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(Article begins on next page)

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**Assessment of safety barrier performance in the  
mitigation of domino scenarios caused by Natech events**

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*Revised version – September 2020*

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16

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18

1 **Abstract**

2 Technological accidents triggered by natural hazards (Natech accidents) are likely to  
3 escalate in cascading scenarios with severe consequences. Indeed, safety barriers  
4 implemented in process plants to prevent and mitigate accidents may be affected by natural  
5 hazards as well. **The present study proposes a novel comprehensive method to assess safety  
6 barriers and protection systems performance modification during natural hazards, as well  
7 as the resulting modification in the expected frequency of secondary technological  
8 scenarios that may arise.** In particular, the probability and frequency of domino scenarios  
9 initiated by Natech events are assessed considering the possible concurrent degradation of  
10 safety barrier performance in case of floods and earthquakes. An approach based on layer  
11 of protection analysis is adopted to quantify safety barrier performance degradation,  
12 accounting for the modification of barrier availability and effectiveness. A dedicated event  
13 tree analysis is applied to domino effect assessment and quantification of overall escalation  
14 scenarios. The results obtained allowed a detailed assessment of the expected frequency of  
15 secondary mitigated escalation scenarios, considering the possible effect of barriers  
16 degradation within Natech events.

17

18 **Keywords**

19 Natech; domino effect; escalation; safety barriers; mitigation.

20

## 21 **1. Introduction**

22 The hazard related to the impact of natural disasters on **installations where relevant**  
23 **quantities of hazardous substances are stored and processed, as the chemical and process**  
24 **industry, the Oil & Gas industry, the nuclear industry and some sectors of the**  
25 **manufacturing industry**, has become a matter of growing concern in the last decades [1–3].  
26 Severe conjoint threats may develop from the interaction between natural hazards and such  
27 critical infrastructures, due to the relevant inventories of hazardous substances handled and  
28 processed in these facilities [4,5]. Among the technical literature, technological accidents  
29 triggered by natural hazards are usually termed as Natech accidents [6–8]. Previous studies  
30 estimated that about 5% of industrial accidents reported in databases have been caused by  
31 natural hazards [9,10]. Nevertheless, the number of disasters is partly growing possibly due  
32 to climate change [11–14], thus these figures may be expected to grow consequently in the  
33 foreseeable future.

34 The consequences of Natech events may be extremely severe when compared to  
35 conventional technological accidents [15–17]. Indeed, multiple simultaneous failures may  
36 occur and the likelihood of accident propagation through domino effect is relevant also due  
37 to the potential impact of the natural event on safety systems [10,18]. For instance, during  
38 the Koaceli earthquake (1999) massive quantities of hazardous chemicals such as  
39 acrylonitrile and diesel fuel were released in the Izmit Bay area [19–21]. Moreover,  
40 multiple fire scenarios developed in a petroleum product storage park due to multiple  
41 simultaneous hydrocarbon releases, and fire was able to spread to nearby tanks since  
42 firefighting intervention was severely hampered due to concurrent damages to water  
43 pumping stations and pipelines [21].

44 Another critical aspect associated with Natech scenarios is related to the possible impact of  
45 the natural event on the safety systems and utilities, thus reducing the possibility of accident  
46 mitigation or even causing specific accident scenarios [22]. For instance, during Hurricane  
47 Harvey (2017), besides multiple oil spills from storage tanks, the prolonged power outage  
48 and the consequent loss of refrigeration of a peroxide storage led to chemical  
49 decomposition and fires [23,24].

50 In the literature, several methodologies to perform Quantitative Risk Assessment (QRA) of  
51 Natech scenarios are available and have been applied to test cases [25–27]. These methods  
52 rely on the adoption of equipment vulnerability models aimed at determining the failure

53 probability of process equipment given the impact of different natural events [28], such as  
54 floods [29–33], earthquakes [34–36], lightning strikes [37,38] and wind [32]. However,  
55 these methodologies feature relevant limitations when considering the role of domino effect  
56 and safety barriers, which should be taken into account for a more realistic and  
57 comprehensive estimation of Natech risk. Moreover, despite established methodologies for  
58 the quantitative assessment of domino propagation are available in the literature [39–41],  
59 the case of escalation during Natech events is seldom considered [42,43].

60 Previous studies evidenced that the impact of natural events may affect the integrity and  
61 availability of safety barriers [23,24]. However, to the knowledge of the authors, no  
62 methods are available in the literature for the quantitative assessment of the effect of the  
63 degradation of safety barriers on system integrity and availability in Natech accident  
64 scenarios. Indeed, a number of studies focus on the role of safety barrier management,  
65 addressing both the general framework related to the protection and integrity of complex  
66 system (e.g. see [44]), and the specific context of domino effect assessment [45-48].  
67 However, such approaches do not address the expected reduction of safety system  
68 performance due to natural hazards, preventing their direct application to the case of Natech  
69 accidents.

70 The present study is aimed at introducing an innovative methodology to include the  
71 concurrent safety barrier degradation due to the impact of the natural event in the  
72 probabilistic assessment of mitigated domino scenarios triggered by Natech events. The  
73 method relies on specific data obtained in a recent study, in which the performance  
74 modification of a set of relevant safety barriers during floods and earthquakes has been  
75 evaluated, based on expert elicitation [49]. The probabilistic framework in which safety  
76 barriers data are implemented is based on a Layer of Protection Analysis (LOPA) approach  
77 [50,51]. Probability and frequency of mitigated domino scenarios during natural hazards  
78 are evaluated through a tailored event tree analysis (ETA) [52–54]. An indicator-based  
79 approach is applied to perform a simplified evaluation and monitoring of the reduction of  
80 barrier performance in domino escalation mitigation/prevention [54].

81 The following parts of the paper are organized as follows. The methodology proposed for  
82 escalation characterization and frequency assessment of mitigated domino scenarios  
83 triggered by Natech accidents is described in Section 2. A case study is presented in Section  
84 3 in order to demonstrate the applicability of the proposed framework. Section 4 is

85 dedicated to the presentation of results and to the discussion on the main findings, and  
86 Section 5 reports the conclusions.

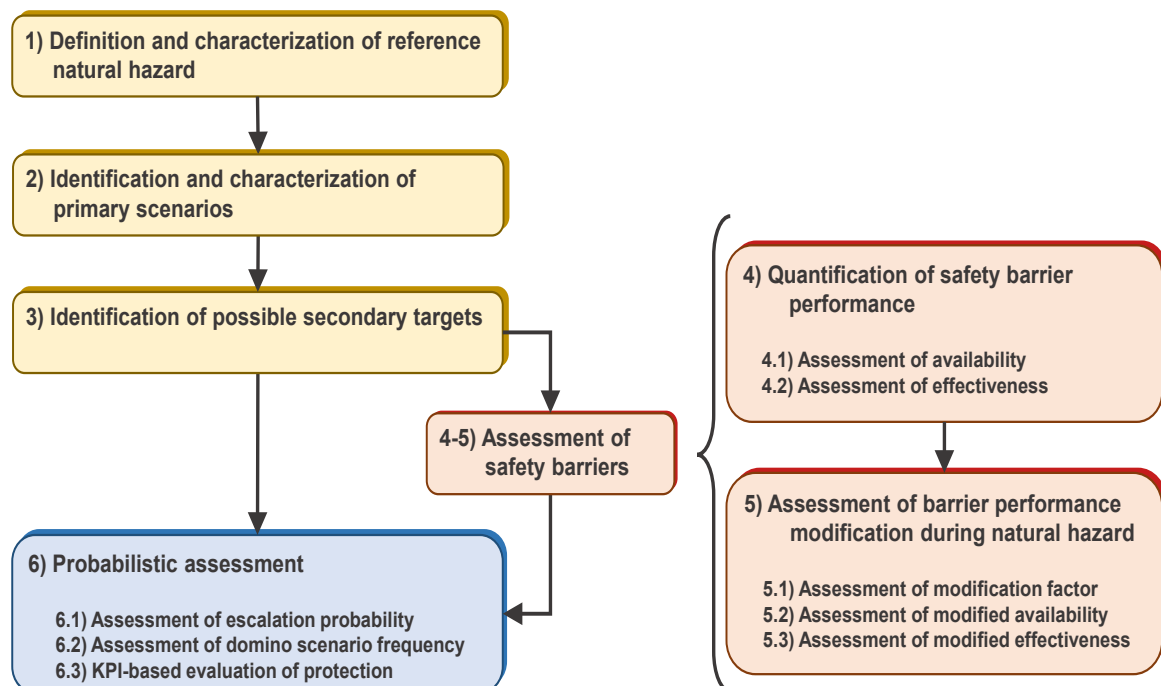
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## 88 2. Methodology

### 89 2.1 Overview

90 Figure 1 outlines the methodology developed in the present study. **With respect to previous**  
91 **methodologies, on the one hand, the proposed procedure allows the evaluation of the**  
92 **probability and frequency of mitigated domino scenarios caused by natural events,**  
93 **considering the possible concurrent depletion of safety barriers. On the other hand, the**  
94 **methodology provides a specific and original approach to the quantitative assessment of**  
95 **the performance of the safety barriers in Natech event, by the calculation of the probability**  
96 **of failure on demand and of the effectiveness of barrier action in the specific conditions**  
97 **occurring during Natech scenarios (steps 5 and 6 in Figure 1).**

98



99

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

102

103 Step 1 (see Figure 1) is aimed at defining the reference natural hazards that may affect the  
104 industrial site under analysis and at performing a characterization of its main features, with

105 a degree of detail suitable for industrial risk assessment studies. The natural hazard should  
106 be defined in terms of time of return, which may be easily related to a frequency of  
107 occurrence, and of magnitude of impact at the site of concern. The present study focuses  
108 on earthquakes and floods, since these events were responsible for the most severe Natech  
109 events reported in industrial accident databases, as highlighted in the dedicated literature  
110 [18], but may be extended to other categories of natural hazards.

111 In the specific framework of Natech, the severity of floods may be characterized in terms  
112 of floodwater height and velocity, while the magnitude of earthquakes is usually assessed  
113 estimating the values of the horizontal component of peak ground acceleration (PGA)  
114 [25,28,55]. This approach leads to the selection of a limited number of reference scenarios  
115 for the natural events, each characterized by a time of return and an intensity, representing  
116 the natural hazard present on the site [25,28,56].

117 Coherently with the state of the art of Natech assessment, the expected time of return and  
118 the effects of the natural hazards are considered independent (that is, the assessment  
119 considers either the effect of a flood or that of an earthquake, and does not consider any  
120 correlation among them or their potential effects). Moreover, barrier degradation due to the  
121 effect of previous natural events is not considered (that is, safety barriers are assumed to  
122 have undergone a regular maintenance).

123 Primary scenarios caused by Natech are then identified and characterized in terms of  
124 frequency and consequences (Step 2 in Figure 1). The identification of primary events is  
125 carried out adopting specific methodologies developed for the framework of Natech  
126 scenarios, described in detail elsewhere [17,56]. The frequency of primary loss of  
127 containment (LOC) events can be calculated multiplying the expected frequency of the  
128 natural event of concern by the conditional probability of equipment damage, obtained  
129 applying equipment vulnerability models [29,30,36], as exemplified in Appendix A.

130 Specific event trees may be used to define the possible primary scenarios following the  
131 LOC events [17,56] and to identify the relevant escalation vectors. Indeed, previous studies  
132 [10,17] highlighted that most of Natech events reported in databases collecting data on  
133 industrial accidents involved the LOC of petrochemical products [23,57], which may lead  
134 to fire scenarios.

135 The possible domino targets may then be identified (Step 3 in Figure 1) through the  
136 application of threshold-based approaches available in the literature [58–60]. These

137 methods are based on the comparison between the actual value of the physical effects  
138 impacting on equipment items (e.g., heat radiation in case of stationary fires, or peak  
139 overpressure in case of explosions) and threshold values below which escalation is  
140 considered not credible.

141 For each identified target, it is then necessary to consider the possible escalation likelihood  
142 modification due to the presence of safety barriers for accident prevention and mitigation  
143 (Steps 4 and 5 in Figure 1). However, these systems may be impacted as well by the natural  
144 hazard [49], thus a specific evaluation of their performance modification is required (Step  
145 5 in Figure 1). Details on the quantification of barrier performance and on its modification  
146 due to the concurrent natural events are discussed respectively in Sections 2.2 and 2.3.

147 The assessment of the frequencies of the overall escalation scenarios may then be carried  
148 out (Step 6 in Figure 1). Probit models based on equipment time to failure (*TTF*) when  
149 exposed to heat load may be applied to assess the probability of escalation due to domino  
150 effect triggered by fire [28,61,62] (Step 6.1 in Figure 1). Dedicated methodologies to  
151 account for safety barriers are then applied to perform mitigated domino scenario  
152 probability and escalation frequency assessment [52–54] (Step 6.2 in Figure 1). These two  
153 steps are discussed in Section 2.4. Finally, a performance analysis of safety barriers and  
154 protection systems is carried out through a specific indicator-based methodology (Step 6.3  
155 in Figure 1), which is presented in Section 2.5.

156

## 157 2.2 *Quantitative performance assessment of safety barriers*

158 Safety barriers are hereby defined as physical and non-physical measures intended to  
159 prevent, mitigate or control dangerous deviations of the industrial system under analysis or  
160 accidents [63–65]. Several frameworks for the classification of safety barriers are available  
161 in the literature [66–69]. In the following, the classification is based on the barrier working  
162 principle [50,70]. This allows classifying safety barriers as:

- 163 • passive barriers: physical protection systems not requiring activation to perform  
164 their function, such as fireproofing or containment dikes [71];
- 165 • active barriers: requiring external activation, such as water deluge systems (WDS)  
166 and sprinklers [72–75];



- 167 • procedural barriers: procedures and contingency plans performed by internal  
168 personnel or external teams to face the occurrence of major accidents (e.g.,  
169 intervention of firefighters).

170 Not every barrier has the same performance in serving the intended safety function, as the  
171 performance may be influenced by several parameters, including reliability, effectiveness  
172 and robustness [76]. As the performance of safety barriers is a critical aspect in evaluating  
173 the probability of accident scenarios caused by Natech events, its characterization is needed  
174 to support the probabilistic assessment of final scenarios.

175 A number of methodologies are available in the literature for barrier performance  
176 characterization, which have been developed in various fields of application of safety  
177 barrier conceptualization and require a variety of input information [50,66,67,70]. In the  
178 present study, a tailored LOPA approach developed for the assessment of mitigated  
179 escalation scenarios is adopted [52] (Steps 4.1 and 4.2 in Figure 1). The approach estimates  
180 the safety barriers performance introducing: i) a probability of failure on demand (PFD),  
181 that is, the probability that the system is unavailable when its safety function is required;  
182 and ii) the barrier effectiveness ( $\eta$ ), that is the probability that the barrier is successful in  
183 performing escalation prevention conditioned to its successful activation.

184 The value of the barrier PFD is related to the system architecture and to the reliability of its  
185 components, and may be assessed with standard reliability techniques, such as fault tree  
186 analysis, in case sufficient data on components can be retrieved in the technical literature.  
187 On the other hand, in case of lack of data, a PFD may still be estimated through the  
188 application of simplified risk-based approaches [77,78]. A comprehensive catalogue of  
189 reliability data sources is reported elsewhere [79].

190 The effectiveness parameter  $\eta$ , being a direct expression of the quality of a barrier function,  
191 should be estimated considering the specificity of the system, as well as other performance  
192 influencing factors (e.g. system installation, maintenance, quality of operations  
193 management, etc.) [52–54].

194 More details on the application of the concepts of PFD and  $\eta$  in the assessment of mitigated  
195 domino escalation are reported elsewhere [52–54].

### 196 *2.3 Assessment of barrier performance modification in Natech events*

197 Once the original performance of safety barriers is quantified, baseline values of PFD and  
 198  $\eta$  are modified taking into account the effect of the natural event (Step 5 in Figure 1),  
 199 adopting the methodology and the dataset developed by Misuri et al. [49]. Performance  
 200 modification factors  $\phi$  were elicited from experts through a covariate approach [80,81],  
 201 and implemented for the assessment of the safety barriers (Step 5.1 in Figure 1). The 2<sup>nd</sup>  
 202 quartile of failure probability distributions obtained was selected as the value of  $\phi$  in order  
 203 to minimize the effect of the outliers [49]. Performance modification factor  $\phi$  can be  
 204 interpreted as the likelihood that barrier systems are impaired or damaged by natural  
 205 hazards, hence higher values (i.e., close to 1) indicate a higher probability that the barrier  
 206 will fail in providing a successful protection action.

207 A subset of relevant safety barriers along with the specific modification factors in case of  
 208 flood ( $\phi_f$ ) and earthquake ( $\phi_e$ ) is reported in Table 1. In the same table, the uncertainty on  
 209 the elicited parameters is expressed as the interval comprised between the 1<sup>st</sup> and the 3<sup>rd</sup>  
 210 quartiles (indicated as Q1 and Q3, respectively) of the distributions obtained.

211 *Table 1: Performance modification factors for safety barriers in case of floods ( $\phi_f$ ) and earthquakes ( $\phi_e$ ).  $Q_1=1^{st}$   
 212 *quartile of distribution;  $Q_3=3^{rd}$  quartile of distribution. Data gathered from [49].**

Safety barrier	$\phi_f$	$[Q_1, Q_3]_f$	$\phi_e$	$[Q_1, Q_3]_e$
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]

213

214 The proposed framework, based on the implementation of the modification factors, thus  
 215 tailoring baseline barrier performance, derives from considerations and lessons learned  
 216 from past Natech accidents [10,19,23] (Steps 5.2 and 5.3 in Figure 1). In particular, in the  
 217 case of active barriers it is assumed that the effect of the natural hazard induces the

218 increment of the PFD of active barriers (i.e., reducing their availability), with a negligible  
 219 effect on effectiveness after successful activation. In case of passive barriers, the  
 220 effectiveness is the sole parameter to be reduced by the impact of the natural event, since  
 221 in this case the barrier does not need any specific activation or action to provide its effect  
 222 (i.e., failure on demand to provide the protective action is not applicable to this barrier  
 223 category).

224 Thus, by the proposed approach, a single modification factor obtained from expert  
 225 elicitation is applied either to modify the PFD (in the case of active barriers) or the  
 226 effectiveness (in the case of passive barriers).

227 Given these premises, while in the case of procedural barriers a specific analysis is always  
 228 needed to assess the expected performance, a general approach may be applied to assess  
 229 the degradation of barrier performance in the case of active and passive barriers.

230 In the case of active barriers, the performance parameters of the  $i$ -th active barrier are  
 231 modified according to Eqs. (1)-(2):

$$232 \quad PFD_{j,i} = 1 + (\phi_{j,i} - 1)(1 - PFD_{0,i}) \quad (1)$$

$$233 \quad \eta_{j,i} = \eta_{0,i} \quad (2)$$

234 where  $\phi_{j,i} \in [0,1]$  is the performance modification factor for  $j$ -th reference natural hazard  
 235 scenario, and  $PFD_{0,i}$  and  $\eta_{0,i}$  are the baseline values for the probability of failure on demand  
 236 and effectiveness, respectively. As discussed above, the impact of natural hazards on the  
 237 effectiveness of active barriers is neglected, thus the effectiveness value is considered equal  
 238 to the baseline value,  $\eta_{0,i}$ . In the case of barriers not specifically designed to resist to natural  
 239 events, it is possible that  $PFD_{0,i}$  is much lower than  $\phi_{j,i}$  (that is: failure in case of natural  
 240 events is significantly higher than conventional failure probability), but a specific  
 241 assessment is always needed.

242 With respect to passive barriers, since the barriers are always available and do not need any  
 243 activation to provide their action, the modification of the performance of the  $i$ -th passive  
 244 barrier may be quantified considering only the effectiveness, as in Eq. (3):

$$245 \quad \eta_{j,i} = (1 - \phi_{j,i}) \eta_{0,i} \quad (3)$$

246 where  $\phi_{j,i} \in [0,1]$  is the performance modification factor of the  $j$ -th reference natural  
247 hazard scenario, and  $\eta_{0,i}$  is the baseline effectiveness value, as shown in Section 2.2.

248 In the case of procedural barriers, modification factors are not available in the literature,  
249 thus a general approach to assess performance degradation during Natech events, as that  
250 proposed for active and passive barriers, is not possible. Specific approaches, depending  
251 on the procedure foreseen, should be developed. An example is provided for the specific  
252 case of a procedural barrier consisting in the emergency response following a fire, aimed  
253 at preventing escalation. The characterization of effectiveness is based on a specific  
254 approach obtained adapting that originally developed by Landucci et al. [54] to Natech  
255 scenarios. In the original approach, the effectiveness  $\eta$  is evaluated based on the  
256 comparison of the time the equipment is expected to withstand the received heat load, the  
257 *TTF*, and the typical time required for the final mitigation of the scenario (*TFM*, time for  
258 final mitigation) [54]. However, the *TFM* obtained by the original methodology, not  
259 accounting for the specific conditions that may arise during a Natech scenario, may be  
260 considered as a “best-case” value. In order to obtain a worst-case estimation of possible  
261 delays due to the complex environmental conditions that may be faced during compound  
262 disasters as earthquakes and floods [82], *TFM* was modified applying a methodology  
263 accounting for delays in response due to harsh environmental conditions. More details on  
264 the evaluation of PFD and  $\eta$  for emergency response to fires are reported in Appendix B.

265

#### 266 2.4 Quantification of domino escalation frequencies

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

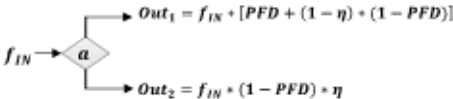
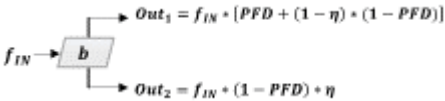
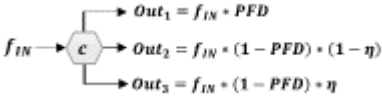
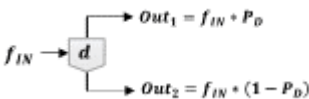
$$272 f_{I,LOC} = f_{nh} \cdot P_{nhd} \quad (4)$$

273 where  $P_{nhd}$  is the equipment damage probability to the impact of the reference natural  
274 hazard scenario. The  $P_{nhd}$  damage probability can be estimated using equipment  
275 vulnerability models or observational fragility curves available in the literature [29,30,36].

276 The description of the vulnerability models applied in the present study is reported in  
 277 Appendix A.

278 Primary Natech scenarios are identified through dedicated methodologies [17,25,56,83]  
 279 and the evaluation of physical effects is performed through conventional integral models  
 280 for consequence assessment [71,84–86]. Subsequently, a tailored ETA is applied to include  
 281 the effect of safety barriers and their performance in escalation probability and frequency  
 282 assessment. The methodology is based on the logical operators described as gates in Table  
 283 2, which are adapted from a previous study [54].

284 *Table 2: Definition of operators to be used in ETA.  $f_{IN}$ : gate input frequency, PFD: Probability of failure on demand,  $\eta$ :  
 285 effectiveness parameter,  $P_D$ : equipment failure probability due to domino escalation. Adapted from [54].*

Gate type	Representation and quantification	Description
a		Simple composite probability gate (type “a”): unavailability, expressed as probability of failure on demand, is combined with a single probability value for the effectiveness.
b		Composite probability distribution gate (type “b”): unavailability, expressed as 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		Discrete probability distribution gate (type “c”): depending on barrier effectiveness, three or more events may originate
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.

286 As shown in the table, the uppermost branch  $Out_1$  of each gate represents the failure of the  
 287 barrier in mitigating escalation. For gates “a” and “b”,  $Out_2$  represents the case of  
 288 successful mitigation. In the specific case of gate “d”, which is a target vessel fragility gate  
 289 rather than a gate expressing barrier performance,  $Out_1$  represents the mechanical failure  
 290 of the target, while  $Out_2$  indicates that the target withstands heat radiation. The probability  
 291 of failure due to domino propagation  $P_D$  to be implemented in gate “d” is identified through  
 292 the application of probit models based on equipment  $TTF$  [61]. Gate “c” instead has been  
 293 specifically designed to assess emergency response performance in escalation prevention  
 294 [52,54]. Thus,  $Out_2$  represents the case of mitigated domino scenarios due to the successful

295 activation of emergency response, but with a  $TFM$  higher than  $TTF$ . On the contrary,  $Out_3$   
296 is the case of successful mitigation due to successful response and  $TFM$  lower than  $TTF$ .

### 297 2.5 Quantification and monitoring of barrier degradation

298 A set of indicators was applied to carry out a simplified quantitative evaluation and  
299 monitoring of barrier performance degradation in preventing/mitigating domino effects  
300 (Step 6.3 in Figure 1). This set of indicators has been developed for passive and active  
301 barriers in previous studies on mitigated domino escalation assessment [54]. In particular,  
302 two Key Performance Indicators (KPIs), namely A and B, are associated to each hardware  
303 barrier. The A KPI is defined as:

$$304 \quad A = \frac{\sigma}{Out_1/f_{IN}} \quad (5)$$

305 where  $\sigma$  is a reference PFD indicating a high performance in reduction of escalation  
306 probability,  $f_{IN}$  is the input frequency to the barrier gate operator and  $Out_1$  is the output  
307 frequency of mitigation failure. Therefore, the ratio  $Out_1/f_{IN}$  is the probability of barrier  
308 failure (either due to lack of activation or ineffectiveness once activated), which is  
309 associated with the uppermost branch of each gate presented in Table 2. The A KPI thus  
310 summarizes the overall probabilistic performance of each barrier compared to a required  
311 safety level. The application of the risk-based methodology defined in IEC61508 and  
312 IEC61511 standards [77,78] evidenced that a safety function with Safety Integrity Level  
313 (SIL) 3 is required for domino escalation prevention [54]. According to the SIL definition,  
314 a safety function with SIL3 has a failure probability on demand between  $10^{-4}$  and  $10^{-3}$ , thus  
315 the latter the value was conservatively assumed for parameter  $\sigma$  in the case-study.

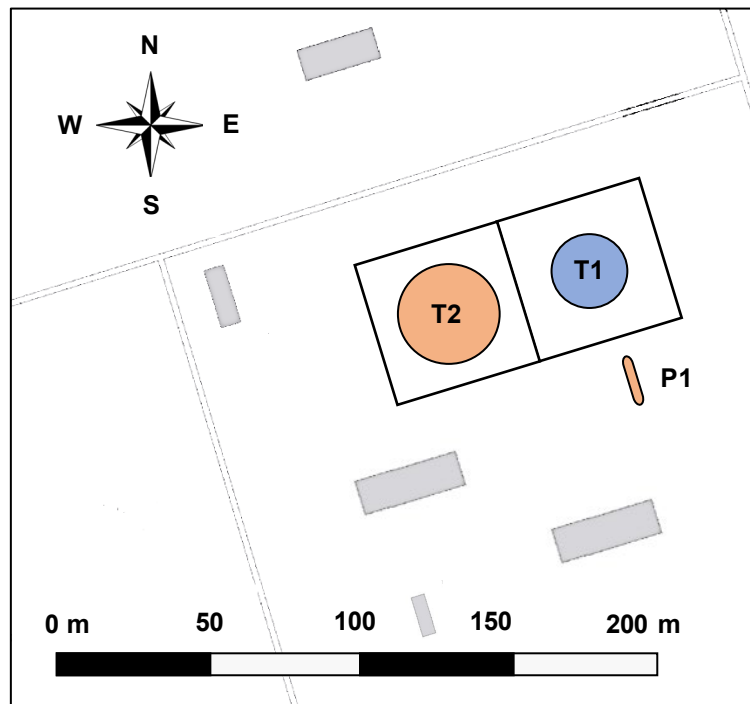
316 The B KPI is defined as:

$$317 \quad B = \frac{TTF - TTF_u}{TFM - TTF_u} \quad (6)$$

318 where  $TTF$  and  $TTF_u$  are the values of the time to failure of the equipment item considered  
319 respectively in presence and in the absence of the barrier, while  $TFM$  is the time required  
320 for final mitigation of the fire, which is highly site specific and may be estimated according  
321 to the simplified methodology presented in a previous study [52]. The B KPI, thus,  
322 specifically quantifies the increase in  $TTF$  achieved through the implementation of fire  
323 protection barriers (e.g. WDS, etc.), with respect to the time required for emergency  
324 intervention at site.

325 **3. Case-study**

326 A reference case study was defined to assess the modification of risk figures caused by  
 327 barrier performance degradation during Natech events. The layout considered is shown in  
 328 Figure 2. The layout is composed of two atmospheric tanks storing liquid flammable  
 329 materials (T1, T2) and of a pressurized vessel storing LPG (P1). The main features of the  
 330 equipment items are summarized in Table 3.



331  
 332 *Figure 2: Layout considered for the case study.*

333

334 *Table 3: Equipment items considered in the case-study. Tank T1 was considered the source of the LOC causing the*  
 335 *primary Natech scenario.*

ID	Type	Capacity [m <sup>3</sup> ]	Diameter [m]	Length/Height [m]	Substance	Inventory [ton]
T1	Atmospheric tank	5000	24.4	10.8	Gasoline	3000
T2	Atmospheric tank	4300	32	5.4	Crude oil	3000
P1	Pressurized vessel	105	2.6	20	LPG	52

336 The facility was assumed to be located in a natural hazard prone area, and to be exposed to  
 337 the risk of severe floods and earthquakes. The reference natural hazards are described in  
 338 Table 4. As shown in the table, the flood with a time of return of 500 years was assumed  
 339 as the reference scenario for flood hazards. The flood scenario with this return time is the  
 340 more severe flood scenario usually considered in flood hazard analysis [25,29,30]. In the  
 341 case of earthquakes, the event with 10% exceedance probability in 50 years is assumed as

342 reference case, which roughly corresponds to a 500 years return time, that, for the sake of  
 343 simplicity, was assumed as the reference value of return time in the analysis of the case-  
 344 study [18]. Thus, the frequency of both the natural hazards assumed in the case-study  
 345 results of  $2.0 \times 10^{-3} \text{ y}^{-1}$ , allowing a straightforward comparison of the results obtained for  
 346 the two different natural hazards.

347 *Table 4: Reference scenarios selected for flood and earthquake in the case study, and consequent LOC and primary*  
 348 *scenario probabilities calculated for tank T1 in Table 3. Ignition probability of 0.9 is assumed.*

ID	Description	Features of the natural event	Return time $t_r$ [y]	Frequency $f_{nh}$ [ $\text{y}^{-1}$ ]	Damage probability of T1 $P_d$	Frequency of primary LOC from T1 $f$ [ $\text{y}^{-1}$ ]	Frequency of primary pool fire $f_{PF}$ [ $\text{y}^{-1}$ ]
W1	High depth flood	$h_w = 2.0 \text{ m}$ $v_w = 0.5 \frac{\text{m}}{\text{s}}$	500	2.00E-03	2.40E-01	4.79E-04	4.31E-04
E1	Severe earthquake	$PGA = 0.5 \text{ g}$	500	2.00E-03	1.74E-01	3.47E-04	3.13E-04

349 Since the aim of the present study is to assess the probability and frequency modification  
 350 of escalation scenarios due to barrier degradation rather than to perform a complete QRA,  
 351 for the sake of simplicity a single primary event due to Natech is considered in the analysis  
 352 of the case-study.

353 The primary Natech scenario is assumed to only involve the atmospheric tank T1, while T2  
 354 and P1 are possible targets for domino effect escalation. The target tanks T2 and P1 are  
 355 equipped with the safety barriers reported in Table 5. Both tanks are protected with pressure  
 356 safety valves (PSV), while tank T2 is equipped with foam-water sprinklers, and P1 with  
 357 water deluge system (WDS) and high rating passive fire protection material (PFP).  
 358 Emergency response plan to a fire involving tank T1 foresees the intervention of emergency  
 359 teams to further protect both items by fire monitors.

360 It should be remarked that the methodology developed allows considering also all the other  
 361 primary Natech scenarios generated by tanks T2 and P1 and the following domino effects.  
 362 This was not done only in order to simplify the case-study and for the sake of brevity.

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

Barrier	Gate	$PFD_o$	$\eta_o$	$PFD_f$	$PFD_e$	$\eta_f$	$\eta_e$	T2	P1
Foam-water sprinkler system	b	5.32E-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
Emergency teams	c	1.00E-01	0;1	1.00E-01	1.00E-01	0;1	0;1	X	X



365 Table 5 shows the original PFD and effectiveness of each barrier, which have been retrieved  
366 from literature sources [52,71,79,87,88], and the modified values calculated according to  
367 Eqs(1)-(3), applying the values of  $\phi_f$  and  $\phi_e$  reported in Table 1. The choice of the  
368 appropriate gate for each barrier is made according to the specific features of the barrier,  
369 the consequence of barrier failure and the specific functionality of the barrier, which  
370 determines how the barrier effectiveness is expressed to model the quality of barrier  
371 function (i.e., as single probability value, or as continuous or discrete probability  
372 distribution). For the case of WDS, PFP and PSV, gate “a” has been selected since their  
373 effectiveness can be expressed as a single value. For the specific case of foam-water  
374 sprinkler systems, gate “b” was selected. This choice is made since sprinkler performance  
375 is generally expressed as the probability distribution of fire extinguishment in technical  
376 literature [52]. Nevertheless, for the sake of simplicity, the minimum value retrieved in the  
377 literature is conservatively adopted in this study to assess foam-water sprinkler  
378 effectiveness. For the case of emergency intervention, gate “c” has been selected to include  
379 partial success in mitigation, as explained in Section 2.4. Further details on gate selection  
380 and specific examples are reported in a previous study to which the reader is referred for  
381 further details [42].

382 The frequencies of the primary Natech scenarios are assessed adopting fragility models  
383 available in the literature (see Section 2.4 and details in Appendix A). In the case of floods  
384 (W1), the vulnerability model developed in [29], considering buckling as the failure  
385 mechanism, has been applied, while in case of earthquake (E1), the tank is conservatively  
386 assumed unanchored and the vulnerability is assessed by the fragility models reported in  
387 [36]. It should be remarked that any alternative appropriate equipment damage model  
388 among those available in the literature could be used for the assessment.

389 A LOC causing the complete release of the tank content in 10 minutes is conservatively  
390 assumed [25,55]. An ignition probability of 0.9 is assumed both in the case of earthquake  
391 and of flood. This choice is in agreement with previous studies, and it is deemed appropriate  
392 to highlight the high likelihood of ignition in case of high magnitude compound disasters  
393 as earthquakes and floods [25,55,56]. Thus, both for flood and for earthquake, the reference  
394 primary Natech scenario is a pool fire involving the total inventory of tank T1.

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

- 398 - unmitigated domino scenarios, developing from the escalation of the primary  
399 scenario in the absence of activation or with the lack of effectiveness of safety  
400 barriers;
- 401 - mitigated domino scenarios, that is, scenarios with potentially reduced  
402 consequences due to partial activation or reduced effectiveness of safety barriers in  
403 the accident sequence;
- 404 - no domino scenarios, in which the escalation is avoided due to activation and  
405 effective response of the safety barriers.

406 The consequence assessment of the primary pool fire was carried out using integral models  
407 [71,85,86]. For the sake of simplicity, a single value of ambient temperature, wind velocity  
408 and atmospheric stability class were considered: 10°C, 2m/s and F. The calculated  
409 maximum incident heat radiation on the surface of each considered target is 60kW/m<sup>2</sup>.

410 The *TTF* of targets and the probability of failure as a function of the heat load caused by  
411 the primary Natech scenario is evaluated by the approach suggested by [61]. Best-case  
412 *TFM* values of 65 and 90 min were obtained for P1 and T2 by the simplified approach,  
413 based on the features of the fire scenario and on the vessel geometries suggested by [52],  
414 not considering the specific conditions of Natech scenarios. A worst-case *TFM* value of  
415 400 min was also estimated, considering the harsh conditions of emergency response in  
416 Natech events (see Appendix B).

417 For the sake of comparison, domino effect causing escalation from a pool fire originated  
418 by the internal failure of Tank T1 is also considered. A LOC causing the release of the  
419 entire inventory of tank T1 in 10 minutes was assumed. A frequency of  $2.5 \times 10^{-6} \text{ y}^{-1}$  was  
420 estimated for the pool fire following the LOC, based on values suggested in the literature  
421 for LOC and immediate ignition [54,84]. Due to the assumptions introduced, the same heat  
422 radiation values calculated for the primary Natech scenarios are associated with this pool  
423 fire. In the absence of a natural hazards acting on the site, the baseline values for PDF and  
424 effectiveness of the safety barriers reported in Table 5 were assumed in the analysis.

425

426 **4. Results and discussion**

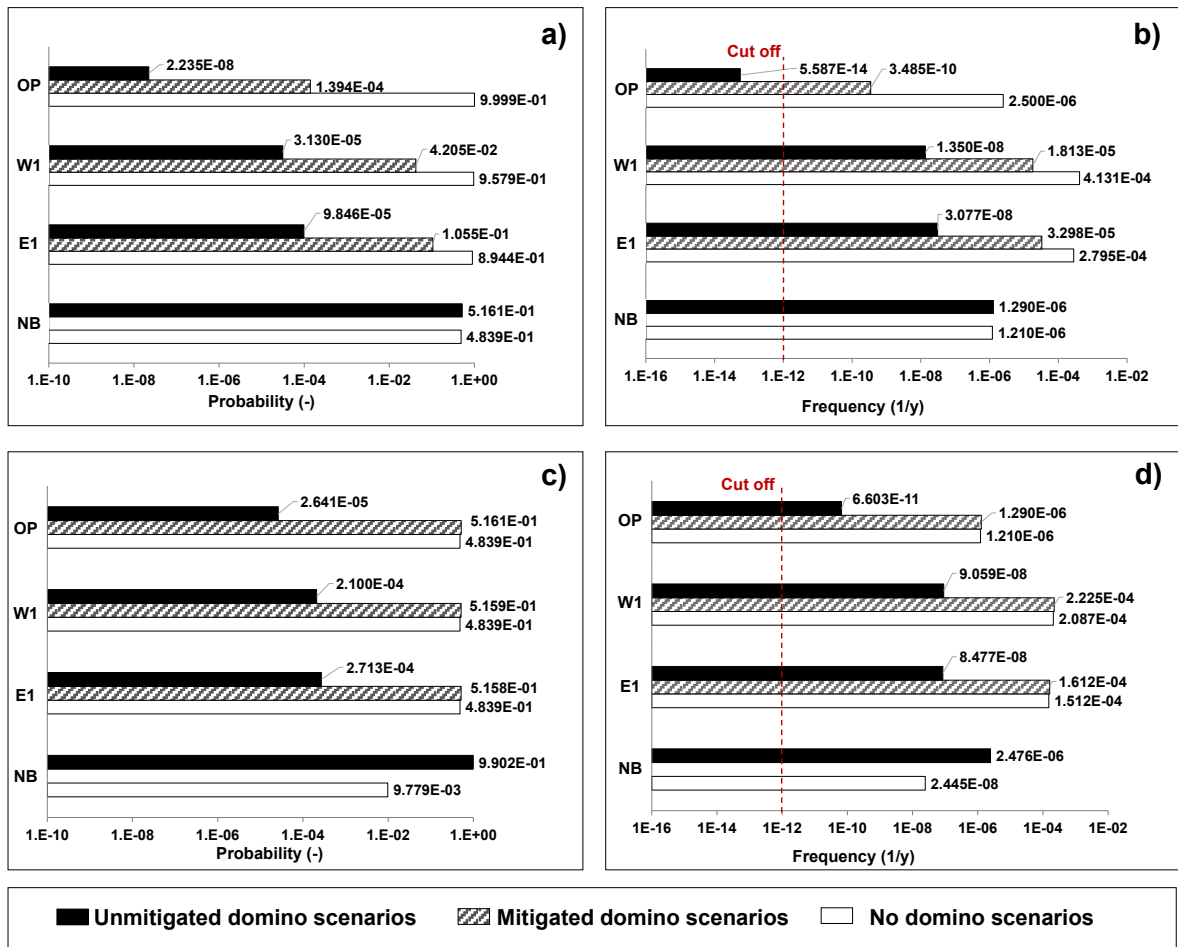
427 *4.1 Assessment of probabilities and frequencies of escalation scenarios*

428 The methodology described in Section 2 has been applied to the case study. The set of event  
429 trees developed to analyse the case study is reported in Appendix C. Since in the case-  
430 study, for the sake of simplicity, the consequences of a single primary event were  
431 considered in all the three cases of domino effect analysed (due to internal causes, due to  
432 flood or due to earthquake), it is possible to directly compare the probabilities of escalation  
433 given the primary event.

434 Figure 3 shows the results obtained for the conditional probability of the three end-point  
435 scenarios considered in the analysis (unmitigated domino scenarios, mitigated domino  
436 scenarios and no domino scenario) calculated considering the possible impact of the natural  
437 event on the safety barriers. The figure also reports the expected overall frequencies of  
438 these final scenarios, considering the frequency estimated for the primary event triggering  
439 the domino sequence, either in the presence or in the absence of natural events. Conditional  
440 probabilities and frequencies of domino scenarios in case of absence of hardware mitigation  
441 (thus without add-on active and passive barriers) and only accounting for generic data for  
442 internal emergency intervention, by the method proposed by Landucci et al. [61]) are also  
443 included in Figure 3 as reference values for the sake of comparison.

444 As shown in the figure, the conditional probability associated with unmitigated scenarios  
445 exhibits a significant increase due to the impact of flood or earthquake on the barriers  
446 considered. For pressurized vessel P1, this increment is of about three orders of magnitude,  
447 while in case of tank T2 it is of about five times the original value. Thus, the degradation  
448 of barrier performance seems to have a greater impact on pressurized vessels rather than on  
449 atmospheric tanks. However, atmospheric storage tanks are inherently more vulnerable to  
450 domino escalation caused by fire (as shown by the values of probability of unmitigated  
451 escalation reported in Figure 3), due to their lower mechanical resistance. Thus, the  
452 probability of unmitigated escalation scenarios affecting T2 is still significantly higher than  
453 the value for P1, even considering barrier performance degradation.

454 It is also worth noting that the effect of barrier performance degradation is different for  
455 earthquakes and floods, depending on the different effects that such events may have on  
456 the degradation of barrier functions, in accordance with previous findings [49].



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Figure 3: 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.

469 The overall frequencies of escalation scenarios given primary Natech events are shown in  
470 Figure 3-b and Figure 3-d. The figures also report a baseline cut-off value ( $1.0 \times 10^{-12} \text{ y}^{-1}$ )  
471 suggested in the literature [54]. As a general remark, it can be observed that the frequencies  
472 of unmitigated escalation scenarios triggered by Natech events are at least three orders of  
473 magnitude higher than those of unmitigated escalation from conventional primary scenarios  
474 due to internal causes. Actually, all escalation scenarios arising from Natech primary  
475 scenarios feature higher frequency values compared to those triggered by conventional  
476 internal failures. This is a direct consequence both of the higher frequency of natural  
477 hazards compared to the frequency of random internal failures (even in case of events  
478 having a high time of return, as those considered in the case study), and of the effect of the  
479 degradation of safety barriers when impacted by natural events.

480 As shown in Figure 3-b, in the case of vessel P1 the frequency of unmitigated scenarios is  
481 negligible in the absence of Natech scenarios. Considering the Natech scenarios and the  
482 simultaneous barrier degradation, the frequency of unmitigated scenarios increases of about  
483 five orders of magnitude, well above the suggested cut-off value. In Figure 3-d a similar  
484 trend is present. However, the frequency of unmitigated escalation scenarios is limited but  
485 may not be neglected, according to the cut-off criteria selected, also in the case of domino  
486 effect due to scenarios caused by internal failures, since the heat load on tank T2 is high  
487 and atmospheric tank resistance is lower than that of pressurized vessels.

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

494

#### 495 *4.2 KPI-based assessment of barrier performance degradation*

496 The approach described in Section 2.5 was applied to monitor the modification of barrier  
497 performance during Natech events. The set of KPIs was calculated both considering  
498 baseline barrier performance and the modified performance due to W1 and E1 reference

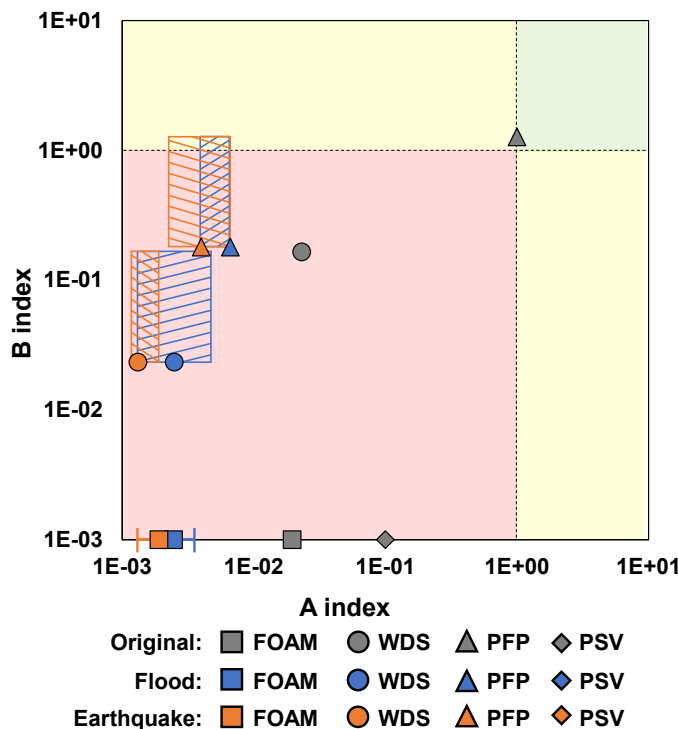
499 Natech scenarios. Results are shown in the chart reported in Figure 4, which is divided into  
500 three parts:

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

508 Grey markers show the baseline performance of the barriers considered, while blue markers  
509 and orange markers show the performance during W1 and E1, respectively. The  
510 performance of barriers aimed at increasing the *TTF* of targets (i.e., WDS and PFP) is  
511 represented together with the area of uncertainty on the value (i.e., area covered by pattern  
512 in Figure 4). The uncertainty on KPI A is expressed calculating the index considering the  
513 1<sup>st</sup> and the 3<sup>rd</sup> quartiles of  $\phi$  distributions (see Table 1), while KPI B is calculated both  
514 considering original *TFM* (best case) and a modified *TFM* based on the methodology for  
515 harsh environment described in Appendix B [82] (worst case). For the barriers not  
516 significantly providing a direct effect on the *TTF* of the target (i.e., foam system and PSV),  
517 a constant minimum value for the B index was set to  $10^{-3}$ . For the foam system, only the  
518 uncertainty on KPI A is available. The values of the KPIs are calculated with the same  
519 method described above and are represented with whiskers. Both during W1 and E1, in the  
520 best case the PFP falls in the yellow-shadowed area of the KPI plot. However, considering  
521 the worst case (i.e., a severely hampered emergency intervention) PFP falls in red-  
522 shadowed area of the plot, indicating that both KPI values are below the reference levels  
523 for high protection. PSV is the only barrier that is not affected either by W1 or by E1 in  
524 accordance with the outcome of a previous study [49], as PSV failure was never reported  
525 in available data on Natech scenarios.

526 It is also worth noting that PFP has the best performance in hampering escalation in domino  
527 scenarios from internal failures. However, in case of natural hazards, the performance of  
528 PFP in preventing escalation from Natech events is reduced, falling into the red area. Figure  
529 4 also shows that in the case-study considered the earthquake E1 affects safety systems

530 more severely than flood W1, as it clearly emerges from the more pronounced shift toward  
 531 lower values of the A index.



532  
 533 *Figure 4: Comparison between original and degraded barrier performance as shown by KPI values, A and B, as*  
 534 *defined by Eqs.(5) and (6) respectively. Legend: FOAM = Foam-water sprinkler system, PSV = Pressure safety valve,*  
 535 *WDS = Water deluge system, PFP = Passive fire protection. Blue-dashed area = Uncertainty for flood W1, orange-*  
 536 *dashed area = Uncertainty for earthquake E1. Uncertainty region for the foam-water sprinkler system is indicated by*  
 537 *whiskers.*

### 538 4.3 Discussion

539 The results obtained highlight the modification of expected conditional probabilities and  
 540 overall frequencies of escalation scenarios when considering also primary scenarios  
 541 induced by Natech events, as in the case of earthquakes and floods affecting a chemical or  
 542 process facility. The method developed provides some key figures needed to develop a  
 543 comprehensive Quantitative Risk Assessment (QRA) procedure accounting for Natech  
 544 events and for the possible domino effects triggered by such scenarios, also considering the  
 545 action of safety barriers and their degradation during Natech events. As shown in Figure 3,  
 546 both the high expected frequency of Natech primary scenarios in areas exposed to natural  
 547 hazards [29] and the critical degradation of barrier availability and effectiveness during  
 548 Natech events [49] were proven to lead to frequencies of both mitigated and unmitigated  
 549 escalation scenarios that may be orders of magnitude higher than those corresponding to  
 550 escalation scenarios from conventional internal failures.

551 Even if by no way the numerical results of the case-study should be generalized, since the  
552 expected frequency of natural events and of Natech accidents may change dramatically  
553 depending on the geographical location of the site and on its exposure to natural hazards,  
554 still the significance of the escalation scenarios induced by primary Natech is clearly shown  
555 by the results obtained.

556 It should also be noted that, despite the case-study illustrated addresses the context of  
557 chemical and process industry, the safety barrier conceptualization is employed in a variety  
558 of industrial sectors [63,89,90]. Thus, the approach proposed can be applied to a broad  
559 number of industrial systems, also considering that several activities beside those of the  
560 chemical and process industry involve the bulk storage and processing of relevant  
561 quantities of hazardous substances: Oil & Gas, mining, industrial ports, nuclear, etc. For  
562 instance, in the in nuclear industry, where there is a clear evidence of the potential severity  
563 of accidents caused by natural events [91], system safety is traditionally based on the  
564 defence-in-depth concept [92–94]. Several studies aim at a more robust safety assessment  
565 of these installations, also widening and consolidating the use of probabilistic safety  
566 assessment (PSA) in this framework [95,96], and specific solutions are proposed to  
567 improve the resilience of these installations to natural events (e.g. see [97]). The specific  
568 approach proposed in the present framework is suitable for application within a “defence  
569 in depth” approach, and may contribute to provide a more realistic assessment of the  
570 performance of the protection layers when affected by natural events as floods and  
571 earthquakes. Indeed, being PSA a reportedly important mean for improving the  
572 understanding of system vulnerabilities, as well as a pivotal tool to enhance defence-in-  
573 depth principle implementation [91,98], the inclusion within the PSA framework of explicit  
574 performance modification of layers of defence during natural hazard might drive better  
575 risk-informed decision-making for accident prevention and mitigation.

576 A further remark concerns the potential importance of the approach in the framework of  
577 Safety Integrity Level (SIL) Assessment [99,100]. The use of SIL Assessment to determine  
578 and verify the safety performance of safety barriers and protection systems, with particular  
579 reference to safety instrumented systems, is a common practice in several industrial sectors,  
580 such as the Oil&Gas, chemical, nuclear and space industry [101]. The quantitative approach  
581 developed in the present study may be easily complemented with the performance  
582 assessment of Safety Instrumented Functions (as several active barriers may be  
583 considered), which is needed both in the SIL determination phase based on LOPA



584 [99,101,102], and in the SIL verification phase [99,100-102]. Moreover, the outcomes of  
585 the present study may be implemented in specific studies dealing with the physical  
586 degradation of safety instrumented systems [103], thus supporting the performance analysis  
587 of depleted safety barriers.

588 As a final remark, it should be considered that the present study only addressed the expected  
589 frequency of escalation scenarios induced by Natech events. In perspective, also the  
590 severity of final escalation scenarios should be assessed, enabling the quantification of  
591 overall risk figure modifications due to the contribution of barrier degradation in Natech  
592 events.

593

## 594 **5. Conclusions**

595 A methodology to include the impact of natural hazards on safety barriers in the  
596 quantification of the probability and frequency of escalation scenarios caused by domino  
597 effect was developed. Specific performance modification factors were implemented and  
598 applied to domino effects triggered by Natech primary scenarios. The results highlight that  
599 the impact of natural hazard on safety barriers leads to a significant increase in the  
600 probability and frequency of unmitigated domino scenarios. As confirmed by the  
601 assessment of specific KPIs, safety barrier performance may be significantly depleted  
602 during Natech events. In addition, the approach developed may support risk-based decision  
603 making addressing the integration of safety barriers and of specific protections aimed at  
604 reducing the potential severity of Natech events. Indeed, the results of the case study show  
605 that the safety barriers addressing the prevention and mitigation of domino effect from  
606 conventional scenario may not be effective to prevent domino effect from Natech primary  
607 scenarios. The development of specific standards to assess the performance of safety  
608 barriers during the impact of natural events may contribute to a more effective control of  
609 risk due to Natech events and to enhance the resilience of chemical and process plants to  
610 the impact of natural hazards.

611

## 612 **Acknowledgments**

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615 involving the release of Hazardous Substances” funded by MIUR - Italian Ministry for  
 616 Scientific Research under the PRIN 2017.

617

## 618 **Appendix A**

619 This appendix shows the equipment vulnerability models for assessing conditional failure  
 620 probability  $P_{nhd}$  given the reference flood W1 and earthquake E1.

621

622 *Table A. 1: Vulnerability model for atmospheric tanks during floods [29], with description of relevant input parameters*  
 623 *and their assumed value for the application to the case study presented in Section 3.*

<b>Vulnerability model equations</b>		
<b>Variable</b>	<b>Definition</b>	<b>Equation</b>
$CFL$	Critical Filling Level	$CFL = \left( \frac{\rho_w k_w}{2} v_w^2 + \rho_w g h_w - P_{cr} \right) / \rho_f g H$
$P_{cr}$	Vessel critical pressure evaluated with the proposed simplified correlation	$P_{cr} = J_1 C + J_2$ in which $J_1 = -0.199$ $J_2 = 6950$
$P_{nhd}$	Vessel vulnerability due to flooding	$P_{nhd} = \frac{CFL - \phi_{min}}{\phi_{max} - \phi_{min}}$
<b>Input parameters</b>		
<b>Item</b>	<b>Definition</b>	<b>Value adopted in Section 3</b>
$C$	Vessel capacity	5000 m <sup>3</sup>
$v_w$	Flood water speed	0.5 m/s
$h_w$	Flood water depth	2.0 m
$\rho_w$	Flood water density	1100 kg/m <sup>3</sup>
$\rho_f$	Stored liquid density	800 kg/m <sup>3</sup>
$k_w$	Hydrodynamic coefficient	1.8
$H$	Vessel height	10.8 m
$g$	Gravity acceleration	9.81 m/s <sup>2</sup>
$\phi_{min}$	Minimum operative filling level	0.01
$\phi_{max}$	Maximum operative filling level	0.75

624

625 For the case of flood W1, the vulnerability model for atmospheric storage tanks developed  
 626 by Landucci et al. [29] is adopted. The model is based on the evaluation of the mechanical  
 627 integrity of the containment under the action of floodwater. In particular, the resulting force  
 628 excerpted by the flood on the item are composed by a static component due to water depth  
 629 and a dynamic component linked to water kinetic energy. The vulnerability of the vessel  
 630 can be determined as function of the liquid level below which the failure due to instability  
 631 may happen. This parameter is named critical filling level ( $CFL$ ) and can be estimated  
 632 together with the vessel  $P_{nhd}$  through the simplified correlation proposed in Table A. 1,  
 633 together with relevant input parameters and their assumed value in this study.

634 For the case of earthquake E1, the vulnerability model for atmospheric storage tanks  
 635 developed by Salzano et al. [36] is adopted. Fragility models are developed for different  
 636 severities in terms of LOC, defined as risk states (RS). In this work, the model for RS=3,  
 637 that is, the most severe release scenario corresponding to a release of the entire inventory  
 638 in less than 10 min is conservatively applied. Moreover, the tank T1 is conservatively  
 639 assumed unanchored, as said in Section 3. The model can be summarized in the form  
 640 reported in Table A. 2.

641 *Table A. 2: Vulnerability model for atmospheric storage tanks during earthquakes adopted in the present study [36].*

<b>Vulnerability model equations</b>		
<b>Variable</b>	<b>Definition</b>	<b>Equation</b>
$P_{nhd}$	Vessel vulnerability to earthquake	$P_{nhd} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y(PGA)-5} \left( \exp \left[ -\frac{u^2}{2} \right] \right) du$
$Y(PGA)$	Probit variable as function of PGA [m/s <sup>2</sup> ] (Unanchored, RS=3)	$Y(PGA) = -0.83 + 1.25 \cdot \ln (10^2 \cdot PGA/g)$
<b>Input parameters</b>		
<b>Item</b>	<b>Definition</b>	<b>Value adopted in Section 3</b>
$PGA$	Horizontal Peak Ground Acceleration	4.9 m/s <sup>2</sup> (0.5g)

642

## 643 **Appendix B**

644 This appendix is intended to provide further details on the calculation of  $PF D$  and of  
 645 effectiveness,  $\eta$ , for the characterization of emergency interventions.

646 The  $PF D$  can be assessed equal to  $1.0 \times 10^{-1}$ , which corresponds to the probability associated  
 647 with human error according to LOPA literature [50] and to recent studies addressing ETA  
 648 for domino escalation [52–54]. The evaluation of the effectiveness,  $\eta$ , may be performed  
 649 according to the comparison between  $TTF$  and  $TFM$  at site, as proposed in Landucci et al.  
 650 [54]. In case the  $TTF$  is lower than  $TFM$ , the emergency intervention should be associated  
 651 to  $\eta = 0$ ; on the contrary, in case the  $TFM$  is lower than  $TTF$  (i.e., in case of accident  
 652 mitigation is achieved before target equipment failure due to fire), emergency intervention  
 653 will be effective, and thus  $\eta = 1$ .

654 The value of time scale for accident mitigation is site specific, and a preliminary estimate  
 655 of  $TFM$  is required to assess  $\eta$ . A simplified methodology based on fire mitigation strategy  
 656 and the relative amount of water rate required for mitigation is applied in this study [52],  
 657 leading to the calculation  $TFM$  values of 65 and 90 min respectively for P1 and T2.  
 658 Nevertheless, the methodology was not developed considering the possibility that the

659 emergency intervention is hindered by the possible unfavourable environment resulting  
 660 from the impact of the natural hazard. Thus, the above reported results should be considered  
 661 as baseline best-case values.

662 In order to perform a preliminary evaluation of the possible delay on emergency  
 663 intervention, an approach originally proposed for assessing *TFM* in harsh environment has  
 664 been adopted [82]. The modified *TFM* for onshore sites may be calculated according to the  
 665 following relation:

$$666 \quad TFM = \sum_{j=1}^5 \tau_j \quad (B.1)$$

667 where  $\tau_j$  are characteristic times required to perform the main operations that are required  
 668 by emergency response.

669 *Table B. 1: Characteristic times to perform main emergency response operations in onshore sites as function of Harsh*  
 670 *Environment Score (HES). Adapted from [82].*

Time	Operation	Correlation	Max $\tau_i$ [min] (HES=1)
$\tau_1$	Time to alert: maximum time required to start the emergency operation, which is usually composed to 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
$\tau_2$	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
$\tau_3$	Time needed by external emergency teams to deploy firefighting equipment	$\log_{10}(\tau_3) = -0.301 \times (1 - HES) + 1.146$	14
$\tau_4$	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
$\tau_5$	Additional time required in case one of more water transport system 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

671

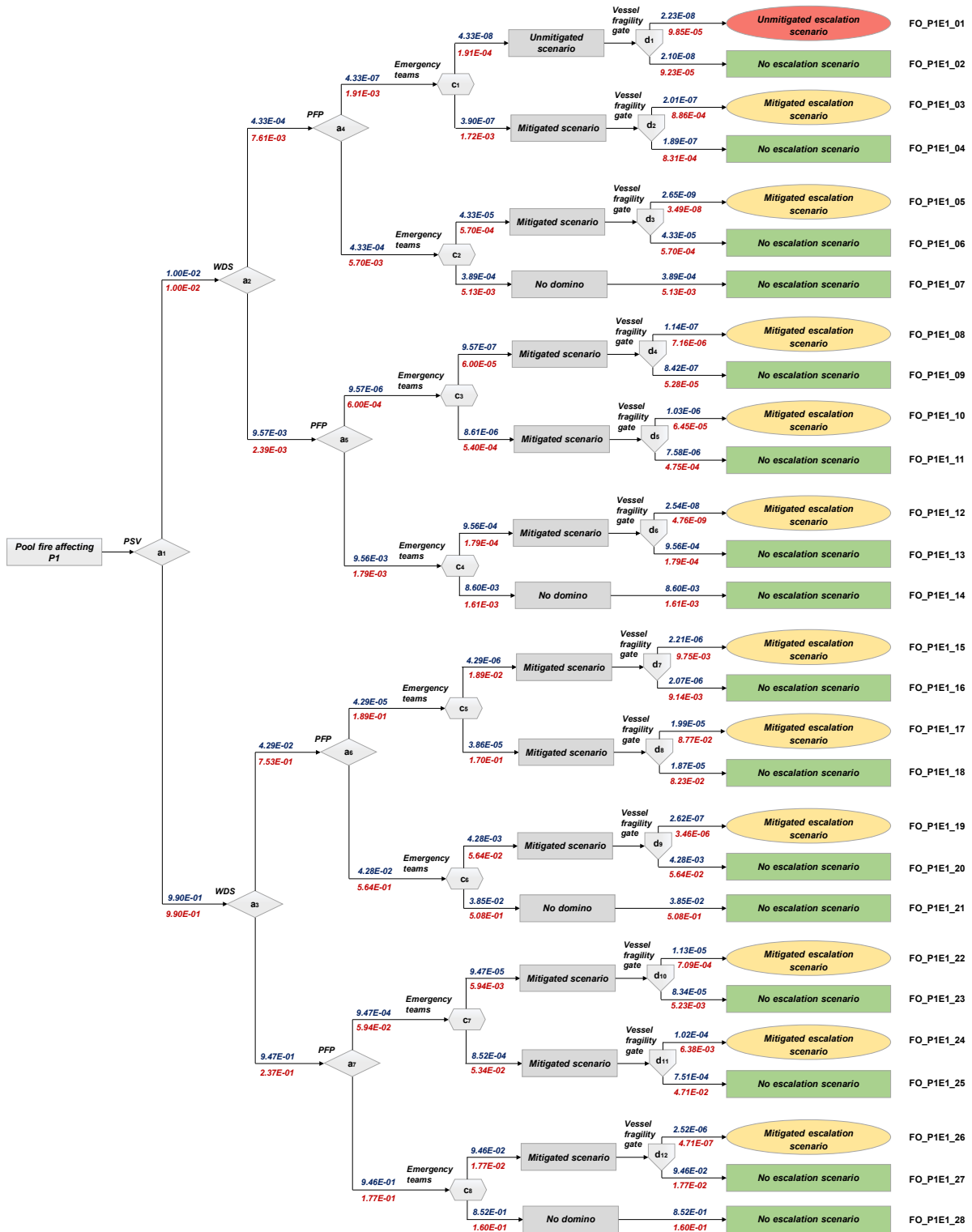
672 The values of  $\tau_j$  can be evaluated through correlations dependent on the Harsh Environment  
 673 Score (HES), a parameter between 0 and 1 expressing the harshness of environmental  
 674 conditions (0: normal conditions; 1: extremely harsh conditions). Conservatively, in the  
 675 present study, a value of HES equal to 1 was assumed, as a worst-case scenario. Description  
 676 of each operation considered, together with the correlation for estimating the characteristic  
 677 times for onshore sites, and the resulting value assumed in this study are presented in Table  
 678 B.1. With respect to the case-study considered, the worst-case value for *TFM* is assessed to  
 679 be equal to 400 min for both P1 and T2.

680

681 **Appendix C**

682 In the following, the event trees developed to analyse the case study are reported. In order  
683 to allow a better comparison of barrier performance, regardless the initial frequency of the  
684 primary scenario, a unitary frequency for primary event is assumed in Figures C.1 – C.4.  
685 The actual frequencies may thus be calculated multiplying by the actual initial frequency  
686 the numbers in the figures. As an example, the frequency of unmitigated escalation scenario  
687 from W1 involving P1 (coded as “FO\_P1W1\_01” in Figure C.1) considering barrier  
688 degradation, can be calculated as the product of  $3.13 \times 10^{-05}$  (uppermost outcome in red from  
689 gate d<sub>1</sub> in Figure C.1) by  $4.31 \times 10^{-04} \text{ y}^{-1}$  (frequency of pool fire from W1 according to Table  
690 4), resulting in  $1.35 \times 10^{-08} \text{ y}^{-1}$ .





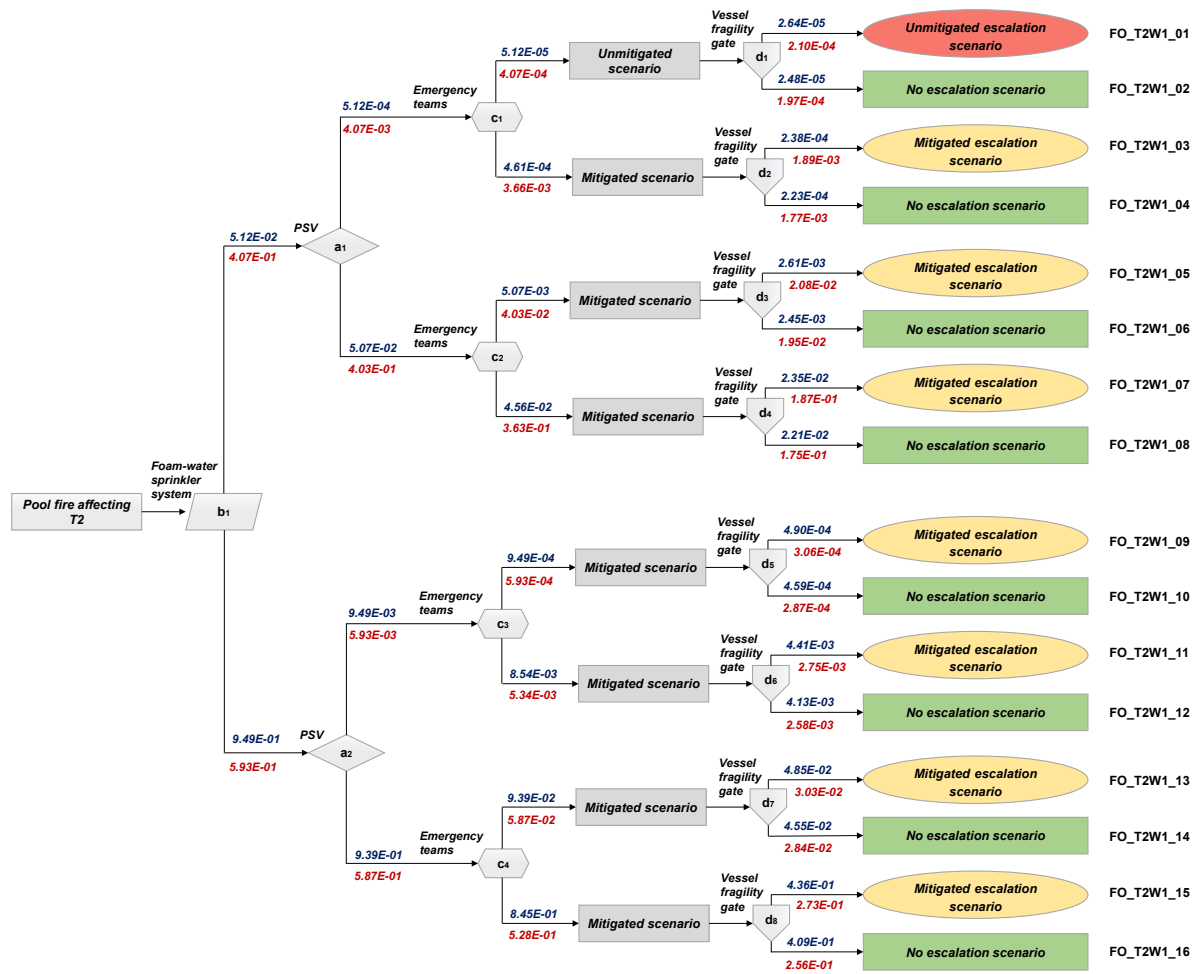
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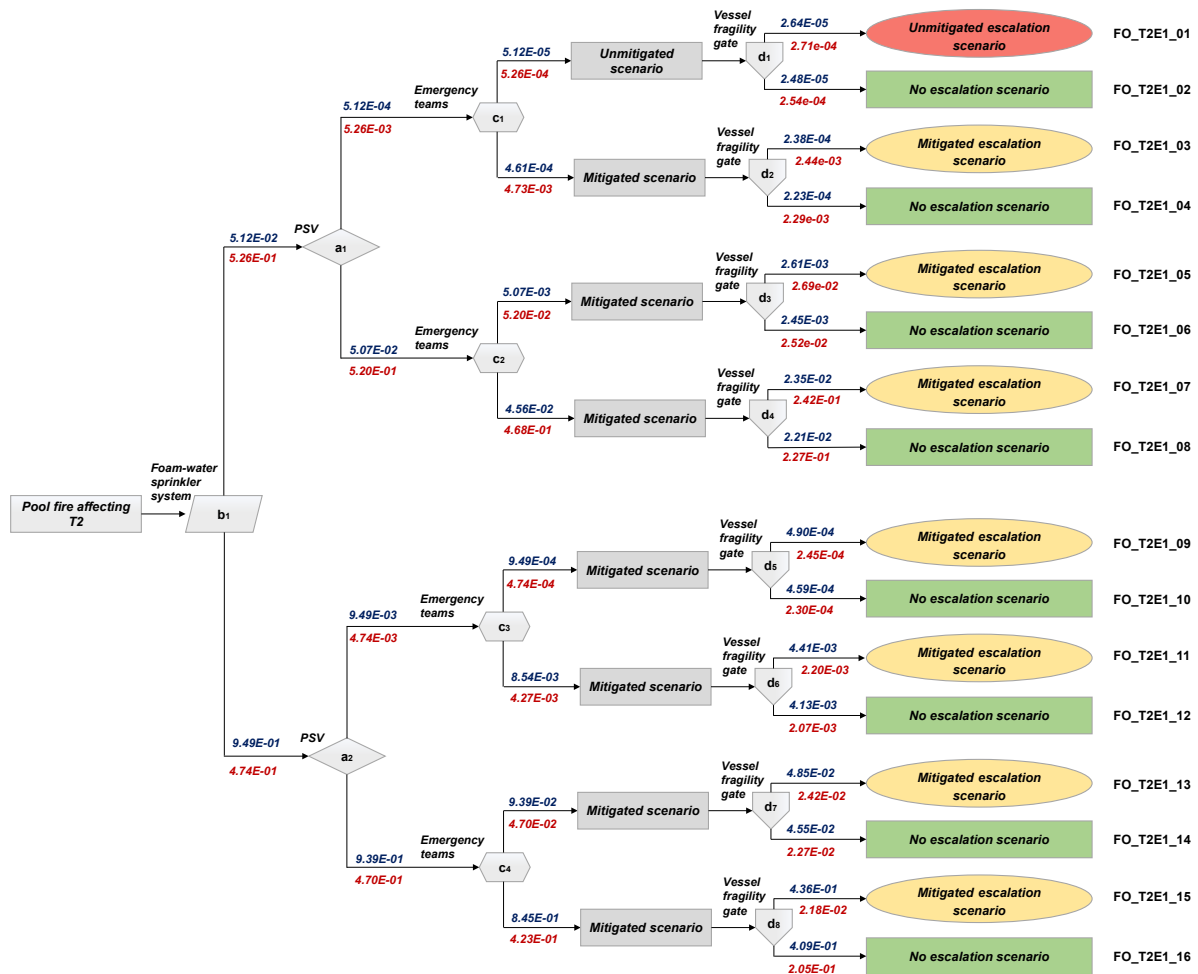
Figure C. 2: Event tree analysis carried out for pressurized vessel P1, in case of E1 earthquake conditions (PGA = 0.5g). The frequency of primary event is assumed unitary. Values in blue are calculated with original barrier performances, while values in red are obtained considering performance degradation.



700

701 Figure C. 3: Event tree analysis carried out for atmospheric tank T2, in case of W1 flooding conditions ( $h_w =$   
 702  $2.0\text{m}$ ,  $v_w = 0.5 \frac{\text{m}}{\text{s}}$ ). The frequency of primary event is assumed unitary. Values in blue are calculated with original  
 703 barrier performances, while values in red are obtained considering performance degradation.





705

706 Figure C. 4: Event tree analysis carried out for atmospheric tank T2, in case of E1 earthquake conditions (PGA=0.5g).  
 707 The frequency of primary event is assumed unitary. Values in blue are calculated with original barrier performances,  
 708 while values in red are obtained considering performance degradation.

709

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