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Assessment of risk modification due to safety barrier performance degradation in Natech events

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10 Abstract

11 Natural hazards may cause severe technological accidents involving hazardous substances (Natech accidents). 12 Along with process equipment also safety critical elements as safety barriers might be impacted by such events, 13 thus reducing the protection provided and the possibility to prevent escalation and cascading effects. In the present study a comprehensive methodology is developed to address the quantitative assessment of the risk 14 15 caused by the escalation of Natech accidents, specifically addressing the effect of the performance modification of safety barriers caused by the impact of the natural hazard. Barrier performance depletion is modelled through 16 17 an innovative multi-level approach, and it is then introduced in the quantitative risk assessment procedure by a 18 modified event tree analysis. A demonstrative application of the proposed methodology to a case study is 19 provided, showing a relevant increase in risk figures deriving from the degradation of safety barrier performance 20 caused by natural events. The proposed framework extends the systemic assessment of Natech scenarios to 21 encompass the specific criticalities introduced by safety barrier performance modification induced by natural 22 events, providing a more effective support to decision-making in the management and control of risk deriving 23 from the interaction of natural hazards with technological installations.

24

25 Keywords

- 26 Natech; domino effect; escalation; safety barriers; quantitative risk assessment.
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- 29

30 List of acronyms

31	EBD	Emergency Blowdown
32	EEI	External Emergency Intervention
33	ESD	Emergency Shutdown
34	ETA	Event Tree Analysis
35	EV	Expectation Value
36	FTA	Fault Tree Analysis
37	FWS	Foam-water system
38	LOC	Loss of Containment
39	LOPA	Layer of Protection Analysis
40	LSIR	Local Specific Individual Risk
41	MCS	Minimal Cut Set
42	PFD	Probability of Failure on Demand
43	PFP	Passive Fire Protection
44	PHM	Proportional Hazard Model
45	PLL	Potential Life Loss
46	PSA	Probabilistic Safety Analysis
47	PSV	Pressure Safety Valve
48	QRA	Quantitative Risk Assessment
49	SEP	Surface Emissive Power
50	WDS	Water Deluge System
51		
52		

53 **1. Introduction**

54 Managing the risk posed by technological accidents following of the impact of natural hazards on critical infrastructures has become a primary concern in the last decade, also due to the effect on climate change on the 55 time of return of climate-related natural disasters [1]. The cascading events in which a sequence of technological 56 57 scenarios involving the release of hazardous substances are triggered by the impact of a natural event as an earthquake or a flood are defined as Natech events [1], and may take place in any industrial facility where 58 59 relevant quantities of chemicals are stored or processed, e.g. in the chemical and process sector, in oil&gas 60 facilities and in other activities in the energy sector [2,3]. Indeed, recent natural disasters remarked the criticality 61 of Natech accidents, highlighting both the vulnerability of technological installations to such events, and the potential severity of such scenarios [4]. For instance, the Tohoku earthquake and tsunami (2011) led to several 62 63 Natech accidents involving chemical and petrochemical companies and to the tragic nuclear disaster at the 64 Fukushima Dai-ichi nuclear power plant [5-7]. Also during Hurricane Harvey (2017) many industrial 65 installations experienced damages that caused the release of hazardous substances, with severe consequences exacerbating the already critical damages brought by the tropical storm [8,9]. Many other examples of past 66 accidents are available in the literature (see for instance [10,11]), demonstrating that Natech scenarios are 67 68 complex and often involve the escalation of the primary technological scenarios. Past accidents also evidence that safety barriers in place for accident prevention and mitigation might be impacted as well. For instance, in 69 70 several accidents safety systems dependent on lifelines (e.g. electric power) or auxiliary systems (e.g. 71 compressed air, cooling water) have recurrently failed [9,12]. The structural damages and loss of integrity of 72 physical barriers, such as catch basins and dikes (e.g., due to ground shaking during earthquakes, or water load 73 during floods) is also documented [1,11].

74 Including these aspects in the assessment of Natech risk is not an easy task since not all the safety barriers may

be degraded to the same extent and specific factors should be evaluated (e.g., barrier features, details on system

architecture, etc.). Furthermore, the characteristics of the natural hazard itself might be critical in determining

77 whether and to what extent these systems may be affected [13]. Whereas barrier performance depletion has been

78 linked to a clear enhancement in the likelihood of accident escalation following primary technological scenarios 79 in Natech events [14], to date no methodologies are available to quantify to what extent this performance shift impacts on risk figures. With the purpose of filling this gap, the present study proposes a comprehensive 80 81 approach for the risk assessment of Natech accidents, integrating the quantitative assessment of the escalation 82 from primary technological scenarios with a novel multi-level barrier assessment methodology. With respect to previous studies based on modification factors retrieved for generic barrier schemes [13], the multi-level 83 84 approach proposed provides a significant advancement, allowing the assessment of barrier performance also 85 considering system complexity into the analysis. Indeed, on the one hand, coarser approaches are suggested for 86 the analysis of simpler systems. On the other hand, the application of more refined and information-intensive methods is proposed for more complex barriers, enabling the evaluation of case-specificities not accountable 87 with generic barrier performance modification factors. 88

A concise state of the art is outlined in Section 2, evidencing the need to modify the current quantitative approaches for Natech quantitative assessment shifting the attention towards the role of safety barriers. The proposed methodology is presented in Section 3, with a specific focus on the steps aimed at safety barrier performance assessment. Then, in order to demonstrate methodology application and to provide an example of how risk figures related the escalation of primary scenarios in Natech events are modified considering updated barrier performance, a case study is defined in Section 4. Results and discussion are presented in Section 5, while Section 6 summarizes the main conclusions of the study.

96 2. State of the art

97 The quantitative assessment of the risk associated with Natech scenarios is a critical task. Most of the 98 methodologies for Natech assessment proposed in the literature have been developed modifying conventional 99 quantitative risk assessment (ORA) procedures to consider the possible multiple simultaneous releases that my be present in Natech events [15–17]. These methodologies allow the assessment of the risk related to primary 100 101 technological scenarios from the release of hazardous substances triggered by equipment damage following the impact of reference natural events [18,19]. In the context of QRA, the equipment damage characterization, along 102 103 with the quantification of the related probability, is performed applying simplified equipment vulnerability 104 models which are available in the literature for a variety of natural hazards, such as earthquake [20–22], wind 105 [23,24], flood [25–27], storm surge [28–30] and lightning strike [31,32]. Whereas the main body of research on 106 Natech quantitative assessment methodologies is focused on these consolidated approaches derived from QRA, 107 some recent publications investigated also the possibility of application of advanced tools for the frequency 108 assessment of Natech scenarios. A relevant example of such research trend is the recent application of Bayesian 109 networks to assess equipment vulnerability to floods [33,34] and to determine wildfire propagation in wildland-110 industrial interfaces, possibly leading to Natech accidents [35].

111 Most of the available methodologies do not consider the escalation of the primary technological events in Natech scenarios, and domino effect is seldom considered. Indeed, although some methodologies have been proposed 112 to assess domino effects in conventional technological scenarios [36,37], both based on the extensions of QRA 113 114 approaches [38–40] and on specific techniques as Bayesian networks [41–44], the possibility of escalation 115 following primary technological scenarios in Natech events was considered only for specific natural hazards 116 and/or for specific scenarios [45-47]. Moreover, to the knowledge of the authors, even in the few works 117 addressing the assessment of domino effect in Natech events, the influence of safety barrier performance 118 modification on overall risk figures was not specifically investigated to date [48], whereas it has been recently 119 evidenced that the specific conditions occurring during natural events may impair or decrease their level of 120 protection [13].

Whereas a number of studies focused on the role of safety systems and safety barriers, both addressing the general framework related to the integrity and protection of complex systems (e.g. see [49]), and the specific

- 123 context of domino effect assessment [50–52], only few recent studies explored the issue of barrier performance
- assessment during or after the impact of natural events [13,14]. Indeed, despite it was demonstrated that the
- 125 likelihood of escalation due to domino effect is significantly higher than expected when accounting for barrier
- 126 degradation in Natech events [14], no specific method is available to date to consider the influence of such
 - 127 phenomenon from a risk assessment perspective.

128 **3. Methodology**

- 129 *3.1 Quantitative assessment of Natech risk*
- In order to fill the gap evidenced in the analysis of the state of the art, a methodology was developed to assess
 the risk due to escalation triggered by domino effect in Natech scenarios, considering the role of safety barriers
 and their possible degradation. An overview of the method is provided in Figure 1.
- 133 As usual, in all the procedures aiming at the quantitative assessment of Natech risk, the starting point of the 134 methodology is the definition and characterization of a reference set of natural hazards that will be considered 135 in the analysis (Step 1 in Figure 1). Specific indications on the approaches to the quantitative characterization 136 of natural hazards in terms of parameters expressing the frequency and the intensity of the events, with a degree of detail suitable for the assessment of Natech events, are available in the literature [19,53,54]. For instance, 137 floods may be characterized in terms of time of return (linked to the frequency of occurrence) and floodwater 138 depth and velocity [17,25,26]. Clearly enough, this step is not intended to provide a detailed characterization of 139 140 natural hazards, but rather to have a concise expression of complex natural phenomena through a limited set of 141 parameters, which is suitable for the framework of QRA [16]. A comprehensive discussion of how the reference 142 events may be identified, on how the time of return of these events may be determined and on the related 143 uncertainty is clearly out of scope of the present paper. Among the established methodologies available to 144 accomplish this task, it is worth to mention the Probabilistic Seismic Hazard Analysis for earthquakes [55] or 145 the use of hazard maps developed from data on past events for the case of floods [56]. Appropriate 146 methodologies need to be selected with the contribution of sectorial experts, also considering the level of detail 147 and the uncertainty compatible with the aims of the analysis. As an example, for the case of flood the accuracy of the estimates of scenario return time might be influenced by several factors as the amount of available data 148 149 (and their related accuracy), the possible effects of climate change or modifications of river drainage area [57].



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

The impact of the natural hazard on equipment items that may lead to the release of hazardous materials and, consequently, to primary technological scenarios is then assessed. Reference equipment items that may lead to a Loss of Containment (LOC) generating primary technological scenarios are identified (Step 2 in Figure 1). Specific criteria developed for the framework of Natech risk assessment for the identification and ranking of equipment to be considered, based on hazardous material inventory, substance features and storage conditions might be adopted (e.g., see [15,58]).

160 The frequency of primary LOC events $f_{I,LOC}$ can be assessed as follows [14]:

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

where f_{nh} is the frequency of the reference natural hazard and P_{nhd} is the conditional probability of equipment failure, estimated applying equipment vulnerability models, as briefly mentioned in Section 2. Equipment vulnerability models are simplified empirical models allowing the assessment of the failure probability of an equipment item given the intensity of the natural event impacting on it [16]. A concise list of reference models has been collected in Section 2, while a more detailed example, applied in the case-study, is reported in theSupplementary Material.

167 The primary technological scenarios following the LOC event then are characterized in terms of frequency (f_P) 168 and consequences by the application of specific event trees, conceptually analogous to those obtained in the 169 conventional assessment of technological scenarios following a release [15,18]. For instance, in the case of 170 floods, water-reacting substances might give rise to specific scenarios after the release, which were object of 171 previous studies [58].

172 The identification of further equipment items that may be the possible secondary targets of domino effects generated by the primary scenarios (Step 3 in Figure 1) is then performed by means of well-established 173 174 threshold-based screening methodologies applied to the escalation vectors generated by the primary 175 technological scenarios [59-61]. It should be remarked that past accident analysis evidenced that most Natech 176 events reported in the literature and in industrial accident databases involved the release of flammable chemicals 177 [12,58,62], which may lead to domino effect due to fire escalation in case of ignition. Thus, in the following, 178 the methodology was focused on domino effects generated by the escalation of fire scenarios. Nevertheless, the methodology may be applied as well to other escalation vectors, when relevant (e.g., fragment projection or 179 180 blast waves).

A thorough assessment of the effect of safety barriers on the likelihood of escalation considering the impact of the natural event on these measures is then required (Steps 4-5 in Figure 1). A multi-level quantitative methodology specifically addressing the Natech framework is developed to consider the presence and performance of safety barriers in the assessment of escalation likelihood. Considering barrier complexity and uncertainties related to the intensity and impact of natural hazards, three levels of assessment are conceptualized, as shown in Figure 1 (Steps 5a to 5c). The approach proposed will be described in detail in Section 3.2.

Probabilistic assessment of domino event frequencies can then be performed (Step 6 in Figure 1). The probability of escalation of stationary fires is evaluated by means of probit models based on the time to failure (*ttf*) of target vessels when impacted by the heat load [16,37,63]. Probabilities and frequencies of the final events are then assessed applying a dedicated event tree (ETA) methodology, which was specifically developed in earlier studies to include safety barriers in the modelling of escalation [40,64,65]. The model allows for the characterization of both unmitigated and mitigated secondary scenarios, based on barrier performance. Further details on fire escalation models and ETA methodology are reported in the Supplementary Material.

The following step of the methodology is the consequence assessment of the secondary domino scenarios (Step 7 in Figure 1), which is carried out adopting literature models [66–68]. In order to obtain a less conservative description of the secondary scenarios, the consequences of mitigated events are modelled considering the mitigation action of the safety barriers, as described in detail in the Supplementary Material.

The final steps of the methodology (Steps 8-10 in Figure 1) involve the characterization of the overall domino scenarios and are described in Section 3.3. The analysis can be extended to the identification and assessment of tertiary events and/or higher level events. In case, the procedure is applied recursively and the selection of possible tertiary/higher level targets possibly affected by escalation needs to be carried out [16,40]. Risk index calculation may be carried out (Step 11 in Figure 1) using the standardized procedures reported in Section 3.4.

203 3.2 Quantitative assessment of safety barrier performance modification in Natech scenarios

The concept of safety barriers is extensively used in the chemical and process industry referring to physical and non-physical means implemented to reduce the possibility of technological accidents or to lessen their impact

206 [69-71]. A well-established classification of safety barriers, particularly suitable within the framework of QRA,

207 is based on barrier working principle and is summarized in Table 1 [64,70,72,73].

208 Table 1: Summary of barrier classification based on working principle [73], applied in the present study.

Classification	Description	Examples				
Passive barriers	All the physical protections available in the	Fireproofing, catch basins, pressure safety				
	plant, which do not require any activation to	valves (PSV), sumps, mounds, firewalls, blast				
	perform their function	walls				
Active barriers	Complex systems requiring external	Foam-water systems (FWS), sprinklers, water				
	automatic and/or manual activation to	deluge systems (WDS), emergency shutdown				
	perform their function	(ESD), emergency blowdown (EBD)				
Procedural barriers	Emergency intervention procedures and	Internal/external emergency team intervention,				
	structured plans for managing and	fire brigade intervention, evacuation plans				
	controlling scenarios					

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210 Performance of safety barriers can be assessed through specific methodologies or retrieving generic data from reliability databases [74–76]. Moreover, methodologies are available in the literature to tailor failure frequencies 211 of equipment items and to include the effect of specificities and environmental factors on reliability figures [77– 212 213 79]. For instance, general failure frequencies may be revised through expert judgment in order to include the 214 effect of item location and other factor not accounted in database values [79]. Proportional hazard models 215 (PHM) have been applied to include the effect of explanatory variables (i.e., covariates) in modification of 216 equipment failure rate and reliability [77,80,81]. More recently, covariate-based models have been applied to 217 evaluate the impact of harsh environment conditions on technical systems availability [78,82]. However, none 218 of these methodologies explicitly address the possibility of performance modification during Natech accidents 219 [83].

220 Therefore, a novel methodology for the assessment of safety barrier performance modification during Natech 221 accidents was developed. The methodology is based on the preliminary evaluation of baseline barrier 222 performance, not accounting for the influence of the natural hazards (Step 4 in Figure 1), through a tailored 223 LOPA approach developed in the context of domino escalation assessment [64,65]. Each safety barrier is 224 categorized according to Table 1. The performance of each barrier is then expressed through a two-parameter 225 metrics: i) the probability of failure on demand (*PFD*), that is the probability that the measure will not be 226 available when required to perform the safety function, and ii) the effectiveness (η), that is, the conditional 227 probability the barrier is able to prevent (or stop) domino escalation once successfully activated. The PFD is 228 linked to barrier system architecture and reliability, and may be determined by means of various reliability 229 approaches according to the available information on the system components, as extensively discussed 230 elsewhere [64,84]. On the other hand, η is the direct quantification of the quality of barrier mitigation or 231 preventive actions, hence it should be estimated considering performance data or statistics, together with other 232 influencing factors as maintenance, operational management and so forth [40,64,65].

233 Once the baseline probabilistic performance of safety barriers is estimated, barrier performance modification 234 due to the natural hazard considered is then assessed, according to a three-level methodology (i.e., Level 0, 235 Level 1, and Level 2 in Step 5 of Figure 1). Level 0 (L0) is based on a simplified evaluation suitable for simpler barrier systems (Step 5a indicated in green in Figure 1). Level 1 (L1) in the assessment is based on the data 236 obtained for reference schemes of safety barriers in previous studies [83] (Step 5b in Figure 1). Level 2 (L2) is 237 based on a detailed analysis of barrier architecture and subsystems, capable of accounting for site-specific 238 239 scenarios and special design provisions (Step 5c in Figure 1). The three levels of assessment are introduced to 240 address barrier systems with increasing level of complexity, thus require an increasing amount of information 241 to be applied. Clearly enough, the selection of the level of the analysis is related to the uncertainty on the possible 242 interaction between the reference natural hazard and the specific features of the barrier under consideration, as 243 explained in the following.

- 244 The basic barrier performance modification assessment level, L0, is adequate when a low uncertainty is present 245 concerning the definition and quantification of the impact of natural hazards on the barrier. This level is 246 conceptually similar to the application of a single-covariate PHM [78,80] and can be regarded as a Boolean approach. In this case the covariate is a feature of the barrier (e.g., the position), identifiable by means of rules-247 of-thumb or basic evaluations, which justify with confidence whether the barrier should be considered affected 248 249 or not by the natural hazard considered. In case the k-th barrier is considered unaffected, it will retain the baseline 250 performance values *PFD*_{0,k} and $\eta_{0,k}$ while in case the covariate indicates the system would be clearly impacted, 251 the k-th barrier should be considered unavailable. In the two-parameter metrics, this is equivalent to setting 252 *PFD*_{*i,k*} = 1 for active systems and $\eta_{i,k} = 0$ for passive protections.
- 253 Level L1 assessment is required where some uncertainty concerning barrier performance is present. This level 254 is an application of the PHM to the two-parameter metrics and is suitable for a wide class of barriers, from 255 passive barriers to the simpler active systems. Modified barrier performance is described by means of a covariate, namely a performance modification factor (ϕ) , representing the likelihood that similar reference 256 257 barriers would fail directly due to the natural event, as proposed in a previous study [83]. It is assumed that the 258 failure mode of active barriers is the lack of activation, leading to barrier unavailability: thus, an increase in the 259 PFD should be considered for this type of barriers. In case of passive barriers, the effectiveness η may be reduced 260 by the impact of the natural event, due to the possible loss of structural integrity of the barrier or to other causes 261 (e.g. in case of flood, catch basins will not be effective in the retention of spills).
- Hence, in the case of an active barrier, performance parameters are modified according to Eqs. (2) and (3) [82]:

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

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

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

266 In the case of a passive barrier, a different modification of performance parameters is introduced:

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

- where $\phi_{j,k} \in [0,1]$ is the performance modification factor for *j*-th reference natural hazard scenario, and $\eta_{0,k}$ is the baseline effectiveness value, determined in Step 4 of the methodology of Figure 1.
- Suggested value for performance modification factors, obtained by an expert survey, are available in the literature [13].

271 The L2 level assessment is required when complex active barrier systems are considered, where the actual 272 consequences of the impact of the reference natural hazard are affected by a high uncertainty. The assessment 273 may also be applied to barriers where the specific system architecture may differ from that of reference configurations, and performance modification factors may not be applicable with confidence. This level of 274 275 analysis is based on a fault tree analysis (FTA) focused on the possible failure of subsystems due to the impact of the natural hazard. Indeed, after the construction of the fault tree considering barrier architecture, the minimal 276 277 cut sets (MCSs) are identified and basic events are screened to explicitly identify which might be influenced by 278 the impact of the natural hazard. The analysis should be performed, considering detailed information on barrier 279 subsystems, including position, fail-safe design, dependence on lifelines, and redundancies. After vulnerable barrier subsystems are identified, the probabilities of the related basic events in the fault tree are updated to 280 281 unitary values (i.e., indicating expected subsystem failure during the reference natural scenario). Therefore, 282 considering the *m*-th MCS of the *k*-th barrier, its updated probability during the *j*-th reference natural scenario 283 $Q_i(MCS_{m,k})$ can be assessed through Eq. (5):

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

where $q_{p,0}$ is the probability of the *p*-th basic event comprised in the *m*-th MCS, and the parameter $\delta_{p,j}$ is equal to 1 in case the *p*-th basic event involves one of the vulnerable barrier subsystems identified (for the *j*-th reference natural scenario), and 0 if not. Conservatively, the updated PFD of the *k*-th barrier, *PFD_{j,k}*, can then be recalculated (as an upper bound) according to Eq. (6):

$$PFD_{j,k} = 1 - \prod_{m} (1 - Q_j(MCS_{m,k}))$$
(6)

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

The application of each of the three levels of barrier assessment will be exemplified in the analysis of the case study, providing further details on the assessment procedure (see Section 5.1 and Appendix A).

Due to the high site-specificity of procedure and emergency response actions, no generalised methodology was developed for the assessment of procedural barriers. A case-by-case assessment is recommended, analysing and assessing how the natural hazard may influence each key procedural step. In the analysis of the case study, a simplified approach is proposed to address the possible failure or delay of first response actions by emergency teams [64,65].

The modified barrier performance parameters obtained by the highest level of assessment, L2, should then be implemented in ETA through specific logical operators [64,65]. These operators are represented as gates on the event trees addressing accident escalation, and influence how each of the barriers contributes to the modification of the probabilities and frequencies of the final domino events. Details on logical operators and on their implementation in ETA are reported in the Supplementary Material.

303 3.3 Characterization of overall domino scenarios

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- According to the ETA defined in barrier performance analysis (e.g., see Section 5), each target equipment can show one out of three possible final events, in agreement with the approach described in [14,40]:
 - State "2": unmitigated secondary domino scenarios, in case all the protection barriers implemented have failed and is clearly a worst-case being the outcome with the most severe consequences;
 - State "1": mitigated secondary domino scenarios, that is, intermediate situations occurring when part of the safety barrier implemented fails in stopping escalation, leading to scenarios with potentially reduced consequences due to partial activation or reduced effectiveness of safety barriers in the accident sequence
- State "0": no domino scenarios, in which the escalation is interrupted due to activation and effective response of the safety barriers.
- The peculiarity of mitigated scenarios is that their consequences might be less severe than unmitigated scenarios, and this feature should be considered for a more accurate risk evaluation. A detailed characterization of mitigated secondary domino scenarios proposed in a previous study [40] might be adopted to account for the specificities of the type of target, the barriers considered and the emergency strategy pursued (see the Supplementary Material for further details). The proposed approach is exemplified in the case-study application (see Section 5.2).
- 320 Once the complete set of the secondary escalation scenarios is characterized, frequency assessment and 321 consequence evaluation of overall domino scenarios can be performed (Steps 8-10 in Figure 1). Considering

the escalation logic with *m* possible states for each of the *n* secondary domino targets, the number of different secondary domino scenarios from a primary Natech scenario (N_c) can be determined as follows:

$$N_c = \prod_{i=1}^n m_i \tag{7}$$

where m_i is the number of possible outcomes for the *i*-th secondary target, assuming that all the targets have three possible escalation states, $N_c = 3^n$. The probability of overall final domino scenarios can thus be assessed assuming that a specific secondary outcome for a given target is independent from that of the other target units, as it is assumed in previous studies addressing escalation due to domino effect [16,38].

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

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

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

The frequency of each generic C^n can then be calculated starting from the frequency of the primary Natech scenario generating the domino escalation f_P according to:

$$f(\mathbf{C}^n) = f_P \times P(\mathbf{C}^n) \tag{9}$$

In order to complete the characterization of overall domino scenarios, once the frequency assessment is performed, the consequence analysis and the calculation of risk indexes should be carried out (Steps 10 and 11 in Figure 1). Since no relevant difference is present with respect to conventional domino scenarios, the method proposed in [39] is applied to these steps. Details are provided in the Supplementary Material.

339 3.4 *Risk calculation and risk metrics*

Once overall domino scenarios are characterized, the calculation of overall risk level may be performed (Step 11 in Figure 1). Individual risk can be expressed by mapping local specific individual risk (LSIR) following standardized procedures, while societal risks can be expressed with F/N plots, being F is the cumulative frequency of scenarios causing N or more expected fatalities, which is calculated directly from the frequency fof scenarios causing N fatalities [67,68,85]. Two further risk indices were selected to provide an overall quantification of risk: the Potential Life Loss (PLL) and the Expectation Value (EV), which are calculated according to Eqs. (10) and (11) respectively:

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

$$EV = \sum_{N} f(N)N^{a} \text{ with } a = 2$$
(11)

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348 **4. Case study**

349 *4.1 Definition of case studies*

350 The equipment lay-out considered in the case study in shown in Figure 2. The layout includes nine atmospheric

storage tanks (T01-T09 in Figure 2), and four pressurized vessels (P01-P04 in Figure 2). The details of the equipment items are summarized in Table 1.



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

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

360	Table 2: Equipment items considered in the case study (see Figure 2 for layout representation; $D = Diameter$; $H = height$; $m_t = stored$
361	mass; $p_o = operating pressure$; $V_n = nominal volume$; $\rho_L = liquid density$; $\rho_V = vapour density$).

ID	D [m]	H [m]	V _n [m ³]	Substance	ρ _L [kg/m ³]	ρν [kg/m ³]	p₀ [bar]	m _t [t]
T01	30	7.2	5087	Gasoline	750	-	1.01	2860
T02	30	7.2	5087	Gasoline	750	-	1.01	2860
T03	30	7.2	5087	Gasoline	750	-	1.01	2860
T05	24	9	4069	H ₂ S (0.4% mol in H ₂ O)	1100	-	1.01	3360
T04	28	9	5539	Benzene	820	-	1.01	3410
T06	20	10.8	3391	NaCl (1% mol in H ₂ O)	1050	-	1.01	2670
T07	20	10.8	3391	NaCl (1% mol in H ₂ O)	1050	-	1.01	2670
T08	28	9	5539	Benzene	820	-	1.01	3410
T09	28	9	5539	Benzene	820	-	1.01	3410
P01	3.4	22	192	Propane	497	18.9	8.4	86.3
P02	3.4	22	192	Propane	497	18.9	8.4	86.3
P03	3.4	22	192	Propane	497	18.9	8.4	86.3
P04	3.2	22	170	Ammonia	600	4.9	8.5	91.9

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

In the specific case-study presented, it is assumed that tank T01, storing gasoline, is the only process unit damaged by the flood. The catastrophic failure of tank T01 starting a pool fire [58] is considered. The damage probability of the tank, $P_{nhd}(T01)$, calculated by the vulnerability model reported in the Supplementary Material,

- is estimated at 0.411. A conservative value of 0.9 is assumed as the ignition probability following the loss of containment (LOC), as suggested in the literature [17]. Hence, the resulting frequency of the primary Natech scenario is obtained as the product of $f_{I,LOC}$, calculated according to Eq. (1), and the assumed ignition probability, resulting in $f_P = 7.395 \times 10^{-4} \text{ y}^{-1}$.
- 374 To further simplify the interpretation of results, four cases were considered in the following:
- Case 1: only the primary Natech scenario described above is considered, to define a baseline risk associated to the impact of the flood on tank T01;
- Case 2: also the possible escalation scenarios due to domino effect are considered. Probability of
 escalation is calculated not considering the action of safety barriers. This case thus represents a
 reference worst-case scenario.
 - Case 3: as case 2, but probability of escalation is calculated considering the action of safety barriers. Baseline values are considered for barrier performance [40]. This case represents the best option for the expected performance of safety barriers, since the possible effects of the impact of the natural hazard on the safety barriers are neglected;
 - Case 4: as case 3, but barrier performance degradation due to the impact of the flood is considered by the methodology presented in Section 3.2.

Moreover, in order to compare the risk due to Natech scenarios triggered by flooding to the risk caused by "conventional" releases from tank T01, a baseline case was also defined (case 0). This case enables the assessment of a baseline "conventional" risk associated with tank T01, thus without considering the contribution of the Natech event. The analysis of case 0, based on consolidated guidelines for risk assessment [85], is documented in the Supplementary Material.

Consequence assessment was performed by means of well-established literature models for physical effect modelling [66–68]. For the sake of simplicity, a uniform wind distribution and a single set of meteorological conditions have been assumed. In particular, wind speed was assumed at 5 m/s, neutral atmospheric stability was considered (class D) [66,85]. Atmospheric temperature was assumed at 20°C and relative humidity at 70%. Clearly enough, different meteorological conditions may be considered in the assessment.

396 In order to model human vulnerability to the physical effects of accidents, literature vulnerability models (i.e., 397 probit and threshold-based) were applied, as detailed in the Supplementary Material. A fictitious uniform population density was assumed to obtain representative societal risk figures not affected by local-specific 398 399 effects. The population density value, equal to 200 people/ha² with 60% presence probability, was considered 400 constant over the entire impact area. For the sake of simplicity, no evacuation was considered and the population 401 was assumed to be affected only by the consequences of the technological scenarios. Risk calculation was 402 performed applying the methodology presented in [46,86]. Alternative approaches are obviously possible for 403 the calculation of the risk indexes considered [68].

- For the sake of brevity, only the probabilistic assessment of case 4 will be detailed thoroughly in the following, limiting the presentation of cases 1, 2 and 3 to the discussion of the results. The complete description of the procedure applied to the analysis of the latter cases is reported in the Supplementary Material.
- 407 *4.2 Domino effect assessment and safety barriers*

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- 408 In order to identify the possible targets for domino escalation, a threshold-based methodology was applied,
- 409 considering the heat radiation from the primary Natech accident as the possible escalation vector. The threshold
- 410 criteria selected to assess the credibility of escalation are 15 kW/m² for atmospheric equipment and 45 kW/m²
- 411 for pressurized tanks, as suggested in specific studies [60,61]. As shown in Table 3, four possible escalation

412 targets were identified: two atmospheric tanks (tanks T02 and T05 in Figure 2), and two pressurized vessels
413 (vessels P03 and P04 in Figure 2).

414 Table 3 also lists the safety barriers associated to each possible target. All the targets identified are equipped

415 with pressure safety valves (PSVs). Tanks T02 and T05 are equipped with foam-water systems (FWS), while

416 vessels P03 and P04 are protected by water deluge systems (WDS). The main assumptions considered for FWS

417 and WDS architectures are reported in Appendix A. As additional layer of protection, passive fire protection

418 (PFP) is also considered for vessels P03 and P04. Beside the technical barriers (both active and passive), external

419 emergency intervention (EEI) is always considered.

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

Target	Radiation from T01 [kW/m ²]	PSV	FWS	WDS	PFP	EEI
T02	43.3	Х	Х			Х
T05	26.5	Х	Х			Х
P03	57.5	Х		Х	Х	Х
P04	82.5	Х		Х	Х	Х

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423 **5. Results and Discussion**

424 5.1 Assessment of safety barriers performance in Natech events

The assessment of safety barrier performance is summarized in Table 4. For each barrier, the original performance values are reported (these are adopted in case 3), together with the classification according to Section 3.2. Barrier performance is modified according to one of the three levels of analysis, as indicated in the table.

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

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

Barrier	Classification	Gate ^a	<i>PFD</i> _ℓ	ηo	Level of Analysis ^c	PFD _f	ηf
PSV	Passive	а	1.00E-02	1.00	L0	1.00E-02	1.00
FWS	Active	b	5.42E-03	9.54E-01	L2	1.00	9.54E-01
WDS	Active	а	4.33E-02	1.00	L2	1.00	1.00
PFP	Passive	а	0	9.99E-01	L1	0	8.49E-01
EEI	Procedural	с	1.00E-01	0;1	n.a.	1.00E-01	0;1 ^b

434 ^aGates are defined in the Supplementary Material.

⁴³⁵ ^bBased on the comparison between time to failure and time to final mitigation, calculated according to Supplementary Material.

436 ^cAnalysis level selected in Step 5 in Figure 1.

437

The L1 analysis was applied to assess the performance of the passive fire protection (PFP). This choice is due

439 to the limited complexity of the barrier, not requiring the application of a more complex level of analysis.

440 Nevertheless, the PFP might be impacted by the natural event and a performance modification factor $\phi_{f,PFP} =$

441 0.15 retrieved from an expert survey [13] was thus adopted to modify barrier effectiveness according to Eq. (4),

442 obtaining $\eta_{f,PFP} = 8.49 \times 10^{-1}$ (see Table 4).

- 443 The L2 analysis was applied to the foam-water system (FWS), since this is a complex active barrier for which
- 444 a deeper understanding of how the flood might impact barrier subsystems is required to determine the expected
- 445 reliability during the Natech event. Therefore, FTA was carried out, considering the main components
- 446 characterizing the architecture of the barrier system, which is reported in Figure 3. The values reported in Figure
- 447 3 were obtained from literature sources and express the expected event frequency considering original 448 component unavailability $q_{p,0}$ [67,87–91]. The contribution of common cause failure is included through a 5%
- 448 component unavailability $q_{p,0}$ [67,87–91]. The contribution of common cause failure is included through a 5% 449 beta factor in *PFD*₀ [67]. The values were used to determine *PFD*₀ (i.e., original barrier performance).
- beta factor in $T^{T}D_{\theta}$ [07]. The values were used to determine $T^{T}D_{\theta}$ (i.e., original barrier period
- The FTA was then examined to identify the subsystems and components critically impacted by the reference flood scenario. In Figure 3 the most vulnerable nodes identified are highlighted in red. The probability of these events is updated to a unitary value since the involved subsystems/components are expected to be not available during the reference flood scenario (i.e., $\delta_p = 1$ for the probability of events reported in red in the quantification of MCSs). Then, the FTA is quantified and an updated value of the PFD in case of flood, *PFD_f*, is calculated by means of Eqs. (5) and (6). The *PFD_f* value is then used in the quantitative ETA.
- 456 As shown in Figure 3, the main contribution to the unavailability of the FWS is given by the lack of electricity. 457 Besides, during floods the main power connections are likely to fail due to power grid disruption [92], and, also 458 considering the relevant water height of the flooding scenario considered ($h_w = 2.0$ m), the backup diesel 459 generators, located at ground level to reduce vibrations, are likely to be submerged. It is relevant to remark that in past Natech accidents involving flooding with relevant water depths, backup supply generators have been 460 461 affected, not being designed to resist to high impact flooding scenarios [8,93]. Moreover, jockey pumps and 462 diesel pumps are likely to be submerged as well. Electric cables and connections are also an issue, although they are usually well insulated and may be unaffected by the flooding [94]. Therefore, considering the 463 464 architecture of the FWS reported in Figure 3 and the updated unavailability of the vulnerable components, the 465 PFD_f resulting from FTA quantification by means of Eqs. (5) and (6) is unitary and the safety barrier is thus considered not available during the Natech accident. 466
- 467 A similar procedure was used to apply L2 analysis to WDS. For the sake of brevity, the FTA of WDS is 468 presented in Appendix A. Considering the updated values for the unavailability of the vulnerable system 469 components in case of flood, the analysis led to a unit value for PFD also in the case of WDS. Hence, the WDS 470 is deemed not available during the reference flood scenario assumed in the case-study.
- 471 As discussed in Section 3.2, a specific assessment is required by the assessment of procedural and emergency 472 barriers. The specific procedure proposed in [64,65] was applied to address the performance of EEI.
- 473 Accordingly, the effectiveness of EEI should be determined considering the comparison of target time to failure
- 474 (ttf) and required time for final mitigation (tfm). Further details are available in the Supplementary Material. On
- the basis of primary fire features and target geometry [64], the *tfm* is estimated at 65 min and 90 min respectively
- 476 for pressurized vessels (i.e., vessels P03 and P04) and atmospheric storages (i.e., tanks T02 and T05).
- 477





479 Figure 3: Fault tree for the foam-water system (FWS) considered in the case study. Values reported are the baseline unavailability 480 values $q_{p,0}$ which have been used to quantify baseline barrier PFD_0 and updated PFD_f , according to Eqs. (5) and (6). Basic events 481 involving components/subsystems which are deemed not available during the reference flooding scenario are highlighted in red.

482 5.2 Assessment of the final outcomes of secondary scenarios

The modified ETA approach presented in Section 3.2 (and detailed in Supplementary Material) was applied to

the identification of the final outcomes of the secondary scenarios caused by domino effect, considering the

485 safety barriers in place and their performance as assessed in Section 5.1. The event trees obtained for tank T02 486 and vessel P03 are reported in Figure 4. The probabilistic assessment of these secondary scenarios is reported

and vessel P03 are reported in Figure 4. The probabilistic assessment of these secondary scenarios is reported
 in Table 5 (tank T02) and Table 6 (vessel P03), while for the sake of brevity the ETs and the results from the

488 probabilistic assessment of domino scenarios for tank T05 and vessel P04 are reported in the Supplementary

489 Material.

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

Final outcome	Escalation scenario	Secondary final outcome	Probability	Frequency [y ⁻¹]
FO_T02_01	Unmitigated domino	Pool fire, maximum	9.49E-04	7.02E-07
		emissive power		
FO_T02_02	Unmitigated domino	No escalation	5.07E-05	3.75E-08
FO_T02_03	Mitigated domino	Pool fire, mitigated emissive	8.54E-03	6.32E-06
		power		
FO_T02_04	Mitigated domino	No escalation	4.56E-04	3.37E-07
FO_T02_05	Mitigated domino	Pool fire, maximum	9.40E-02	6.95E-05
		emissive power		
FO_T02_06	Mitigated domino	No escalation	5.02E-03	3.71E-06
FO_T02_07	Mitigated domino	Pool fire, mitigated emissive	8.46E-01	6.25E-04
		power		
FO_T02_08	Mitigated domino	No escalation	4.52E-02	3.34E-05

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493 *Table 6: Probabilistic assessment of the final outcomes of secondary scenarios caused by domino effect for tank P03. Final outcomes* 494 *with frequency equal to zero are not reported.*

Final outcome	Escalation scenario	Secondary final outcome	Probability	Frequency [y ⁻¹]
FO_P03_01	Unmitigated domino	Fireball	5.11E-05	3.78E-08
FO_P03_02	Unmitigated domino	No escalation	9.97E-05	7.38E-08
FO_P03_03	Mitigated domino	Fireball	4.60E-04	3.40E-07
FO_P03_04	Mitigated domino	No escalation	8.98E-04	6.64E-07
FO_P03_05	Mitigated domino	Fireball	3.88E-08	2.87E-11
FO_P03_06	Mitigated domino	No escalation	8.49E-04	6.28E-07
FO_P03_07	No domino	No escalation	7.64E-03	5.65E-06
FO_P03_15	Mitigated domino	Fireball	5.06E-03	3.74E-06
FO_P03_16	Mitigated domino	No escalation	9.88E-03	7.30E-06
FO_P03_17	Mitigated domino	Fireball	4.55E-02	3.37E-05
FO_P03_18	Mitigated domino	No escalation	8.89E-02	6.57E-05
FO_P03_19	Mitigated domino	Fireball	3.84E-06	2.84E-09
FO_P03_20	Mitigated domino	No escalation	8.41E-02	6.22E-05
FO_P03_21	No domino	No escalation	7.57E-01	5.59E-04





498Figure 4: Event trees reporting the quantification of the frequencies (in y^{-1}) of final outcomes of: a) escalation scenarios involving499tank T02 and b) escalation scenarios involving vessel P03. The branches indicated with a red cross are not further considered, as500consequence of the failure of FWS (in panel a) and WDS (in panel b) caused by the flooding, as indicated by FTAs in L2 analysis.501FO= Final Outcome.

- As shown in Figure 4, the application of the barrier assessment methodology (Step 5 in Figure 1) results in the elimination of part of the ETA branches. In particular, the downward output branches of the logic operators associated to the FWS (node b_1 in Figure 4-a) and WDS (nodes a_2 and a_3 in Figure 4-b) systems are no more present, since these two systems are considered unavailable during the reference flood scenario according to the results obtained from L2 analysis.
- 508 Thus, the methodology led to the identification and characterization of the set of final outcomes reported in
- 509 Table 7. The table also reports the calculated frequencies and probabilities of the final outcomes. As shown in
- 510 the table, mitigated scenarios (indicated with number "1" in the column "State" of the table) are not considered
- 511 likely for the pressurized equipment items, as the vessels P03 and P04. Indeed, in the case of escalation caused
- 512 by domino effect due to a fire involving pressurized equipment, the action of fire brigades may not be able to
- 513 mitigate the violent vaporization of the fluid, as described in Supplementary Material.
- Table 7: Probabilities and frequencies of the final outcomes identified through the ETA. State (see Section 3.3): 0=no escalation;
 1=mitigated escalation; 2=unmitigated escalation. SEP=surface emissive power.

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

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517 5.3 Assessment of the overall domino scenarios

Starting from the final outcomes of the secondary events reported in Table 7, the number of different overall domino scenarios is determined by Eq. (7). Considering that escalation involving tanks T02 and T05 can lead to three alternative final outcomes each, while in the case of vessels P03 and P04 two alternative final outcomes are only possible, the number of overall domino scenarios, N_c , is equal to 36. For the sake of simplification, only secondary domino scenarios are considered in the case study. Nevertheless, the proposed methodology is recursively applicable for further level assessment, as it is explained in Section 3 (see Figure 1).

The probabilities and frequencies of the overall domino scenarios are assessed applying Eqs. (8) and (9), as described in Section 3.3. The results are presented in Table 8. As shown in the table, the frequencies of the overall scenarios span between 10^{-8} to 10^{-4} y⁻¹, and many combinations have probability values close to that of the primary Natech scenario, as well as to the conventional scenarios considered as benchmarks.

529 Table 8: Overall domino scenarios (final event combinations) considered for risk assessment. State (see Section 3.3): 0=no escalation;

530 *1=mitigated escalation; 2=unmitigated escalation.*

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

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532 5.4 Results of the risk assessment

Figure 5 shows the LSIR results for the case-study analysed. It is worth to remind that in all the risk figures reported, the baseline contribution of conventional scenarios is included (i.e., case 0, as explained in Section 4.1). Figure 5-a shows the baseline Natech LSIR from tank T01 (i.e., case 1). Figure 5-d shows the overall LSIR obtained applying the methodology developed in Section 2 (i.e., case 4), while Figure 5-b and Figure 5-c represent the worst-case and the best-case considering escalation caused by domino effect (i.e., case 2 and case 3 respectively, see Section 3).

539 Comparing Figure 5-a and Figure 5-c, it is clear that including the contribution of escalation scenarios caused by domino effect considering mitigation due to safety barriers with baseline performance produces a limited 540 increase in the LSIR value. However, the risk caused by escalation scenarios increases dramatically when 541 542 considering the degradation of safety barriers due to the flooding (Figure 5-d). Indeed, in the latter case, the tank farm area is entirely exposed to LSIR values higher that 10⁻⁵ y⁻¹, while this value is present only in a limited 543 area of the layout in Figure 5-c. Thus, the LSIR is clearly underestimated if the possible barrier degradation 544 caused by natural events is overlooked when assessing Natech scenarios. Nevertheless, comparing Figure 5-d 545 546 and Figure 5-b (where no barriers are considered), it is clear that the residual barrier performance still contributes to reduce the risk level, since in case of completely unmitigated escalation the tank farm area is exposed to LSIR 547 548 values as high as 10⁻⁴ y⁻¹, an order of magnitude higher than in the case of mitigated escalation with degraded 549 barriers.



551 552

Figure 5: LSIR values calculated for: a) case 1, b) case 2, c) case 3, d) case 4.

Figure 6 describes the societal risk calculated for the four cases considered, obtained considering the simplifying assumptions discussed in Section 4. The severity of the primary Natech scenario (i.e., case 1) is limited (up to 100 expected fatalities). Escalation scenarios have a higher magnitude (up to 1000 expected fatalities), as shown in Figure 6. As expected, the F/N curve of case 4 has an intermediate severity (between that of case 2 and 3), highlighting, on the one hand, that considering unmitigated escalation would be possibly over-conservative, and, on the other hand, that overlooking barrier degradation would lead to a critical underestimation of risk.



560

561 Figure 6: F/N curves calculated for the case-study. Case 0 is reported to provide baseline risk figures related to conventional scenarios.



562

563 Figure 7: Potential Life Loss (PLL) and expectation value (EV) values calculated for the case study. Case 0 is also reported (in grey) to 564 provide baseline PLL and EV values from conventional scenarios.

565 The above results are confirmed by the PLL and EV values reported in Figure 7. The values calculated 566 considering the primary Natech accident (i.e., case 1) are about 10³ times higher than the figures obtained from 567 baseline conventional scenarios (i.e., case 0). Considering escalation caused by domino effect does not affect

568 significantly the PLL, possibly because F and N are equally weighed in the index definition (see Eq. (9)), and 569 the most severe domino scenarios (i.e., scenarios ID 10-36 in Table 8, featuring the rupture of at least one 570 pressurized vessel among P03 and P04) have frequency values considerably lower than that of the primary Natech accident (i.e., 1 to 4 orders of magnitude difference). Thus, the effect of escalation scenarios triggered 571 572 by Natech is better highlighted by the analysis of the EV index. Indeed, as shown in Figure 7, in case of mitigated 573 escalation considering barrier degradation (i.e., case 4) there is an increase of more than 6 times of the EV with 574 respect to that calculated not considering escalation (i.e., case 1). Adopting baseline barrier performance (i.e., 575 case 3, best-case scenario), the increase is limited to about 1.5 times, while not considering barriers (i.e., case 576 2, worst-case scenario) the value of EV is about 6 times higher than that of case 4.

577 5.5 Discussion

578 The results shown in Sections 5.3 and 5.4 allow determining the key role of safety barriers in preventing the 579 escalation of primary Natech accidents by domino effect. Nevertheless, in Natech scenarios, safety barriers 580 might not be as effective as expected in preventing domino effect, due to the impact of natural events that may damage barrier components or impair barrier action. As shown in the case study assessment, the two active 581 582 firefighting systems considered are found to be not available during a flooding (i.e., the FWS and WDS 583 systems), thus no mitigation will come from the presence of these devices in a Natech scenario triggered by 584 flood. However, the methodology proposed avoids over-conservative results that may be obtained by a worst-585 case approach that completely neglects the action of all safety barriers. Indeed, passive barriers (e.g., passive 586 fire protection materials) considered in the case study are more robust due to the absence of external activation, 587 and may be considered to resist to the impact of the flooding scenario.

588 The results obtained show that a relevant increase in the risk indexes is detected when the performance 589 modification of the barriers with respect to baseline values is considered in quantitative risk assessment. The 590 increase in risk figures is not limited to the vicinity of the source of the primary Natech scenario, but rather to 591 the entire facility, involving as well the areas near the equipment items that are potential targets accident. This 592 is clearly related to the high likelihood of high magnitude escalation scenarios and is confirmed by the F/N 593 curves reported in Figure 6, where the contribution of escalation caused by domino effect is mainly related to 594 the presence of specific high impact scenarios. The comparison of the F/N curves for cases 2, 3 and 4 to that 595 obtained for case 1 makes evident this point. Nevertheless, according to the results obtained in the case study, 596 the increase in the risk figures is critical specifically for the scenarios having a higher magnitude. Indeed, the 597 PLL value obtained for the unmitigated case (case 2 in Figure 7) is comparable with the values obtained considering safety barriers (cases 3 and 4 in Figure 7). Differently, the EV parameter, that weights more the 598 599 scenarios with a higher number of expected fatalities, is about 25 times higher for the unmitigated case (case 2 600 in Figure 7) with respect to the case considering baseline barrier performance (case 3 in Figure 7), and about 7 601 times higher than the case considering modifications in barrier performance (case 4 in Figure 7).

602 Clearly enough, a critical point of the analysis is the selection of the appropriate level of detail for the application of the safety barrier performance degradation analysis. This step is influenced by the available information, in 603 particular on complex barrier systems of interest in the analysis. On the one hand, the selection of L2 level is 604 605 more information-intensive and is time demanding, although it allows the analyst to take into account specific barrier design provisions (e.g., the application of design standards or solutions explicitly considering natural 606 607 hazards). On the other hand, if the adoption of L1 and L0 provides sufficiently accurate results and the system 608 may be hardly divided in components, as in the case of simple systems as passive barriers, these levels of 609 analysis provide a straightforward approach to consider performance modification of barriers in risk assessment 610 procedures.

Even if a detailed L2 analysis is applied, uncertainty may still be present in the results, due to the difficulty in assessing the actual behaviour of some components of safety functions when impacted by a natural hazard.

- 613 However, the upper and lower risk bounds can be clearly identified by the application of unmitigated domino
- escalation [46] and mitigated domino escalation considering baseline barrier performance [40] (cases 2 and 3
- 615 respectively in the case-study).
- 616 The application of the methodology may also be used to drive decision-making in implementing specific
- 617 provisions for each barrier, with the purpose of shifting the risk level from a situation close to absence of
- 618 mitigation toward the identified lower risk bound. This approach may be of specific interest considering the L2
- 619 analysis, which allows identifying the critical components of the safety barriers that may be considered for
- 620 upgrading and protection from the impact of the natural event.
- 621 Although the multi-level assessment procedure developed for the quantitative assessment of barrier performance
- 622 modification in Natech scenarios was integrated in a conventional QRA procedure for risk assessment, Steps 4
- and 5 may be adopted also in different approaches to quantitative risk assessment. In particular, the quantitative
- approach to the degradation of barrier performance may be easily integrated with approaches based on Bayesian
- 625 Networks [33–35] or other graph theoretical approaches [43,44] for the quantitative assessment of the risk of
- 626 Natech scenarios.

627 Finally, it should be remarked that the present multilevel approach is not restricted to chemical and process 628 sector and it might be beneficial also in industries where the conceptualization of safety barrier is adopted. For 629 instance, in the nuclear sector, where the system safety is based on defence-in-depth principle [95,96], the 630 methodology might be applied within probabilistic safety assessment (PSA) studies to model explicitly the performance of layers of defence during natural hazards. In doing so, the PSA might drive better risk-informed 631 632 decisions on how to reduce the likelihood and the impact of accidents originated by natural hazards [97], which, 633 as Fukushima Dai-ichi nuclear disaster (2011) recently demonstrated [6,93,98], safety management might not 634 be ready to face.

635 6. Conclusions

636 A comprehensive methodology for the risk assessment of the escalation of Natech scenarios caused by domino 637 effect was developed. The methodology was specifically conceived to allow considering the performance 638 modification of safety barriers during Natech scenarios, caused by the impact of the natural event. A three-level 639 approach was proposed to assess barrier performance modification. The methodology was applied to a case 640 study, and the results obtained are compared with the outcomes of reference methodologies for risk assessment 641 of escalation scenarios caused by domino effect. Risk figures obtained including the modification in barrier 642 performance are of an order of magnitude higher than those obtained considering baseline barrier performance. 643 Still, in particular in the case of high-severity scenarios, even when impacted by a natural event, the layers of 644 protection provided by the safety barriers are effective in reducing of about an order of magnitude the risk with 645 respect to a worst-case scenario where safety barriers are considered absent. The methodology also provides a guidance to the identification of the most critical components of technical safety barriers, supporting risk-based 646 647 decision-making concerning the upgrading of these systems to improve their resistance to natural events.

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654 Appendix A

The main assumptions considered for the reference architectures of FWS and WDS in conducting the FTA arereported in Section A.1. The FTA for the WDS, along with the further details on the related application of the

L2 level of the proposed methodology (L2 - Step 5c in Figure 1) are reported in Section A.2.

658 A.1 Assumptions on FWS and WDS architectures

659 The FTA shown in Figure 3 is based on a reference FWS equipped on tanks T02 and T05 and featuring the following barrier system architecture. A single foam module is conservatively considered, not accounting for 660 the possible presence of redundancies. An in-line eductor system is considered for realizing the intended foam-661 662 water mixture [99]. The foam solution is stored in a permanent foam supply tank. The water supply is provided by a permanent firewater tank located inside plant premises which is connected to water main network from the 663 closest inhabited area. The foam/water delivery is accomplished by means of a single fire diesel pump, or by 664 two electric pumps with half nominal capacity compared to the former. Two jockey pumps are considered to 665 666 maintain the water network to the required pressure balancing small pressure drops due to possible leaks over 667 time [94]. Electric power can be provided from three independent supplies: main power connection, backup 668 supply and diesel generator.

669 The main features of the reference WDS implemented for protection of vessels P03 and P04 which have been 670 considered in the FTA (see Figure A.1) are reported in the following. The water supply is provided by a permanent firewater tank located inside plant premises which is connected to water main network from the 671 672 closest inhabited area. The water delivery is accomplished by means of a single fire diesel pump, with a single deluge unit. System actuation can be either automatic or manual from fire area. The electrical actuation system 673 674 is composed of one solenoid valve receiving electric signal from the control panel receiving fire detection signal 675 from heat detectors. Manual actuation can be performed from fire area following the activation of a fire alarm. Electric power can be provided from three independent supplies: main power connection, backup supply and 676 677 diesel generator. No fail-safe design is conservatively considered.

678 *A.2 FTA of the reference WDS and details on L2 level application*

679 The FTA for the WDS is reported in Figure A.1. The system probability of failure on demand indicated in 680 Figure A.1 is used as baseline performance value PFD_0 (i.e., in absence of natural hazard) reported in Table 3. 681 The input data $q_{p,0}$ for FTA have been retrieved from standard reliability databases and literature sources [67,87– 682 91]. A 5% beta factor is assumed also in the case of WDS to include the contribution of common cause failure 683 in PFD_0 [67].

684 The fault tree was then examined to determine critical subsystems considering the reference flood scenario. The most vulnerable nodes identified are highlighted in red in the FTA. As for the case of FWS, the main 685 686 contribution to the unavailability is linked to the lack of electricity. Indeed, during floods main power connection 687 is likely interrupted due to power grid disruption [92], and given the relevant water height ($h_w = 2.0$ m) floodwater is deemed to submerge also diesel generators which are usually located at ground level [8,93]. The 688 diesel pump can be considered submerged as well in case special provisions for positioning the equipment above 689 ground level had not been previously adopted. Manual actuation is deemed not possible as well, since the 690 691 releasing panel will not actuate the alarm sound in case of lack of power connection (fail-safe design is conservatively not considered in this study as explained above) and the area might not be reached by operators 692 693 in case of relevant floodwater height. Therefore, by the application of Eqs. (5) and (6), the PFD_f of the WDS is 694 assessed at unitary value and thus the WDS is considered not available during the Natech accident considered 695 in Section 3.



Figure A. 1: Fault tree for the water deluge system (WDS) considered in the case study. Values reported are the baseline

 $\begin{array}{l} 699\\ \text{unavailability values } q_{p,0} \text{ which have been used to quantify baseline barrier } PFD_0 \text{ and updated } PFD_f, according to Eqs. (5) and (6).\\ 700\\ \text{Basic events involving components/subsystems which are deemed not available during the reference flooding scenario are highlighted in red.}\\ \end{array}$

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