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Analysis of Firewater Runoff in SEVESO Chemical Plant

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Fire in the establishment falling under SEVESO Directive III is one of the most recurring accident scenarios both at a European level and in the Czech Republic. Runoff of firewater can cause a major accident leading to serious danger to the environment, especially to water environment. Although the Directive pays attention to the possibility of dangerous substance release in case of fires, still there are no united requirements for firewater treatment in European Union. This leads to unpreparedness of SEVESO chemical plants to a major fire, where large quantities of firewater require sufficient containment system and next liquidation. Implementation of effective safety containment system situated near the facility and verified by emergency training seems to be the best preventive approach. Lessons learned from past accidents clearly demonstrate negative effect of firewater to the environment. Approximately 80% of them reported in major accident database (eMARS) have occurred near watercourses (eMARS, 2018). Firewater may contain dissolved dangerous chemical substances and particulate materials from combustion processes or foams depending on the facility and nearby surroundings. Also standard tests of toxicity show their high ecotoxicological hazard, e.g. the acute toxicity tests with marine luminous bacteria *Vibrio Fischeri* (Sikorova et al., 2017b).
This paper is focused on analysis of firewater runoff in selected SEVESO chemical plant. First, risk sources with direct impact to the environment were identified. Next accident scenarios were determined. Contaminated firewater runoff was evaluated from different facilities affected by a major fire to endangered aquatic environment. The spread was considered via process sewerage system, rainwater sewerage system and own wastewater treatment plant to nearby watercourse. For estimation of consequences to the environment a calculation with H&V Index methodology was used. This methodology is highly recommended for the purposes of risk analysis according to SEVESO Directive III in the Czech Republic (Danihelka et al, 2006). In conclusion, effective safety measures for environmental impact reduction were proposed.

1. Introduction

Major accident is defined as an occurrence such as a major emission, fire, or explosion resulting from uncontrolled developments in the course of the operation of any establishment covered by SEVESO Directive III, and leading to serious danger to human health or the environment, immediate or delayed, inside or outside the establishment, and involving one or more dangerous substances (European Commission, 2013). Dangerous substances and their hazard categories in accordance with Regulation (European Commission, 2008) are listed in the Annex I of SEVESO Directive III (European Commission, 2013). Environmental hazards are defined according to hazard categories together with qualifying quantity (tonnes) of dangerous substances, where only aquatic environment is considered (see Table 1).

Table 1: Environmental hazards

Hazard categories	Lower-tier requirements	Upper-tier requirements
Hazardous to the Aquatic Environment in Category Acute 1 or Chronic 1	100 t	200 t
Hazardous to the Aquatic Environment in Category Chronic 2	200 t	500 t

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Major fire in SEVESO chemical plant will require several millions litter of water. Water is widely used in chemical process facilities as an active protection layer, and it is successful in tackling most of the fires (Han et al., 2017). In case of long-lasting fires large quantities of firewater can occur, which perform an extraordinary hazard to the environment. Firewater quantity estimations are therefore needed to keep costs and harm to the receiving environment down (Scholz, 2014).
Firewater may contain dissolved dangerous chemical substances depending on the facility being extinguished or foams, which due to biochemical oxygen demand can cause decrease of the concentration of oxygen and make the water quality worse (see Figure 1). Aquatic environment is the most vulnerable to the pollution from all emergency incidents (Geynes and Wood, 2014). Runoff of firewater containing dangerous substance can spread in water environment very fast and over long distances. Environmental damage may be short and/or long term and, in the case of groundwater, may persist for decades. Plant sewerage system, rainwater drainage system, wastewater treatment plant (Wang et al., 2017) and other services all present routes for the transport of pollutants off-site (De Rademaeker, 2014). The environmental threat is the strongest where levels of toxicity are particularly high (Marlair et al., 2004). Smart firewater management will help reduce water use and protect the environment from pollution (Scholz, 2014; Sun, 2017).
This paper focuses on analysis of firewater runoff in chemical plant classified under the SEVESO Directive III. Lower-tier plant located in the north-east of Czech Republic was selected as a case study area for analysis of different scenarios considering firewater runoff with direct impact to the watercourse. A simple case study is performed, in order to provide the capability of the H&V Index methodology in the firewater runoff risk assessment.

Figure 1: Firefighting foam captured in the wastewater treatment plant

2. Methodology

H&V Index methodology was primarily developed for assessment of short-term emergency releases into the environment with the presence of dangerous substance, which does not exceed hours or days over their time horizons. The approach of methodology does not allow evaluating long-term releases or old environmental burdens in the environment. For these reasons, the methodology does not count with the biodegradation of substances in the environment, as they are not relevant for massive releases of hazardous substances to the environment. The methodology also does not consider synergy and domino effect (Danihelka et al., 2006).
The purpose of this methodology is risk analysis related to the major accident from which follows the possibility of environmental threat. If the parts of the environment are not seriously affected, they will not be evaluated. Otherwise, the probability of release of the hazardous substance into the environment is determined in the risk analysis section. By quantitative assessment of the scenarios, it is possible to determine the amount of release. For the environmental impact assessment, the results from the risk analysis are used, which present the possibility of environmental hazard, the amount of substance released into the environment and the probability of the release. If a risk analysis has not yet been performed and therefore there are no scenarios and their probability, a deterministic approach may be used. Then it is assumed that any hazardous substance present in the facility can escape (Sikorova et al., 2017a)
H&V Index is based on the evaluation of the hazard index of the substance for the environment and the vulnerability index of the territory against the potential accident involving the dangerous substance. The hazard index performs combination of the (eco) toxic properties of the substance, the physical-chemical properties of the substance and the potential spread of the substance. The vulnerability index can be determined separately for the different parts of the environment (e.g. surface and groundwater, soil environment, biotic component of the landscape. It includes the characteristics of these parts of the

environment (e.g. soil permeability, permeability of hydrogeological subsoil, land use, use of underground and surface water, specially protected nature areas, protection zones etc.). Using synthesis of both indexes (hazard index and vulnerability index) partial indexes is obtained that inform about the hazards of selected substance for the site being evaluated. In conclusion of the evaluation the consequence of the environmental impact is determined. Consequence (A-E) is calculated as a combination of the amount of released substance and partial indexes. Negative effects to different parts of the environment can be estimated:

- effects of toxic substances in surface water, soil, groundwater and biotic components of the environment are estimated
- toxic and flammable effects on the biotic component of the environment are estimated

In 2012, H&V Index passed through a major revision related to new classification according to CLP Regulation (European Commission, 2008). Due to the fact that the released amount of dangerous substance into the environment has a key importance for the consequence of the accident, the revised version of the methodology put more emphasis on its correct determination. Simple rule for the estimation of released amount to the environment has been adopted. If none of the implemented safety measures can clearly demonstrate its use to prevent the spreading of a dangerous substance towards an environment, then the total amount stored or manipulated in the facility is considered. Effective preventive measure performs especially sufficient capacity of the "catchment system" (e.g. emergency reservoirs, retention tanks etc.). However, for the evaluation of the sufficient capacity of the containment system, it is necessary to take into account not only the maximum amount of dangerous substance in the facility but also other extraordinary events such as the presence of rainwater in case of accident, fire or cooling water, floods, emergency destruction of containment system and others..

3. Applicative case study

SEVESO chemical plant, where liquid and solid forms of medicines and pharmaceutical substances are produced, was selected for purposes of this study. The whole area of this plant is located in the valley of the river with the altitude about 240 meters above sea level (see Figure 2). The terrain is mostly flattened. Towards the north slightly descends to the river. Because the river drains the water from the nearest mountains, usually it has enough water almost all year round. The highest flow rates reach at the end of the spring and the lower one at the end of the summer. The average flow rate is about 17,6 m^3/s. Hydrological characteristics (e.g. minimal flow rate) are particularly important to know for the possibility of dilution of polluted waters into the river in case of extraordinary events which major accidents or floods can be. In 1997, the most extensive floods in Moravian-Silesian Region changed the flow of the river in many places and some sections were left in a state close to the nature. Fortunately, this establishment was not flooded in 1997 in comparison with other SEVESO plants situated in the same region (Sikorova and Bernatik, 2012).

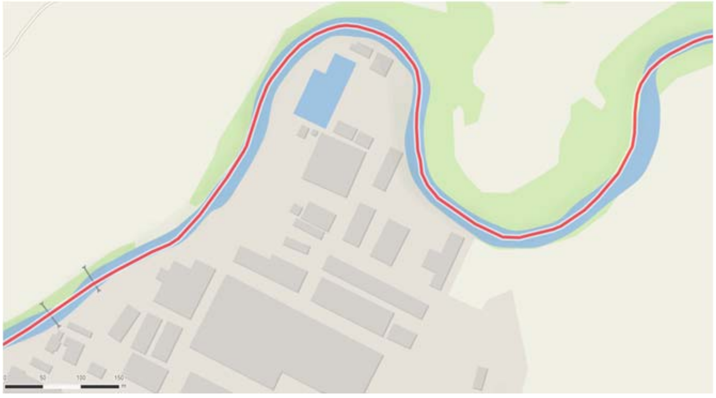

Figure 2: River flowing from the north around the SEVESO chemical plant

The subject of this study is an analysis of extraordinary release of selected dangerous substances (including fire waters) directly to the river. Surface waters are endangered especially due to the location of the SEVESO plant, the amount of dangerous substances stored in the industrial area (i.e. classified as toxic or hazardous to the aquatic environment) and the probability of major accident occurrence. First risk sources with the possible threat for the river were identified. Next scenarios and consequence categories for the aquatic environment were determined.

3.1 Risk site identification

For the identification of risk sources were selected storages which are surrounded by rainwater sewerage system which is connected directly to the river (see Table 2). This sewerage is unprotected to any undesirable release to the aquatic environment. No system of detection is implemented inside. Only safety valve disabling the liquid flow to the river is at end of one sewer branch proposed (No. VIII). Major disadvantage is that it is the manual one (see Figure 3).

Table 2: Identification of risk sources with direct environmental impact to the river

Storage No.	Dangerous Substance	Quantity (tonnes)	Facility	Classification	Distance to the river (m)
S1	Hexane	0,870	Tank	H411	170
		0,680	Tank		
		0,680	Tank		
S2	Mix	12,000	Barrels	H400, H410	260
		17,000	Barrels	H411	
S3	Mix	2,000	Barrels	H400, H410	90
		15,000	Barrels	H411	
	Mix	20,000	Barrels	H331	
S4	Methanol	3,555	Tank	H301, H311, H331	110

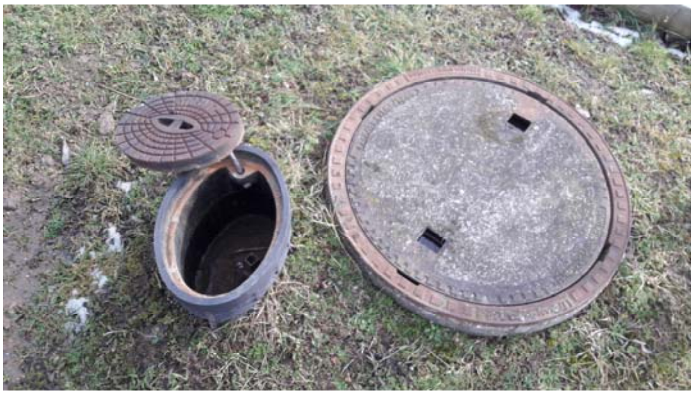

Figure 3: Safety valve for closure of rainwater sewerage system at the outflow to the river

3.2 Scenarios

For identified risk sources were considered different types of emergency scenarios resulting in a major impact to the aquatic environment (see Table 3). The cause may be a human error in handling with dangerous substance, traffic accident and major fire in the plant or others. Frequency of these events has not been determined. All scenarios perform a release of dangerous substance or firewater via sewerage system. The sewerage system in the plant is a both, process and rainwater. Process sewerage system is primarily used for a transport of contaminated waste waters from production facilities. This sewerage system is completely connected to the wastewater treatment plant located in the north part of the plant. Rainwaters are flowing by a separate sewerage system. Historically, related to the development of the plant, several outflows were built. At the present time, 8 permits according to IPPC Directive (EC, 2008a) for discharging of rainwaters directly to the river are issued (called No. I to VIII). Rainwater sewerage system is from 70% protected from undesirable direct release to the river and connected to the wastewater treatment plant. However, the remaining 30% flowing right to the aquatic environment with no possibility to stop them automatically (remotely) in case of extraordinary release (without outflow No. VIII, manual safety valve was implemented).
In general, major impact to the nearest river can be predicted when:

- dangerous substance leaks out on the paved area and is not captured by sewerage system, which can be transferred to wastewater treatment plant → direct impact to the aquatic environment (firewater considered)

- dangerous substance leaks out on the paved area and is captured by process or rainwater sewerage system leading to the wastewater treatment plant, which does not work due to major accident too → direct impact to the aquatic environment (firewater considered)
- dangerous substance leaks out on the paved area in places where is no entry to the sewerage system and due to slope of terrain it flows right to the river → direct impact to the aquatic environment (firewater considered)

Table 3: Summary of data used in scenarios determination

Storage No.	Dangerous Substance	Facility	Firewater considered	Rainwater sewerage system	Outflow to the river No.	Direct impact to the river
S1	Hexane	Tank	✓	✓	VIII	✓
S2	Mix	Barrel	✓	✓	VIII	✓
S3	Mix	Barrel	✓	✓	VIII	✓
S4	Methanol	Tank	✓	✓	II, III	✓

3.3 Environmental impact assessment

According to H&V Index, substance or mixture is evaluated as a hazardous to the water environment if it is classified as a substance with acute or chronic toxicity to the aquatic environment in category 1-4 (H phrases – H400, H410, H411, H412, and H413). Hazard to the biota and terrestrial ecosystems then follows from acute toxicity in category 1-4 (H phrases – H300, H301, H302, H310, H311, H312, H330, H331, and H332). For hazard index calculation (T_W) information from safety data sheet were used. If substance or mixture were classified by H phrase 400 and more, direct index was assigned (e.g. for hexane tank and substances stored in barrels). In case of the tank with methanol final index T_W was calculated as a combination of acute toxicity and selected physical properties of substance (see Table 3).
Index of vulnerability to the aquatic environment was evaluated on the base of presence of hydrological categories in the distance of possible accident effects. Final vulnerability index (I_{SW}) was calculated as a maximum value found. In case of extraordinary event (including major fire), around or inside of evaluated storages, there is a high possibility of release via rainwater sewerage system with direct outflow to the river. Therefore, the index of average vulnerability of the territory was assigned in all cases (see Table 4).
By synthesis of indexes, both hazard and vulnerability indexes (T_W and I_{SW}), a final index of toxicity to the aquatic environment (I_{TSW}) was calculated (see Equation 1 and Table 4).

$$I_{TSW} = max\left(\frac{Isw + Tw}{2}\right) \tag{1}$$

In conclusion, consequence categories depending on considered amount release (Am) and toxicity to the aquatic environment (I_{TSW}) were calculated (see Table 4). Resulting consequence categories (A-E) perform the prediction of the impact to the aquatic environment, where “B category” presents small impact to the river, “C category” significant impact and “D category” very significant impact (see Table 4).

Table 4: Environmental impact assessment – H&V Index

		Indexes			
Storage No.	Substance	T_W	I_{SW}	I_{TSW}	A – E
S1	Hexane	3	3	3	B
S2	Mix	4/3	3	3,5/3	D/C
S3	Mix	4/3/3	3	3,5/3/3	C/C/C
S4	Methanol	2	3	2,5	C

4. Conclusion

Water is the most used medium for firefighting. However, major accident can occurred when water used for firefighting, where dangerous substance stored is, has been runoff to nearby aquatic environment. How the dangerous substance (fire water) will spread in surface water it follows from physical-chemical properties and actual climatic and hydrological characteristics that determine the behaviour of the dangerous substance in aquatic environment after the release. These facts cannot be completely covered by one screening methodology. In the event of a direct major release to the river, it is also necessary to critically evaluate the intervention procedures and the real times for accident recovery, including the possibility of building retaining protection walls etc.

The goal of this paper was to perform an analysis of possible fire water runoff on the example of applicative case study. SEVESO chemical plant situated near the aquatic environment together with H&V Index methodology were selected for this purpose. Storages S1 to S4 with the presence of different dangerous substance or substances, located near the rainwater sewerage system, were identified as potential risk sources for the close watercourse. In general, 3 types of scenarios with direct impact to the river were considered. For purposes of this analysis frequency of the events was excluded. Deterministic approach for calculation of hazard index was applied. The vulnerability was determined as an average threat for the river, which can be relatively fast recovered. In conclusion, the consequence of the impact to water environment was evaluated. From obtained data, the highest impact to the environment resulted for storage No. 2. Various substances classified as hazardous to the aquatic environment are stored or it is manipulated with them on the inside or outside of the storage No. 2. Recommendations for elimination or mitigation of major impact to the environment were in final report proposed (e.g. drain covers in sufficient quantity, remote-controlled sluice valves in the outflows to the river, bounded space for purposes of manipulation with dangerous substances or major fire using absorbent booms and pad, land booms, available geographical information systems (GIS) drainage sewerage maps and others. Implementation of such effective safety measures or containment systems in practise may contribute to decrease of major impact to the aquatic environment due to undesirable release via rainwater sewerage system.

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