general failure frequencies may be revised through expert judgment to include the effect of item location and other factors not accounted for in database values (Pitblado et al., 2011). Proportional hazard models (PHM) have been applied to include the effect of explanatory variables (i.e., covariates) in modification of equipment failure rate and reliability (Bendell et al., 1991; Cox, 1972; Kumar and Klefsjö, 1994). More recently, covariate-based models have been applied to evaluate the impact of harsh environmental conditions on technical systems availability (Gao et al., 2010; Landucci et al., 2017a). However, none of these methodologies explicitly address the possibility of performance modification during Natech accidents (Misuri et al., 2020b).

Therefore, a novel methodology for the assessment of safety barrier performance modification during Natech accidents will be applied in the following, in analogy with Section 6.1. As can be noticed from Step 4 of Figure 6.3. 1, the methodology is based on the preliminary evaluation of baseline barrier performance through a tailored LOPA approach developed in the context of domino escalation assessment (Landucci et al., 2016, 2015), overlooking the possible influence of the natural hazards. Each safety barrier is categorized according to the passive/active/procedural classification based on the barrier working principle already discussed in Section 5.3.2. The performance of each barrier is then expressed through two-parameter metrics: i) the probability of failure on demand (*PFD*), that is the probability that the measure will not be available when required to perform the safety function, and ii) the effectiveness (η), that is, the conditional probability the barrier is able to prevent (or stop) domino escalation once successfully activated. The *PFD* is linked to barrier system architecture and reliability, and may be determined through various reliability approaches according to the available information on the system components, as extensively discussed elsewhere (Landucci et al., 2015; Necci et al., 2014b). On the other hand, η is the direct quantification of the quality of barrier mitigation or preventive actions, hence it should be estimated considering performance data or statistics, together with other influencing factors as maintenance, operational management, and so forth (Landucci et al., 2017b, 2016, 2015).

Once the baseline probabilistic performance of safety barriers is estimated, barrier performance modification due to the natural hazard considered is then assessed, according to a three-level methodology (i.e., Level 0, Level 1, and Level 2 in Step 5 of Figure 6.3. 1). Level 0 (L0) is based on a simplified evaluation suitable for simpler barrier systems (Step 5a indicated in green in Figure 6.3. 1). Level 1 (L1) in the assessment is based on the data obtained for reference schemes of safety barriers in previous studies (Misuri et al., 2020b) (Step 5b in Figure 6.3. 1). Level 2 (L2) is based on a detailed analysis of barrier architecture and subsystems, capable of accounting for site-specific scenarios and special design provisions (Step 5c in Figure 6.3. 1). The three levels of assessment are introduced to address barrier systems with increasing levels of complexity in analogy to those introduced in Section 6.1, although they are here applied to the case of barriers intended to prevent the escalation. Clearly enough, the selection of the level of the analysis is related to the uncertainty on the possible interaction between the reference natural hazard and the specific features of the barrier under consideration, as explained in Section 6.1.

The basic barrier performance modification assessment level, L0, is adequate for low uncertainty situations concerning the definition and quantification of the impact of natural hazards on the barrier and is conceptually similar to the application of a single-covariate PHM (Cox, 1972; Gao et al., 2010). Thus, as discussed in Section 6.1, Level L0 can be regarded as a Boolean approach where the covariate is a feature of the barrier (e.g., the position), identifiable using rules-of-thumb or basic evaluations, which justify with sufficient confidence whether the barrier should be considered affected or not by the natural event. In case the *k*-th barrier is considered unaffected, it will retain the baseline performance values $PFD_{0,k}$ and $\eta_{0,k}$ while in case the covariate indicates the system would be clearly impacted, the *k*-th barrier should be considered unavailable. In the two-parameter metrics, this is equivalent to setting $PFD_{j,k} = 1$ for active systems and $\eta_{j,k} = 0$ for passive protections.

Level L1 assessment is required where some uncertainty concerning barrier performance is present. This level is an application of the PHM to the two-parameter metrics and is suitable for a wide class of barriers, from passive barriers to simpler active systems. Modified barrier performance is described by a covariate, namely a performance modification factor (ϕ), representing the likelihood that similar reference barriers would fail directly due to the natural event, as proposed in a previous study (Misuri et al., 2020b). It is assumed that the failure mode of active barriers is the lack of activation, leading to barrier unavailability: thus, an increase in the *PFD* should be considered for this type of barrier. In the case of passive barriers, the effectiveness η may be reduced by the impact of the natural event, due to the possible loss of structural integrity of the barrier or to other causes (e.g., in case of flood, catch basins will not be effective in the retention of spills).

Hence, in the case of an active barrier, performance parameters are modified according to Eqs. (6.3.2) and (6.3.3) (Misuri et al., 2020b):

$$PFD_{j,k} = 1 + (\phi_{j,k} - 1)(1 - PFD_{0,k}) \tag{6.3. 2}$$

$$\eta_{j,k} = \eta_{0,k} \tag{6.3. 3}$$

where $\phi_{j,k} \in [0,1]$ is the performance modification factor of the *k*-th active barrier for *j*-th reference natural hazard scenario, and $PFD_{0,k}$ and $\eta_{0,k}$ are the baseline performance parameters of the *k*-th active barrier determined in Step 4 of the methodology of Figure 6.3. 1.

In the case of a passive barrier, a different modification of performance parameters is introduced following Eq. (6.3.4):

$$\eta_{j,k} = (1 - \phi_{j,k})\, \eta_{0,k} \tag{6.3. 4}$$

where $\phi_{j,k} \in [0,1]$ is the performance modification factor for *j*-th reference natural hazard scenario, and $\eta_{0,k}$ is the baseline effectiveness value, determined in Step 4 of the methodology of Figure 6.3. 1. The suggested value for performance modification factors, obtained by an expert survey, are available in the literature (Misuri et al., 2020b).

The L2 level assessment, on the contrary, is required when complex active barrier systems are considered, where the actual impact of the reference natural event is affected by high uncertainty, as explained in Section 6.1. The assessment may also be applied to barriers where the specific system architecture may differ from that of reference configurations, and performance modification factors $\phi_{j,k}$ may not be applicable with confidence. This level of analysis is based on a fault tree analysis (FTA) focused on the possible failure of subsystems due to the impact of the natural hazard. Indeed, after the construction of the fault tree considering barrier architecture, the minimal cut sets (MCSs) are identified and basic events are screened to explicitly identify which might be influenced by the impact of the reference natural event on the basis of detailed information on barrier subsystems (e.g., position, fail-safe design, dependence on lifelines, redundancies). After vulnerable barrier subsystems are identified, the probabilities of the related basic events in the fault tree are updated to unitary values (i.e., indicating the expected subsystem failure during the natural event). Therefore, considering the *m*-th MCS of the *k*-th barrier, its updated probability during the *j*-th reference natural scenario $Q_j(MCS_{m,k})$ can be assessed through Eq. (6.3.5):

$$Q_j(MCS_{m,k}) \ = \prod_p (q_{p,0} + \delta_{p,j}(1 - q_{p,0})) \tag{6.3. 5}$$

where $q_{p,0}$ is the probability of the p-th basic event comprised in the m-th MCS, and the parameter $\delta_{p,j}$ is equal to 1 in case the p-th basic event involves one of the vulnerable barrier subsystems identified (for the j-th reference natural scenario), and 0 if not. Conservatively, the updated *PFD* of the k-th barrier, $PFD_{j,k}$, can then be recalculated (as an upper bound) according to Eq. (6.3.6):

$$PFD_{j,k} = 1 - \prod_m (1 - Q_j(MCS_{m,k})) \tag{6.3. 6}$$

Therefore, the output of the L2 level assessment is a scenario-based quantification of barrier updated unavailability in case the reference natural event will impact the site, calculated considering the impact on each system component.

The application of each of the three levels of barrier assessment will be exemplified in the analysis of the case study, providing further details on the assessment procedure (see Section 6.3.5).

Due to the high site-specificity of procedure and emergency response actions, also in this case no generalized methodology was developed for the assessment of procedural barriers. In the analysis of the case study, a simplified approach is proposed to address the possible failure or delay of first response actions by emergency teams (Landucci et al., 2016, 2015).

6.3.3 Characterization of domino scenarios and risk calculation

The modified barrier performance parameters obtained by the highest level of assessment, L2, should then be implemented in ETA through specific logical operators (Landucci et al., 2016, 2015). These operators are represented as gates on the event trees addressing accident escalation and influence how each of the barriers contributes to the modification of the probabilities and frequencies of the final domino events. Details on logical operators and on their implementation in ETA have been already discussed in Chapter 5 (e.g., see Section 5.1 and Section 5.3).

According to the ETA defined in barrier performance analysis (e.g., see Section 5.3), each target equipment can show one out of three possible final events, in agreement with the approach described in (Landucci et al., 2017b; Misuri et al., 2021b):

- State "2": unmitigated secondary domino scenarios, in case all the protection barriers implemented have failed and is a worst-case being the outcome with the most severe consequences;
- State "1": mitigated secondary domino scenarios, that is, intermediate situations occurring when part of the safety barrier implemented fails in stopping escalation, leading to scenarios

with potentially reduced consequences due to partial activation or reduced effectiveness of safety barriers in the accident sequence

- State “0”: no domino scenarios, in which the escalation is interrupted due to activation and effective response of the safety barriers.

The peculiarity of mitigated scenarios is that their consequences might be less severe than unmitigated scenarios, and this feature should be considered for a more accurate risk evaluation.

Table 6.3. 1: Description of the main assumptions for consequence assessment of final domino events. State: 0=no escalation; 2=unmitigated escalation. Fl: flammable; SEP: surface emissive power; Tox: toxic.

Storage type	Substance	State	Final event description	Final event modelling	Notes
Atmospheric	Fl	0	No escalation	-	SEP_u: unmitigated SEP [kW/m^2]
		1	Pool fire, mitigated SEP	Pool fire model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005) $SEP_m = \Psi_f \times SEP_u$; $\Psi_f = 0.5$	SEP_m: mitigated SEP [kW/m^2] Ψ_f: attenuation
		2	Pool fire, maximum SEP	Pool fire model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005)	parameter linked to performance of water spray systems (Landucci et al., 2017b; Liu and Kim, 2000).
	Tox	0	No scenario	-	V_u: evaporation rate
		1	Toxic dispersion, mitigated evaporation rate	Pool evaporation model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005) Gas dispersion model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005) $V_m = \Psi_t \times V_u$; $\Psi_t = 0.4$	from the toxic liquid pool surface [kg/(m^{2}s)] V_m: mitigated evaporation rate from the toxic liquid pool surface [kg/(m^{2}s)] Ψ_t: attenuation
		2	Toxic dispersion, max evaporation rate	Pool evaporation model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005) Gas dispersion model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005)	parameter linked to evaporation reduction strategies (Landucci et al., 2017b).
Pressurized	Fl	0	No scenario	-	Mitigated scenario not credible*
		2	Fireball	Fireball model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005)	
	Tox	0	No scenario	-	Mitigated scenario not credible*
		2	Toxic dispersion	Gas dispersion model (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005)	

*catastrophic failure of the containment is generally followed by violent vaporization due to instantaneous depressurization of liquefied gas

A detailed characterization of mitigated secondary domino scenarios has been proposed in a previous study (Landucci et al., 2017b). The main assumptions related to this characterization have been reported in Table 6.3. 1, while the reader can refer to the original publication for further details on the concepts behind this approach. It should be noted that this approach for the characterization of mitigated domino scenarios was selected in the case study developed in the following section because it allows accounting for the specificities of the type of target, the barriers considered and the emergency strategy pursued.

Once the complete set of the secondary escalation scenarios is characterized, frequency assessment and consequence evaluation of overall domino scenarios can be performed (Steps 8-10 in Figure 6.3. 1). Considering the escalation logic with *m* possible states for each of the *n* secondary domino targets, the number of different secondary domino scenarios from a primary Natech scenario (N_c) can be determined through Eq. (6.3.7) (i.e., including the case of primary scenario only, given the absence of escalation):

$$N_c = \prod_{i=1}^{n} m_i \qquad (6.3.\ 7)$$

where m_i is the number of possible outcomes for the *i-th* secondary target, assuming that all the targets have three possible escalation states, $N_c = 3^n$. The probability of overall final domino scenarios can thus be assessed assuming that a specific secondary outcome for a given target is independent of that of the other target units, as it is assumed in previous studies addressing escalation due to domino effect (Cozzani et al., 2014, 2006a).

Indeed, each overall final scenario $\boldsymbol{C^n}$ can be represented as a vector of *n* elements indicating the combination of the events involving each of the *n* possible domino targets. Defining C_i^n as the generic element of $\boldsymbol{C^n}$ that represents the final event of the generic *i-th* target, the joint probability of the generic overall final scenario $P(\boldsymbol{C^n})$ might be calculated by Eq. (6.3.8):

$$P(\boldsymbol{C^n}) = \prod_{i=1}^{n} P(C_i^n) \qquad (6.3.\ 8)$$

where $P(C_i^n)$ is the probability of the state of the *i-th* target, assessed with the ETA.

The frequency of each generic $\boldsymbol{C^n}$ can then be calculated starting from the frequency of the primary Natech scenario generating the domino escalation f_I according to Eq. (6.3.9):

$$f(\boldsymbol{C^n}) = f_I \times P(\boldsymbol{C^n}) \qquad (6.3.\ 9)$$

In order to complete the characterization of overall domino scenarios, once the frequency assessment is performed, the consequence analysis and the calculation of risk indexes should be carried out (Steps 10 and 11 in Figure 6.3. 1). Conventional consequence models are not applicable directly to describe multiple simultaneous scenarios, given the possibility of heterogeneous physical effects from different sources (e.g., two target items simultaneously, the former leading to the dispersion of toxic gas, while the latter releasing flammable substance igniting and leading to fire). Therefore, a simplified approach based on the calculation of vulnerability widely adopted in the framework of risk assessment of domino and Natech accidents is applied (Cozzani et al., 2014, 2005). The consequence assessment of each final event is carried out independently by means of conventional literature models for physical effect modeling and human vulnerability evaluation (CCPS, 2000; Uijt de Haag and Ale, 2005; Van Den Bosh and Weterings, 2005). Then, the probability of death of generic overall domino scenario $V(\boldsymbol{C^n})$ is estimated as the normalized sum of the probabilities of death due to each domino event $V(C_i^n)$ (i.e., the death probability in case the *i*-th target is in the state "0" is null) and the probability of death directly linked to the primary Natech event V_I according to Eq. (6.3.10):

$$V(\boldsymbol{C^n}) = \min[(V_I + \sum_{i=1}^{n} V(C_i^n)), 1] \tag{6.3. 10}$$

Once overall domino scenarios are characterized, the calculation of the overall risk level may be performed (Step 11 in Figure 6.3. 1). Individual risk can be expressed by mapping local specific individual risk (LSIR) following standardized procedures, while societal risks can be expressed with F/N plots, being *F* is the cumulative frequency of scenarios causing *N* or more expected fatalities, which is calculated directly from the frequency *f* of scenarios causing *N* fatalities (CCPS, 2000; Mannan, 2005; Uijt de Haag and Ale, 2005). The *PLL* and *EV* risk indices adopted in the previous sections were selected also in this case to provide a summarized visualization of societal risk and are calculated according to Eqs. (6.3.11) and (6.3.12):

$$PLL = \sum_N f(N)N = \sum_N F(N) \tag{6.3. 11}$$

$$EV = \sum_N f(N)N^a \ with\ a = 2 \tag{6.3. 12}$$

6.3.4 Definition of case studies

The equipment layout considered in the case study is shown in Figure 6.3. 2. The layout includes nine atmospheric storage tanks (T01-T09 in Figure 6.3. 2), and four pressurized vessels (P01-P04 in Figure 6.3. 2). The details of the equipment items are summarized in Table 6.3. 2.

Figure 6.3. 2: Layout considered in the case study. Tank T01 (in red) is considered to generate the primary Natech scenario. All other items are considered as possible domino targets.

In order to exemplify the methodology, a single flooding scenario was selected as the reference natural hazard: a flood with a time of return of 500 years (f_w = 2.00 × 10^{-3} y^{-1}), characterized by a water depth, $h_{w,}$ of 2.0 m and a speed, $v_{w,}$ of 1.0 m/s was assumed. It should be noted that despite in this case study a flood scenario is considered, the methodology allows addressing also other types of natural hazards (e.g., earthquakes).

Table 6.3. 2: Equipment items considered in the case study represented in Figure 6.3.2; D = Diameter; H = height; m_t = stored mass; p_o = operating pressure; V_n = nominal volume; ρ_L = liquid density; ρ_V = vapour density.

ID	D [m]	H [m]	V_n [m^3]	Substance	ρ_L [kg/m^3]	ρ_V [kg/m^3]	p_o [bar]	m_t [t]
T01	*30*	*7.2*	*5087*	*Gasoline*	*750*	-	*1.01*	*2860*
T02	30	7.2	5087	Gasoline	750	-	1.01	2860
T03	30	7.2	5087	Gasoline	750	-	1.01	2860
T05	24	9	4069	H_2S (0.4% mol in H_2O)	1100	-	1.01	3360
T04	28	9	5539	Benzene	820	-	1.01	3410
T06	20	10.8	3391	NaCl (1% mol in H_2O)	1050	-	1.01	2670
T07	20	10.8	3391	NaCl (1% mol in H_2O)	1050	-	1.01	2670
T08	28	9	5539	Benzene	820	-	1.01	3410
T09	28	9	5539	Benzene	820	-	1.01	3410
P01	3.4	22	192	Propane	497	18.9	8.4	86.3
P02	3.4	22	192	Propane	497	18.9	8.4	86.3
P03	3.4	22	192	Propane	497	18.9	8.4	86.3
P04	3.2	22	170	Ammonia	600	4.9	8.5	91.9

Since the aim of the case study is not to perform a complete QRA, but rather to show the contribution of specific barrier performance modifications on the overall risk figures, a single primary scenario is considered to be generated by the flood for the sake of simplicity. Clearly enough, the methodology is capable of considering also the escalation of multiple primary scenarios, resulting from the damage of more than a single tank.

In the specific case study presented, it is assumed that tank T01, storing gasoline, is the only process unit damaged by the flood. The catastrophic failure of tank T01 starting a pool fire (Cozzani et al., 2010) is considered. The damage probability of the tank, P_{nhd}(T01), calculated by the vulnerability model reported in Appendix E, is estimated at 0.411. A conservative value of 0.9 is assumed as the ignition probability following the LOC, as suggested in the literature (Antonioni et al., 2015). Hence, the resulting frequency of the primary Natech scenario is obtained as the product of $f_{I,LOC}$, calculated according to Eq. (6.3.1), and the assumed ignition probability, resulting in $f_P = 7.395 \times 10^{-4}$ y^{-1}.

To further simplify the interpretation of results, four cases were considered in the following:

- Case 1: only the primary Natech scenario described above is considered, to define a baseline risk associated with the impact of the flood on tank T01;
- Case 2: also the possible escalation scenarios due to domino effect are considered. The probability of escalation is calculated not considering the action of safety barriers. This case thus represents a reference worst-case scenario.
- Case 3: as case 2, but the probability of escalation is calculated considering the action of safety barriers. Baseline values are considered for barrier performance (Landucci et al., 2017b). This case represents the best option for the expected performance of safety barriers since the possible effects of the impact of the natural hazard on the safety barriers are neglected;
- Case 4: as case 3, but barrier performance degradation due to the impact of the flood is considered by multi-level methodology presented in Section 6.3.2.

Moreover, in order to compare the risk due to Natech scenarios triggered by flooding to the risk caused by “conventional” releases from tank T01, a baseline case was also defined (case 0). This case enables the assessment of a baseline “conventional” risk associated with tank T01, thus without considering the contribution of the Natech event. The analysis of case 0, based on consolidated guidelines for risk assessment (Uijt de Haag and Ale, 2005), is documented in Appendix E.

Consequence assessment was performed by means of well-established literature models for physical effect modeling (CCPS, 2000; Mannan, 2005; Van Den Bosh and Weterings, 2005). For the sake of simplicity, a uniform wind distribution and a single set of meteorological conditions have been assumed. In particular, the wind speed was assumed at 5 m/s, neutral atmospheric stability was considered (class D) (Uijt de Haag and Ale, 2005; Van Den Bosh and Weterings, 2005). The atmospheric temperature was assumed at 20°C and relative humidity at 70%. Clearly enough, different meteorological conditions may be considered in the assessment.

To model human vulnerability to the physical effects of accidents, literature vulnerability models (i.e., probit and threshold-based) were applied in analogy with what was done in Section 6.1 and Section 6.2, as detailed in Appendix D.1. A fictitious uniform population density was assumed to obtain representative societal risk figures not affected by local-specific effects. The population density value, equal to 200 people/ha^2 with 60% presence probability, was considered constant over the entire impact area. For the sake of simplicity, no evacuation was considered and the population was assumed to be affected only by the consequences of the technological scenarios. Risk calculation was performed applying the methodology presented in (Egidi et al., 1995; Misuri et al., 2020a). Alternative approaches are possible for the calculation of the risk indexes considered (CCPS, 2000). For the sake of brevity, only the probabilistic assessment of case 4 will be detailed thoroughly in the following, limiting the presentation of cases 1, 2, and 3 to the discussion of the results. Further details on the intermediate results from the analysis of cases 1, 2, and 3 are reported in Appendix E.

In order to identify the possible targets for domino escalation, a threshold-based methodology was applied, considering the heat radiation from the primary Natech accident as the possible escalation vector. The threshold criteria selected to assess the credibility of escalation are 15 kW/m^2 for atmospheric equipment and 45 kW/m^2 for pressurized tanks, as suggested in specific studies (Alileche et al., 2015; Cozzani et al., 2013b). As shown in Table 6.3. 3, four possible escalation targets were identified: two atmospheric tanks (tanks T02 and T05 in Figure 6.3. 2), and two pressurized vessels (vessels P03 and P04 in Figure 6.3. 2).

In addition, the safety barriers associated with each possible target are also reported in Table 6.3. 3. All the targets identified are equipped with pressure safety valves (PSVs). Tanks T02 and T05 are equipped with foam-water systems (FWS), while vessels P03 and P04 are protected by water deluge systems (WDS). As an additional layer of protection, passive fire protection (PFP) is also considered for vessels P03 and P04. Besides the technical barriers (both active and passive), external emergency intervention (EEI) is always considered.

Table 6.3. 3: Escalation targets with assumed set of barriers; I(T01) = radiation from T01; PSV=pressure safety valve; FWS=foam-water system; WDS=water deluge system; PFP=passive fire protection (fireproofing); EEI=external emergency intervention.

Target	**I(T01) [kW/m^2]**	**PSV**	**FWS**	**WDS**	**PFP**	**EEI**
T02	43.3	X	X			X
T05	26.5	X	X			X
P03	57.5	X		X	X	X
P04	82.5	X		X	X	X

6.3.5 Results obtained for the case studies

Assessment of safety barrier performance

The assessment of safety barrier performance is summarized in Table 6.3. 4. For each barrier, the original performance values are reported (these are adopted in case 3), together with the classification according to Section 6.3.2. Barrier performance is modified according to one of the three levels of analysis, as indicated in the table.

In particular, L0 analysis is applied to the PSVs, since these components may be considered unaffected by the flooding scenario. This can be assessed with sufficient confidence since the PSV is a single-hardware device located on top of the equipment items and its action does not depend on utilities as instrument air or electricity.

Table 6.3. 4: Barrier performance assessment and modification. 0=original performance, f=performance during the reference flood event. Barrier coding is defined according to Table 6.3. 3.

Barrier	Classification	Gate[a]	PFD_0	η_0	Level of Analysis[c]	PFD_f	η_f
PSV	Passive	a	1.00E-02	1.00	L0	1.00E-02	1.00
FWS	Active	b	5.42E-03	9.54E-01	L2	1.00	9.54E-01
WDS	Active	a	4.33E-02	1.00	L2	1.00	1.00
PFP	Passive	a	0	9.99E-01	L1	0	8.49E-01
EEI	Procedural	c	1.00E-01	0;1	n.a.	1.00E-01	0;1[b]

[a]Gates are defined in Section 5.3.
[b]Based on the comparison between time to failure and time to final mitigation, calculated according to Appendix C.
[c]Analysis level selected in Step 5 in Figure 6.3.1.

The L1 analysis was applied to assess the performance of the passive fire protection (PFP). This choice is due to the limited complexity of the barrier, not requiring the application of a more complex level of analysis. Nevertheless, the PFP might be impacted by the natural event and a performance modification factor $\phi_{f,PFP}$ = 0.15 retrieved from an expert survey (Misuri et al., 2020b) was thus adopted to modify barrier effectiveness according to Eq. (6.3.4), obtaining $\eta_{f,PFP} = 8.49 \times 10^{-1}$ (see Table 6.3. 4).

The L2 analysis was applied to the foam-water system (FWS) since this is a complex active barrier for which a deeper understanding of how the flood might impact barrier subsystems is required to determine the expected reliability during the Natech event. Therefore, FTA was carried out, considering the main components characterizing the architecture of the barrier system, which is reported in Figure 6.3. 3.

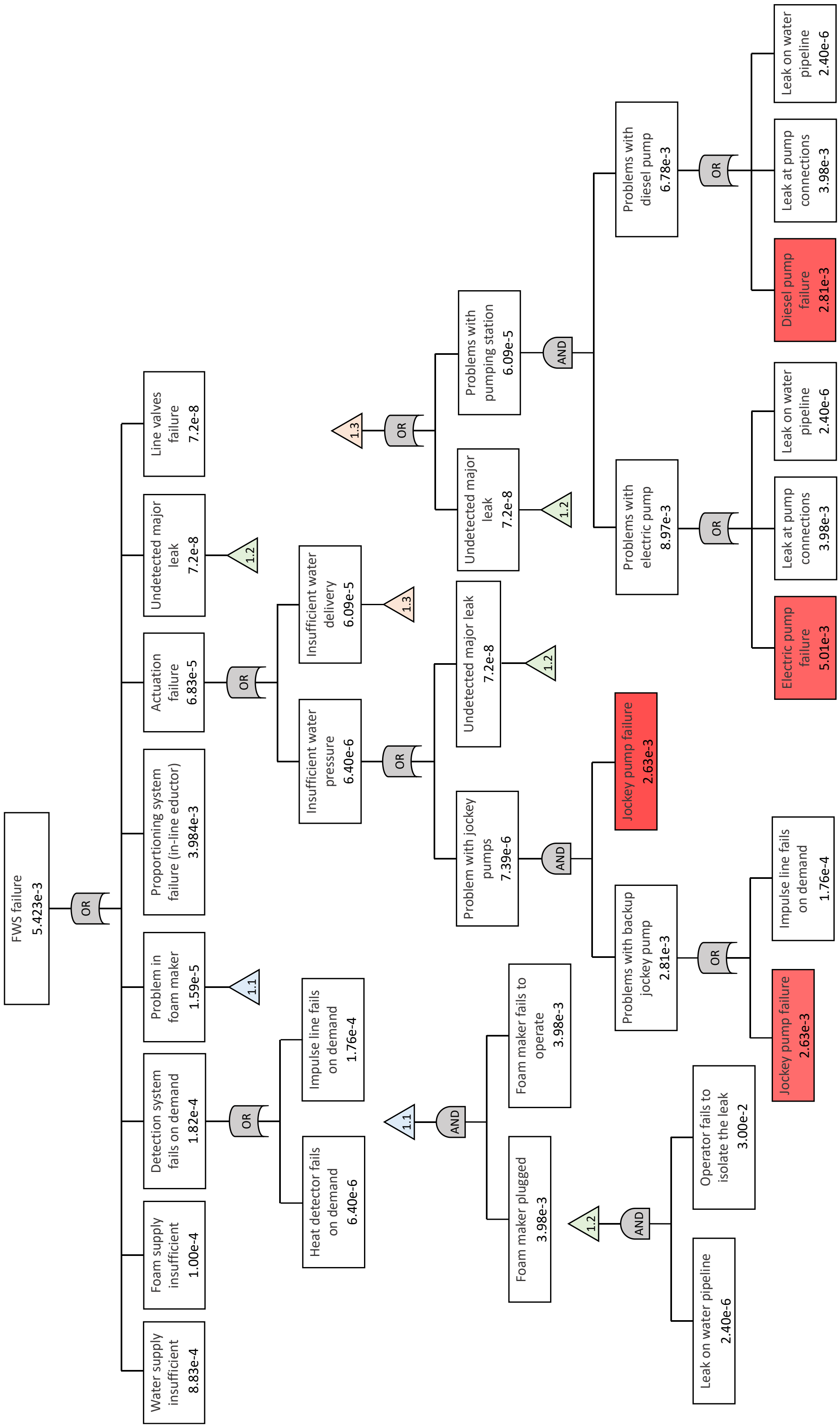


Figure 6.3. 3: Fault tree for the foam-water system (FWS) considered in the case study. Values reported are the baseline unavailability values $q_{p,0}$ which have been used to quantify baseline barrier PFD_0 and updated PFD_f, according to L2 analysis. Basic events involving components/subsystems which are deemed not available during the reference flooding scenario are highlighted in red.

The values reported in Figure 6.3. 3 were obtained from literature sources and express the expected event frequency considering original component unavailability $q_{p,0}$ (API, 2008; Cadwallader, 1995; DNV, 1997; Madonna et al., 2009; Mannan, 2005; New Zealand Fire Service Commission, 2008). The contribution of common cause failure is included through a 5% beta factor in PFD_0 (Mannan, 2005). The values were used to determine PFD_0 (i.e., original barrier performance).

The FTA was then examined to identify the subsystems and components critically impacted by the reference flood scenario. In Figure 6.3. 3 the most vulnerable nodes identified are highlighted in red. The probability of these events is updated to a unitary value since the involved subsystems/components are expected to be not available during the reference flood scenario ($\delta_p = 1$ for the probability of events reported in red in the quantification of MCSs). Then, the FTA is quantified and an updated value of the *PFD* in case of flood, PFD_f, is calculated utilizing Eqs. (6.3.5) and (6.3.6). The PFD_f value is then used in the quantitative ETA.

As shown in Figure 6.3. 3, the main contribution to the unavailability of the FWS is given by the lack of electricity. Besides, during floods the main power connections are likely to fail due to power grid disruption (Karagiannis et al., 2017), and, also considering the relevant water height of the flooding scenario considered (h_w = 2.0m), the backup diesel generators, located at ground level to reduce vibrations, are likely to be submerged. It is relevant to remark that in past Natech accidents involving flooding with relevant water depths, backup supply generators have been affected, not being designed to resist to high impact flooding scenarios (Labib and Harris, 2015; U.S. CSB, 2018). Moreover, jockey pumps and diesel pumps are likely to be submerged as well. Electric cables and connections are also an issue, although they are usually well insulated and may be unaffected by the flooding (NFPA, 2007). Therefore, considering the architecture of the FWS reported in Figure 6.3. 3 and the updated unavailability of the vulnerable components, the PFD_f resulting from FTA quantification is unitary and the safety barrier is thus considered not available during the Natech accident.

A similar procedure was used to apply L2 analysis to WDS. The FTA for the WDS is reported in Figure 6.3. 4. Also in this case, the system probability of failure on demand indicated in the figure is used as baseline performance value PFD_0 reported in Table 6.3. 4. Consistently with the case of FWS, the same standard reliability databases and a 5% beta factor have been adopted also for the WDS (API, 2008; Cadwallader, 1995; DNV, 1997; Madonna et al., 2009; Mannan, 2005; New Zealand Fire Service Commission, 2008).

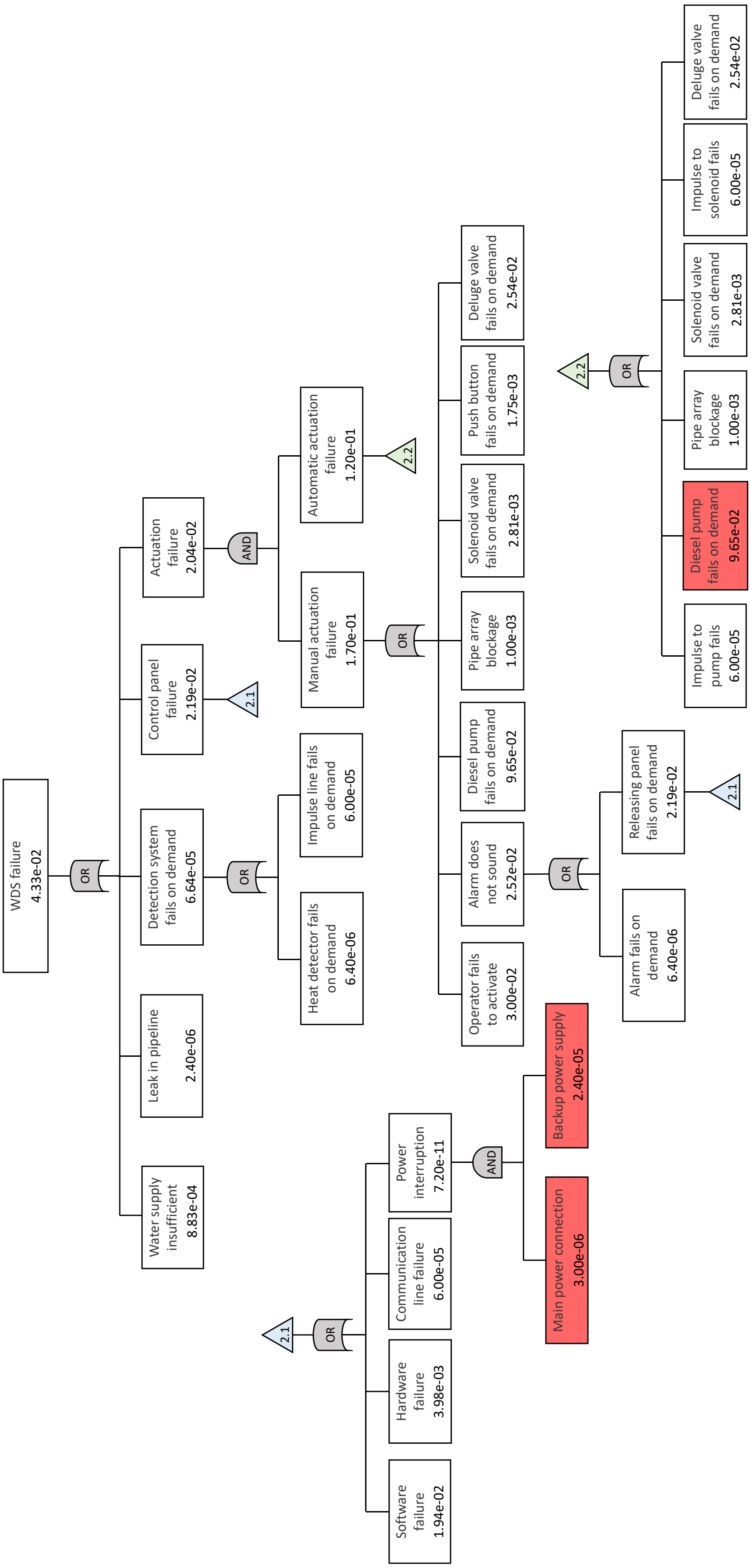


Figure 6.3. 4: Fault tree for the water deluge system (WDS) considered in the case study. Values reported are the baseline unavailability values $q_{p,0}$ which have been used to quantify baseline barrier PFD_0 and updated PFD_f, according to L2 analysis. Basic events involving components/subsystems which are deemed not available during the reference flooding scenario are highlighted in red.

The fault tree was then examined to determine critical subsystems considering the reference flood scenario. The most vulnerable nodes identified for the WDS system are highlighted in red in Figure 6.3. 4. As for the case of FWS, the main contribution to the unavailability is linked to the lack of electricity. Indeed, during floods, the main power connection is likely interrupted due to power grid disruption (Karagiannis et al., 2017), and given the relevant water height (h_w = 2.0m) floodwater is deemed to submerge also diesel generators which are usually located at ground level (Labib and Harris, 2015; U.S. CSB, 2018). The diesel pump can be considered submerged as well in case special provisions for positioning the equipment above ground level had not been previously adopted. Manual actuation is deemed not possible as well since the releasing panel will not actuate the alarm sound in case of lack of power connection (fail-safe design is conservatively not considered in this study as explained above) and the area might not be reached by operators in case of relevant floodwater height. Therefore, by the application of the L2 methodology, the PFD_f of the WDS is assessed at unitary value and thus the WDS is considered not available during the Natech accident.

It should be noted that the FTA realized to apply the L2 analysis to FWS and WDS systems have been based on some assumptions considered for the architecture of these complex systems. For the sake of brevity, the main assumptions considered in the construction of the FTs are reported in Appendix F.

Considering the updated values for the unavailability of the vulnerable system components in case of flood, the analysis led to a unit value for *PFD* also in the case of WDS. Hence, the WDS is deemed not available during the reference flood scenario assumed in the case study.

As discussed in Section 6.3.2, a specific assessment is required by the assessment of procedural and emergency barriers. The specific procedure proposed in (Landucci et al., 2016, 2015) was applied to address the performance of EEI. Accordingly, the effectiveness of EEI should be determined considering the comparison of target time to failure (*TTF*) and the required time for final mitigation (*TFM*). Further details are available in Appendix C. On the basis of primary fire features and target geometry (Landucci et al., 2015), the *TFM* is estimated at 65 min and 90 min respectively for pressurized vessels (i.e., vessels P03 and P04) and atmospheric storages (i.e., tanks T02 and T05).

Assessment of the final outcomes and of overall domino scenarios

The modified ETA approach was applied to the identification of the final outcomes of the secondary scenarios caused by domino effect, considering the safety barriers in place and their performance as assessed in Table 6.3. 4. The ETs obtained are reported in Figure 6.3. 5 and Figure 6.3. 6.

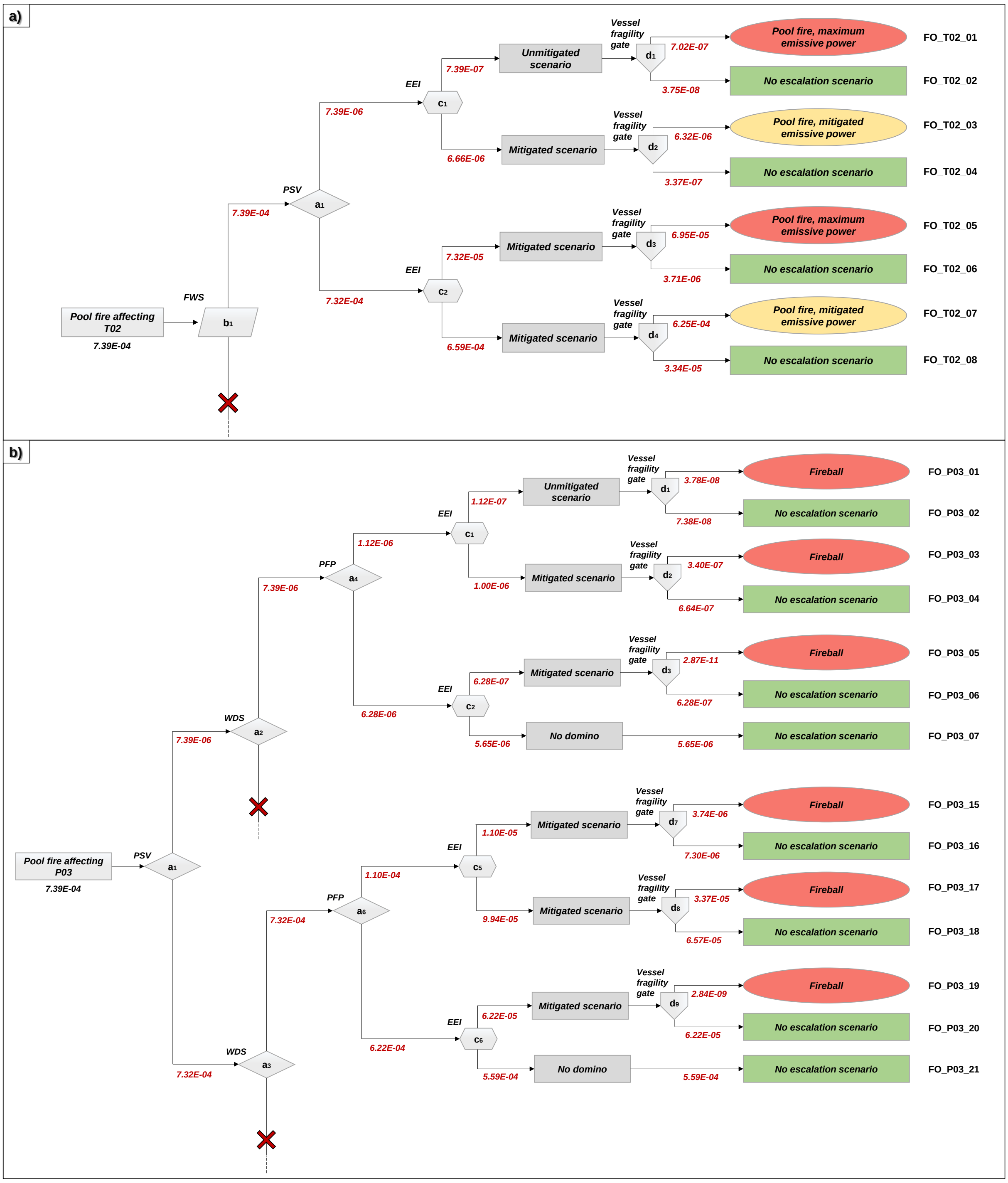


Figure 6.3. 5: Event trees reporting the quantification of the frequencies (in y^{-1}) of final outcomes of a) escalation scenarios involving tank T02 and b) escalation scenarios involving vessel P03. The branches indicated with a red cross are not further considered, as a consequence of the failure of FWS (in panel a) and WDS (in panel b) caused by the flooding, as indicated by FTAs in L2 analysis. FO= Final Outcome.

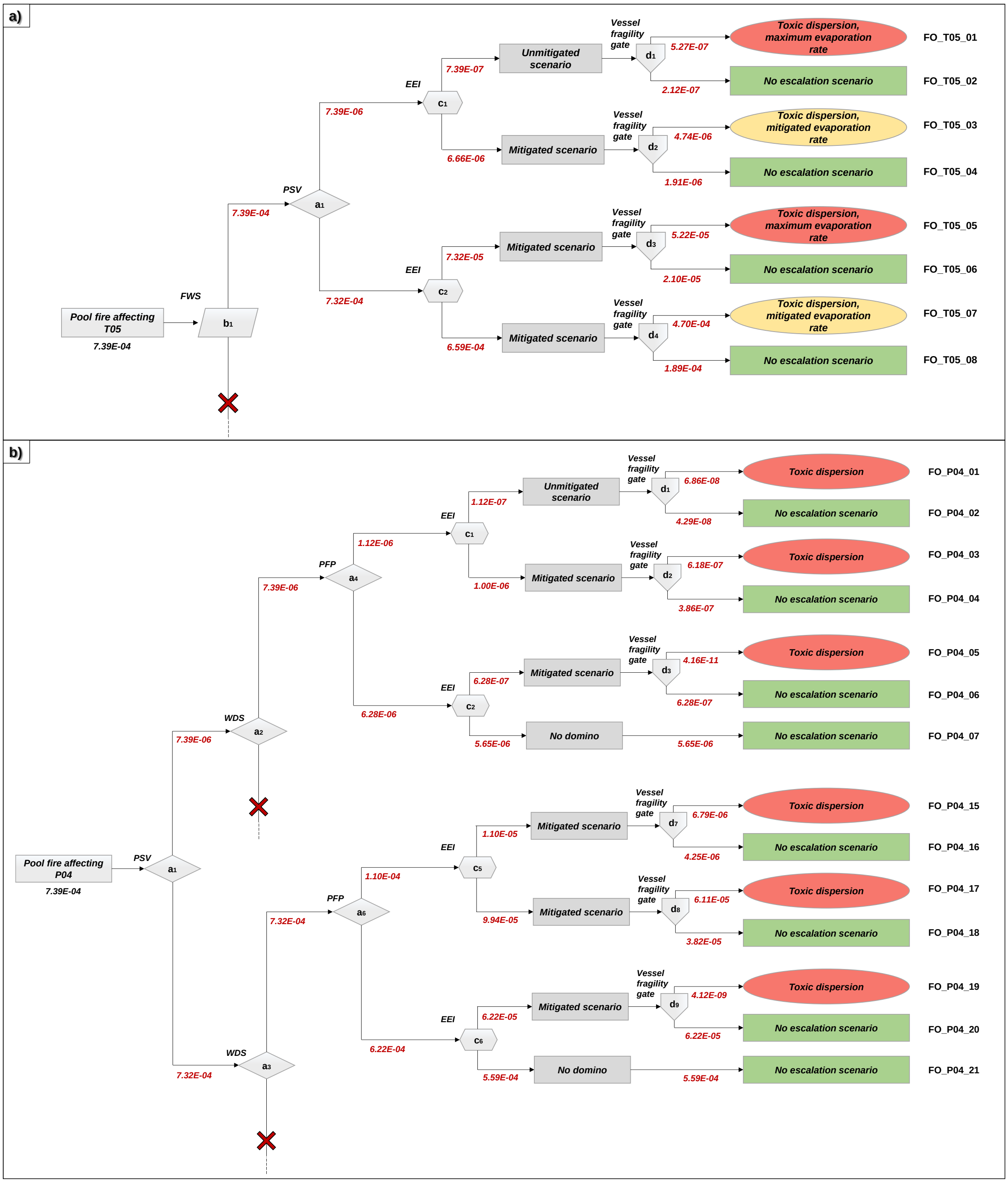


Figure 6.3. 6: Event trees reporting the quantification of the frequencies (in y^{-1}) of final outcomes of a) escalation scenarios involving tank T05 and b) escalation scenarios involving vessel P04. The branches indicated with a red cross are not further considered, as a consequence of the failure of FWS (in panel a) and WDS (in panel b) caused by the flooding, as indicated by FTAs in L2 analysis. FO= Final Outcome.

Once the ETs were drawn, the probabilistic assessment of the secondary scenarios could be completed. The results of this step are summarized in Table 6.3. 5. As it can be noticed from the table, only final outcomes with non-zero frequencies have been reported.

Table 6.3. 5: Probabilistic assessment of the final outcomes of secondary scenarios caused by domino effect for tank T02. Final outcomes with a frequency equal to zero are not reported. SEP = Surface emissive power

Final outcome	Escalation scenario	Secondary final outcome	Probability	Frequency [y^{-1}]
FO_T02_01	Unmitigated domino	Pool fire, maximum SEP	9.49E-04	7.02E-07
FO_T02_02	Unmitigated domino	No escalation	5.07E-05	3.75E-08
FO_T02_03	Mitigated domino	Pool fire, mitigated SEP	8.54E-03	6.32E-06
FO_T02_04	Mitigated domino	No escalation	4.56E-04	3.37E-07
FO_T02_05	Mitigated domino	Pool fire, maximum SEP	9.40E-02	6.95E-05
FO_T02_06	Mitigated domino	No escalation	5.02E-03	3.71E-06
FO_T02_07	Mitigated domino	Pool fire, mitigated SEP	8.46E-01	6.25E-04
FO_T02_08	Mitigated domino	No escalation	4.52E-02	3.34E-05
FO_T05_01	Unmitigated domino	Toxic dispersion, maximum evaporation rate	7.13E-04	5.27E-07
FO_T05_02	Unmitigated domino	No escalation	2.87E-04	2.12E-08
FO_T05_03	Mitigated domino	Toxic dispersion, mitigated evaporation rate	6.41E-03	4.74E-06
FO_T05_04	Mitigated domino	No escalation	2.59E-03	1.91E-06
FO_T05_05	Mitigated domino	Toxic dispersion, maximum evaporation rate	7.06E-02	5.22E-05
FO_T05_06	Mitigated domino	No escalation	2.84E-02	2.10E-05
FO_T05_07	Mitigated domino	Toxic dispersion, mitigated evaporation rate	6.35E-01	4.70E-04
FO_T05_08	Mitigated domino	No escalation	2.56E-01	1.89E-04
FO_P03_01	Unmitigated domino	Fireball	5.11E-05	3.78E-08
FO_P03_02	Unmitigated domino	No escalation	9.97E-05	7.38E-08
FO_P03_03	Mitigated domino	Fireball	4.60E-04	3.40E-07
FO_P03_04	Mitigated domino	No escalation	8.98E-04	6.64E-07
FO_P03_05	Mitigated domino	Fireball	3.88E-08	2.87E-11
FO_P03_06	Mitigated domino	No escalation	8.49E-04	6.28E-07
FO_P03_07	No domino	No escalation	7.64E-03	5.65E-06
FO_P03_15	Mitigated domino	Fireball	5.06E-03	3.74E-06
FO_P03_16	Mitigated domino	No escalation	9.88E-03	7.30E-06
FO_P03_17	Mitigated domino	Fireball	4.55E-02	3.37E-05
FO_P03_18	Mitigated domino	No escalation	8.89E-02	6.57E-05
FO_P03_19	Mitigated domino	Fireball	3.84E-06	2.84E-09
FO_P03_20	Mitigated domino	No escalation	8.41E-02	6.22E-05
FO_P03_21	No domino	No escalation	7.57E-01	5.59E-04
FO_P04_01	Unmitigated domino	Toxic dispersion	9.28E-05	6.86E-08
FO_P04_02	Unmitigated domino	No escalation	5.80E-05	4.29E-08
FO_P04_03	Mitigated domino	Toxic dispersion	8.35E-04	6.18E-07
FO_P04_04	Mitigated domino	No escalation	5.22E-04	3.86E-07
FO_P04_05	Mitigated domino	Toxic dispersion	5.63E-08	4.16E-11
FO_P04_06	Mitigated domino	No escalation	8.49E-04	6.28E-07
FO_P04_07	No domino	No escalation	7.64E-03	5.65E-06
FO_P04_15	Mitigated domino	Toxic dispersion	9.19E-03	6.79E-06
FO_P04_16	Mitigated domino	No escalation	5.75E-03	4.25E-06
FO_P04_17	Mitigated domino	Toxic dispersion	8.27E-02	6.11E-05
FO_P04_18	Mitigated domino	No escalation	5.17E-02	3.82E-05
FO_P04_19	Mitigated domino	Toxic dispersion	5.58E-06	4.12E-09
FO_P04_20	Mitigated domino	No escalation	8.41E-02	6.22E-05
FO_P04_21	No domino	No escalation	7.57E-01	5.59E-04

As shown in Figure 6.3. 5, the application of the barrier assessment methodology (Step 5 in Figure 6.3. 1) results in the elimination of part of the ETA branches. In particular, the downward output branches of the logic operators associated with the FWS (node b_1 in Figure 6.3. 5-a) and WDS (nodes a_2 and a_3 in Figure 6.3. 5-b) systems are no more present, since these two systems are considered unavailable during the reference flood scenario according to the results obtained from L2 analysis.

Thus, the methodology led to the identification and characterization of the set of final outcomes reported in Table 6.3. 6. The table also reports the calculated frequencies and probabilities of the final outcomes. As shown in the table, mitigated scenarios (indicated with number "1" in the column "State" of the table) are not considered likely for the pressurized equipment items, as the vessels P03 and P04. Indeed, in the case of escalation caused by domino effect due to a fire involving pressurized equipment, the action of fire brigades may not be able to mitigate the violent vaporization of the fluid, as described in previous publications (Landucci et al., 2017b).

Table 6.3. 6: Probabilities and frequencies of the final outcomes identified through the ETA. State: 0=no escalation; 1=mitigated escalation; 2=unmitigated escalation. SEP=surface emissive power.

Target	State	Secondary final event	Probability	Frequency [y^{-1}]
T02	0	No scenario	5.070E-02	3.749E-05
T02	1	Pool fire, mitigated SEP	8.544E-01	6.318E-04
T02	2	Pool fire, max SEP	9.493E-02	7.020E-05
T05	0	No scenario	2.873E-01	2.124E-04
T05	1	Toxic dispersion, mitigated evaporation rate	6.514E-01	4.744E-04
T05	2	Toxic dispersion, maximum evaporation rate	7.127E-02	5.271E-05
P03	0	No scenario	9.489E-01	7.017E-04
P03	2	Fireball	5.110E-02	3.779E-05
P04	0	No scenario	9.072E-01	6.708E-04
P04	2	Toxic dispersion	9.281E-02	6.863E-05

Starting from the final outcomes of the secondary events reported in Table 6.3. 6, the number of different overall domino scenarios is determined by Eq. (6.3.7). Considering that escalation involving tanks T02 and T05 can lead to three alternative final outcomes each, while in the case of vessels P03 and P04 two alternative final outcomes are only possible, the number of overall domino scenarios, N_C, is equal to 36. For the sake of simplification, only secondary domino scenarios are considered in the case study. Nevertheless, the proposed methodology is recursively applicable for further level assessment, as it is explained in Section 6.3.1.

The probabilities and frequencies of the overall domino scenarios are assessed as described in Section 6.3.3. The results are presented in Table 6.3. 7. As shown in the table, the frequencies of the overall scenarios span between 10^{-8} to 10^{-4} y^{-1}, and many combinations have probability values close to that of the primary Natech scenario, as well as to the conventional scenarios considered as benchmarks.

Table 6.3. 7: Overall domino scenarios (final event combinations) considered for risk assessment. State: 0=no escalation; 1=mitigated escalation; 2=unmitigated escalation.

ID	Target state				Probability	Frequency [y^{-1}]	ID	Target state				Probability	Frequency [y^{-1}]
	T02	T05	P03	P04				T02	T05	P03	P04		
1	0	0	0	0	1.254E-02	9.270E-06	19	0	0	0	2	1.283E-03	9.484E-07
2	0	1	0	0	2.800E-02	2.070E-05	20	0	1	0	2	2.864E-03	2.118E-06
3	0	2	0	0	3.111E-03	2.300E-06	21	0	2	0	2	3.182E-04	2.353E-07
4	1	0	0	0	2.113E-01	1.562E-04	22	1	0	0	2	2.161E-02	1.598E-05
5	1	1	0	0	4.718E-01	3.489E-04	23	1	1	0	2	4.827E-02	3.569E-05
6	1	2	0	0	5.242E-02	3.876E-05	24	1	2	0	2	5.363E-03	3.966E-06
7	2	0	0	0	2.347E-02	1.736E-05	25	2	0	0	2	2.402E-03	1.776E-06
8	2	1	0	0	5.242E-02	3.876E-05	26	2	1	0	2	5.363E-03	3.966E-06
9	2	2	0	0	5.824E-03	4.307E-06	27	2	2	0	2	5.959E-04	4.406E-07
10	0	0	2	0	6.752E-04	4.993E-07	28	0	0	2	2	6.907E-05	5.108E-08
11	0	1	2	0	1.508E-03	1.115E-06	29	0	1	2	2	1.542E-04	1.141E-07
12	0	2	2	0	1.675E-04	1.239E-07	30	0	2	2	2	1.714E-05	1.267E-08
13	1	0	2	0	1.138E-02	8.414E-06	31	1	0	2	2	1.164E-03	8.608E-07
14	1	1	2	0	2.541E-02	1.879E-05	32	1	1	2	2	2.599E-03	1.922E-06
15	1	2	2	0	2.823E-03	2.088E-06	33	1	2	2	2	2.888E-04	2.136E-07
16	2	0	2	0	1.264E-03	9.349E-07	34	2	0	2	2	1.293E-04	9.564E-08
17	2	1	2	0	2.823E-03	2.088E-06	35	2	1	2	2	2.888E-04	2.136E-07
18	2	2	2	0	3.137E-04	2.320E-07	36	2	2	2	2	3.209E-05	2.373E-08

Risk figures

The LSIR results obtained for the case study are shown in Figure 6.3. 7. It is worth reminding that in all the risk figures reported, the baseline contribution of conventional scenarios is included (i.e., case 0, as explained in Section 6.3.4). Figure 6.3. 7-a shows the baseline Natech LSIR from tank T01 (i.e., case 1). Figure 6.3. 7-d shows the overall LSIR obtained applying the methodology of Figure 6.3. 1 (i.e., case 4), while Figure 6.3. 7-b and Figure 6.3. 7-c represent the worst-case and the best-case considering escalation caused by domino effect (i.e., case 2 and case 3 respectively).

Comparing Figure 6.3. 7-a and Figure 6.3. 7-c, it is clear that including the contribution of escalation scenarios caused by domino effect considering mitigation due to safety barriers with baseline performance produces a limited increase in the LSIR value. However, the risk caused by escalation scenarios increases dramatically when considering the degradation of safety barriers due to the flooding (Figure 6.3. 7-d). Indeed, in the latter case, the tank farm area is entirely exposed to LSIR values higher than 10^{-5} y^{-1}, while this value is present only in a limited area of the layout in Figure 6.3. 7-c. Thus, the LSIR is clearly underestimated if the possible barrier degradation caused by natural events is overlooked when assessing Natech scenarios. Nevertheless, comparing Figure 6.3. 7-d and

Figure 6.3. 7-b (where no barriers are considered), it is clear that the residual barrier performance still contributes to reducing the risk level, since in case of completely unmitigated escalation the tank farm area is exposed to LSIR values as high as 10^{-4} y^{-1}, an order of magnitude higher than in the case of mitigated escalation with degraded barriers.

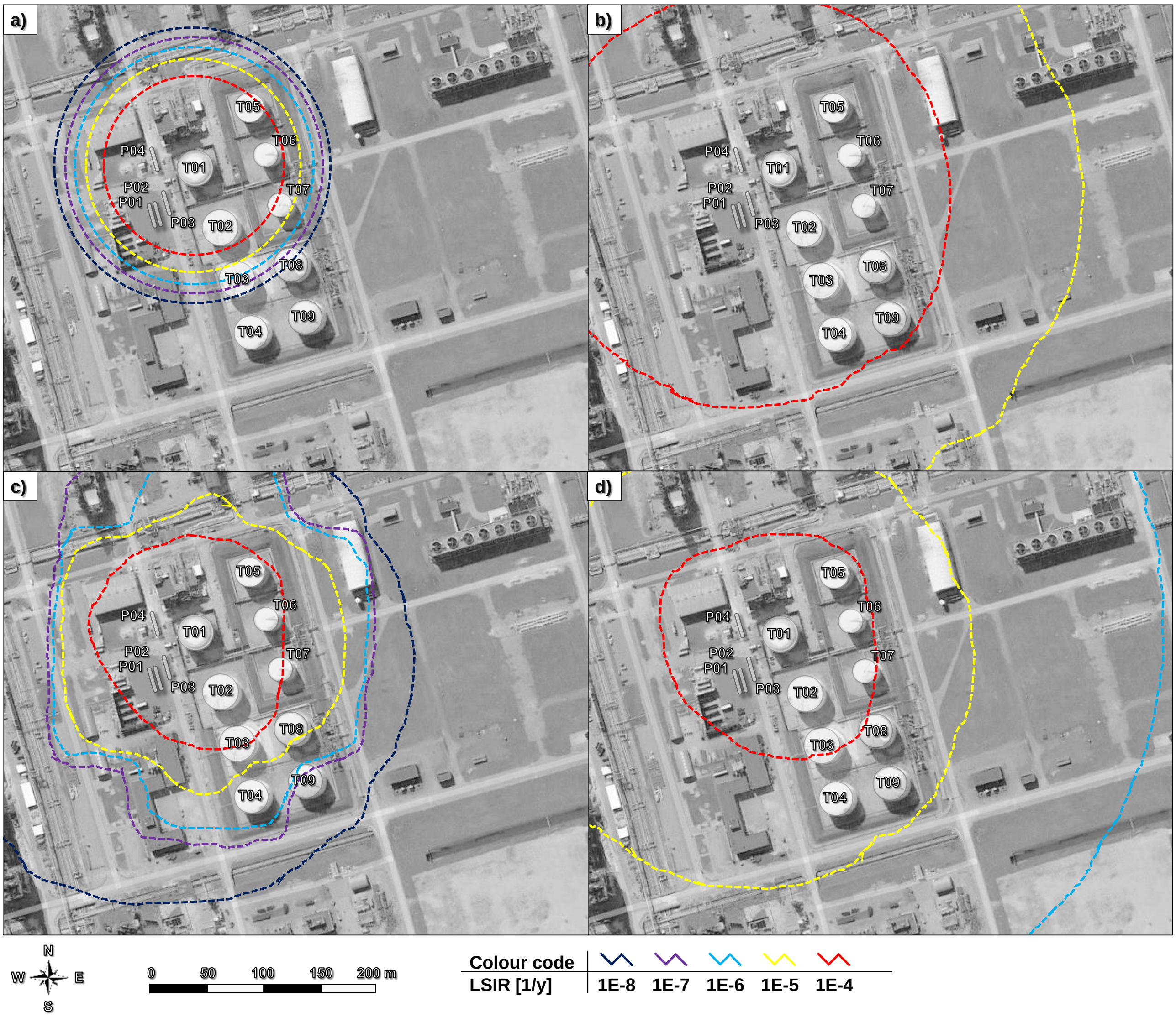


Figure 6.3. 7: LSIR values calculated for: a) case 1, b) case 2, c) case 3, d) case 4.

Figure 6.3. 8 describes the societal risk calculated for the four cases considered, obtained considering the simplifying assumptions discussed in Section 6.3.4. The severity of the primary Natech scenario (i.e., case 1) is limited (up to 100 expected fatalities). Escalation scenarios have a higher magnitude (up to 1000 expected fatalities), as shown in Figure 6.3. 8. As expected, the F/N curve of case 4 has an intermediate severity (between that of case 2 and 3), highlighting, on the one hand, that considering unmitigated escalation would be possibly over-conservative, and, on the other hand, that overlooking barrier degradation would lead to a critical underestimation of risk.

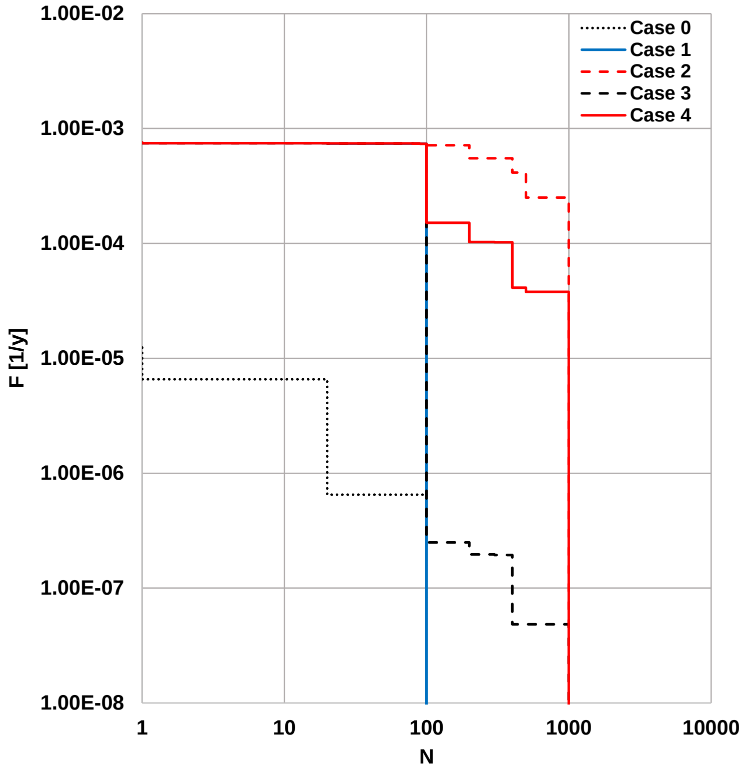


Figure 6.3. 8: F/N curves calculated for the case study. Case 0 is reported to provide baseline risk figures related to conventional scenarios.

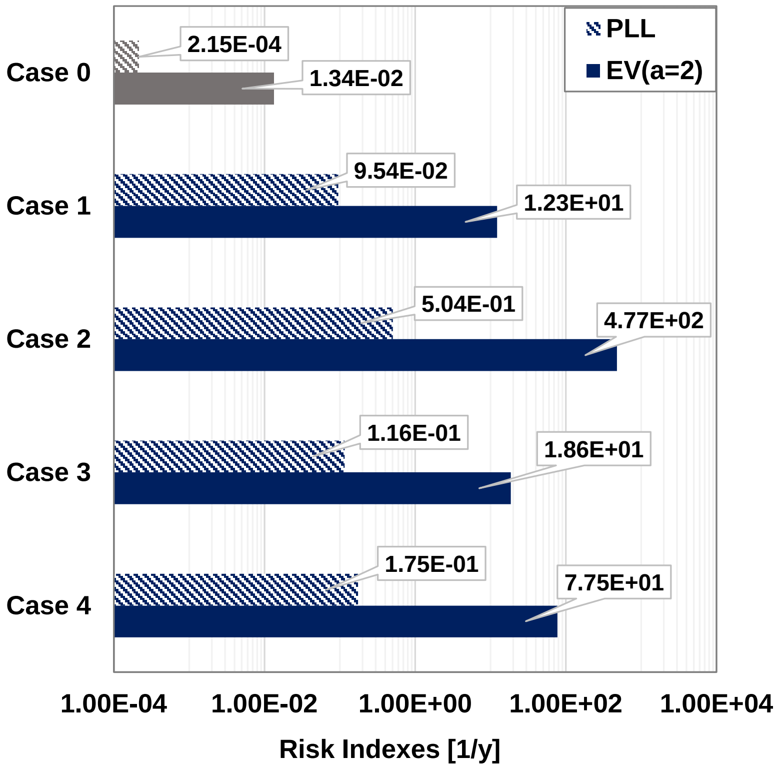


Figure 6.3. 9: Potential Life Loss (PLL) and expectation value (EV) values calculated for the case study. Case 0 is also reported (in grey) to provide baseline PLL and EV values from conventional scenarios.

The above results are confirmed by the *PLL* and *EV* indices reported in Figure 6.3. 9. The values calculated considering the primary Natech accident (i.e., case 1) are about 10^3 times higher than the figures obtained from baseline conventional scenarios (i.e., case 0). Considering escalation caused by domino effect does not affect significantly the *PLL*, possibly because *F* and *N* are equally weighed in the index definition, and the most severe domino scenarios (i.e., scenarios ID 10-36 in Table 6.3. 7, featuring the rupture of at least one pressurized vessel among P03 and P04) have frequency values considerably lower than that of the primary Natech accident (i.e., 1 to 4 orders of magnitude difference). Thus, the effect of escalation scenarios triggered by Natech is better highlighted by the analysis of the *EV* index. Indeed, as shown in Figure 6.3. 9, in case of mitigated escalation considering barrier degradation (i.e., case 4) there is an increase of more than 6 times of the *EV* compared to that calculated not considering escalation (i.e., case 1). Adopting baseline barrier performance (i.e., case 3, best-case scenario), the increase is limited to about 1.5 times, while not considering barriers (i.e., case 2, worst-case scenario) the value of *EV* is about 6 times higher than that of case 4.

6.3.6 Discussion

The results shown in Section 6.3.5 allow determining the key role of safety barriers in preventing the escalation of primary Natech accidents by domino effect. Nevertheless, in Natech scenarios, safety barriers might not be as effective as expected in preventing domino effect, due to the impact of natural events that may damage barrier components or impair their action. As shown in the case study assessment, the two active firefighting systems considered are found to be not available during a flooding (i.e., the FWS and WDS systems), thus no mitigation will come from the presence of these devices in a Natech scenario triggered by a flood. However, the methodology proposed avoids over-conservative results that may be obtained by a worst-case approach that completely neglects the action of all safety barriers. Indeed, passive barriers (e.g., passive fire protection materials) considered in the case study are more robust due to the absence of external activation and may be considered to resist the impact of the flooding scenario.

The results obtained show that a relevant increase in the risk indexes is detected when the performance modification of the barriers instead of baseline values is considered in quantitative risk assessment. The increase in risk figures is not limited to the vicinity of the source of the primary Natech scenario, but rather to the entire facility, involving as well the areas near the equipment items that are potential targets of accident propagation. This is clearly related to the high likelihood of high magnitude escalation scenarios and is confirmed by the F/N curves reported in Figure 6.3. 8, where the contribution of escalation caused by domino effect is mainly related to the presence of specific high impact scenarios. The comparison of the F/N curves for cases 2, 3, and 4 to that obtained for case 1 makes evident this point. Nevertheless, according to the results obtained in the case study, the increase in the risk figures is critical specifically for the scenarios having a higher magnitude. Indeed, the *PLL* value obtained for the unmitigated case (case 2 in Figure 6.3. 9) is comparable with the values obtained considering safety barriers (cases 3 and 4 in Figure 6.3. 9). Differently, the *EV* index, that weights more the scenarios with a higher number of expected fatalities, is about 25 times higher for the unmitigated case (case 2 in Figure 6.3. 9) compared to the case considering baseline barrier performance (case 3 in Figure 6.3. 9), and about 7 times higher than the case considering modifications in barrier performance (case 4 in Figure 6.3. 9).

Clearly enough, a critical point of the analysis is the selection of the appropriate level of detail for the application of the safety barrier performance degradation analysis. This step is influenced by the available information, in particular on complex barrier systems of interest in the analysis. On the one hand, the selection of L2 level is more information-intensive and is time demanding, although it allows the analyst to take into account specific barrier design provisions (e.g., the application of design standards or solutions explicitly considering natural hazards). On the other hand, if the adoption of L1 and L0 provides sufficiently accurate results and the system may be hardly divided into components, as in the case of simple systems as passive barriers, these levels of analysis provide a straightforward approach to consider performance modification of barriers in risk assessment procedures.

Even if a detailed L2 analysis is applied, uncertainty may still be present in the results, due to the difficulty in assessing the actual behavior of some components of safety functions when impacted by a natural hazard. However, the upper and lower risk bounds can be clearly identified by the application of unmitigated domino escalation (Misuri et al., 2020a) and mitigated domino escalation considering baseline barrier performance (Landucci et al., 2017b) (i.e., respectively cases 2 and 3).

The application of the methodology may also be used to drive decision-making in implementing specific provisions for each barrier, with the purpose of shifting the risk level from a situation close to the absence of mitigation toward the identified lower risk bound. This approach may be of specific interest considering the L2 analysis, which allows identifying the critical components of the safety barriers that may be considered for upgrading and protection from the impact of the natural event.

Although the multi-level assessment procedure developed for the quantitative assessment of barrier performance modification in Natech scenarios was integrated into a conventional QRA procedure for risk assessment, Steps 4 and 5 may be adopted also in different approaches to quantitative risk assessment. In particular, the quantitative approach to the degradation of barrier performance may be easily integrated with approaches based on Bayesian Networks (Khakzad, 2019; Khakzad and Van

Gelder, 2018, 2017) or other graph-theoretical approaches (Khakzad et al., 2017; Khakzad and Reniers, 2015) for the quantitative assessment of the risk of Natech scenarios.

Finally, it should be remarked that the present multilevel approach is not restricted to the chemical and process sector and it might be beneficial also in industries where the conceptualization of safety barrier is adopted. For instance, in the nuclear sector, where the system safety is based on the defense-in-depth principle (Fleming and Silady, 2002; IAEA, 1996), the methodology might be applied within probabilistic safety assessment (PSA) studies to model explicitly the performance of layers of defence during natural hazards. In doing so, the PSA might drive better risk-informed decisions on how to reduce the likelihood and the impact of accidents originated by natural hazards (Apostolakis, 2004), which, as the Fukushima Dai-ichi nuclear disaster (2011) recently demonstrated (Labib and Harris, 2015; Watanabe et al., 2015; Yang, 2014), safety management might not be ready to face.

6.3.7 Conclusions

A comprehensive methodology for the risk assessment of the escalation of Natech scenarios caused by domino effect was developed. The methodology was specifically conceived to allow considering the performance modification of safety barriers during Natech scenarios, caused by the impact of the natural event. A three-level approach was proposed to assess barrier performance modification. The methodology was applied to a case study, and the results obtained are compared with the outcomes of reference methodologies for risk assessment of escalation scenarios caused by domino effect. Risk figures obtained including the modification in barrier performance are of an order of magnitude higher than those obtained considering baseline barrier performance. Still, in particular in the case of high-severity scenarios, even when impacted by a natural event, the layers of protection provided by the safety barriers are effective in reducing of about one order of magnitude the risk compared to a worst-case scenario where safety barriers are considered absent. The methodology also guides the identification of the most critical components of technical safety barriers, supporting risk-based decision-making concerning the upgrading of these systems to improve their resistance to natural events.

Chapter 7. Conclusive remarks and future directions

From the dawn of civilization, humankind has always striven to find effective means to protect itself and relevant assets from the impact of natural calamities. This issue has probably become even more critical with the development of modern societies, which heavily rely on complex technologies and critical infrastructures to provide goods and services. Indeed, a great share of industrial facilities designed to provide commodities, specialty chemicals, or even energy, handles relevant quantities of hazardous substances as part of the production process, and in the case of their release following the impact of natural phenomena, high-consequence technological scenarios can be triggered. This Ph.D. project was focused on this typology of complex industrial accidents, that is, on Natech events. After the analysis of severe past accidents and of the related lessons which can be extracted from accident databases, the tools available nowadays to address the quantification of the Natech risk have been screened in order to identify their possible limitations. The most fundamental gap identified is that the current accident paradigm, which is the basis of the majority of the established Natech risk assessment methodologies, completely overlooks the possibility of the systemic impact of natural hazards on site utilities, lifelines, and safety barriers for accident prevention and mitigation. On the one side, this feature systematically prevented the identification of technological scenarios that can be indirectly generated when these services are unavailable and substances requiring their permanent functioning are present on the site. On the other side, it could not fully reproduce the cascading nature of Natech events since the central role of the concurrent depletion of safety barriers during natural disasters in possibly enhancing the likelihood of accident propagation and escalation was not recognized. Therefore, the first task addressed in this Ph.D. project was to conceive an updated paradigm to realistically reproduce the systemic impact of natural disasters at chemical and process sites and the cascading nature of Natech events, and to propose a roadmap for its implementation in quantitative risk assessment methodologies. The framework enables the identification of possible technological scenarios following the unavailability of auxiliary systems during natural disasters and stresses the accent on the role of safety barriers on the characterization of primary events and on further scenarios derived from their escalation.

Related to the latter point, the methodologies available in the literature to address the quantification of the performance of safety barriers were analyzed and it was recognized that none of the established approaches explicitly allowed to estimate their expected depletion during natural disasters. In addition, despite the recurrent failure of accident prevention and mitigation measures reported in past Natech events, information from database analysis was not sufficiently detailed to draw statistical indications on this issue. Thus, an explorative study based on expert elicitation was performed to obtain data on the performance of common safety barriers adopted in chemical and process plants during natural hazards. Some safety barriers were clearly identified as particularly vulnerable to natural hazards, and a set of failure probability parameters was obtained distilling the opinions expressed by the involved panel of experts. These parameters were included as barrier performance modification factors in a novel methodology to assess the likelihood of Natech accident escalation through domino effects and tested against a case study, demonstrating that the impact of natural hazards on safety barriers directly leads to an enhanced frequency of unmitigated secondary scenarios.

Then, in agreement with the roadmap for a comprehensive Natech risk assessment developed in the first part of the research activity, an updated methodology for the detailed assessment of the risk related to primary Natech scenarios considering the role of safety barriers has been developed and applied to case studies, highlighting the influence of safety barrier depletion also from the viewpoint of risk figures. The barrier assessment step was further improved in a multi-level methodology that can be effectively used to obtain risk-based indications useful for ranking strategies to enhance the performance of technical safety barriers, a key step forward in the effort to enhance the resilience of chemical and process facilities to the possible effects of climate change. Moreover, as explained, barrier depletion does not only contribute to enhancing the severity of Natech events directly caused by the impact of natural disasters but can also influence the severity and the likelihood of accident propagation to nearby equipment by domino effects. Hence, the successive step of the research activity was dedicated to the formalization of a comprehensive methodology to address the quantification of the risk related to domino effects generated in Natech accidents considering the role of barrier depletion in this complex accident dynamics. The methodology was tested developing case studies and considering also the cases of barriers with baseline performance and of complete absence of barriers, clearly showing that results are more realistic when compared with the worst-case scenario, still of an order of magnitude higher than those obtained for the best-case of barriers operating normally.

The methodologies conceptualized within this Ph.D. project represent landmark advancements in respect of the gaps identified in previous Natech risk assessment approaches. The developed tools and metrics pave the way for a substantial improvement in the possibility of defining risk-informed proactive strategies to enhance the resilience of chemical and process plants against natural disasters, a key feature considering the possibility that climate change will further exacerbate the severity of extreme natural phenomena in the foreseeable future. Nevertheless, further research effort dedicated to several open issues is required for the effective implementation of the updated accident paradigm. Indeed, ad-hoc approaches to characterize indirect scenarios from auxiliary system failure are not available. Related to the same point, the key-enabling models employed in established Natech risk assessment approaches to estimate the vulnerability or the fragility of equipment to natural phenomena cover only some classes of items and some categories of natural hazards. These issues might pose severe limitations to the capabilities of Natech risk management processes, and the investigation of possible solutions to characterize scenarios following the failure of auxiliary systems when unstable substances are processed and to evaluate the likelihood of releases from a broader class of equipment exposed to a broader set of natural hazards should be given priority. In addition, research effort should be dedicated also to the development of proper strategies to perform a more realistic consequence modelling, capturing the possible specificities of releases during natural hazards (e.g., in the case of release of substances underwater during floods), and to extend the characterization of Natech scenarios considering also their possible medium-to-long term effects on population and on other risk receptors (e.g., environmental contaminations).

Another open issue that was identified during the research activity is related to the performance modeling of emergency response during Natech events. Indeed, in previous past accidents, it was evidenced that situations of unexpected complexity due to the simultaneity of a natural disaster and a technological scenario might impair the action of emergency teams. Nevertheless, to date, a general approach to evaluate the extent of their possible performance depletion is not available and the thorough description of Natech accident dynamics would significantly benefit from advancements in this specific research direction.

Finally, is it worth noting that despite the proposed implementation of a comprehensive quantitative risk assessment approach is based on the well-established QRA framework, other possibilities should be also investigated. For instance, in perspective flexible tools as Bayesian Networks might be also leveraged to solve the possible burdens connected to the QRA rationale when a significantly high number of items are included in the analysis.

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Appendix A. Transcription of the expert survey forms

The details on the survey forms adopted to carry out the expert elicitation procedure described in Chapter 5.2 are reported in this appendix. The transcription of the forms is reported in Table A. 1.

Table A. 1: Transcription of the survey forms adopted in the expert elicitation (Misuri et al., 2020b).

The scope of the present questionnaire is to gather experts' opinions on the possibility that several common safety barriers used in chemical and process plants could fail if impacted by natural events. The safety barriers considered are described in the file that you received attached to the e-mail including the link to the survey.

The survey is limited to the impact of generic FLOOD and SEISMIC events (i.e., EARTHQUAKES) affecting the site where the barrier is present. The term "generic" in this context means that the opinion has to be expressed independently of the intensity of the event: in answering the questions you should evaluate how plausible is the failure of a protection measure in case of such events. It must be remarked that the present elicitation is to gather performance estimates: you should assess the plausibility of barrier failure and/or inefficient response considering its architecture (e.g., subsystems, dependence on power-grid connection, position of pumps, pipework, fail-safe design, etc.).

In case you do not know (or you are not familiar with) a specific system mentioned in the survey, you can skip the question. In case you know the system, but you are not sure about the answer you can skip the question as well.

In line with EU research standards, this survey is strictly anonymous. This research is purely academic, it is only intended to further and improve knowledge on the performance of protection measures adopted in industrial facilities.

<u>*Personal information*</u>

You are kindly asked to answer to a couple of questions for understanding your background.

1. Which kind of institution do you belong to?

Answers: [Academia/Industry/Consultancy/Other: (specify)…………]

2. How many years of experience do you have in the context of safety barrier management?

Answers: [No experience/ From 1 to 5/From 5 to 10/From 10 to 20/More than 20]

<u>*SB1. Inert Gas Blanketing System*</u>

With inert gas blanketing system we refer to the whole system for padding tanks containing flammable liquids, comprising the inert supply tank, and the relative distribution piping.

3. Do you think in case of a flood event impacting process facilities, the inert gas blanketing system could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

4. Based on your experience and judgement, how likely do you think it is that the inert gas blanketing system is unavailable in case of demand, as an immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

5. Do you think in case of a seismic event impacting process facilities, the inert gas blanketing system could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

6. Based on your experience and judgement, how likely do you think it is that the inert gas blanketing system is unavailable in case of demand, as an immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

<u>*SB.2 Automatically Actuated Rim-Seal Fire Extinguishers*</u>

With automatically actuated rim-seal fire extinguishers we refer to a safety system against rim-seal fires located on the roof of flammable liquid storage tanks.

7. Do you think in case of a flood event impacting process facilities automatically actuated rim-seal fire extinguishers could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

8. Based on your experience and judgement, how likely do you think it is that automatically actuated rim-seal fire extinguishers are unavailable in case of demand, as an immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

9. Do you think in case of a seismic event impacting process facilities automatically actuated rim-seal fire extinguishers could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

10. Based on your experience and judgement, how likely do you think it is that automatically actuated rim-seal fire extinguishers are unavailable in case of demand, as an immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.3 Fixed/Semi-Fixed Foam Systems

With fixed/semi-fixed foam systems we refer to systems for tank fire extinction by providing water-based foam to the fire area.

11. Do you think in case of a flood event impacting process facilities fixed/semi-fixed foam systems could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

12. Based on your experience and judgement, how likely do you think it is that fixed/semi-fixed foam systems are unavailable in case of demand, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

13. Do you think in case of a seismic event impacting process facilities fixed/semi-fixed foam systems could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

14. Based on your experience and judgement, how likely do you think it is that fixed/semi-fixed foam systems are unavailable in case of demand, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.4 Water Deluge System / Water Curtains & Sprinklers

With water deluge system, water curtains we refer to safety systems to mitigate the risk posed by external fire to critical areas where the fire shall not spread. With sprinklers we refer to the system providing water to burning area.

15. Do you think in case of a flood event impacting process facilities water deluge system, water curtains & sprinklers could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

16. Based on your experience and judgement, how likely do you think it is that water deluge system, water curtains & sprinklers are unavailable in case of demand, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

17. Do you think in case of a seismic event impacting process facilities water deluge system, water curtains & sprinklers could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

18. Based on your experience and judgement, how likely do you think it is that water deluge system, water curtains & sprinklers are unavailable in case of demand, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.5 Hydrants

With hydrants we refer to sources where fire brigades can connect firehoses to deliver water to burning areas. The system of firefighting water distribution to hydrants can be supposed the same to provide water to WDS and sprinklers.

19. Do you think in case of a flood event impacting process facilities hydrants could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

20. Based on your experience and judgement, how likely do you think it is that hydrants are unavailable in case of demand, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

21. Do you think in case of a seismic event impacting process facilities hydrants could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

22. Based on your experience and judgement, how likely do you think it is that Hydrants are unavailable in case of demand, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.6 Fire Walls

With fire walls we refer to physical barriers to protect assets from fire.

23. Do you think in case of a flood event impacting process facilities fire walls could be damaged and could be unavailable?

Answers: [YES/NO/NOT SURE]

24. Based on your experience and judgement, how likely do you think it is that fire walls are unavailable, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

25. Do you think in case of a seismic event impacting process facilities fire walls could be damaged and could be unavailable?

Answers: [YES/NO/NOT SURE]

26. Based on your experience and judgement, how likely do you think it is that fire walls are unavailable, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.7 Blast Walls

With blast walls we refer to physical barriers resistant to blast waves.

27. Do you think in case of a flood event impacting process facilities blast walls could be damaged and could be unavailable?

Answers: [YES/NO/NOT SURE]

28. Based on your experience and judgement, how likely do you think it is that blast walls are unavailable, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

29. Do you think in case of a seismic event impacting process facilities blast walls could be damaged and could be unavailable?

Answers: [YES/NO/NOT SURE]

30. Based on your experience and judgement, how likely do you think it is that blast walls are unavailable, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.8 Fireproofing

With fireproofing we refer to specific coating material intended to protect equipment from fire.

31. Do you think in case of a flood event impacting process facilities fireproofing could be damaged and could be ineffective?

Answers: [YES/NO/NOT SURE]

32. Based on your experience and judgement, how likely do you think it is that fireproofing is ineffective, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

33. Do you think in case of a seismic event impacting process facilities fireproofing could be damaged and could be ineffective?

Answers: [YES/NO/NOT SURE]

34. Based on your experience and judgement, how likely do you think it is that fireproofing is ineffective, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.9 Bunds / Catch Basins

With bunds / catch basins we refer to physical barriers around tanks storing hazardous liquids, sized to retain the whole content of the tank preventing liquid spread. Concrete, earth, or steel are used to build these structures.

35. Do you think in case of a flood event impacting process facilities bunds / catch basins could be damaged and could be ineffective?

Answers: [YES/NO/NOT SURE]

36. Based on your experience and judgement, how likely do you think it is that bunds / catch basins are ineffective, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

37. Do you think in case of a seismic event impacting process facilities bunds / catch basins could be damaged and could be ineffective?

Answers: [YES/NO/NOT SURE]

38. Based on your experience and judgement, how likely do you think it is that bunds / catch basins are ineffective, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.10 Fire Activated Valves

With fire activated valves we refer to valves activated through melting elements or by heat detectors. The valves instrument air to operate correctly.

39. Do you think in case of a flood event impacting process facilities fire activated valves could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

40. Based on your experience and judgement, how likely do you think it is that fire activated valves are unavailable in case of demand, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

41. Do you think in case of a seismic event impacting process facilities fire activated valves could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

42. Based on your experience and judgement, how likely do you think it is that fire activated valves are unavailable in case of demand, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.11 Fire and Gas Detectors

With fire and gas detectors we refer to sensors located in the field to detect fire, heat, smoke, or gas leaks, cabled to an alarm in control room.

43. Do you think in case of a flood event impacting process facilities fire and gas detectors could be damaged and could be unavailable?

Answers: [YES/NO/NOT SURE]

44. Based on your experience and judgement, how likely do you think it is that fire and gas detectors are unavailable, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

45. Do you think in case of a seismic event impacting process facilities fire and gas detectors could be damaged and could be unavailable?

Answers: [YES/NO/NOT SURE]

46. Based on your experience and judgement, how likely do you think it is that fire and gas detectors are unavailable, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.12 Shut Down Valves (SDVs)

With shut down valves (SDVs) we refer to fail-close valves aimed at the isolation of the equipment when activated. SDVs may be activated manually or by process/local/emergency shut-down logic.

47. Do you think in case of a flood event impacting process facilities shut down valves (SDVs) could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

48. Based on your experience and judgement, how likely do you think it is that shut down valves (SDVs) are unavailable in case of demand, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

49. Do you think in case of a seismic event impacting process facilities shut down valves (SDVs) could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

50. Based on your experience and judgement, how likely do you think it is that shut down valves (SDVs) are unavailable in case of demand, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.13 Blow Down Valves (BDVs)

With blow down valves (BDVs) we refer to fail-open valves venting process fluid to flare, aimed at providing a fast depressurization of the equipment. BVDs may be activated manually or by emergency shut-down logic.

51. Do you think in case of a flood event impacting process facilities blow down valves (BDVs) could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

52. Based on your experience and judgement, how likely do you think it is that blow down valves (BDVs) are unavailable in case of demand, as immediate consequence of a flood event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

53. Do you think in case of a seismic event impacting process facilities blow down valves (BDVs) could be damaged and could be unavailable in case of demand?

Answers: [YES/NO/NOT SURE]

54. Based on your experience and judgement, how likely do you think it is that blow down valves (BDVs) are unavailable in case of demand, as immediate consequence of a seismic event?

Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

SB.14 Emergency Blow Down (EBD) line to flare stack

The BDV is activated to depressurize equipment through opening a line to flare stack. The EBD line connecting the equipment to the flare is likely to have a flash KO drum for liquid separation.

55. Do you think in case of a flood event impacting process facilities the emergency blow down (EBD) line to flare stack could be damaged and could be unavailable?
Answers: [YES/NO/NOT SURE]
56. Based on your experience and judgement, how likely do you think it is that the emergency blow down (EBD) line to flare stack is unavailable in case of demand, as immediate consequence of a flood event?
Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]
57. Do you think in case of a seismic event impacting process facilities the emergency blow down (EBD) line to flare stack could be damaged and could be unavailable?
Answers: [YES/NO/NOT SURE]
58. Based on your experience and judgement, how likely do you think it is that the emergency blow down (EBD) line to flare stack is unavailable, as immediate consequence of a seismic event?
Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]
SB.15 Mounding storage
With mounding storage we refer to locating tanks into above-ground piles of gravel/earth (i.e., mounds) for protection from external fire.
59. Do you think in case of a flood event impacting process facilities mounds protecting the tanks could be damaged and could become ineffective in protecting tanks in case of fire?
Answers: [YES/NO/NOT SURE]
60. Based on your experience and judgement, how likely do you think it is that the protection given by mounds becomes ineffective, as immediate consequence of a flood event?
Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]
61. Do you think in case of a seismic event impacting process facilities mounds protecting the tanks could be damaged and could become ineffective in protecting tanks in case of fire?
Answers: [YES/NO/NOT SURE]
62. Based on your experience and judgement, how likely do you think it is that the protection given by mounds becomes ineffective, as immediate consequence of a seismic event?
Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]
SB.16 Burying storage
With burying storage (underground) we refer to positioning storage tanks below ground level.
63. Do you think in case of a flood event impacting process facilities the protection given by earth covering buried tanks could be compromised?
Answers: [YES/NO/NOT SURE]
64. Based on your experience and judgement, how likely do you think it is that the protection given by earth covering buried tanks becomes ineffective, as immediate consequence of a flood event?
Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]
65. Do you think in case of a seismic event impacting process facilities the protection given by earth covering buried tanks could be compromised?
Answers: [YES/NO/NOT SURE]
66. Based on your experience and judgement, how likely do you think it is that the protection given by earth covering buried tanks becomes ineffective, as immediate consequence of a seismic event?
Answers: [Certain/Probable/Expected/Fifty-Fifty/Uncertain/Improbable/Impossible]

Appendix B. Details of the elicited failure probability distributions

In this appendix, the details of the distributions obtained from experts' answers to the quantitative part of the survey are reported. The results obtained for floods are presented in Table B. 1 for floods, while the ones obtained for earthquakes are presented in Table B. 2.

Table B. 1: Description of performance parameter distribution for each safety barrier for floods. The reader can refer to Table 5.2. 1 for concise barrier descriptions and classification.

Safety barrier	Barrier ID	Performance modification factor	Distribution description
Inert-gas blanketing system	*SB.1*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 0.85 Average = 0.441 Sample Std.Dev. = 0.259
Automatic rim-seal fire extinguishers	*SB.2*	0.15	Minimum=0 1st quartile = 0.15 2nd quartile = 0.15 3rd quartile = 0.25 Maximum = 0.85 Average = 0.284 Sample Std.Dev. = 0.217
Fixed / Semi-fixed foam systems	*SB.3*	0.375	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.375 3rd quartile = 0.5 Maximum = 0.85 Average = 0.434 Sample Std.Dev. = 0.236
WDS / Water Curtains / Sprinklers	*SB.4*	0.375	Minimum=0 1st quartile = 0.175 2nd quartile = 0.375 3rd quartile = 0.75 Maximum = 0.85 Average = 0.439 Sample Std.Dev. = 0.279
Hydrants	*SB.5*	0.5	Minimum=0 1st quartile = 0.25 2nd quartile = 0. 5 3rd quartile = 0.75 Maximum = 1 Average = 0.493 Sample Std.Dev. = 0.308
Fire activated valves	*SB.6*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.5 Maximum = 0.85 Average = 0.418 Sample Std.Dev. = 0.238
Fire and gas detectors	*SB.7*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 1 Average = 0.537

			Sample Std.Dev. = 0.281
SDVs	*SB.8*	0.25	Minimum=0.15 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 1 Average = 0.343 Sample Std.Dev. = 0.238
BDVs	*SB.9*	0.25	Minimum=0.15 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 0.85 Average = 0.318 Sample Std.Dev. = 0.222
Fire walls	*SB.10*	0.2	Minimum=0 1st quartile = 0.15 2nd quartile = 0.2 3rd quartile = 0.25 Maximum = 0.85 Average = 0.282 Sample Std.Dev. = 0.245
Blast walls	*SB.11*	0.15	Minimum=0 1st quartile = 0.15 2nd quartile = 0.15 3rd quartile = 0.75 Maximum = 0.85 Average = 0.274 Sample Std.Dev. = 0.240
Fireproofing	*SB.12*	0.15	Minimum=0 1st quartile = 0.15 2nd quartile = 0.15 3rd quartile = 0.25 Maximum = 0.85 Average = 0.261 Sample Std.Dev. = 0.252
Bunds / Catch basins	*SB.13*	0.75	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.75 3rd quartile = 0.85 Maximum = 1 Average = 0.597 Sample Std.Dev. = 0.275
Emergency Blowdown line to flare stack	*SB.14*	0.25	Minimum=0 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 1 Average = 0.334 Sample Std.Dev. = 0.236
Mounding tanks	*SB.15*	0.25	Minimum=0 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 0.85 Average = 0.357 Sample Std.Dev. = 0.275
Burying tanks	*SB.16*	0.15	Minimum=0 1st quartile = 0.15 2nd quartile = 0.15

			3rd quartile = 0.5 Maximum = 0.85 Average = 0.289 Sample Std.Dev. = 0.230

Table B. 2: Description of performance parameter distribution for each safety barrier for earthquakes. The reader can refer to Table 5.2. 1 for concise barrier descriptions and classification.

Safety barrier	**Barrier ID**	**Performance modification factor**	**Distribution description**
Inert-gas blanketing system	*SB.1*	0.625	Minimum=0.15 1st quartile = 0.5 2nd quartile = 0.625 3rd quartile = 0.85 Maximum = 1 Average = 0.607 Sample Std.Dev. = 0.238
Automatic rim-seal fire extinguishers	*SB.2*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 0.85 Average = 0.489 Sample Std.Dev. = 0.255
Fixed / Semi-fixed foam systems	*SB.3*	0.5	Minimum=0.15 1st quartile = 0.5 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 0.85 Average = 0.571 Sample Std.Dev. = 0.238
WDS / Water Curtains / Sprinklers	*SB.4*	0.75	Minimum=0.15 1st quartile = 0.5 2nd quartile = 0.75 3rd quartile = 0.85 Maximum = 1 Average = 0.620 Sample Std.Dev. = 0.246
Hydrants	*SB.5*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 0.85 Average = 0.482 Sample Std.Dev. = 0.282
Fire activated valves	*SB.6*	0.375	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.375 3rd quartile = 0.6875 Maximum = 0.85 Average = 0.445 Sample Std.Dev. = 0.262
Fire and gas detectors	*SB.7*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 1 Average = 0.480 Sample Std.Dev. = 0.264
SDVs	*SB.8*	0.5	Minimum=0.15 1st quartile = 0.25

			2nd quartile = 0.5 3rd quartile = 0.5 Maximum = 1 Average = 0.433 Sample Std.Dev. = 0.246
BDVs	*SB.9*	0.25	Minimum=0.15 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 0.85 Average = 0.368 Sample Std.Dev. = 0.236
Fire walls	*SB.10*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 1 Average = 0.514 Sample Std.Dev. = 0.271
Blast walls	*SB.11*	0.25	Minimum=0 1st quartile = 0.25 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 0.85 Average = 0.405 Sample Std.Dev. = 0.257
Fireproofing	*SB.12*	0.25	Minimum=0 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.4375 Maximum = 0.75 Average = 0.314 Sample Std.Dev. = 0.234
Bunds / Catch basins	*SB.13*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 0.85 Average = 0.464 Sample Std.Dev. = 0.249
Emergency Blowdown line to flare stack	*SB.14*	0.5	Minimum=0.15 1st quartile = 0.25 2nd quartile = 0.5 3rd quartile = 0.75 Maximum = 1 Average = 0.530 Sample Std.Dev. = 0.234
Mounding tanks	*SB.15*	0.25	Minimum=0.15 1st quartile = 0.15 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 1 Average = 0.411 Sample Std.Dev. = 0.259
Burying tanks	*SB.16*	0.25	Minimum=0 1st quartile = 0.175 2nd quartile = 0.25 3rd quartile = 0.5 Maximum = 0.85 Average = 0.391 Sample Std.Dev. = 0.251

Appendix C. Details of emergency intervention performance characterization

This appendix is intended to provide further details on the calculation of *PFD* and η, for the characterization of emergency interventions adopted in Sections 5.3 and 6.3.

The *PFD* can be assessed equal to 1.0×10^{-1}, which corresponds to the probability associated with human error according to LOPA literature (CCPS, 2001b) and to recent studies addressing ETA for domino escalation (Landucci et al., 2017b, 2016, 2015). The evaluation of the effectiveness, η, may be performed according to the comparison between *TTF* and *TFM* at the site, as proposed in Landucci et al. (Landucci et al., 2016). In case the *TTF* is lower than *TFM*, the emergency intervention should be associated to $\eta = 0$; on the contrary, in case the *TFM* is lower than *TTF* (i.e., in case of accident mitigation is achieved before target equipment failure due to fire), the emergency intervention will be effective, and thus $\eta = 1$.

The value of time scale for accident mitigation is site-specific, and a preliminary estimate of *TFM* is required to assess η. A simplified methodology based on fire mitigation strategy and the relative amount of water rate required for mitigation is applied in the case studies developed in Section 5.3 and Section 6.3 (Landucci et al., 2015), leading to the calculation of *TFM* values of 65 and 90 min respectively for pressurized vessels and atmospheric tanks. Nevertheless, the methodology was not developed considering the possibility that the emergency intervention is hindered by the possible unfavorable environment resulting from the impact of the natural hazard. Thus, the above-reported results should be considered as baseline best-case values.

For what concerns the case study presented in Section 5.3, in the assessment of the modification of domino scenario frequencies given barrier depletion, it was decided to perform a preliminary evaluation of the possible delay on emergency intervention, adopting an approach originally proposed for assessing *TFM* in operations carried out in harsh environments (Landucci et al., 2017a). In the following, the approach is briefly described together with the final *TFM* values calculated for the case study of Section 5.3.5.

The modified *TFM* for onshore sites may be calculated according to the following relation:

$$TFM = \sum_{j=1}^{5} \tau_j \qquad \text{(C. 1)}$$

where τ_j are characteristic times required to perform the main operations that are required by emergency response. The values of τ_j can be evaluated through correlations dependent on the Harsh Environment Score (*HES*), a parameter between 0 and 1 expressing the harshness of environmental conditions (0: normal conditions; 1: extremely harsh conditions).

Conservatively, in the case study presented in Chapter 5.3, a value of *HES* equal to 1 was assumed, as a worst-case scenario. Description of each operation considered, together with the correlation for estimating the characteristic times for onshore sites, and the resulting value assumed in this study are presented in Table C. 1. With respect to the case study considered, the worst-case value for *TFM* is assessed to be equal to 400 min for both P1 and T2.

Table C. 1: Characteristic times to perform main emergency response operations in onshore sites as a function of Harsh Environment Score (HES). Adapted from (Landucci et al., 2017a).

Time	**Operation**	**Correlation**	**Max τ_i [min]**
τ_1	Time to alert: the maximum time required to start the emergency operation, which is usually composed of the detection time and the time needed to alarm onsite personnel and offsite teams	$\log_{10}(\tau_1) = -0.301 \times (1 - HES) + 1.000$	10
τ_2	Time needed by external emergency teams to turn out and reach the site	If $HES < 0.8$: $\log_{10}(\tau_2) = -0.301 \times (1 - HES) + 1.380$ If $HES \geq 0.8$: $\tau_2 = 60$	60
τ_3	Time needed by external emergency teams to deploy firefighting equipment	$\log_{10}(\tau_3) = -0.301 \times (1 - HES) + 1.146$	14
τ_4	Time needed by external emergency teams to carry out extra set-up operations	$\log_{10}(\tau_4) = -0.301 \times (1 - HES) + 1.204$	16
τ_5	Additional time required in case one of more water transport systems or interregional assistance are needed	If $HES < 0.8$: $\log_{10}(\tau_5) = -0.301 \times (1 - HES) + 2.079$ If $HES \geq 0.8$: $\tau_5 = 300$	300

Appendix D. Details of the benchmark cases defined in Section 6.1

D.1 Case 0: QRA of conventional scenarios

The set of conventional scenarios considered for benchmarking the results obtained in the case study of Section 6.1 is described in the following. The case is indicated as case 0 in Section 6.1.

The frequencies of each LOC have been determined by adopting generic values available in standard references (Uijt de Haag and Ale, 2005). For what concerns the event trees for the release of flammable substances, reference values for ignition probabilities were derived by the application of UKOOA look-up correlations (Energy Institute, 2019; IOGP, 2019). The correlations provided in the UKOOA model are developed for typical scenarios and can be used to evaluate a total ignition probability as a function of substance release rate (Energy Institute, 2019). The values obtained for the various releases considered are reported in Table D. 1. Additionally, the model suggests deriving the immediate and delayed ignition probability from the total ignition probability using a 30:70 ratio (Energy Institute, 2019).

Table D. 1: Reference frequencies for LOCs and ignition probabilities obtained from UKOAA look-up correlations adopted in the QRA of conventional scenarios involving the equipment considered in the case study. f_{LOC} = frequency of LOC; P_{ign} = immediate ignition probability; $P_{ign}^{delayed}$ = delayed ignition probability.

Item involved	LOC	f_{LOC} [y^{-1}]	P_{ign}	$P_{ign}^{delayed}$
T1 – T4	Catastrophic rupture	5.00E-06	1.50E-02	3.50E-02
	Continuous release in 10 min	5.00E-06	1.50E-02	3.50E-02
	Leak from 10 mm hole	1.00E-04	5.28E-04	1.23E-03
P1 – P2	Catastrophic rupture	-	-	-
	Continuous release in 10 min	-	-	-
	Leak from 10 mm hole	-	-	-
P3	Catastrophic rupture	5.00E-07	1.95E-01	4.55E-01
	Continuous release in 10 min	5.00E-07	1.20E-01	2.80E-01
	Leak from 10 mm hole	1.00E-05	9.75E-04	2.27E-03

In developing the conventional scenarios, the barriers summarized in Table 6.1. 3 have been considered. In particular, some assumptions were required on barrier action and performance:

- Consequence simulation of liquid spills in the case of catch basin failure is made assuming a pool spreading over an area equal to two times the original area of the catch basin. This assumption is made to avoid over-conservative results which might be generated considering unconfined liquid spills. In case of 10-mm releases, the flammable liquid pool area is calculated considering the maximum burning rate of the substance, and the status of the catch basin does not influence consequence calculation;

- The FWS is assumed to reduce the surface emissive power (SEP) of scenarios following immediate ignition by 50% (i.e., pool fires) and to lower the evaporation rate of scenarios related to delayed ignition by 40% (i.e., flash fires and VCEs), in analogy with indications on previous publications (Landucci et al., 2017b);
- WCs are assumed to be designed only to cope with continuous gaseous releases (i.e., the case of 10-min release can be mitigated). Several publications report different approaches to evaluate the effectiveness of WC action in mitigating release consequences, depending on the substance involved and on the specific design features of the protection (Fthenakis and Blewitt, 1995). For the sake of simplicity, a reduction of 75% in the hazmat release flowrate has been assumed for the continuous releases from vessels P1 to P3 (Fthenakis et al., 1995; Fthenakis and Blewitt, 1995). On the contrary, no mitigation is deemed credible for instantaneous releases following the catastrophic failure of the containment due to the intense momentum generated by substance vaporization (Landucci et al., 2017b).

Therefore, the event trees obtained for tanks T1 – T4 are reported in Figure D. 1 and Figure D. 2.

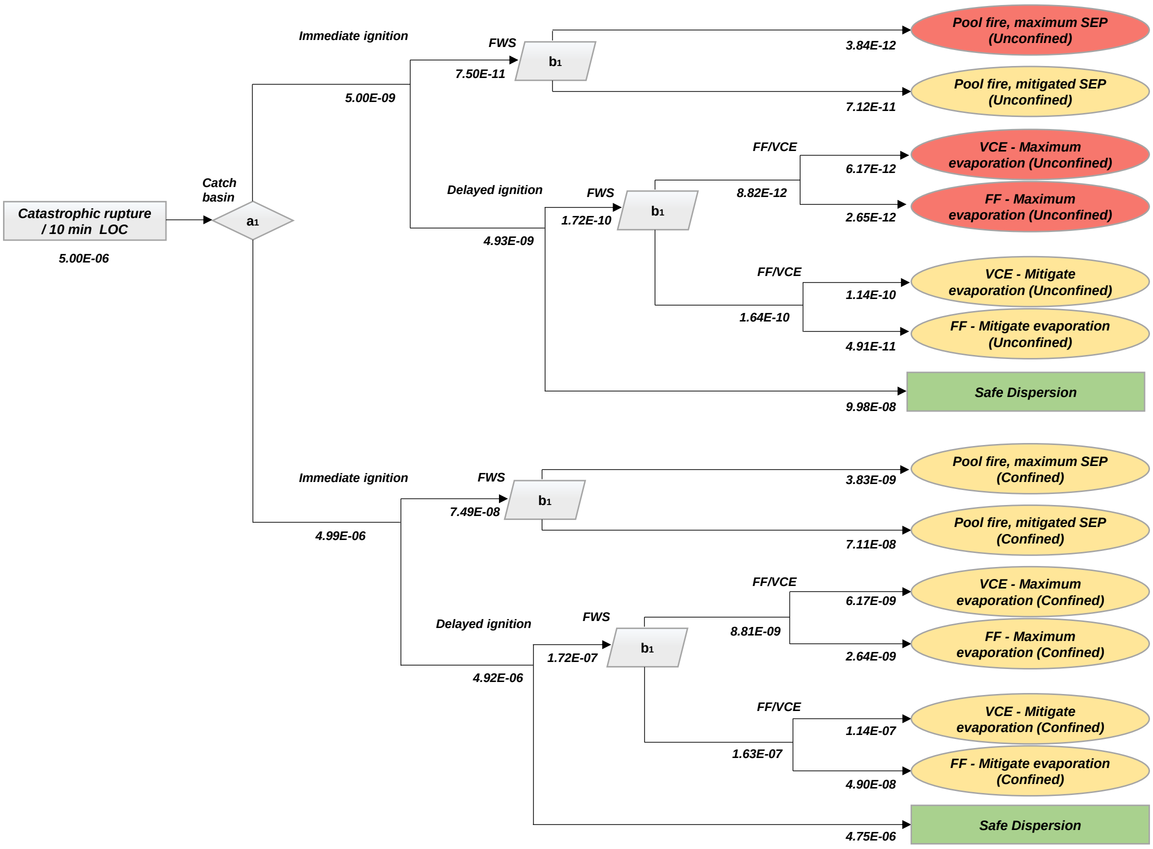

Figure D. 1: Event tree for conventional scenarios following catastrophic ruptures or 10-min continuous releases from tanks T1 – T4, considering the presence of catch basin and FWS (see Table 6.1. 3). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow.

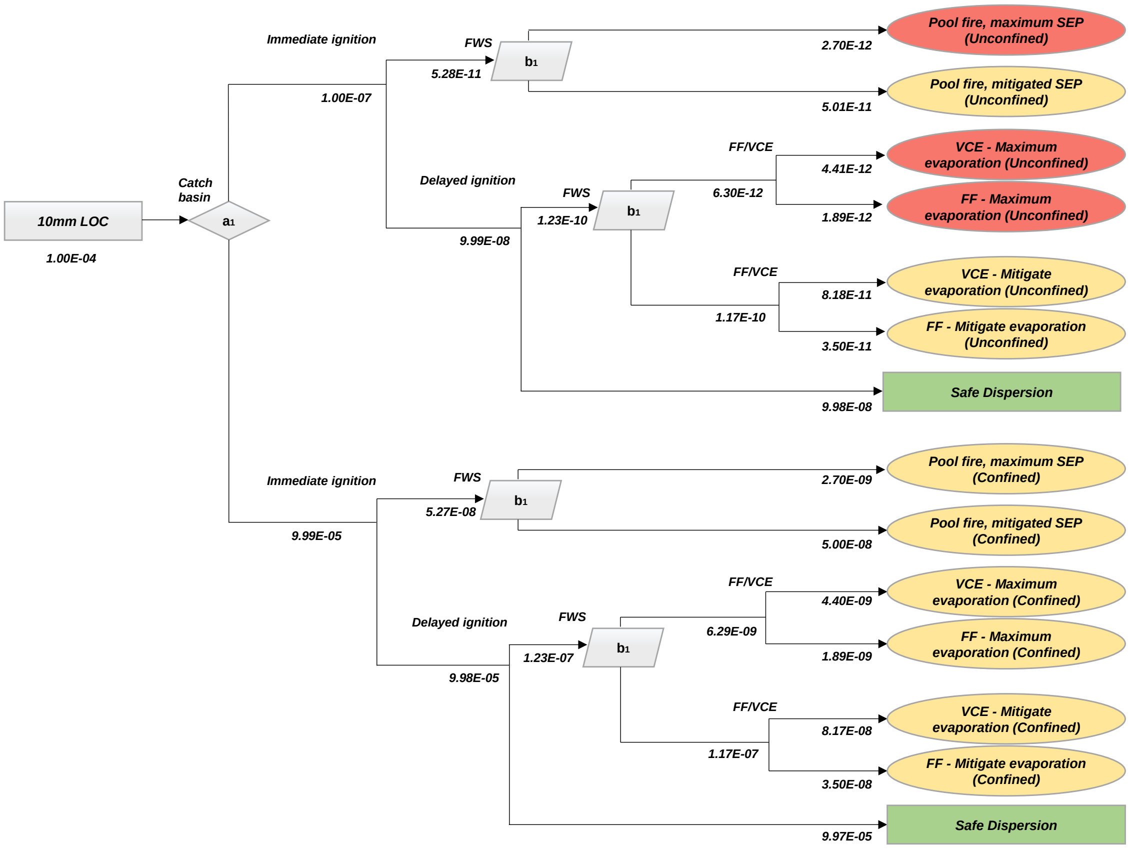

Figure D. 2: Event tree for conventional scenarios following catastrophic ruptures or 10-min continuous releases from tanks T1 – T4, considering the presence of catch basin and FWS (see Table 6.1. 3). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow.

For vessels P1 and P2 instead, the scenarios obtained are reported in Figure D. 3. As already mentioned above, the mitigation in case of vessel catastrophic rupture is not deemed possible (panel a), while the WC are included in the ETs for continuous releases (panels b and c).

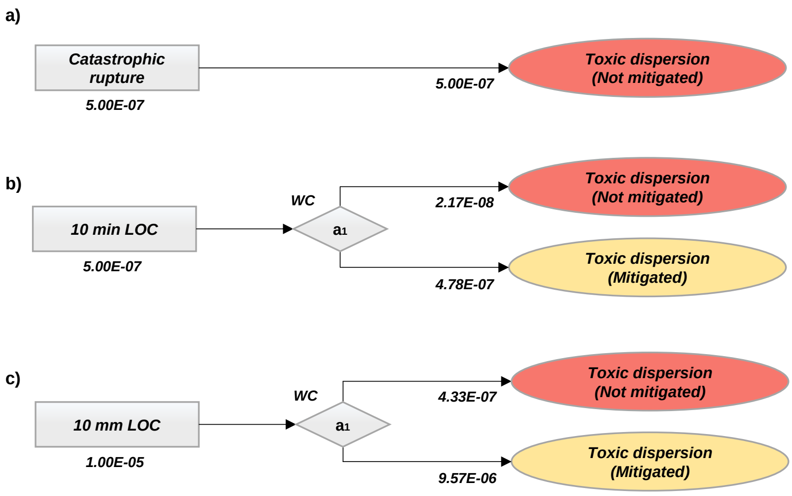

Figure D. 3: Event tree for conventional scenarios following a) catastrophic ruptures, b) 10-min continuous releases and c) 10 mm continuous releases from vessels P1 and P2, considering the presence of WC (see Table 6.1. 3). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow.

Lastly, Figure D. 4 shows the ETs that have been obtained for horizontal vessel P3. Also in this case the possibility of mitigation provided by WC is not deemed credible in case of catastrophic ruptures (panel a), while it is considered for all the continuous releases (panel b and panel c).

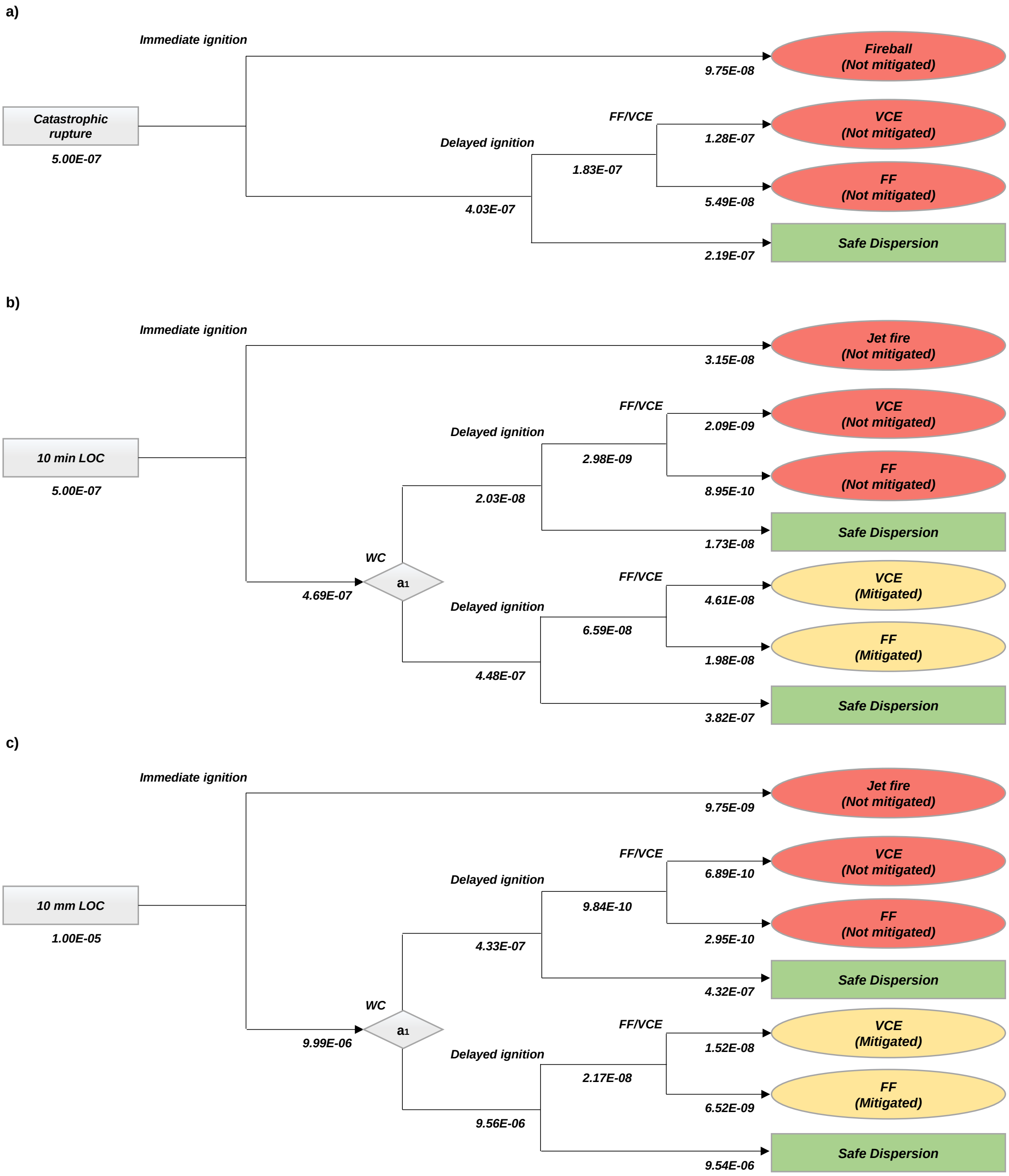

Figure D. 4: Event tree for conventional scenarios following a) catastrophic ruptures, b) 10-min continuous releases and c) 10 mm continuous releases from vessel P3, considering the presence of WC (see Table 6.1. 3). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow

The summary of damage models for the human target adopted is summarized in Table D. 2. It should be noted that the models described in Table D. 2 have been consistently applied also in the case study presented in Section 6.2 and Section 6.3.

Table D. 2: Human vulnerability models adopted in this case study. P=death probability

Physical effect	**Human vulnerability model**
Heat radiation	Probit equation: $Y = -14.9 + 2.56\ln(t_{exp} \times I^{\frac{4}{3}})$ Vulnerability (Finney, 1971): $P = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{Y-5} e^{-\frac{u^2}{2}}\,du$
Heat radiation (flash fire)	Threshold-based: $\begin{cases} P = 1\ if\ C_f \geq \frac{LFL}{2} \\ P = 0\ if\ C_f < \frac{LFL}{2} \end{cases}$
Overpressure	Threshold-based: $\begin{cases} P = 1\ if\ P_s \geq 0.3bar \\ P = 0\ if\ P_s < 0.3bar \end{cases}$
Toxic dispersion	Probit equation: $Y = k_1 + k_2\ln({C_t}^n \times t_{exp})$ Vulnerability (Finney, 1971): $P = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{Y-5} e^{-\frac{u^2}{2}}\,du$

Notes

t_{exp} [s]: exposure time
I [kW/m^2]: heat radiation
C_f [ppm]: concentration in air
LFL [ppm]: lower flammability limit
P_S [bar]: peak static overpressure
C_t [mg/m^3]: toxic concentration in air
Ammonia: $k_1 = -15.6$; $k_2 = 1$; $n = 2$;
H_2S: $k_1 = -11.5$; $k_2 = 1$; $n = 1.9$; (see Section 6.3)

The models have been taken from standardized literature on QRA (CCPS, 2000; Finney, 1971; Mannan, 2005; Uijt de Haag and Ale, 2005; Van Den Bosh, 1992; Van Den Bosh and Weterings, 2005), and the ARIPAR procedure for risk recomposition has been applied (Egidi et al., 1995).

The results obtained in terms of local specific individual risk (LSIR) are shown in Figure D. 5.

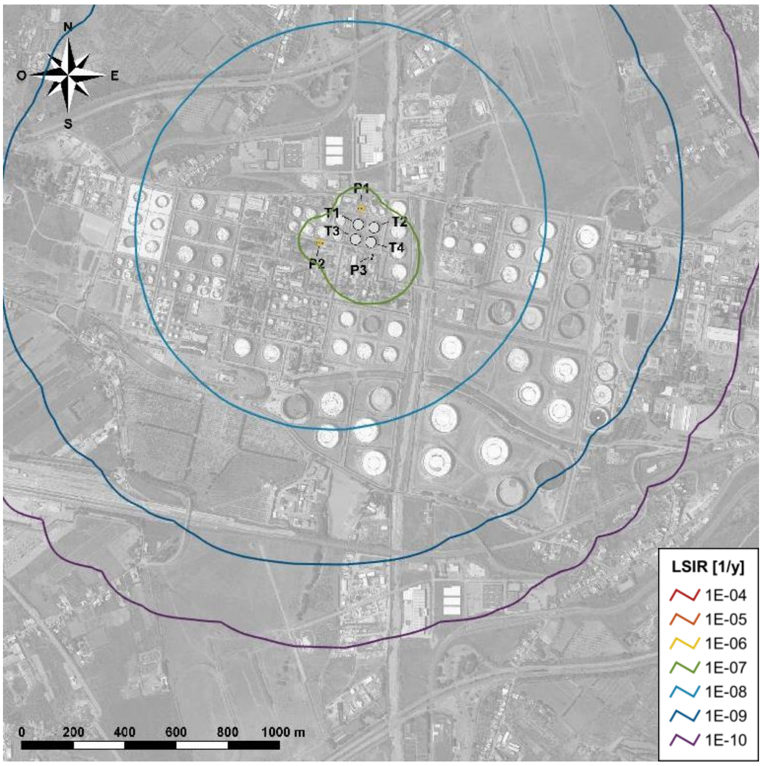

Figure D. 5: LSIR contours for conventional scenarios obtained for the case study of Section 6.1 considering the presence of barriers (case 0).

The results in terms of societal risk are expressed through the F/N plot reported in Figure D. 6.

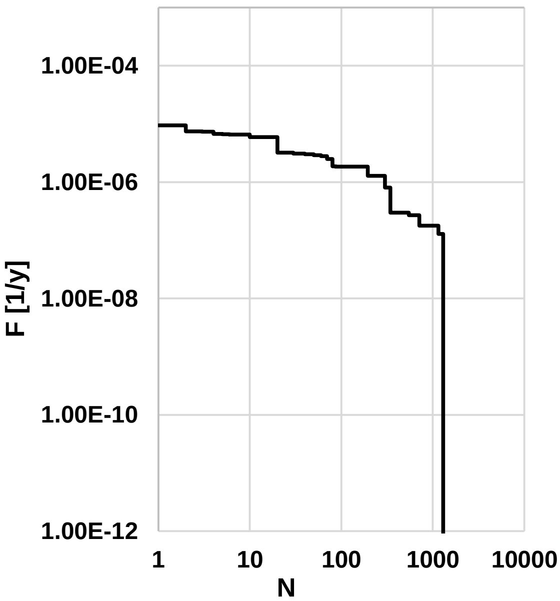

Figure D. 6: Societal risk for scenarios obtained for the case study of Section 6.1 considering the presence of barriers (case 0).

D.2 Case 1: QRA of primary Natech scenarios in absence of safety barriers

In this section, additional details on the primary Natech scenario in absence of safety barriers (i.e., worst-case situation) developed for the case study of Section 6.1 will be provided. The probability of damage due to the reference earthquake event and the frequency of the related LOCs have been calculated leveraging the fragility models proposed in (Salzano et al., 2009), as already presented in Table 6.1. 4.

As already mentioned, the values reported in (Ricci et al., 2021) for ignition probabilities were considered in the development of post-release event trees following the impact of the reference earthquake event. According to the original publication, the overall ignition probability for liquid releases of flammable substances during earthquakes might be assumed at 5.80E-02, while for the cases of liquefied flammable gases a reference value of 3.21E-01 is suggested. A 30/70 ratio between immediate and delayed ignition probabilities has been assumed also in case 1, consistently with the approach adopted in case 0 for conventional scenarios (Energy Institute, 2019).

The results obtained from frequency assessment are reported in Table D. 3.

*Table D. 3: Details of the frequencies and probabilities of final scenarios considered in case 1 (worst-case, absence of barriers). f_{LOC} = frequency of LOC; P_{ign} = immediate ignition probability; $P_{ign}^{delayed}$ = delayed ignition probability; VCE = Vapour cloud explosion; FF = Flash fire; $f(N_k^7)$ = frequency of a final scenario from the k-th equipment involved (out of 7 total elements of the layout); $P(N_k^7)$ = probability of a final scenario from the k-th equipment involved (out of 7 total elements of the layout) (see Section 6.1.3). * = reference event considered in the validation of the outcomes of case 1 against the application of the methodology of Section 2.2.2 (based on a single final scenario per target).*

Item involved	LOC	f_{LOC} [y^{-1}]	P_{ign}	$P_{ign}^{delayed}$	Final scenario	$f(N_k^7)$ [y^{-1}]	$P(N_k^7)$
T1 – T4	Catastrophic rupture	6.75E-04	1.74E-02	4.06E-02	Pool fire*	1.18E-05	5.88E-03
					FF	8.08E-06	4.04E-03
					VCE	1.89E-05	9.43E-03
P1 – P2	Continuous release in 10 min	2.02E-04	-	-	Toxic dispersion*	2.02E-04	1.01E-01
P3	Continuous release in 10 min	2.02E-04	9.63E-02	2.25E-01	Jet fire	1.94E-05	9.72E-03
					FF*	1.23E-05	6.15E-03
					VCE	2.87E-05	1.43E-02

Considering the application of the methodology shown in Section 6.1, assuming all the barriers unavailable, the expected total number of combinations involving technological scenarios is assessed at 4095 using Eq. (6.1.6). Indeed, three final scenarios plus the safe state have been considered for items T1 to T4 and P3, and a single final scenario plus the safe state has been included for items P1 and P2. The probability and frequency of each overall primary Natech scenario have been calculated respectively according to Eq. (6.1.7) and Eq. (6.1.8). Consequence simulation has been performed utilizing established models. It should be noted that for the calculation of the consequences of liquid releases from tanks T1 – T4, the presence of the catch basin is not considered in this case to model the worst-case scenario of barrier absence. Therefore, in analogy with case 0 (see Appendix D.1), it was assumed a pool spreading over an area two times greater than the original catch basin area (see Table 6.1. 2). Finally, the death probability related to each overall primary Natech scenario is assessed by means of Eq. (6.1.9).

Given that case 1 is analyzed through the methodology developed in Section 6.1.3, but assuming the absence of barriers, a preliminary validation of results against the ones which can be obtained from the current approach to Natech QRA is performed (see Section 2.2.2). As already pointed out, in previous publications the simplifying assumption of a single reference outcome associated with each piece of equipment is made (see Eqs. (2.2.1) to (2.2.3)). Therefore, the most severe final scenario associated with the failure of each item among the ones reported in Table D. 3 is identified (i.e., the one leading to the highest number of fatalities, marked with "*" in the table). This scenario is used as a reference scenario to apply the QRA methodology of Section 2.2.2.

The comparison of the results obtained in terms of LSIR is shown in Figure D. 7.

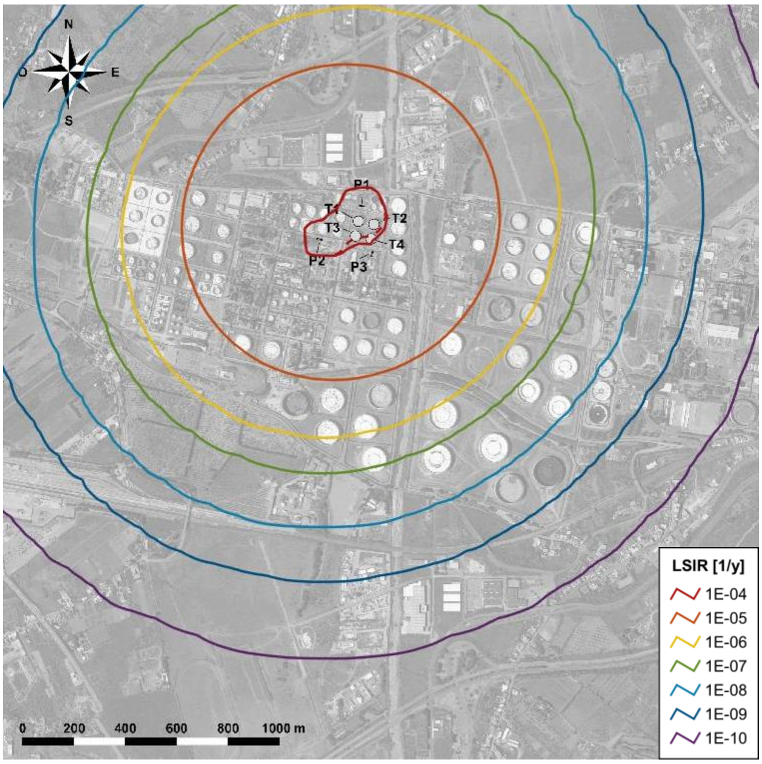

Figure D. 7: Comparison of LSIR contours for case 1 (worst-case) assessed by the methodology presented in Section 6.1.3 (continuous lines), and contours obtained from the application of the methodology described in Section 2.2.2 considering a single reference-scenario per equipment (see Table D. 3) (dashed lines).

The LSIR contours associated with case 1 (i.e., considering all the possible final scenarios from the event tree without the presence of safety barriers) are shown as continuous lines, while the figures resulting from the application of the current QRA methodology described in Section 2.2.2 are depicted as dashed lines. As can be seen, the contours are almost superimposed, and the sole region of the layout featuring a slight difference is the one occupied by tanks T1 – T4.

Additional proof of the substantial agreement between the two approaches can be obtained by analyzing the F/N curves calculated for the two cases, as shown in Figure D. 8.

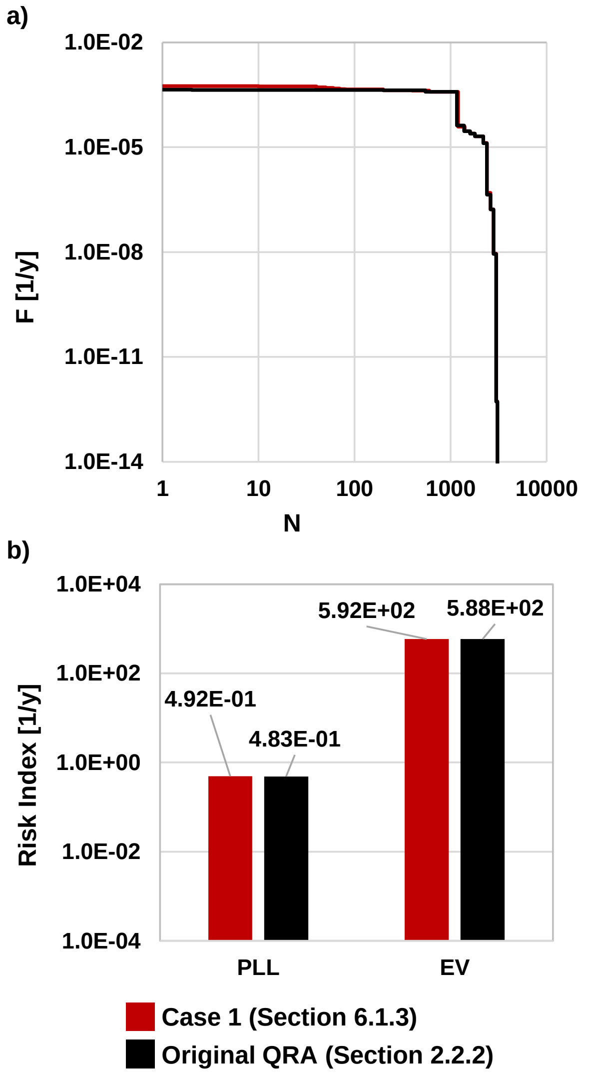

Figure D. 8: Societal risk curves (panel a) and PLL and EV indexes (panel b) for case 1 (worst-case) assessed by the methodology presented in Section 6.1.3 (in red), and obtained from the application of the methodology described in Section 2.2.2 considering a single reference-scenario per equipment (see Table D. 3) (in black).

As clear also from Figure D. 8, the results are consistent with the current QRA approach (i.e., there is only a minor increase in risk figure related to the inclusion of additional scenarios of the post-release event tree beside the worst-outcome). Therefore, the results obtained for case 1 are validated and can be effectively used in Section 6.1 as a worst-case situation.

D.3 Case 2: QRA of primary Natech scenarios considering safety barriers with baseline performance

This section is aimed at providing additional details on the probabilistic assessment of primary Natech scenarios considering the set of safety barriers reported in Table 6.1. 3, assuming their baseline performance. This case can thus be seen as a best-case situation of absence of barrier depletion during the reference earthquake event, and it is termed case 2 in Section 6.1.

The set of ETs developed for this case are reported in Figure D. 9, Figure D. 10, and Figure D. 11.

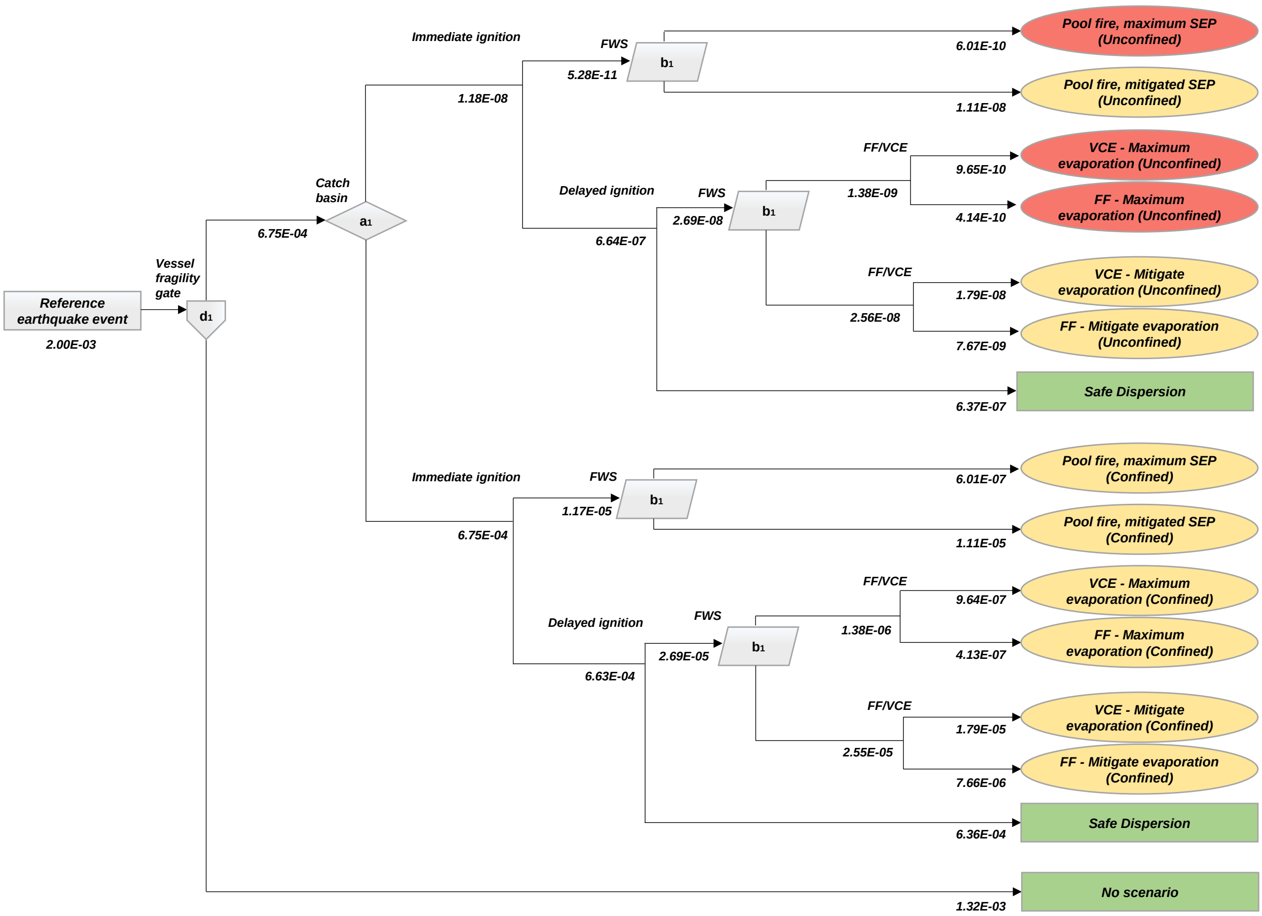

Figure D. 9: Event tree for primary Natech scenarios from tanks T1 – T4 following the reference earthquake event, considering the presence of catch basin and FWS with baseline performance (see Table 6.1. 3 and Table 6.1. 5). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow.

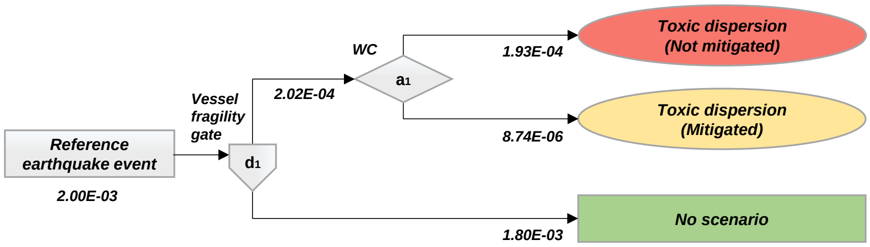

Figure D. 10: Event tree for primary Natech scenarios from vessels P1 and P2 following the reference earthquake event, considering the presence of WC with baseline performance (see Table 6.1. 3 and Table 6.1. 5). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow.

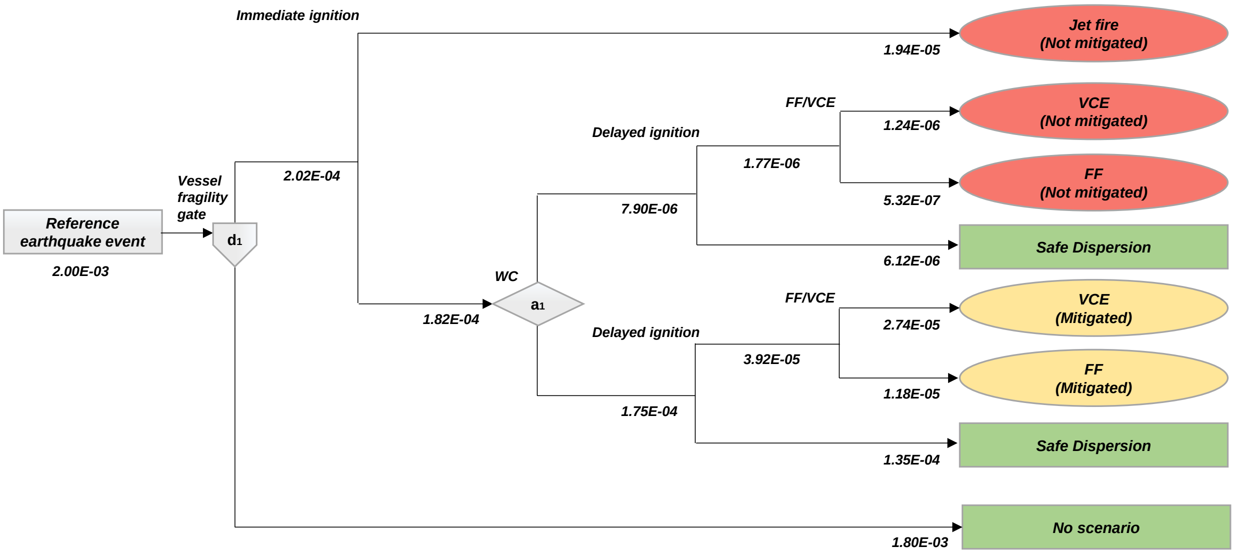

Figure D. 11: Event tree for primary Natech scenarios from vessel P3, following the reference earthquake event, considering the presence of WC with baseline performance (see Table 6.1. 3 and Table 6.1. 5). All the frequencies are in y^{-1}. Unmitigated scenarios are reported in red, while mitigated scenarios are reported in yellow.

For the sake of clarity, the final probabilities and frequencies for the set of primary Natech scenarios identified for each item damaged by the reference earthquake event, are reported in Table D. 4.

As can be seen from the table, each atmospheric tank is associated with 12 hazardous technological scenarios plus a safe condition (i.e., safe dispersion or absence of scenario due to vessel resistance to seismic load). The pressurized vessels P1 and P2 instead are assumed to lead only to 2 possible technological scenarios plus the safe condition of absence of equipment failure, while the release from vessel P3 is assumed to cause 5 different hazardous outcomes plus a safe condition (i.e., also in this case assessed as the sum of safe dispersion and no-failure cases). Therefore, applying Eq. (6.1.6) the total number of overall Natech scenarios for case 2 is assessed at 1542293 possible different combinations of final scenarios involving the 7 items considered in the case study (i.e., the combination with all the items in a safe condition is not considered according to Eq. (6.1.6) since it does not constitute an accidental situation).

Table D. 4: Details of the frequencies and probabilities of final scenarios considered in case 2 (best-case, barriers with baseline performance). SEP=surface emissive power; VCE = Vapour cloud explosion; FF = Flash fire; $f(N_k^7)$ = frequency of a final scenario from the k-th equipment involved (out of 7 total elements of the layout); $P(N_k^7)$ = probability of a final scenario from the k-th equipment involved (out of 7 total elements of the layout) (see Section 6.1.3).

Item involved	LOC	*Final scenario*	$f(N_k^7)$ [y^{-1}]	$P(N_k^7)$
T1 – T4	Catastrophic rupture	Pool fire, maximum SEP (Unconfined)	6.01E-10	3.01E-07
		Pool fire, mitigated SEP (Unconfined)	1.11E-08	5.55E-06
		VCE – Maximum evaporation rate (Unconfined)	9.65E-10	4.83E-07
		FF – Maximum evaporation rate (Unconfined)	4.14E-10	2.07E-07
		VCE – Mitigated evaporation rate (Unconfined)	1.79E-08	8.95E-06
		FF – Mitigated evaporation rate (Unconfined)	7.67E-09	3.84E-06
		Pool fire, maximum SEP (Confined)	6.01E-07	3.01E-04
		Pool fire, mitigated SEP (Confined)	1.11E-05	5.55E-03
		VCE – Maximum evaporation rate (Confined)	9.64E-07	4.82E-04
		FF – Maximum evaporation rate (Confined)	4.13E-07	2.07E-04
		VCE – Mitigated evaporation rate (Confined)	1.79E-05	8.95E-03
		FF – Mitigated evaporation rate (Confined)	7.66E-06	3.83E-03
		Safe dispersion / No scenario	1.96E-03	9.78E-01
P1 – P2	Continuous release in 10 min	Toxic dispersion (Not mitigated)	1.93E-04	9.65E-02
		Toxic dispersion (Mitigated)	8.74E-06	4.37E-03
		No scenario	1.80E-03	9.00E-01
P3	Continuous release in 10 min	Jet fire (Not mitigated)	1.94E-05	9.70E-03
		VCE (Not mitigated)	1.24E-06	6.20E-04
		FF (Not mitigated)	5.32E-07	2.66E-04
		VCE (Not mitigated)	2.74E-05	1.37E-02
		FF (Not mitigated)	1.18E-05	5.90E-03
		Safe dispersion / No scenario	1.94E-03	9.71E-01

The probability and frequency of overall primary Natech scenarios have been calculated by Eq. (6.1.7) and Eq. (6.1.8), although given the great number of combinations the results will not be explicitly reported here. Nevertheless, it should be noted that the same Matlab scripts used in the validation of the results of case 1 against the ones obtained applying the established methodology presented in Section 2.2.2 (see Appendix D.2) are used also in this case. Therefore, the methodology for the frequency assessment of overall primary Natech scenarios proposed in Section 6.1.3 can be considered validated also for case 2. Finally, the death probabilities related to the 1542293 overall primary Natech scenarios of case 2 are assessed by Eq. (6.1.9). The results obtained in terms of LSIR and F/N curves for case 2 have been already shown in Section 6.1.5 and will not be repeated in this appendix.

Appendix E. Details of the benchmark cases defined in Section 6.3

E.1 Case 0: QRA of conventional scenarios

The set of conventional scenarios considered for benchmarking the results obtained in the case study is described in this section. The case is indicated as case 0 in Section 6.3. Only conventional scenarios involving T01 (see Figure E. 1) are considered.

Table E. 1: Summary of characterization conventional scenarios from tank T01.

LOC	f_{LOC} [y^{-1}]	P_{ign}	$P_{ign}^{delayed}$	$P_{flashfire}/P_{VCE}$	Final scenario	f_{SCE} [y^{-1}]
					Pool fire	3.25E-07
Catastrophic rupture	5.00E-06	0.065	0.90	0.3/0.7	Flash fire	1.26E-06
					VCE	2.95E-06
					Pool fire	3.25E-07
Continuous release in 10 min	5.00E-06	0.065	0.90	0.3/0.7	Flash fire	1.26E-06
					VCE	2.95E-06
Leak from 10 mm hole	1.00E-04	0.065	-	-	Pool fire	6.50E-06

Scenario frequencies have been determined adopting generic LOC frequencies and even trees available in standard references (Uijt de Haag and Ale, 2005), and have been reported in Table E. 1. The same damage models summarized in Table D. 2 and taken from standardized literature on QRA (CCPS, 2000; Finney, 1971; Mannan, 2005; Uijt de Haag and Ale, 2005; Van Den Bosh, 1992; Van Den Bosh and Weterings, 2005) have been consistently adopted also in the case study presented in Section 6.2 and Section 6.3, thus they will not be repeated in this appendix.

Standard procedures for QRA have been applied (CCPS, 2000; Mannan, 2005; Uijt de Haag and Ale, 2005). The results in terms of local specific individual risk (LSIR) are presented in Figure E. 1.

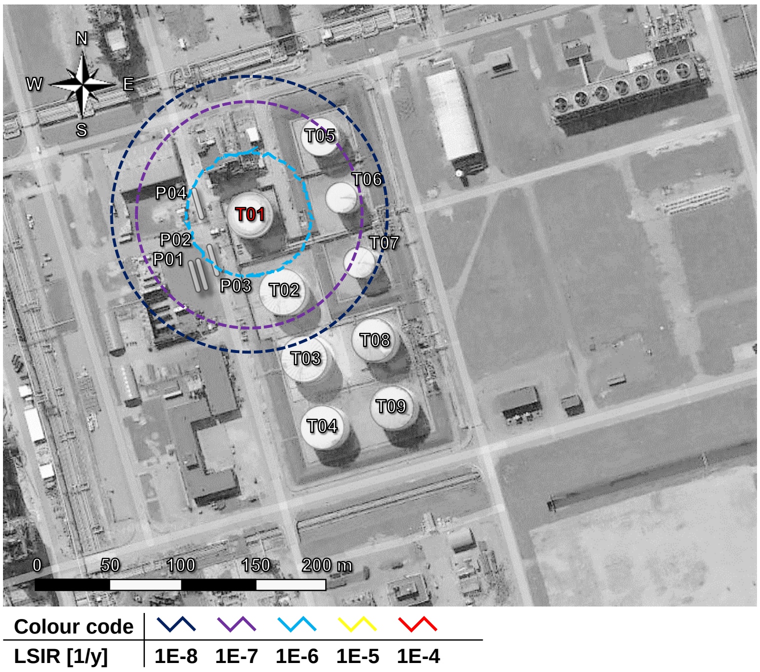

Figure E. 1: LSIR contours for conventional scenarios from tank T01 (case 0).

The results in terms of societal risk are expressed through the F/N plot reported in Figure E. 2.

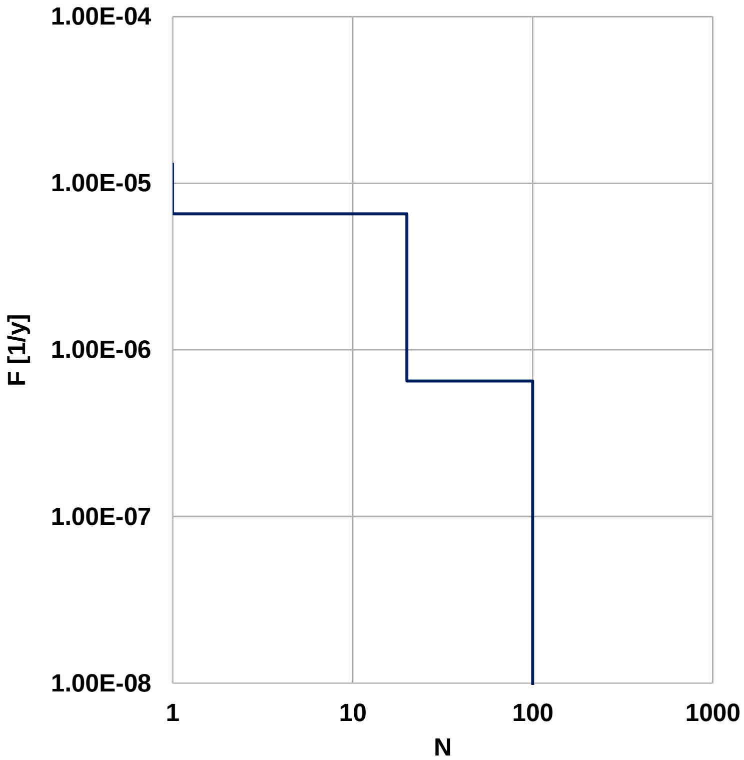

Figure E. 2: Societal risk for conventional scenarios from tank T01 (case 0).

E.2 Case 1: QRA of the Natech scenario triggered by flood

In this section, additional details on the primary Natech scenario involving T01 are provided. The probability of damage due to the natural hazard and the related frequency of LOC from T01 have been calculated taking the advantage of the vulnerability model presented in (Landucci et al., 2012), to which the reader is referred for more details. Nevertheless, for the sake of clarity the main equations and necessary input parameters considered in the application are reported in Table E. 2. Applying the simplified relationships shown in the table, the probability of failure of tank T01 given the reference flood scenario is estimated at P_{nhd}(T01) = 0.411.

Table E. 2: Vulnerability model for atmospheric tanks during flood, with a description of relevant input parameters and their assumed value for the application (Landucci et al., 2012).

Vulnerability model equations		
Variable	**Definition**	**Equation**
CFL	Critical Filling Level	$CFL = \left(\frac{\rho_w k_w}{2} v_w^2 + \rho_w g h_w - P_{cr}\right) / \rho_L g H$
P_{cr}	Vessel critical pressure evaluated with the proposed simplified correlation	$P_{cr} = J_1 V_n + J_2$ in which J_1 = -0.199; J_2 = 6950
P_{nhd}	Vessel vulnerability due to flooding	$P_{nhd} = \frac{CFL - \phi_{min}}{\phi_{max} - \phi_{min}}$
Input parameters		
Item	**Definition**	**Value adopted in Section 6.3**
V_n	Vessel nominal capacity	5087 m^3
v_w	Flood water speed	1 m/s
h_w	Flood water depth	2.0 m
ρ_w	Flood water density	1100 kg/m^3
ρ_L	Stored liquid density	750 kg/m^3
k_w	Hydrodynamic coefficient	1.8
H	Vessel height	7.2 m
g	Gravity acceleration	9.81 m/s^2
ϕ_{min}	Minimum operative filling level	0.01
ϕ_{max}	Maximum operative filling level	0.75

The results obtained in terms of LSIR and F/N curves for the case that considers only the primary Natech scenario from T01 (indicated as case 1 in Section 6.3) have been already shown and discussed in Section 6.3.5, thus will not be repeated here.

E.3 Case 2: QRA of unmitigated domino scenarios

This section summarizes the case of unmitigated domino escalation (i.e., accident escalation through domino effect was modeled without considering the presence of safety barriers). This case was used as a worst-case scenario to compare the results obtained in mitigated domino escalation from primary Natech accident and is assessed applying the general methodology for unmitigated domino escalation in Natech events discussed in Section 6.2 (Misuri et al., 2020a). This case is indicated as case 2 in Section 6.3.

The final probabilities and frequencies for the set of endpoint scenarios identified for each target equipment involved are reported in Table E. 3. It should be noted that in this case only two possible states for each target are considered, that is "0" and "2", corresponding respectively to no escalation and unmitigated escalation, in analogy to what is reported in Section 6.3.

Table E. 3: Endpoint scenarios in case of unmitigated domino escalation (case 2). State: 0=no escalation; 2=unmitigated escalation. SEP=surface emissive power.

Target	State	Secondary final outcome	Probability	Frequency [y^{-1}]
T02	0	No scenario	5.070E-02	3.749E-05
T02	2	Pool fire, max SEP	9.493E-01	7.020E-04
T05	0	No scenario	2.873E-01	2.124E-04
T05	2	Toxic dispersion, max. evap. rate	7.127E-01	5.271E-04
P03	0	No scenario	6.613E-01	4.890E-04
P03	2	Fireball	3.387E-01	2.505E-04
P04	0	No scenario	3.848E-01	2.845E-04
P04	2	Toxic dispersion	6.152E-01	4.549E-04

Identified target state combinations have been summarized in Table E. 4. The probabilities and frequencies of overall domino scenarios are calculated applying the methodology presented in (Misuri et al., 2020a) (i.e., see Section 6.2).

Table E. 4: Overall domino scenarios (final scenario combinations) identified for unmitigated domino escalation (Case 2). State: 0=no escalation; 2=unmitigated escalation.

ID	Target state				Probability	Frequency [y^{-1}]	ID	Target state				Probability	Frequency [y^{-1}]
	T02	T05	P03	P04				T02	T05	P03	P04		
1	0	0	0	0	3.707E-03	2.741E-06	9	2	0	0	0	6.940E-02	5.132E-05
2	0	0	0	2	5.926E-03	4.382E-06	10	2	0	0	2	1.110E-01	8.205E-05
3	0	0	2	0	1.898E-03	1.404E-06	11	2	0	2	0	3.555E-02	2.629E-05
4	0	0	2	2	3.035E-03	2.244E-06	12	2	0	2	2	5.683E-02	4.202E-05
5	0	2	0	0	9.195E-03	6.799E-06	13	2	2	0	0	1.722E-01	1.273E-04
6	0	2	0	2	1.470E-02	1.087E-05	14	2	2	0	2	2.752E-01	2.035E-04
7	0	2	2	0	4.709E-03	3.483E-06	15	2	2	2	0	8.818E-02	6.521E-05
8	0	2	2	2	7.529E-03	5.568E-06	16	2	2	2	2	1.410E-01	1.042E-04

E.4 Case 3: QRA of mitigated domino scenarios with baseline barrier performance

This section summarizes the frequencies obtained for case 3, that is, applying the methodology for risk assessment of mitigated domino scenarios from tank T01 (Landucci et al., 2017b), considering baseline barrier performance (*PFD_0* and η_0 in Table 6.3. 4). In this application, the effect of the natural hazard on mitigation and protection systems is neglected, thus this case is used for exemplifying the analysis of mitigated domino escalation without applying the methodology described in Section 6.3.2 for barrier performance modification.

The set of event trees obtained applying the modified ETA (Landucci et al., 2017b, 2016, 2015) is reported in Figure E. 3 to Figure E. 6.

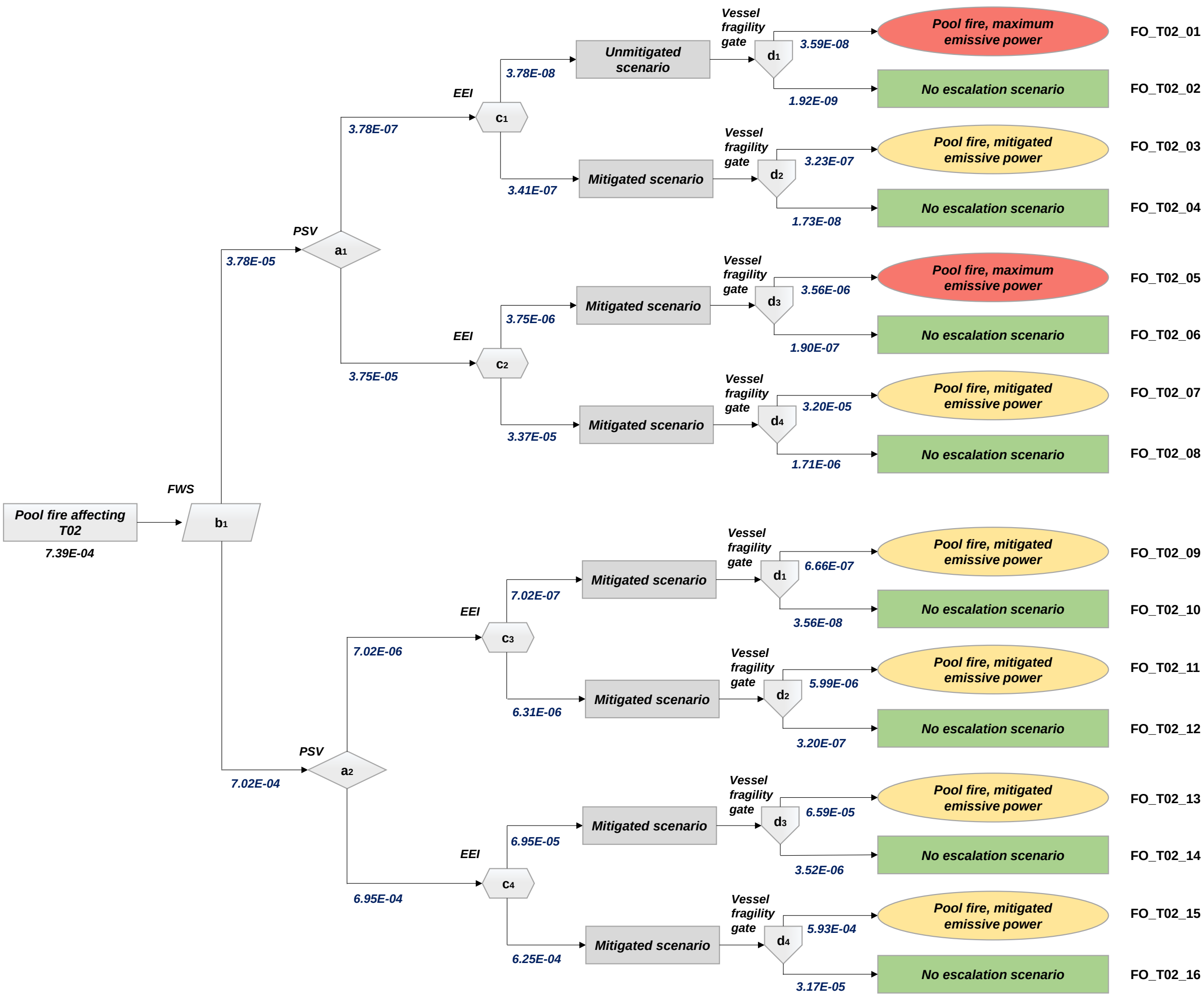

Figure E. 3: Event tree for mitigated escalation on tank T02 (case 3 of Section 6.3). All the frequencies are in y^{-1}. Baseline values have been used for safety barrier performance. FO= Final Outcome.

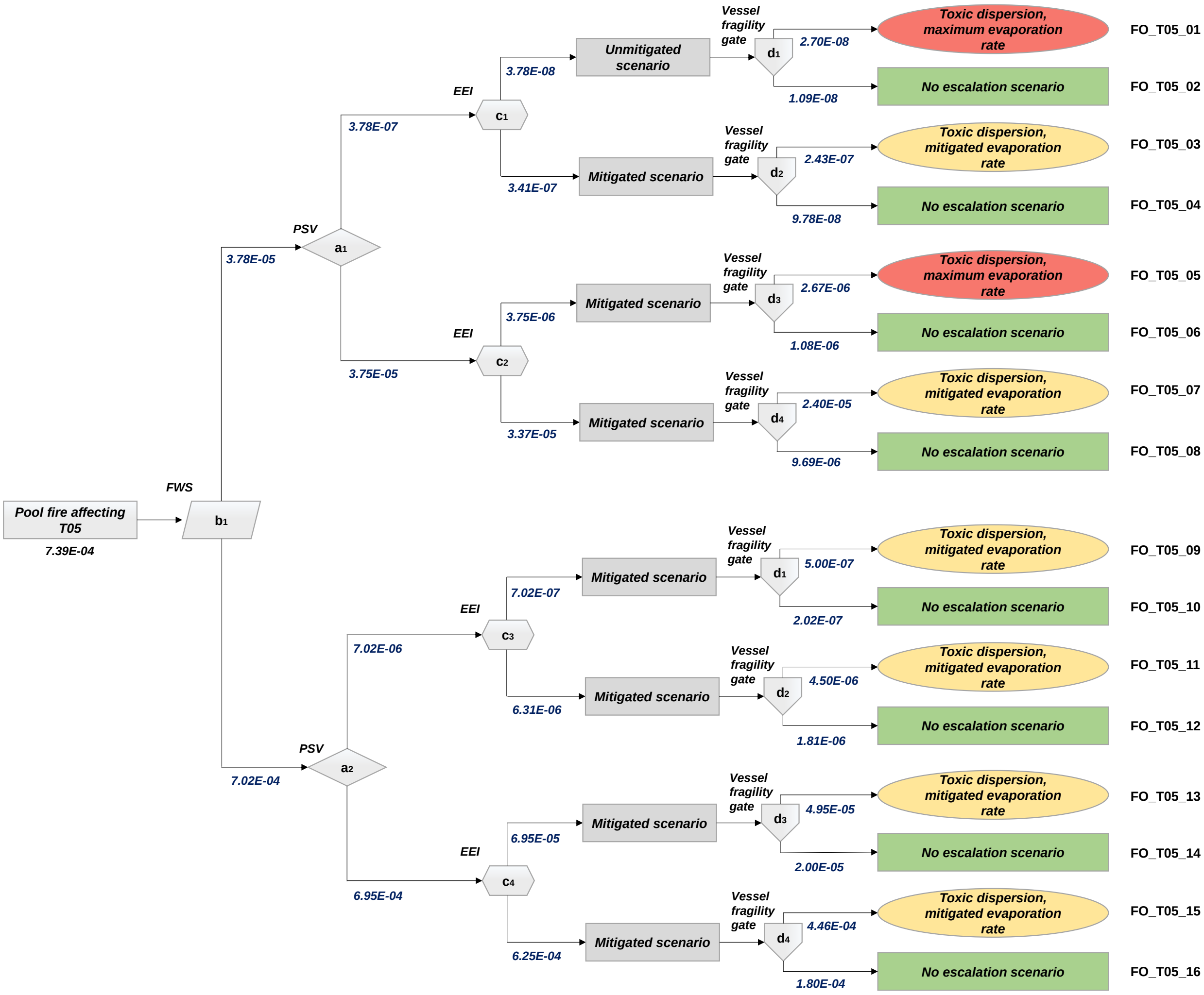

Figure E. 4: Event tree for mitigated escalation on tank T05 (case 3 of Section 6.3). All the frequencies are in y^{-1}. Baseline values have been used for safety barrier performance. FO= Final Outcome.

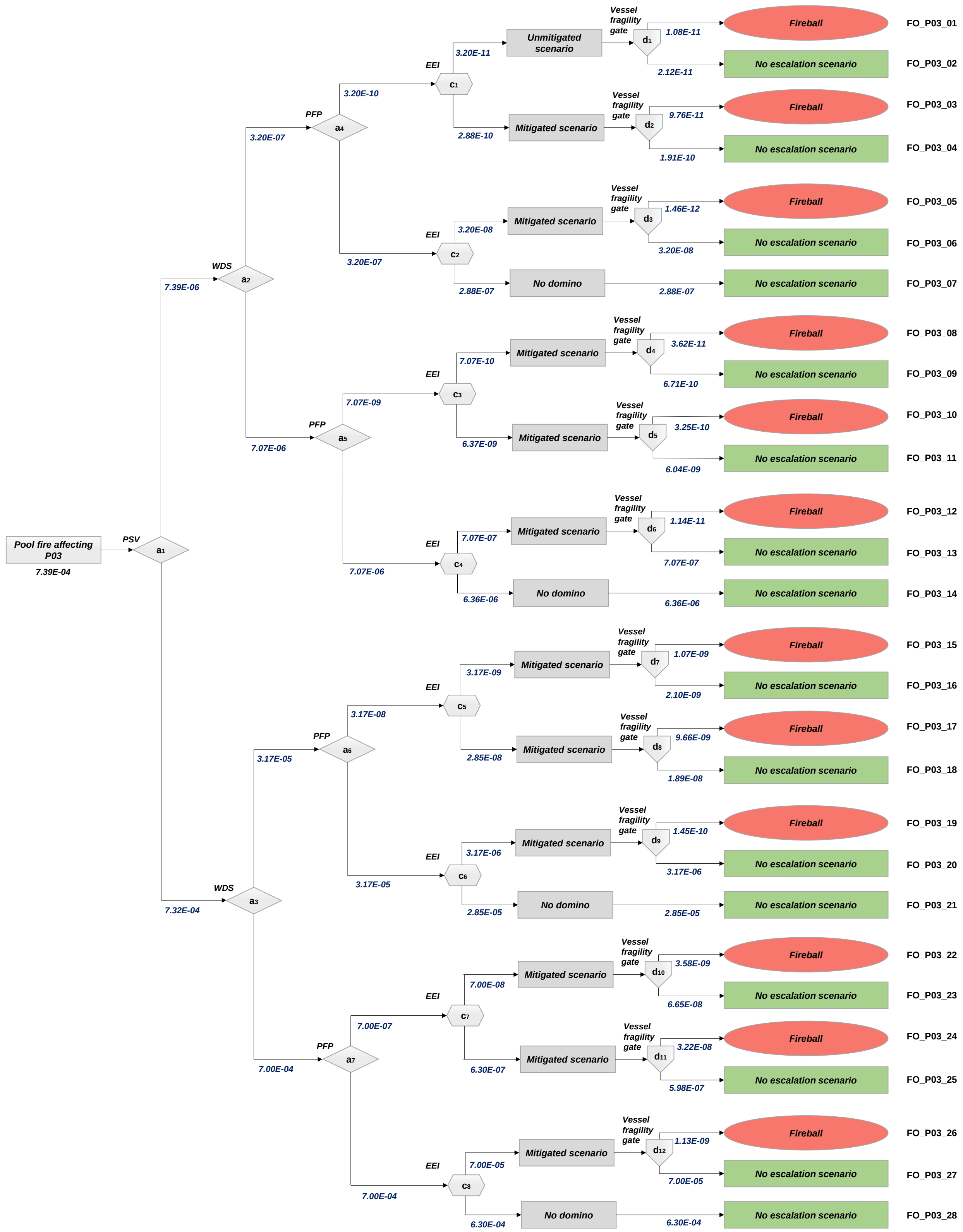

Figure E. 5: Event tree for mitigated escalation on vessel P03 (case 3 of Section 6.3). All the frequencies are in y^{-1}. Baseline values have been used for safety barrier performance. FO= Final Outcome.

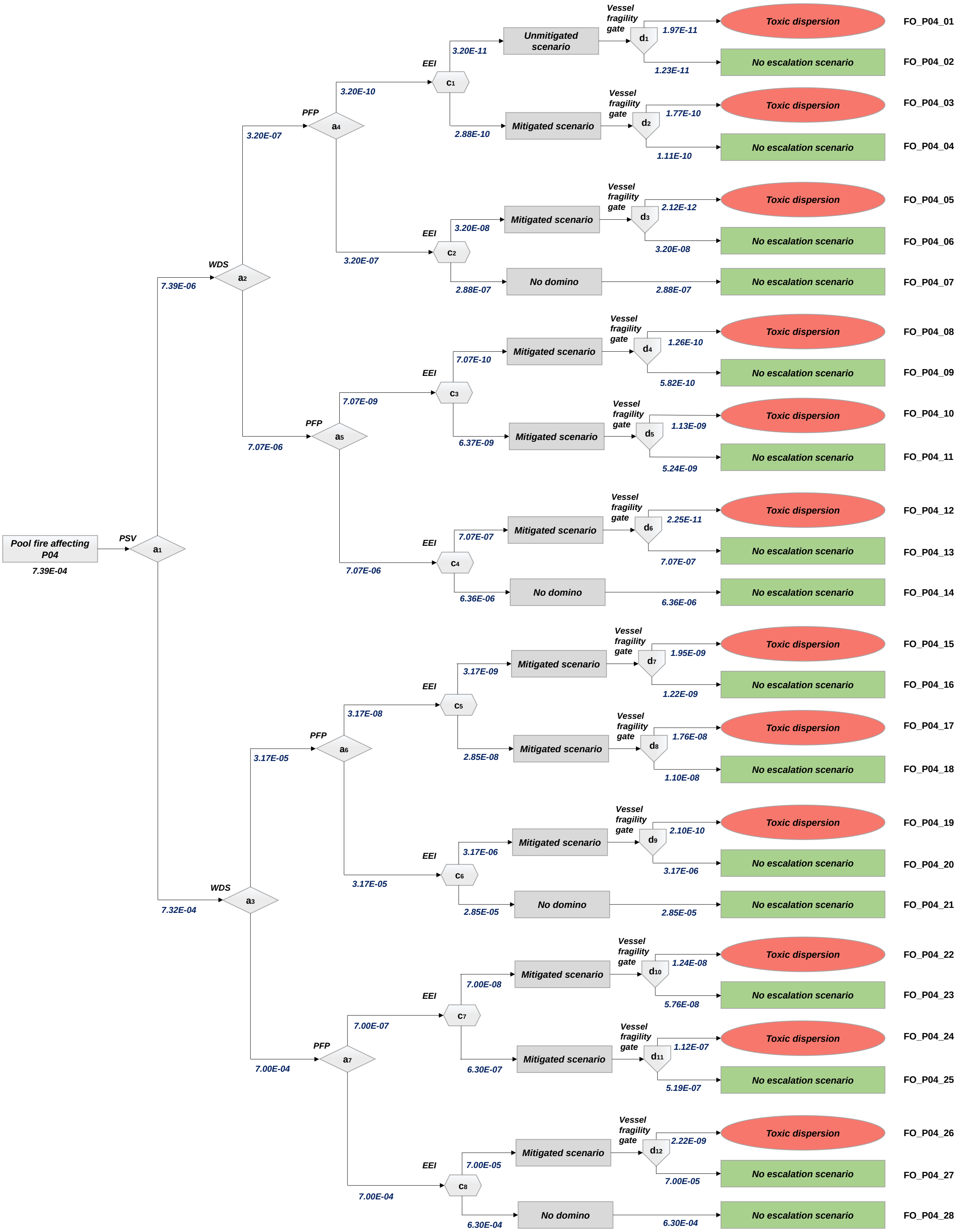

Figure E. 6: Event tree for mitigated escalation on vessel P04 (case 3 of Section 6.3). All the frequencies are in y^{-1}. Baseline values have been used for safety barrier performance. FO= Final Outcome.

The final probabilities and frequencies for the set of endpoint scenarios identified for each target equipment involved in case 3 are reported in Table E. 5. The terminology used for the state of the targets is consistent with Section 6.3.3.

Table E. 5: Endpoint scenarios calculated with ETA with baseline barrier performance (case 3). State (see Section 6.3.3): 0=no escalation; 1=mitigated escalation; 2=unmitigated escalation. SEP=surface emissive power.

Target	State	Secondary final outcome	Probability	Frequency [y^{-1}]
T02	0	No scenario	5.070E-02	3.749E-05
T02	1	Pool fire, mitigated SEP	9.493E-01	7.020E-04
T02	2	Pool fire, max SEP	4.859E-05	3.593E-08
T05	0	No scenario	2.873E-01	2.124E-04
T05	1	Toxic dispersion, mitigated evaporation rate	7.127E-01	5.270E-04
T05	2	Toxic dispersion, maximum evaporation rate	3.648E-05	2.698E-08
P03	0	No scenario	9.999E-01	7.394E-04
P03	2	Fireball	6.532E-05	4.830E-08
P04	0	No scenario	9.998E-01	7.393E-04
P04	2	Toxic dispersion	1.997E-04	1.477E-07

The probabilities and frequencies of overall domino scenarios are calculated with an analogous methodology as the one presented in Section 6.3.3. Identified target state combinations have been summarized in Table E. 6.

Table E. 6: Overall domino scenarios (final scenario combinations) identified for mitigated domino escalation with baseline barrier performance (case 3). State (see Section 6.3.3): 0=no escalation; 1=mitigated escalation; 2=unmitigated escalation.

ID	Target state				Probability	Frequency [y^{-1}]
	T02	T05	P03	P04		
1	0	0	0	0	1.456E-02	1.077E-05
2	0	1	0	0	3.612E-02	2.671E-05
3	0	2	0	0	1.849E-06	1.367E-09
4	1	0	0	0	2.726E-01	2.016E-04
5	1	1	0	0	6.764E-01	5.002E-04
6	1	2	0	0	3.462E-05	2.560E-08
7	2	0	0	0	1.395E-05	1.032E-08
8	2	1	0	0	3.462E-05	2.560E-08
9	2	2	0	0	1.772E-09	1.310E-12
10	0	0	2	0	9.511E-07	7.033E-10
11	0	1	2	0	2.360E-06	1.745E-09
12	0	2	2	0	1.208E-10	8.931E-14
13	1	0	2	0	1.781E-05	1.317E-08
14	1	1	2	0	4.418E-05	3.267E-08
15	1	2	2	0	2.261E-09	1.672E-12
16	2	0	2	0	9.114E-10	6.740E-13
17	2	1	2	0	2.261E-09	1.672E-12
18	2	2	2	0	1.157E-13	8.559E-17
19	0	0	0	2	2.908E-06	2.150E-09
20	0	1	0	2	7.215E-06	5.335E-09
21	0	2	0	2	3.693E-10	2.731E-13
22	1	0	0	2	5.445E-05	4.026E-08
23	1	1	0	2	1.351E-04	9.990E-08
24	1	2	0	2	6.914E-09	5.113E-12
25	2	0	0	2	2.787E-09	2.061E-12
26	2	1	0	2	6.914E-09	5.113E-12
27	2	2	0	2	3.539E-13	2.617E-16
28	0	0	2	2	1.900E-10	1.405E-13
29	0	1	2	2	4.713E-10	3.485E-13
30	0	2	2	2	2.412E-14	1.784E-17
31	1	0	2	2	3.557E-09	2.630E-12
32	1	1	2	2	8.825E-09	6.526E-12
33	1	2	2	2	4.517E-13	3.340E-16
34	2	0	2	2	1.820E-13	1.346E-16
35	2	1	2	2	4.517E-13	3.340E-16
36	2	2	2	2	2.312E-17	1.709E-20

Appendix F. Assumptions on FWS, WC and WDS systems considered in Section 6.1 and Section 6.3

The FTA shown in Figure 6.1. 3 and Figure 6.3. 3 is based on a reference FWS featuring the following barrier system architecture. A single foam module is conservatively considered, not accounting for the possible presence of redundancies. An in-line eductor system is considered for realizing the intended foam-water mixture (NFPA, 2005). The foam solution is stored in a permanent foam supply tank. The water supply is provided by a permanent firewater tank located inside plant premises which is connected to the water main network from the closest inhabited area. The foam/water delivery is accomplished by means of a single fire diesel pump, or by two electric pumps with half nominal capacity compared to the former. Two jockey pumps are considered to maintain the water network to the required pressure balancing small pressure drops due to possible leaks over time (NFPA, 2007). Electric power can be provided from three independent supplies: main power connection, backup supply, and diesel generator.

The WC considered in Section 6.1 for the mitigation of scenarios from horizontal vessels (see Figure 6.1. 4) and the WDS considered in Section 6.3 (see Figure 6.3. 4) are assumed to feature similar system architectures based on the assumptions reported in the following. The water supply is provided by a permanent water tank located inside plant premises which is connected to the water main network from the closest inhabited area. The water delivery is accomplished through a single diesel pump, with a single deluge unit. System actuation can be either automatic or manual from the area close to the scenario. The electrical actuation system is composed of one solenoid valve receiving an electric signal from the control panel receiving a gas detection signal from gas detectors (in case of WC) or a fire detection signal from heat detectors (in case of WDS). Electric power can be provided from three independent supplies: main power connection, backup supply, and diesel generator. No fail-safe design is conservatively considered.

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