



The Effect of Safety Barrier Degradation on the Severity of Primary Natech Scenarios^{*}

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ABSTRACT

The impact of natural events on technological infrastructures may lead to severe accident scenarios involving hazardous materials, generating the so-called Natech events. This typology of accidents is particularly critical since, besides damaging process or storage equipment items, natural hazards might concurrently impair safety barriers implemented to prevent and mitigate technological scenarios, reducing the overall safety of the system and increasing the likelihood of unmitigated outcomes and domino effects. In this study, a novel methodology to perform the quantitative risk assessment of the primary Natech scenarios directly caused by the impact of natural hazards considering the presence of safety barriers with depleted performance is proposed. A multi-level approach is tailored to assess the performance modification of safety systems designed to mitigate the primary technological scenarios. An innovative procedure for the quantitative assessment of these scenarios is proposed to enable the characterization of the final outcomes considered in the quantitative risk assessment accounting for depleted barrier performance. A case study is developed to demonstrate the application of the methodology, evidencing a relevant increase in risk compared to that assessed considering the baseline performance of safety systems. The proposed methodology thus enables a more comprehensive assessment of the final outcomes of primary Natech events, fostering the development of a holistic framework for Natech quantitative risk assessment.

1. Introduction

When critical infrastructures handling relevant quantities of hazardous materials are impacted by natural hazards, severe technological scenarios such as fires, explosions, and toxic releases can be triggered [1]. These events generate a further threat to the exposed population, and an additional burden for emergency teams [2]. In the literature, industrial accidents where the sequence of cascading events begins with the impact of natural hazards on main or auxiliary equipment are termed Natech [3]. Natech accidents are particularly critical in terms of their growing incidence and of associated societal risk, as evidenced in a comprehensive review of the information available in major accident databases [4]. In addition, recent studies suggest that climate change is exerting a key role in enhancing the severity of some categories of natural hazards [5–7]. Thus, the likelihood of Natech accidents is expected to further increase in case adaptation measures are not implemented [8,9].

Whereas the first steps of Natech research can be dated back to the

nineties (e.g., see [10–14]), many severe accidents in the last decades raised the flag on the need to develop appropriate risk management tools [15–17]. These studies evidenced both the substantial lack of company preparedness in dealing with such complex, yet frequent, events and the deficiencies in risk governance oversight [1]. For instance, in 2017 Hurricane Harvey hit many industrial sites leading to the release of hazardous materials [18,19], causing complex accidents with serious consequences as the one that involved a peroxide production site in Crosby, Texas [20]. Also during the Great East Japan Earthquake and Tsunami (GEJET) of 2011, several petrochemical and process sites were affected, triggering severe cascading scenarios [21–23]. Despite these examples, Natech events are not limited to the chemical and process industry, but also affect other industrial sectors [24]. Indeed, the nuclear disaster at the Fukushima Dai-ichi nuclear power station caused by the GEJET can be considered a specific type of Natech event [3,25]. Recently, several Natech events were also caused by extreme flooding events due to heavy rain impacting steelworks and ironworks companies [26–28].

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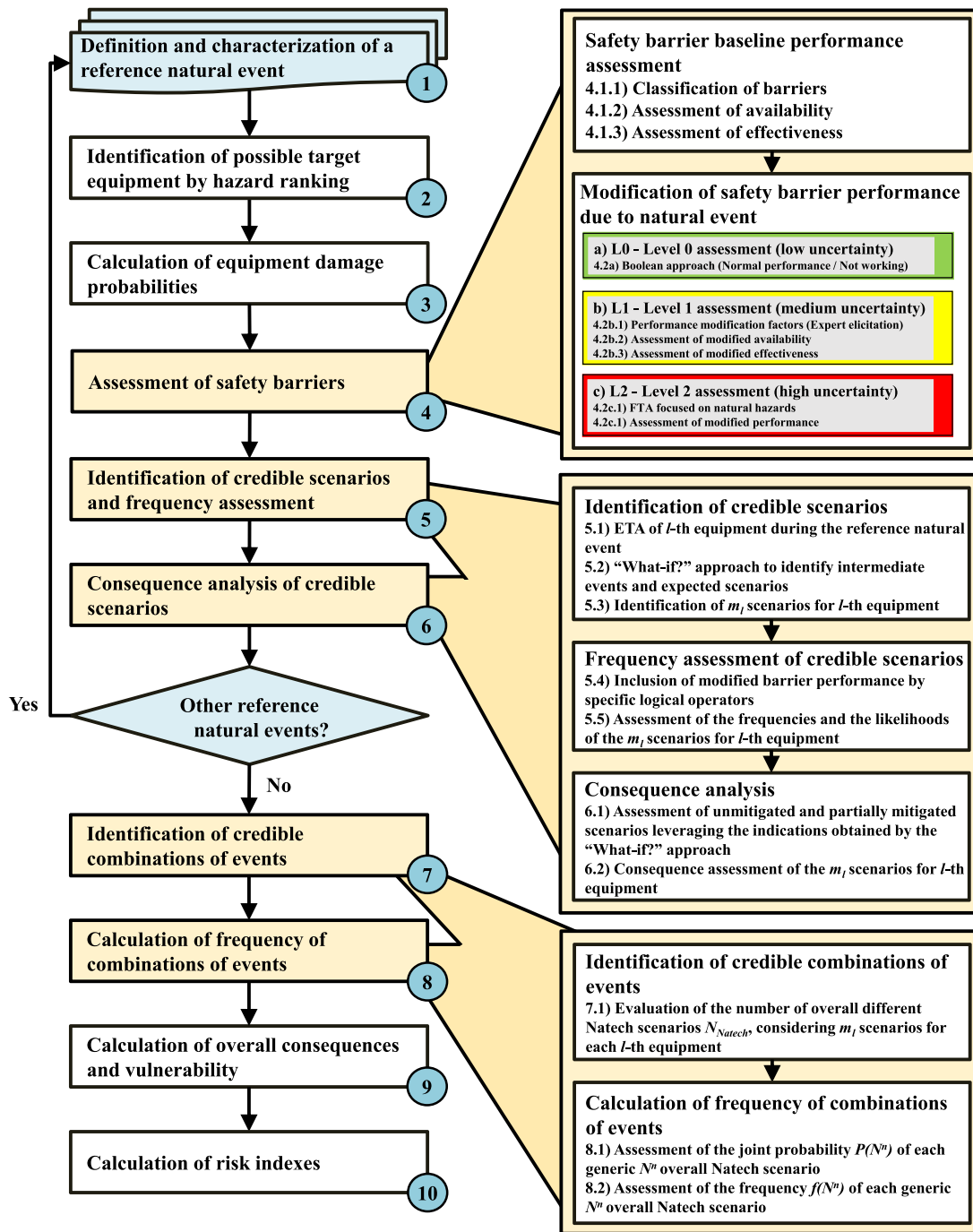


Fig. 1. Flowchart of the methodology proposed for the risk assessment of primary Natech scenarios considering safety barriers.

The growing number of accidents fostered the development of appropriate methodologies to effectively manage Natech risks [15]. Nowadays consolidated approaches are available to carry out the quantitative assessment of Natech scenarios. Many of such approaches rely on quantitative risk assessment (QRA) frameworks [29–31], although alternative strategies based on different probabilistic frameworks as graph theory or Bayesian Networks have been also proposed [32–35]. Most of the methodologies proposed for Natech assessment enable the estimation of the risk figures associated with scenarios following the release of hazardous substances from process or storage equipment (e.g., see [16,17,36–38]). These approaches use simplified equipment vulnerability models to characterize expected damages and to estimate the probability of Loss of Containment (LOC) [39]. In the

literature, several vulnerability models have been proposed covering the impact of natural hazards as floods [40–44], storm surges [45–47], earthquakes [48,49], and lightning strikes [50,51].

Nevertheless, Natech events are inherently complex scenarios, and not all their features can be easily described by the existing methodologies. For instance, in spite of the evidence of the relevant role of the domino effect in Natech events (e.g., see [22,23]), methodologies to include technological accident escalation in Natech quantitative assessment were formalized only recently [52–54]. In addition, the current Natech QRA methodologies do not consider the presence and the possible failure of safety systems during the accident, even if there is evidence of their recurrent damage in past Natech events [18,20,55]. This gap was partially addressed in recent studies proposing an

Table 1
Summary of the approach to assess safety barrier performance [54].

| Safety barrier classification | | |
|-------------------------------|---|--|
| Category | Description | Examples |
| Passive | Physical technical systems permanently available and not requiring external activation to perform their function. | Pressure safety valves, containment dikes, bunds, catch basins, fireproofing |
| Active | Technical barriers that require activation (e.g., automatic through a detection-processing-actuation loop, by operators) to perform their function. | Sprinklers, water deluge systems, water curtains |
| Procedural | Operative measures based on specific procedures performed by personnel or emergency teams. | Intervention of firefighting teams, emergency evacuation |

| Baseline barrier performance | | |
|------------------------------|----------------------------------|---|
| Parameter | Definition | Description |
| $PF_{D_{0,k}}$ | Probability of failure on demand | Probability that the k -th barrier will not be available when required to perform its function. |
| $\eta_{0,k}$ | Effectiveness | Conditional probability the k -th barrier is able to perform its safety function after successful activation. |

| Modification of safety barrier performance due to natural event* | | |
|--|--|--|
| Level | Description | Performance modification |
| L0 | Application of rules-of-thumb to justify with confidence if the barrier should be considered affected or operating normally during the natural event. Suitable for simple barriers (low-uncertainty situation). | Is the k -th barrier deemed affected? - NO: $PF_{D_{0,k}}$ and $\eta_{0,k}$ - YES: o Active barriers: $PF_{D_{j,k}} = 1$ o Passive barriers: $\eta_{j,k} = 0$ |
| L1 | Application of performance modification factors ϕ developed in [59]. Suitable for a broad set of barriers, from passive barriers to the simpler active systems (medium-uncertainty situation). | For the k -th active barrier: - $PF_{D_{j,k}} = 1 + (\phi_{j,k} - 1)(1 - PF_{D_{0,k}})$ - $\eta_{j,k} = \eta_{0,k}$ For the k -th passive barrier: - $\eta_{j,k} = (1 - \phi_{j,k}) \eta_{0,k}$ with $\phi_{j,k}$ for the k -th barrier during the j -th natural event |
| L2 | Analysis of barrier architecture through the application of a fault tree analysis (FTA) focused on the possible failure of subsystems during the reference natural event. Suitable for complex active barriers (high-uncertainty situation). | For the k -th active barrier: - $Q_j(MCS_{m,k}) = \prod_p (q_{p,0} + \delta_{p,j}(1 - q_{p,0}))$ - $PF_{D_{j,k}} = 1 - \prod_m (1 - Q_j(MCS_{m,k}))$ with - $Q_j(MCS_{m,k})$ unavailability of the m -th minimal cut set (MCS) identified from the FTA - $q_{p,0}$ is the probability of the p -th basic event in the m -th MCS - $\delta_{p,j} = 1$ if the p -th basic event involves one of the vulnerable barrier subsystems identified for the j -th natural event (otherwise, $\delta_{p,j} = 0$). |

approach to assess the effect of safety barrier degradation on the likelihood of domino effects following primary Natech events [54,56]. However, these studies focused only on the effect of safety barrier degradation on the prevention of escalation leading to domino effects. Nonetheless, Misuri and Cozzani [3] evidenced that the failure of safety barriers in Natech events also plays a crucial role in the severity of the consequences of the primary technological scenarios.

In the present study, a novel methodology is proposed to consider the effects of safety barrier degradation on the frequency and severity of

primary technological scenarios involved in a Natech event. The method aims at including the effect on the overall risk figures of the unmitigated technological scenarios that may arise from the failure, unavailability or degraded performance of safety barriers in the technological scenarios taking place during Natech events. Differently from previous approaches, a detailed characterization of all the expected final outcomes following LOC events from each piece of equipment impacted by natural events is considered. Thus, a comprehensive set of final outcomes following a reduced probability of successful mitigation by safety barriers is introduced in the assessment, enabling a more realistic representation of the primary technological scenarios during Natech events.

The novel approach to the characterization and quantitative assessment of the primary Natech events is presented in Section 2. A case study is introduced in Section 3 to provide a reference application of the methodology. The results are then presented in Section 4, along with the discussion on their importance and implications. Finally, the conclusions of the study are summarized in Section 5.

2. Methodology

2.1. Overview of the methodology

The developed methodology is shown in Fig. 1. The overall approach was derived from the established framework proposed by Cozzani et al. [17] for the QRA of Natech scenarios, introducing a step specifically addressing safety barrier performance assessment (Step 4 in Fig. 1). The introduction of a step dedicated to safety barrier assessment requires to adapt four other steps of the methodology: the identification of credible scenarios and their frequency assessment considering the presence of safety barriers (Step 5 in Fig. 1), the consequence analysis of the identified set of credible scenarios (Step 6 in Fig. 1), the identification of credible combinations of scenarios (Step 7 in Fig. 1), and the calculation of the frequency of combinations of events (Step 8 in Fig. 1).

The main element of novelty of the methodology concerns the build-up of the primary scenarios that need to be considered. Actually, the definition of primary scenario is inherently more complex when safety barriers are considered and needs the evaluation of intermediate events linked to the number of safety barriers considered, to their safety functions, and to their actual state during the escalation. Thus, a specific approach based on “What-if?” analysis was introduced to build a tailored event tree describing the event sequence leading to the final outcomes of the primary scenarios. Event tree analysis (ETA) is then applied to assess the frequencies of the alternative final outcomes identified.

In the following sections, the novel specific steps introduced in the Natech QRA flowchart will be discussed in detail. The other steps of the procedure are summarized in the Supplementary Material and are discussed in detail in previous publications [17,36].

2.2. Metrics for safety barrier performance assessment

The specific methodology proposed by Misuri et al. [54] is applied in the present approach to the assessment of safety barrier performance. Barriers are preliminarily classified according to their operating principle, as in several QRA approaches [54,57], and are then grouped into three main categories, as listed in Table 1. Their baseline performance is assessed using two parameters, namely a probability of failure on demand (PF_{D_0}) and an effectiveness value (η_0), as shown in Table 1. Further details on barrier classification and on approaches for baseline performance evaluation are reported elsewhere [58].

A three-level assessment is then considered to modify barrier performance according to system complexity, as shown in Table 1. The methodology enables on the one hand the evaluation of simpler systems according to rules-of-thumb (i.e., L0 in Table 1), while on the other hand, it provides an ad-hoc approach based on fault tree analysis (FTA) for complex barrier systems (i.e., L2 in Table 1). An intermediate level may also be chosen (i.e., L1 in Table 1), applying performance

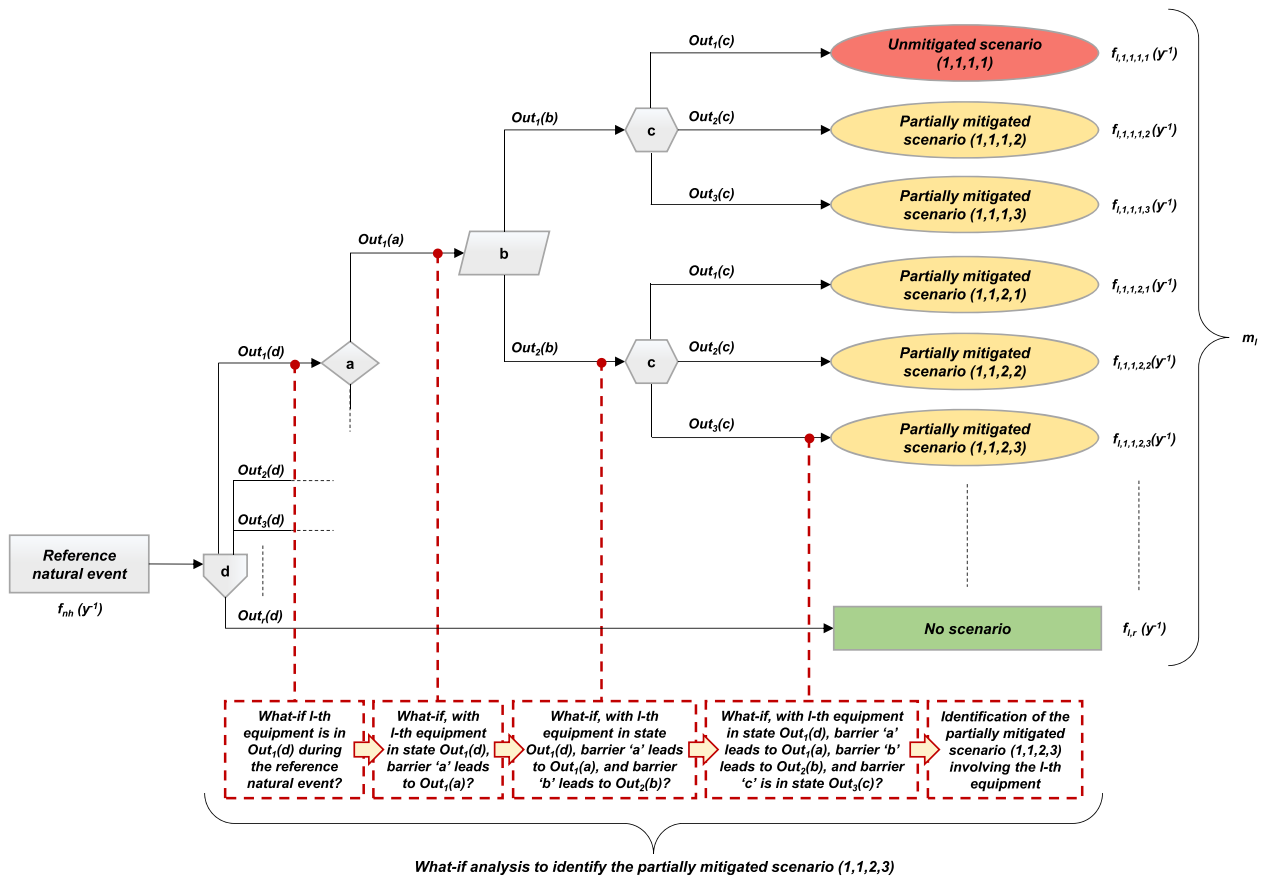


Fig. 2. Example of event tree to support the identification and assessment of unmitigated and partially mitigated scenarios considering the impact of a reference natural event on the generic l -th equipment including the results of what-if analysis (red-dashed boxes). m_l = Total expected number of primary Natech scenarios involving l -th target.

modification factors obtained in previous studies for a broad set of safety barriers considering a reference architecture [59]. The methodology described in Table 1 may be applied to technical barriers only (i.e. passive and active barriers), while for procedural barriers a site-specific assessment is suggested [54]. Further details on the approach described

in Table 1 are reported in the Supplementary Material and in a previous publication [54].

Updated performances are obtained with respect to $PF_{j,k}$ and $\eta_{j,k}$, for the generic k -th barrier during each j -th natural event as an output of the methodology described in Table 1.

Table 2

Operators defined for the ETA of primary Natech scenarios considering the presence of safety barriers (f_{IN} = gate input frequency, f_{nh} = reference natural event frequency assessed in Step 1 of Fig. 1, PFD: Probability of failure on demand, η = effectiveness parameter, P_{nhd} = equipment probability of one of the $(r - 1)$ possible LOCs given the reference natural event).

| Gate type | Representation and quantification | Description |
|-----------|-----------------------------------|---|
| a | | Simple composite probability gate (type “a”): unavailability, expressed as PFD , is combined with a single probability value for η . |
| b | | 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 | | Discrete probability distribution gate (type “c”): depending on barrier η , three or more events may originate. |
| d | | Vessel fragility gate (type “d”): based on the resistance of the equipment to the reference natural event, a set of $(r - 1)$ failure outcomes can be originated, each with a related P_{nhd} calculated in Step 3 of Fig. 1 by equipment vulnerability models, plus the r -th outcome representing the safe state. |

2.3. Characterization of primary technological scenarios

The inclusion of safety barriers requires relaxing the assumption of binary targets included in most of the previous approaches to Natech quantitative risk assessment (i.e., an item is safe or is involved in the accident leading to the worst-case scenario). Indeed, the possibility of mitigated outcomes should be also considered to account for the action of safety barriers and/or safety systems. This requires to define a proper approach to the identification and frequency assessment of the expected scenarios (Step 5 in Fig. 1), and a method to evaluate their consequences (Step 6 in Fig. 1).

Differently from previous studies [17], in the present approach, the mitigative action of safety barriers is considered by introducing a set of final outcomes, depending on the set of implemented barriers, on their safety function and on their performance. For instance, the presence of secondary containments (e.g., catch basins) to mitigate liquid spills leads to two possible groups of outcomes in case of a release. The first group considers their proper operation, thus leading to liquid pools confined into the containment area of the catch basin. The second group accounts for their misoperation leading to liquid pools spreading over broader areas. The probabilities of these two groups of scenarios depend on the integrity and effectiveness of the secondary containments during and after the natural event.

Clearly enough, in case multiple safety barriers are associated with a generic piece of equipment, a set of unmitigated and partially mitigated final outcomes are generated, depending on the success and/or failure of each of the barriers implemented. Therefore, the identification of the set of expected final outcomes and their frequency assessment is performed in the present approach building a specific event tree (ET) using “What-If” analysis [62] and calculating the conditional probabilities of the final outcomes by event tree analysis (ETA). An example of the ET obtained by this procedure is provided in Fig. 2, while the logical operators used to consider the intermediate events are described in Table 2.

The starting point of the procedure is the characterization of the possible LOCs that can involve a generic l -th equipment during the reference natural event. As shown in Fig. 2, the gate “d” reported in Table 2 is used to include in the ET all the possible r states that the l -th equipment can feature during a reference natural event, that is, all the failure modes leading to LOCs, and the possibility that the target will not undergo any failure leading to LOC ($Out_r(d)$ in the bottom branch of Fig. 2). Indeed, while in some cases the vulnerability models consider only two possible states for the equipment item (i.e., failure with LOC, or safe), other models feature multiple risk states. For instance, the vulnerability model for vertical atmospheric tanks exposed to flood developed in [40] addresses buckling failure and provides a single P_{nhd} value representative of the likelihood of this failure mode. On the other hand, several fragility models for atmospheric equipment exposed to seismic load consider multiple possible damage states, each with an associated likelihood value P_{nhd} (e.g., see [61]).

With reference to Fig. 1, it should be noted that when this step of the procedure is carried out, the $(r - 1)$ values of P_{nhd} have been already estimated (in Step 3 of the procedure), and may thus be used as an input to the quantification of the “d” gates in the ETA.

As mentioned above, the characterization of unmitigated and partially mitigated outcomes following intermediate events is carried out applying a “What if?” approach [62]. In Fig. 2, an example of application of the “What-if?” approach is shown. In particular, the identification of the partially mitigated scenario resulting from the l -th target in the state ‘1’ (i.e., $Out_1(d)$ in Fig. 2), and the three barriers considered, ‘a’, ‘b’, and ‘c’, respectively in the states ‘1’ (i.e., $Out_1(a)$ in Fig. 2), ‘2’ (i.e., $Out_2(b)$ in Fig. 2), and ‘3’ (i.e., $Out_3(c)$ in Fig. 2) is described. This procedure is repeated for each of the r expected states of the l -th equipment, leading to the identification of m_l possible different primary scenarios (i.e., right-hand side of Fig. 2).

A top-down approach starting from the expected LOCs is suggested to define the intermediate events in the ETA, that are dependent on the

specific safety function of each safety barrier, and on its performance. Each barrier is included in the ETA by means of the logical gates reported in Table 2. The logical rules associated with each gate are consistent with those discussed in previous studies [56,58,60].

Starting from the first expected state of the l -th equipment during the reference natural event, the sequences of intermediate events are identified considering the safety function of each barrier. The ETA is then used to support the evaluation of the frequencies of each of the m_l different primary scenarios starting from the f_{nh} (i.e., assessed in Step 1 of Fig. 1). This is achieved including the updated performance of each barrier in terms of $PFD_{i,k}$ and $\eta_{j,k}$ values calculated in Step 4 of the methodology by the operators shown in Table 2.

Once the calculation of the likelihood of each scenario is completed, consequence analysis should be performed (Step 6 in Fig. 1). The analysis of the physical effects of each outcome can be carried out through the application of established literature models, as for instance those reported by the TNO Yellow Book [63].

Differently from previous approaches to Natech QRA, the method developed requires also to assess the influence of barriers on scenario consequences. The “What-if?” approach applied to identify the scenarios may be used also to support the identification of the consequences of unmitigated or partially mitigated scenarios, taking into account the set of safety barriers implemented, their function, and their state during the escalation. For instance, as shown in Fig. 2, in the case of water curtains for toxic vapour abatement from a liquid pool, the reduction in evaporation should be accounted for by appropriate dispersion models in case of a successful outcome of the safety function. On the contrary, the normal evaporation rate should be considered in case of barrier failure. A practical example of application is given in the case study discussed in the following.

2.4. Identification and frequency assessment of combination of events

After completing the characterization of each single Natech event, the methodology requires the evaluation of the possibility of multiple simultaneous scenarios (Steps 7 – 8 in Fig. 1). These steps have important differences compared to those adopted in previous approaches to Natech QRA, not considering the presence and action of safety barriers on technological scenarios [17,36].

Considering the presence of n items, a single Natech scenario can involve the contemporary damage of l out of n units resulting in l final outcomes (i.e., one related to each item involved). Thus, relaxing the assumption of binary targets, m_l possible outcomes can be identified by the ETA for each generic l -th primary target impacted (i.e., see the right-hand side of Fig. 2). The total number of hazardous combinations N_{Natech} is assessed by Eq. (1):

$$N_{Natech} = \prod_{l=1}^n m_l - 1 \quad (1)$$

As shown in Eq. (1), the safe state of a single element is considered a possible outcome, although the case when all the elements are in the safe state does not count as an overall primary Natech scenario. It can be easily verified that in case all the targets feature only two possible outcomes (i.e., a single LOC per item, and assuming no safety barriers), the equation would lead to the same result as in previous Natech QRA approaches [64].

Hence, each Natech scenario can be represented by a vector \mathbf{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 Eq. (1), N_{Natech} different \mathbf{N}^n vectors are possible during the reference natural event. Each l -th element N_l^n of a generic vector \mathbf{N}^n represents the state of the l -th target in the Natech scenario considered. As consequence, the overall probability of a generic Natech scenario $P(\mathbf{N}^n)$ can be calculated by Eq. (2):

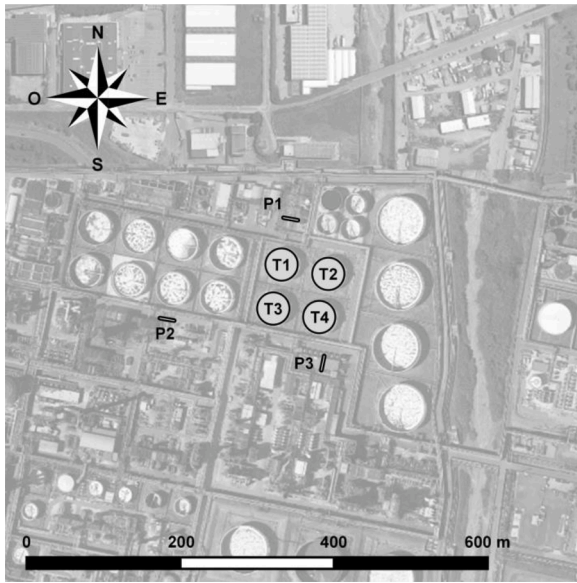


Fig. 3. Layout considered in the case study. Equipment features are summarized in Table 3.

$$P(N^m) = \prod_{l=1}^n P(N_l^m) \quad (2)$$

where $P(N_l^m)$ is the probability of a given state of the l -th target, assessed using the ETA of Section 2.3.

It should be remarked that the gates defined in Table 2 lead to the calculation of the frequency of each state for a generic l -th target. Thus, in order to obtain a probability value $P(N_l^m)$ of a generic state of the l -th target to be used in Eq. (2), a unit value of f_{nh} should be adopted in the gate “d”. The actual frequency of the natural hazard f_{nh} obtained from the characterization performed in Step 1 of Fig. 1 is then introduced in the following step of the analysis by Eq. (3), to calculate the frequency of a generic overall Natech scenario $f(N^m)$:

$$f(N^m) = f_{nh} \times P(N^m) \quad (3)$$

The following part of the procedure (i.e., Steps 9 and 10 in Fig. 1) is analogous to the previous approaches proposed for Natech QRA [16,17, 36,64]. For the sake of clarity, a brief explanation of Steps 9 and 10 is reported in the Supplementary Material.

3. Case study

3.1. Definition of the case study

A case study was defined to demonstrate the application of the methodology and analyse the results obtained. The layout considered for the case study, derived from that of an existing industrial facility, is shown in Fig. 3.

Table 3

Equipment items considered in the case study (see Fig. 3 for equipment layout). 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 = Atmospheric storage tank (unanchored); 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] | Vessel type | 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 | - |

Four atmospheric storage tanks (T1 to T4 in Fig. 3) and three horizontal pressurized vessels (P1 to P3 in Fig. 3) are considered in the case study. The substances stored and the sizes of the equipment are reported in Table 3.

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

The characterization of the expected LOCs for the equipment considered is summarized in Table 4. The probit models reported by [61] were applied to the case study to assess equipment vulnerability and to calculate the probability of LOC (P_{nhd}). For what concerns items T1 to T4, only a catastrophic rupture has been considered as a LOC. Indeed, according to [61], 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 is considered, since the threshold PGA value of 0.526g required for RS = 3, in this case, is not exceeded [61].

The risk associated with the layout shown in Fig. 3 was calculated considering three different sets of assumptions, to ease the interpretation and the discussion of the results:

- Case 1: primary Natech scenarios assuming the complete absence of safety barriers, to define a worst-case situation associated with the impact of the earthquake on the site;
- Case 2: primary Natech scenarios assuming the presence of safety barriers with baseline performance (i.e., not considering the

Table 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; RS = Release State).

| ID | k_1 | k_2 | RS | LOC assumed |
|---------|-------|-------|----------|---------------------------|
| T1 – T4 | 5.51 | 1.34 | 3 | Catastrophic rupture |
| P1 – P3 | 4.50 | 1.12 | ≥ 2 | 10-min continuous release |

Table 5

Safety barriers considered for each item included in the layout. FWS = Foam-water systems; WC = Water curtains.

| ID | Catch basin | FWS | WC |
|----|-------------|-----|----|
| T1 | X | X | |
| T2 | X | X | |
| T3 | X | X | |
| T4 | X | X | |
| P1 | | | X |
| P2 | | | X |
| P3 | | | X |

Table 6

Probability of LOC and overall LOC expected frequency calculated for the equipment considered in the case study. LOC = loss of containment; P_{nhd} = Probability of LOC given the reference natural event; f_{LOC} = Expected frequency of the LOC.

| ID | LOC assumed | P_{nhd} | f_{LOC} [y^{-1}] |
|---------|---------------------------|-----------|------------------------|
| T1 – T4 | Catastrophic rupture | 3.38E-01 | 6.76E-04 |
| P1 – P3 | 10-min continuous release | 1.01E-01 | 2.02E-04 |

possibility that the earthquake might impair their operation), to define a best-case situation;

- Case 3: primary Natech scenarios assuming the presence of safety barriers and accounting for the possibility of their failure caused by the earthquake, by the methodology presented in Section 2.2.

In addition to these cases, a conventional QRA, termed case 0 in the following, was also developed to obtain baseline risk figures. Case 0 was carried out only considering conventional scenarios generated by LOCs from the equipment included in the layout, accounting for the safety barriers implemented for their mitigation (see Table 5) with their baseline performance $PFDO$ and η_0 in normal operating conditions. The description of the procedure applied to carry out the QRA of case 0, based on consolidated guidelines for risk assessment [65] and on specific methodologies for the estimation of ignition probability [66], is reported in the Supplementary material. The risk figures calculated for cases 1 to 3 were added to that obtained from case 0, in order to derive overall risk figures.

In the assessment of cases 1 to 3, the complete post-release event trees have been considered in the characterization of primary Natech scenarios, applying the methodology described in Section 2. In order to obtain the probabilities and frequencies of the final scenarios related to cases 1 to 3, specific values of ignition probabilities retrieved from the comprehensive database analysis performed in [4] were adopted. Further details on the ignition probability used in the case study are reported in the Supplementary material.

The consequence analysis of each scenario was performed by applying well-established literature models for the evaluation of the physical effects of accident scenarios [63,67,68]. Further details on the assumptions considered are reported in the supplementary information.

The methodology presented in [52,69] was applied to carry out risk calculations. Other alternative approaches to accomplish this step are available in the literature and can be applied without conceptually modifying the methodology presented in Fig. 1 [67].

3.2. Definition of the safety barriers

The set of safety barriers associated with each piece of equipment considered is shown in Table 5. As shown in the table, catch basins and foam-water systems (FWS) are considered to protect atmospheric equipment, while in 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 assumed to prevent any possibility of mitigation [57].

Table 7

Safety barriers performance assessed by means of the methodology presented in Section 2.2. FWS = Foam-water systems; WC = Water curtains; $PFDO$ = Baseline value for probability of failure on demand; $PFDeq$ = Probability of failure on demand after the reference earthquake; η_0 = Baseline value for barrier effectiveness; ηeq = Barrier effectiveness after the reference earthquake.

| Barrier | Classification | Gate | $PFDO$ | η_0 | Level of analysis ^a | $PFDeq$ | ηeq |
|-------------|----------------|------|----------|----------|--------------------------------|----------|----------|
| 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 Refer to Step 4 in Fig. 1.

4. Results and Discussion

4.1. Assessment of equipment vulnerability to the reference natural event

The values of the probability and expected frequency of LOC calculated considering the reference earthquake assumed in the case study are reported in Table 6. As discussed in Section 3, for the atmospheric vertical tanks T1 to T4 a catastrophic rupture leading to an instantaneous release of the entire content of the tank was considered, while for pressurized vessels (P1 to P3) the entire content was assumed to be released in 10 minutes.

4.2. Assessment of safety barrier performance

Table 7 reports the results of the barrier performance assessment carried out for the case study by the methodology described in Section 2.2.

For each safety barrier, the table reports the barrier category and the gate used for its inclusion in the post-release ETA presented in Section 2.3. The table also includes the modified barrier performance parameters obtained by Step 4 of the methodology presented in Fig. 1. The L1 level analysis was applied to the catch basins to consider the possibility that these elements would undergo structural failure under seismic loads. Catch basins feature relatively limited complexity not requiring the application of a higher-level assessment procedure (although L0 was not considered appropriate due to uncertainties on the possible impact of the seism with respect to the different materials and design strategies that might be adopted for their construction). Therefore, a specific performance modification factor for barrier effectiveness was derived from the expert survey carried out in a previous study [59].

The foam-water system (FWS) installed on tanks T1 – T4 and the water curtain (WC) installed on horizontal vessels P1 – P3 required a L2 level analysis due to their complexity. Indeed, assessing the performance of these two complex active barrier systems requires a deeper understanding of how the earthquake might impact barrier subsystems, leading to the modification of their expected availability (and in turn their $PFDO$). Figs. 4 and 5 report the Fault Trees (FT) obtained respectively for FWS and WC in the present study. The details and the assumptions concerning the design of FWS and WC considered in the development of the FTs are reported in the Supplementary Material.

When considering the L2 analysis of FWS, the values reported in Fig. 4 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 [68,70-74]. The contribution of common cause failure was included by a 5% beta factor in $PFDO$ [68]. On top of the FTA, the value of $PFDO$ is reported, expressing the baseline 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 Fig. 4). As reported in [75], even if structures related to electricity production were only marginally affected by earthquakes with PGA values up to 0.97g, a power outage is frequent following earthquakes, 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

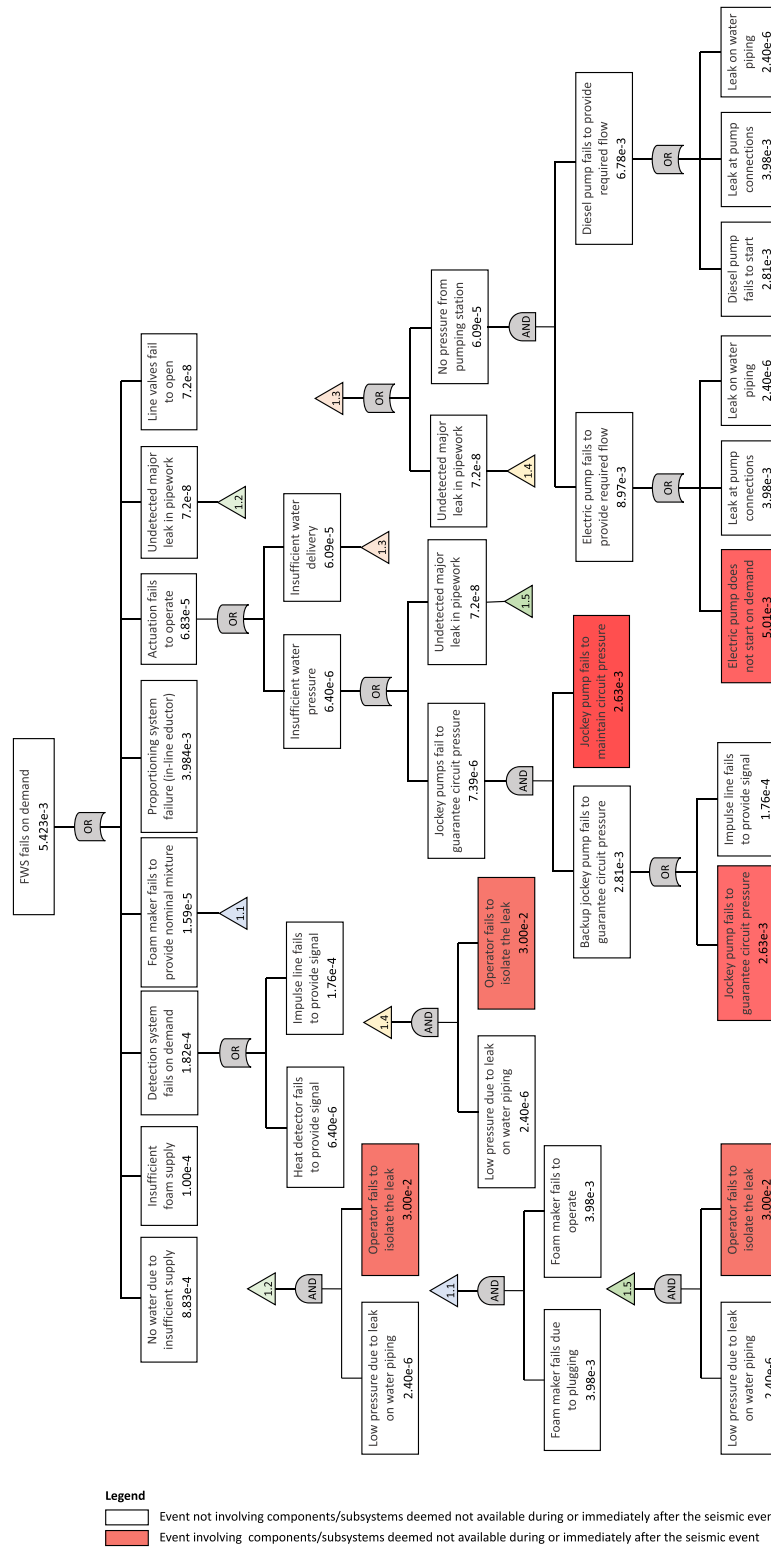


Fig. 4. Fault tree (FT) for the foam-water system (FWS) considered in the case study. Values reported in the FT boxes are the baseline unavailability values $q_{p,0}$ used to quantify $PFDO$.

immediately after the earthquake. This is consistent with evidence reported during past Natech accidents triggered by severe earthquakes (e.g., during the Kocaeli earthquake, only pumps driven by diesel motors could be operated, while all the electricity-dependent subsystems were not operating [55]).

In addition, after 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 should be considered. For instance, several Japanese petrochemical facilities experienced damages to internal roads during the Tohoku earthquake of 2011 [22,76]. This pattern was identified also during other severe seismic events (e.g., see [55,77]). This in turn might lead to the impossibility for operators to restore

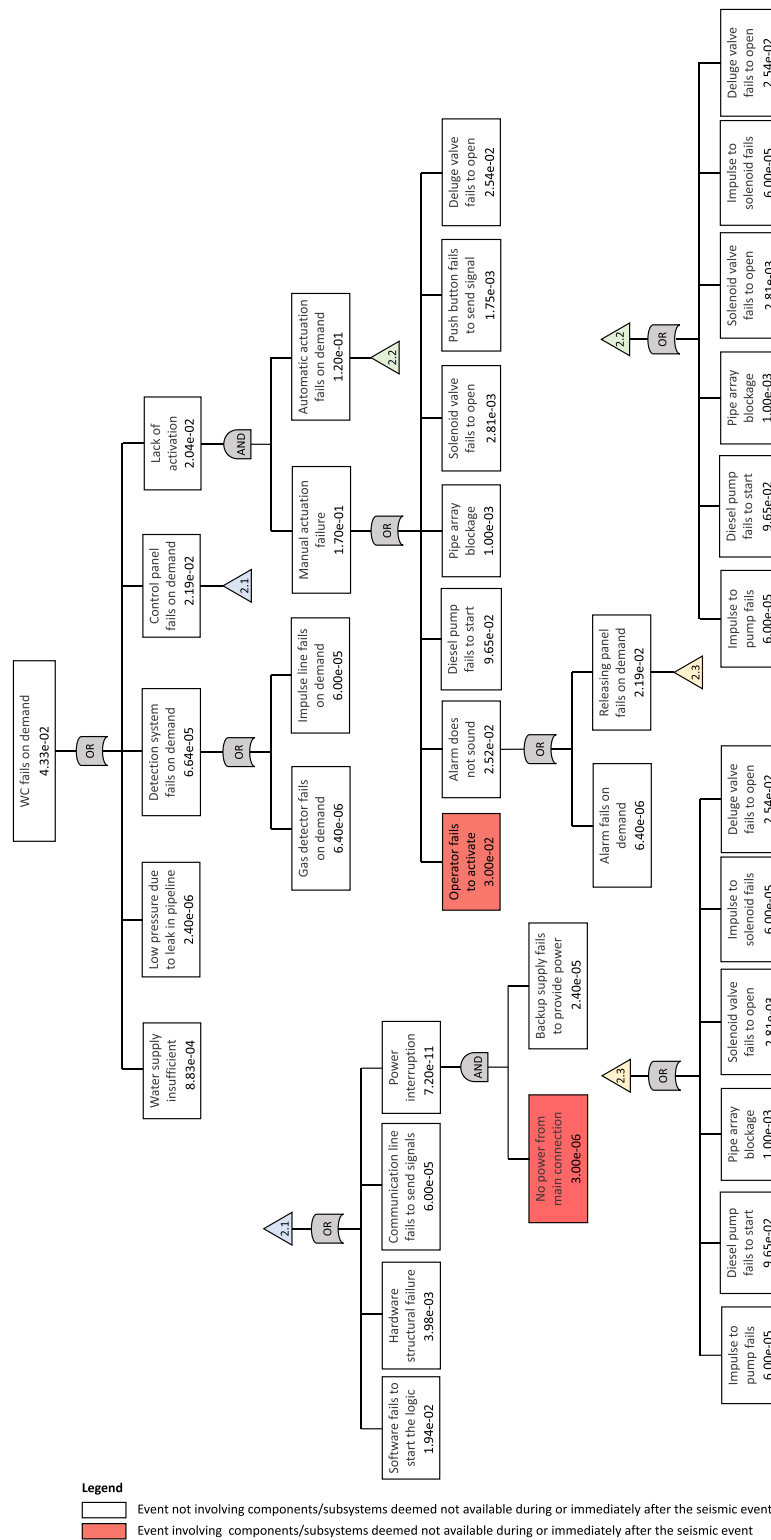


Fig. 5. Fault tree (FT) for the water curtains (WC) considered in the case study. Values reported in the FT boxes are the baseline unavailability values $q_{p,0}$ used to quantify $PFDO$.

failures of 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 Fig. 4).

Thus, a unit failure probability was assumed for these elements in the FTA (i.e., $\delta_p = 1$ in the application of equations related to L2 level according to Table 1 for the events reported in red in Fig. 4). The updated

values of $PFDeq$ are then calculated according to the expressions in Table 1. Thus, a unit value of $PFDeq$ is obtained from the FTA of the FWS, and the barrier is considered unavailable during the accident. Clearly enough, the results obtained apply to the assessment of a generic system, where no specific design measure was introduced to contrast earthquake damage. Thus, the components in red in Fig. 4 represent the more critical elements of the FWS, whose improvement should be considered to

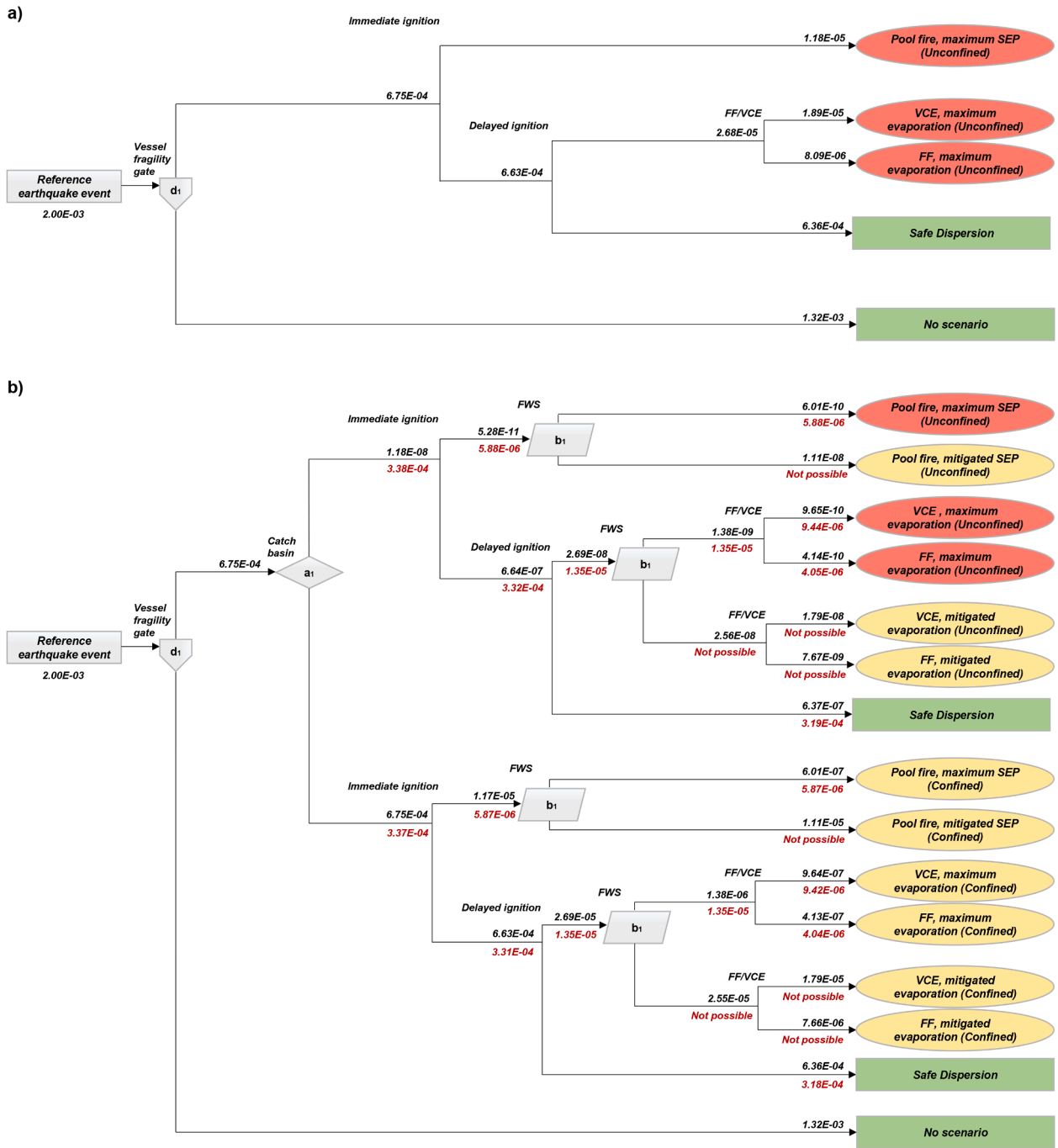


Fig. 6. Event trees reporting the quantification of the frequencies (in y^{-1}) of primary Natech scenarios involving tanks T1 to T4 for case 1 (panel a), and cases 2 and 3 (panel b). In panel b, values in black are obtained with baseline barrier performance (case 2), while values in red are obtained considering barrier depletion caused by the reference earthquake event (case 3).

reduce system vulnerability.

With respect to WC, the same standard reliability databases and a 5% beta factor were used to calculate consistently with the case of FWS the baseline value of the probability of failure on demand PF_{D0} [68,70-74].

The most vulnerable nodes identified for the WC are highlighted in red in Fig. 5. Also in this case, the main factor influencing barrier unavailability is the power outage. The activation of the barrier in the case of an earthquake thus can rely only on a backup power supply. In addition, the intervention of operators to manually activate the barrier is deemed not credible considering the possible damages to site passages and the presence of rubbles. Therefore, the $PF_{D_{eq}}$ of the WC is calculated as equal to 1.44×10^{-1} , as shown in Table 7.

4.3. Assessment of the final outcomes

The approach based on the modified gates presented in Table 2 was applied to the identification and the frequency assessment of primary Natech scenarios, considering the set of safety barriers listed in Table 7. The set of ETs obtained are reported in Fig. 6, Fig. 7, and Fig. 8, respectively for atmospheric equipment (i.e., T1 to T4), pressurized vessels containing ammonia (i.e., P1 and P2), and pressurized equipment storing propane (i.e., P3).

Important differences are present between the ETs obtained in the three cases considered. With respect to atmospheric tanks T1 – T4, the ET obtained in case 1 is shown in Fig. 6a, while the ET obtained for cases

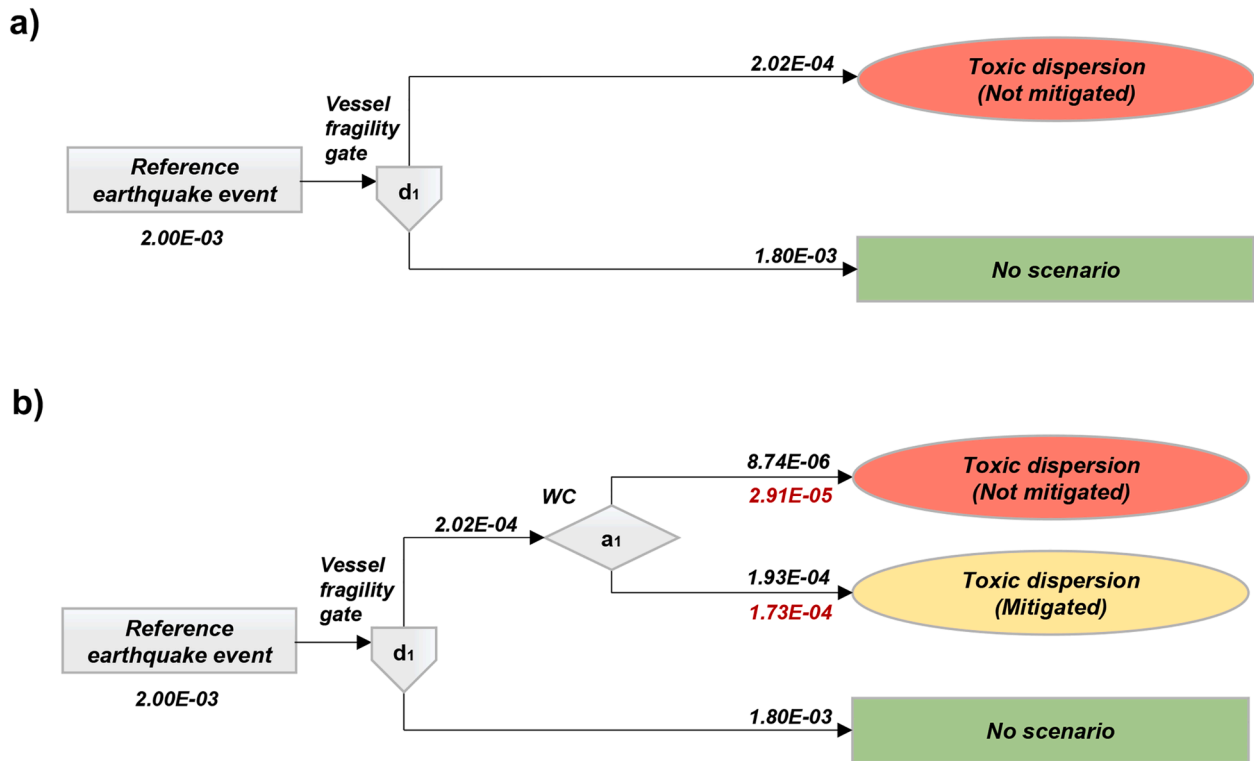


Fig. 7. Event trees reporting the quantification of the frequencies (in y^{-1}) of primary Natech scenarios involving vessels P1 and P2, for case 1 (panel a), and cases 2 and 3 (panel b). In panel b, values in black are obtained with baseline barrier performance (case 2), while values in red are obtained considering barrier depletion caused by the reference earthquake event (case 3).

2 and 3 is shown in Fig. 6b. In the latter panel, the values in black are obtained considering baseline barrier performance (i.e., case 2), while values in red consider barrier depletion due to the earthquake (i.e., case 3). It is evident that, when cases 1 and 2 are compared (i.e., values in Fig. 6a and value in black color in Fig. 6b), several scenarios are effectively mitigated by the action of safety barriers and most of the unmitigated scenarios feature very low frequencies when baseline barrier performance is assumed.

However, when considering the action of the reference earthquake on safety barriers (i.e., case 3, red values in Fig. 6b), some of the mitigated scenarios are no more possible (e.g., outcomes with mitigated SEP or reduced evaporation), due to the expected unavailability of the FWS, as resulting from the L2 analysis (i.e., the branches marked with a red 'Not possible' label in Fig. 6b). Similar findings are obtained also looking at Fig. 7 and Fig. 8, even if the L2 analysis of the WC system did not lead to the complete exclusion of mitigated scenarios, but only to the reduction of their probability.

In addition, the frequency of the most severe outcomes features a relevant increase when the performance degradation of safety barriers is considered, in agreement with previous studies addressing the performance of technical and emergency barriers aimed at preventing domino effects [56]. A comparison of the expected probabilities and frequencies calculated for the primary Natech scenarios in the three cases considered, that is, in absence of safety barriers (i.e., case 1), with safety barriers with baseline performance (i.e., case 2) and with barriers featuring depleted performance (i.e., case 3) is reported in Table 8. The table highlights that most of the more severe unmitigated scenarios would have an almost negligible probability if the baseline performance of safety barriers is assumed (see the probabilities of the scenarios in *italic* in Table 8). However, when the impact of the reference natural event on safety barriers is accounted for, the resulting depletion (and possibly complete impairment, as in the case of FWS) of safety barriers increases the conditional probability of unmitigated scenarios to values

that in some cases are comparable to those obtained in the absence of safety barriers (e.g., see $P(N_i^7)$ values obtained for "Pool fire, maximum SEP (Unconfined)" in cases 1 and 3).

This is even more relevant when cut-off criteria are considered. Actually, in the current practice, scenarios that have very low expected frequencies in most approaches are dropped from safety reports. For instance, in some European Union Member States, in the framework of issuing the safety report for sites falling under the obligations of the Seveso-III Directive (Directive 2012/18/EU), scenarios with expected frequencies below a cut-off value of $10^{-8} y^{-1}$ are considered not credible. Thus, such scenarios are not included in the report and are excluded from the final safety assessment and safety management system of the site. As shown in Table 8, assuming baseline safety barrier performance, the application of this approach to the case study would lead to the exclusion of all the unmitigated scenarios from tanks T1 – T4, since they all feature frequencies of the order of $10^{-10} y^{-1}$ (e.g., scenarios from T1 – T4 in *italic* in Table 8). However, the actual frequency of such unmitigated scenarios raises dramatically (up to four orders of magnitude, as shown in Table 8) when considering the impairment or degradation of safety barriers due to natural events as the reference earthquake considered in the case study.

4.4. Individual and societal risk

Based on the expected final outcomes listed in Table 8 for each of the tanks considered in the case study, the final scenarios consisting of all the credible combinations of final outcomes were identified and their frequencies were evaluated by the application of Eqs. (1) – (3). The local-specific individual risk (LSIR) was then calculated tailoring the approach adopted in previous Natech QRAs [17]. For the sake of brevity, the applied equations are described in the Supplementary Material. Fig. 9 reports the LSIR values calculated for the case study. As shown in the figure, the increase in LSIR values is relevant when Natech scenarios

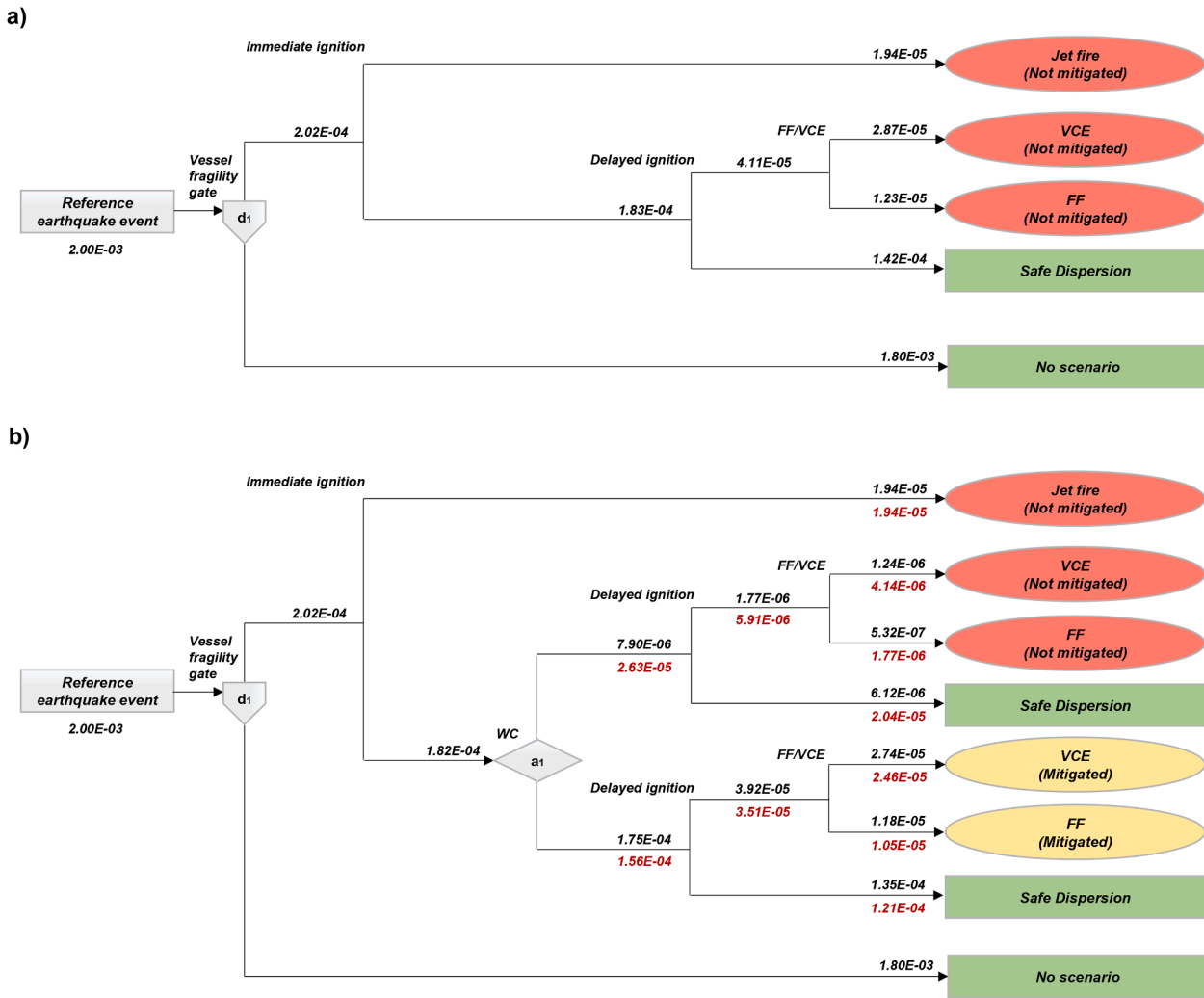


Fig. 8. Event trees reporting the quantification of the frequencies (in y^{-1}) of primary Natech scenarios involving vessel P3, for case 1 (panel a), and cases 2 and 3 (panel b). In panel b, values in black are obtained with baseline barrier performance (case 2), while values in red are obtained by barrier depletion caused by the reference earthquake event (case 3).

are considered in the analysis.

The positive effect of safety barriers on risk reduction is clearly shown by the comparison of Fig. 9b with figure Fig. 9c, with a reduction of LSIR values up to two orders of magnitude. Nonetheless, when comparing Fig. 9c to d it is evident that the depletion in barrier performance caused by the reference earthquake leads to a relevant increase of risk figures, with LSIR values increasing of more than an order of magnitude when considering the possible degradation of barrier performance due to earthquake impact. Indeed, the areas where LSIR is higher than $10^{-6} y^{-1}$ and $10^{-7} y^{-1}$ in Fig. 9d (case 3, depleted barriers) are respectively 1.6 and 1.2 times greater than those in Fig. 9c (case 2, baseline barrier performance). In addition, the highest LSIR value calculated in case 2 is lower than $10^{-4} y^{-1}$, as shown in Fig. 9c, while in case 3 (Fig. 9d) values higher than $10^{-4} y^{-1}$ (similar to those present in Fig. 9b, obtained for case 1, not considering safety barriers) are obtained in some areas of the layout considered.

The results obtained considering the LSIR contours are confirmed also by the societal risk figures calculated for the three cases considered, reported in Figs. 10 and 11. In particular, the F/N plot reported in Fig. 10 clearly shows that the societal risk related to case 3 (depleted barriers, continuous red curve) lies in between the best-case (case 2, black-dashed curve) and the worst-case (case 1, no barriers, red-dashed curve).

The intermediate position of the F/N curve obtained for case 3 thus indicates that previous QRA methodologies not considering safety

barriers in primary Natech scenarios characterization would lead to possibly over-conservative results (as shown by the comparison of the thick-red curve with the red-dashed curve). Nevertheless, considering safety barriers without including the possibility of their depletion during the seismic would have led to a substantial underestimation of societal risk figures (as shown by the comparison of the thick-red curve with the black-dashed curve).

The results discussed above are further confirmed by the values of the Potential Life Loss (PLL) and Expectation Value (EV) indexes calculated for the case study, reported in Fig. 11. The definition and the procedure for the calculation of these risk indexes are briefly summarized in Section 3 of the Supplementary Material. As shown in Fig. 11, the PLL values obtained considering Natech scenarios are more than 2 orders of magnitude higher than those calculated for the conventional scenarios (i.e., case 0), indicating that the influence of Natech contribution to PLL is 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 about 3 orders of magnitude higher.

On the one hand, it is clear that considering the worst-case scenario (case 1 - absence of barriers) leads to extremely high values of the indicators. Indeed, the 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 hand, considering the presence of barriers with baseline performance

Table 8

Frequencies and probabilities of final scenarios considered in cases 1, 2 and 3 (respectively: no safety barriers, barriers with baseline performance and barriers with depleted performance due to the earthquake). SEP=surface emissive power; VCE = Vapour cloud explosion; FF = Flash fire; $P(N_i^j)$ = conditional probability of a final scenario from the i -th equipment involved (out of 7 total elements of the layout). Scenarios in italic are the most severe outcomes that can be expected from each item category,

| Item involved | LOC | Final scenario | Case 1 | | Case 2 | | Case 3 | |
|------------------------------|------------------------------|---|------------------------------|---|-------------------------|------------|-------------------------|------------|
| | | | $f(N_i^j)$ [y^{-1}] | $P(N_i^j)$ | $f(N_i^j)$ [y^{-1}] | $P(N_i^j)$ | $f(N_i^j)$ [y^{-1}] | $P(N_i^j)$ |
| T1 – T4 | Catastrophic rupture | <i>Pool fire, maximum SEP (Unconfined)</i> | 1.18E-05 | 5.90E-03 | 6.01E-10 | 3.01E-07 | 5.88E-06 | 2.94E-03 |
| | | Pool fire, mitigated SEP (Unconfined) | - | - | 1.11E-08 | 5.55E-06 | - | - |
| | | <i>VCE, maximum evaporation rate (Unconfined)</i> | 1.89E-05 | 9.45E-03 | 9.65E-10 | 4.83E-07 | 9.44E-06 | 4.72E-03 |
| | | <i>FF, maximum evaporation rate (Unconfined)</i> | 8.09E-06 | 4.05E-03 | 4.14E-10 | 2.07E-07 | 4.05E-06 | 2.03E-03 |
| | | 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 | 5.87E-06 | 2.94E-03 |
| | | Pool fire, mitigated SEP (Confined) | - | - | 1.11E-05 | 5.55E-03 | - | - |
| | | VCE, maximum evaporation rate (Confined) | - | - | 9.64E-07 | 4.82E-04 | 9.42E-06 | 4.71E-03 |
| | | FF, maximum evaporation rate (Confined) | - | - | 4.13E-07 | 2.07E-04 | 4.04E-06 | 2.02E-03 |
| | | 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 | 9.79E-01 | 1.96E-03 | 9.79E-01 | 1.96E-03 | 9.79E-01 |
| | | P1 – P2 | Continuous release in 10 min | <i>Toxic dispersion (Not mitigated)</i> | 2.02E-04 | 1.01E-01 | 8.74E-06 | 4.37E-03 |
| Toxic dispersion (Mitigated) | - | | | - | 1.93E-04 | 9.65E-02 | 1.73E-04 | 8.65E-02 |
| No scenario | 1.80E-03 | | | 8.99E-01 | 1.80E-03 | 8.99E-01 | 1.80E-03 | 8.99E-01 |
| P3 | Continuous release in 10 min | <i>Jet fire (Not mitigated)</i> | 1.94E-05 | 9.70E-03 | 1.94E-05 | 9.70E-03 | 1.94E-05 | 9.70E-03 |
| | | <i>VCE (Not mitigated)</i> | 2.87E-05 | 1.44E-02 | 1.24E-06 | 6.20E-04 | 4.14E-06 | 2.07E-03 |
| | | <i>FF (Not mitigated)</i> | 1.23E-05 | 6.15E-03 | 5.32E-07 | 2.66E-04 | 1.77E-06 | 8.85E-04 |
| | | VCE (Mitigated) | - | - | 2.74E-05 | 1.37E-02 | 2.46E-05 | 1.23E-02 |
| | | FF (Mitigated) | - | - | 1.18E-05 | 5.90E-03 | 1.05E-05 | 5.25E-03 |
| | | Safe dispersion / No scenario | 1.94E-03 | 9.71E-01 | 1.94E-03 | 9.71E-01 | 1.94E-03 | 9.71E-01 |

during primary Natech scenarios leads to a relevant underestimation of the risk indicators, not representative of the actual figures related to Natech risk (i.e., the values of PLL and EV obtained for case 3 are respectively 1.3 and 1.9 times higher than the values obtained for case 2).

4.5. Discussion

The results obtained highlight the important role that safety barriers play in influencing the likelihood and the severity of primary Natech scenarios.

On the one hand, the significant depletion of safety barrier performance during/after natural hazards significantly influences the possibility of mitigation of the technological scenarios following the release of hazardous substances during Natech accidents. Assuming that safety barriers will retain their baseline performance might lead to an inaccurate evaluation of risk figures when considering primary Natech scenarios. Indeed, as shown in the analysis of the case study, the safety barriers considered are expected to feature significantly lower performances compared to the baseline case (e.g., the FWS is found to be not available at all during/after the earthquake), thus a reduced level of protection should be considered during/after a natural event when assessing Natech scenarios.

On the other hand, it should be observed that a residual level of protection exerted by safety barriers is still present, as evidenced by the results obtained for case 3, indicating the importance of their inclusion in Natech QRA.

The methodology developed enables considering the expected safety barrier performance during or after natural events, avoiding the application of possibly over-conservative approaches based on the worst-case assumption and supporting the definition of possible risk-based strategies to enhance barrier resilience to natural events. The approach also allows the identification of critical components of complex safety barriers and safety systems, contributing to address the design of barriers with higher resilience to the impact of natural events.

It is also worth remarking that the results obtained are even more relevant when considered in the light of previous findings, evidencing the higher probability of escalation caused by the reduced performance

of safety barriers aiming specifically at the prevention of domino effects [54,56]. Indeed, both the relevance of domino effects on Natech risk [52,53] and the specific contribution of barrier depletion on further increasing overall figures [54,56] have been clearly shown in recent studies.

Differently, the present study focused on primary scenarios, not considering the domino effect. However, the results evidence that the likelihood of domino effects in Natech accidents can potentially soar also due to the increased frequency of unmitigated primary scenarios (i.e., featuring more intense escalation vectors compared to mitigated scenarios). This represents an additional pathway to domino scenarios, not considered in previous studies.

The credibility of unmitigated primary scenarios in Natech events due to safety barriers degradation provides an additional contribution to the overall likelihood of domino effects, different from that related to the depletion of the safety barriers specifically aimed at preventing escalation, since it involves different safety systems.

Finally, it should be remarked that the proposed approach has a general validity, as it may be included also in alternative methodologies for the quantitative assessment of risk due to Natech scenarios, as those proposed by other authors [33,34,78].

5. Conclusions

An innovative approach to the detailed assessment of the risk related to Natech scenarios was developed, including the effect of safety barriers and safety systems performance degradation on the overall severity of primary technological scenarios. The proposed methodology specifically addresses the modification in frequency and severity of the primary scenarios, accounting for the mitigated and unmitigated final outcomes deriving from the updated performance of the safety barriers during/after the impact of the natural event. A specific multi-level assessment was adopted to enable the inclusion of safety barrier performance reduction caused by the natural event.

The results of the case study carried out confirm the importance of considering the impairment and/or degradation of safety barrier performance in the assessment of Natech scenarios, highlighting that overlooking the possibility of reduced protection/mitigation leads to a

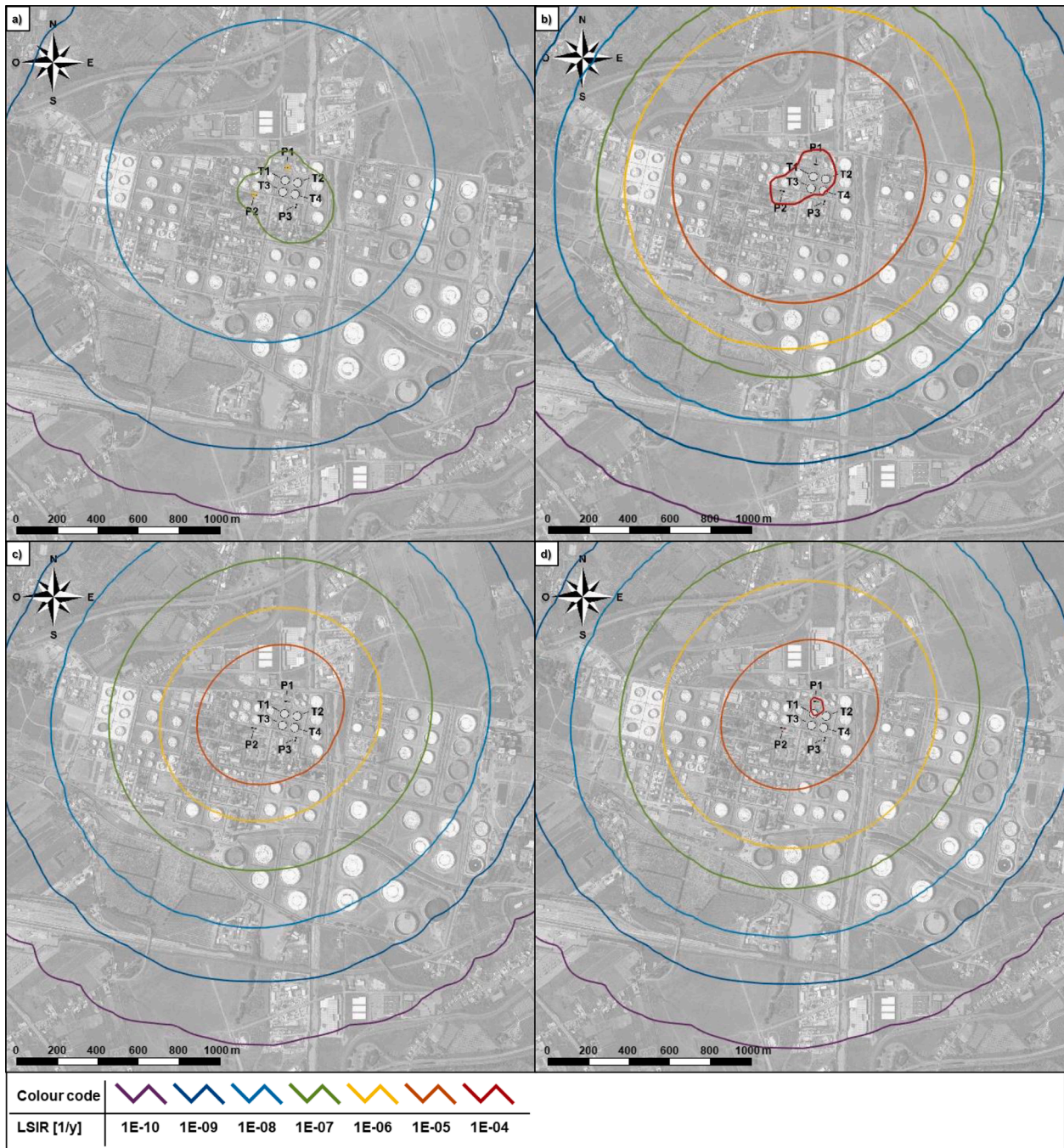


Fig. 9. LSIR contours obtained for: a) case 0 (baseline case, conventional scenarios with barriers with baseline performance); b) case 1 (worst-case, conventional scenarios + Natech scenarios not considering safety barriers mitigating primary Natech scenarios); c) case 2 (best-case, conventional scenarios + Natech scenarios considering barriers with baseline performance); d) case 3 (conventional scenarios + Natech scenarios accounting for barriers with depleted performance due to the impact of the reference earthquake).

significant underestimation of risk figures. The specific ET analysis techniques embedded in the methodology allow capturing the relevant modification of the expected frequency of unmitigated primary scenarios. These events, which may be considered unlikely and that are usually dropped in conventional quantitative risk assessment practices when baseline performance of safety barriers is considered, actually provide a relevant contribution to the overall risk figures when the degradation of safety barriers due to the impact of natural events is considered.

In addition, the results obtained may be used to extract risk-based indications on the most critical subsystems of technical safety barriers, allowing the identification of effective design strategies to improve

safety barrier resilience to natural events, reducing the gap between the actual level of protection provided in Natech accidents and that available in normal conditions, where the baseline performance of safety barriers may be assumed.

Finally, it should be remarked that the approach proposed for barrier assessment is consistent with previous studies focused on the propagation phase of Natech accidents through domino effects. Hence, the methodology proposed in the present study is a further step towards a more comprehensive framework aimed at the exhaustive description and risk assessment of the cascading nature of Natech accidents.

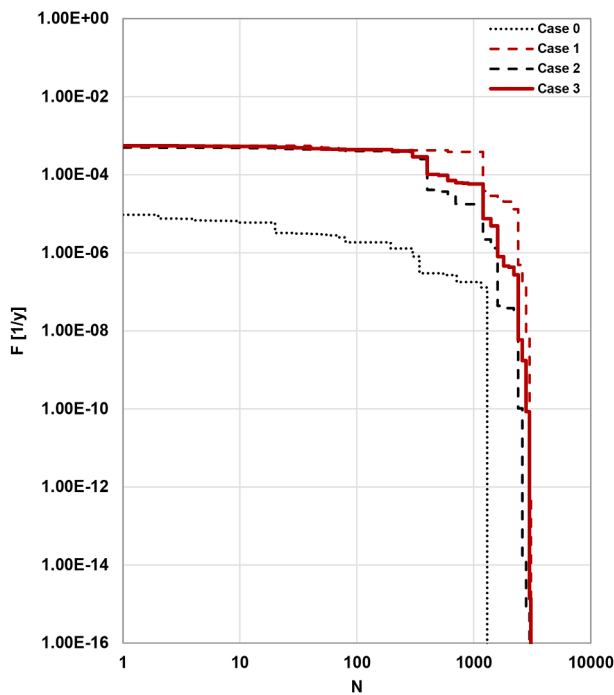


Fig. 10. Societal risk (F/N curves) for case 0 (black-dotted line – conventional failures), case 1 (red dashed line – conventional scenarios + Natech scenarios, no barriers), case 2 (black dashed line – conventional scenarios + Natech scenarios, baseline barrier performance), and case 3 (continuous red line, conventional scenarios + Natech scenarios, depleted barrier performance).

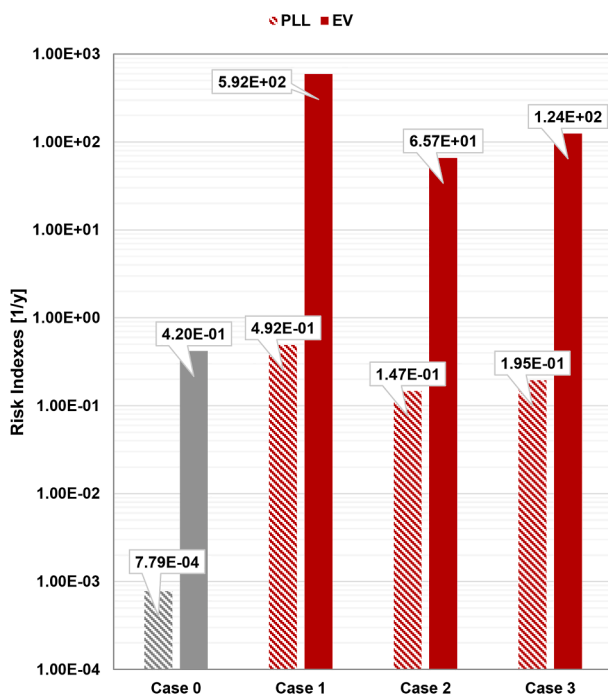


Fig. 11. Potential Life Loss (PLL) and expectation value (EV) values calculated for the case study (see Section 3 of the Supplementary Material for the definition and calculation procedure adopted for these risk indexes).

CRediT authorship contribution statement

Alessio Misuri: Conceptualization, Methodology, Writing – original draft. **Federica Ricci:** Conceptualization, Methodology, Writing – original draft. **Riccardo Sorichetti:** Investigation, Data curation.

Valerio Cozzani: Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.res.2023.109272](https://doi.org/10.1016/j.res.2023.109272).

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