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RISK ASSESSMENT OF HAZARDOUS WASTE MANAGEMENT PROCESS

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ABSTRACT. Urbanization and industrial activities are responsible for the increasing quantities of wastes each year leading to environmental and health consequences. Wastes are also generated from household, commercial, agricultural or medical activities industrial, mining or metallurgical sectors. Hazardous wastes can be identified as any solid, liquid, or gaseous waste that, in its chemical and physical characteristics, represents a potential harm to human health and/or the environment. Therefore, it requires specific management, such as compliance with the EU Waste Framework Directive for waste prevention and reduction. This study explores the hazardous waste management process to identify potential hazards during the treatment phase. It analyses the risk to the population using the qualitative preliminary hazard analysis (PHA) method and performs consequence analysis using Effects modelling software. The results of the PHA indicate a low to moderate risk, if specific safety measures are applied. The most severe accident scenario may result in reversible effects outside the establishment over short distances. These analyses can support decision-making in land-use and emergency planning procedures.

Key words: *hazardous waste, risk assessment, PHA method.*

INTRODUCTION

After the Chinese ban on imported waste in 2017, many countries around the world, such as the UK, US, and member states of the EU, have realized the importance of changing their waste management policies and moving towards an advanced level of recycling instead of seeking an alternative importer for their waste (Wen et al., 2021). The growing population and urbanization, along with economic and industrial growth, were the main factors that increased the demand for raw materials, and in turn, increased the waste generated each year, especially hazardous waste, which can endanger human health and the environment when improperly managed. The traditional ways of waste disposal have become ineffective and can't cope with the high level of environmental contamination. Poor waste management would certainly contaminate the natural environment and hinder economic development (Kaza et al., 2018).

Wastes have different characteristics and therefore belong to various categories. The most common way of classifying waste is based on their source, environmental impact, and physical state. Waste sources can include households, industrial facilities, commercial establishments, mining or agricultural operations, residues from construction activities, or medical sector (Zhang et al., 2022; Xu et al., 2019).

Environmental impact categorizes waste into two main categories: hazardous and non-hazardous. Physical state provides another method of waste categorization, where waste can be classified as solid, gaseous, or liquid (Amasuomo and Baird, 2016; Zhang et al., 2022).

Solid waste includes municipal solid waste (MSW), industrial waste, and hazardous waste (HW) (EPA, 2022). MSW encompasses organic and inorganic waste resulted in urban areas. Organic waste can be further categorized as fermentable, non-fermentable, or putrescible. Fermentable and putrescible wastes decompose rapidly, while non-fermentable waste resists decomposition and breaks down slowly (UNEP, 2015).

Industrial waste is a type of solid waste that is not classified as hazardous waste, resulting from manufacturing processes. It may include materials such as rubber, plastic, glass, clay, stones, water treatment by-products, steel, iron, organic and inorganic chemicals, and other waste generated by industrial activities, excluding the oil and mining industry (EPA, 2022).

Hazardous waste (HW) can be defined as any solid, liquid, or gaseous waste that, due to its chemical and physical characteristics, such as toxicity, flammability, or ecotoxicity, poses a potential threat to human health and/or the environment, necessitating specific management practices (Hyder, 2012). Classifying waste as hazardous is a complex process, and therefore, the United States Environmental Protection Agency has developed regulations to determine whether a waste falls under the hazardous waste definition (EPA, 2022). Hazardous wastes include acids, alkali, asbestos, inorganic cyanide, non-ferrous metals, and mineral oils (Yang et al., 2020). Moreover, metallurgical and chemical industries, such as of pesticides, fertilizers, sulfuric acid and ammonia, are the main generators of hazardous waste (Peizhe and Leisheng, 1993). Cooking oil is another source of hazardous waste that presents challenges in the disposal and landfilling process due to its high annual generation from households, restaurants, and industries (Hosseinzadeh-Bandbafha et al., 2022). Incineration residues and household wastes such as batteries are also included in this category. These types of wastes are subject to specific regulations and restrictions (Hyder, 2012), such as the European Regulation No. 1272/2008 (EP and EC, 2008) and the EU Waste Framework Directive (WFD) for waste prevention and reduction (EP and EC, 2018).

This study aims to explore hazardous waste management to identify potential sources of hazards that may arise during the treatment and disposal processes of hazardous wastes at a HW management plant in Romania. The objectives of the study include identifying hazards through qualitative Preliminary Hazard Analysis (PHA) method and quantitatively calculating the consequences of potential accidents using EFFECTS software. The results of the study can support decision making for land-use planning and emergency planning processes.

European Regulations on Chemicals and Wastes

Industrial accidents can result in environmental contamination and pose risks to human health due to the release of hazardous substances both inside and outside the industrial facility. Additionally, explosion or fire accidents can also cause property damage, further threatening environmental safety (Hollá et al., 2021).

After the accident in the Italian city of Seveso (1976) and the release of dioxins, in 1982 the Seveso I Directive (Directive 82/501/EEC) was adopted. This directive required member states of the EU to identify the probable risks associated with industrial activities, particularly those in dangerous industries, with the aim of preventing similar accidents and taking preventive measures.

Following the Bhopal accident in 1984, the Seveso II Directive (Directive 96/82/EC) was introduced with the aim of enforcing a classification mechanism for substances, categorizing them as toxic, flammable, explosive, or environmentally hazardous. Subsequent accidents, including the Enschede fireworks explosion in 2000, the Baia Mare cyanide waste spill in 2000, and the Toulouse ammonium nitrate explosion in 2001, prompted amendments to the Seveso II Directive, all aimed at reducing the consequences of such incidents (EC and EP, 2012; Laurent et al., 2021; Peeters and Vanhoenacher, 2022). Later, the Seveso III Directive (Directive 2012/18/EU), which focuses on the control of major accident hazards involving dangerous substances, was introduced as a result of changes and updates in the European Regulation (EC) No. 1272/2008 on Classification, Labelling, and Packaging of Substances and Mixtures (CLP) (EC and EP, 2012; HSE, 2015; Laurent et al., 2021; Peeters and Vanhoenacher, 2022). Seveso III Directive provides governments with the legislative tools to establish the necessary measures to prevent chemical accidents, and these policies are typically reflected in emergency and land-use planning (Török et al., 2011a). However, this latest directive has faced fundamental criticism on various fronts. For example, issues related to land-use planning in Slovakia have been raised (Hollá et al., 2021), and there are concerns about its ability to ensure a high level of safety to prevent accidents (Laurent et al., 2021). It is worth noting that the Seveso directives fall short in addressing the environmental impact beyond establishment boundaries (Sikorova et al., 2017).

The Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation (EC 1907/2006) aims to reduce the diverse effects of chemical substances in the EU, and to facilitate the movement of hazardous substances while also protecting the human health and the environment, and providing a reference for effective ways of replacing them with less harmful substitutes (EP and EC, 2006).

Additionally, the EU Waste Framework Directive (WFD) for waste prevention and reduction (EP and EC, 2018) lays down measures for preventing the generation and management of waste, by reducing overall impacts of resource use. Its contribution is introducing the waste hierarchy, based on theory of circular economy. Furthermore, the WFD also addresses hazardous waste, which poses significant environmental and health risks, ensuresuring that hazardous waste is managed safely and responsibly, in compliance with established regulations and best practices, to protect both the European environment and its citizens.

Hazard identification and Risk assessment

The improper handling and management of HW can endanger human health and the environment (Peizhe and Leisheng, 1993). HW possess potential hazards, and risk assessment is a tool for determining their impact on human health and the environment (Mari et al., 2009). However, the impact of HW on human health depends on various factors, including the receptor's exposure, duration, frequency of exposure, as well as the individual's weight, age, gender, and occupation (Li et al., 2012).

An explosion of a container containing magnesium alloy debris at Tianjiayi Chemical Co., Ltd. in Xiangshui Industrial Park (Yang et al., 2020) was caused by the illegal storage of HW for more than seven years, without the use of specially designed facilities for its disposal or temporary storage.

Hazard, according to The United Nations Office for Disaster Risk Reduction (UNDRR, 2022), takes different forms, it can be of natural origin, man-made, associated with human factors and socio-natural which results from both natural and human activities such as deforestation and climate change. Risk comprises three major components: the hazardous event with a potential of causing negative consequences; the likelihood of occurrence, which can be calculated from historical data or by using logic tree models; and the vulnerability of potentially affected factors, such as human, environment or infrastructure. Vulnerability refers to the ability to experience adverse consequences when exposed to a hazardous event (Renjith and Madhu, 2010).

Characterizing wastes as hazardous is related to their potential for flammability, corrosivity, toxicity, and/or reactivity. The HW-based risk depends on the type of these wastes, the environmental and physical conditions around it (Das et al., 2012).

Risk assessment is a process which aims to ensure that all possible accident scenarios and their effects are being taken into account and safety measures are imposed to create a safely controlled environment (BSC, 2022; Lindhout and Reniers, 2017). It is a complex process that requires deep knowledge and specialists to conduct such assessment. Moreover, it gives authorities guidelines towards creating their risk management policies and approaches for protecting natural environment, human health, economy, security, technology, infrastructure and others (EFSA, 2012; Gormley et al., 2011). The process of risk assessment serves to raise awareness regarding the importance of health and safety, thereby prompting proactive measures against potential hazards (Minett, 2022).

In the risk assessment all possible components should be accounted in order to conclude an updated complete assessment. Such results can confirm the credibility of the risk assessment in which decision-makers can rely on in prioritizing the intervention (Lindhout and Reniers, 2017). The potential risk from hazardous substances or wastes can't, unfortunately, be reduced to zero. Therefore, it's important to put control on these substances or wastes in order to properly understand their potential consequences (Dhurandher et al., 2015). Laurent et al. (2021) also consider the worst-case scenario that might occur and emergency and land-use planning (LUP) procedures can include also these scenarios.

METHOD AND MATERIALS

Many methods and techniques for risk assessment, such as risk matrices, fault tree and event tree analysis (Ericson, 2005), HAZard and OPerability study (HAZOP) etc., have been developed and many of these techniques are supported also by computerized software.

Qualitative or semi-quantitative methods are applied to identify potential hazards and to categorize the risk levels associated with dangerous substances, or even HW, that may have adverse effects on the environment and human health. Scenario probabilities and consequences are combined within a risk matrix from which the risk can be categorized either accepted, tolerated or unacceptable (Sikorova et al., 2017), These methods help in assessing and managing the risks associated with hazardous materials and wastes, allowing for informed decision-making and the implementation of appropriate safety measures and controls (Sikorova et al., 2019).

A preliminary hazard analysis (PHA) represents an initial phase in the qualitative risk assessment process, in which the hazards associated with the technological process are identified and evaluated and the risk level of each identified threat is estimated in a qualitative manner. The main purpose of the PHA is to identify at an early stage the critical security requirement for the system and to identify the incidents most likely to occur, so that informed decisions can be made about security measures and risk reduction (Ericson, 2005). However, PHA is also suitable for other phases in the lifecycle of an installation, such as operation, maintenance, planned changes etc., offering a general level of understanding on hazards and risks (Török et al., 2011b). Table 1 present the risk matrix used in PHA.

Table 1. *Risk matrix used in PHA (Török et al., 2011b)*

			Consequences				
			Insignificant	Minor	Moderate	Major	Catastrophic
			1	**2**	**3**	**4**	**5**
Likelihood	Improbable	**1**	*1*	*2*	*3*	*4*	*5*
	Isolated	**2**	*2*	*4*	*6*	*8*	*10*
	Occasional	**3**	*3*	*6*	*9*	*12*	*15*
	Probable	**4**	*4*	*8*	*12*	*16*	*20*
	Frequent	**5**	*5*	*10*	*15*	*20*	*25*

Where: Risk = C x L; C – Consequences; L – Likelihood.

Risk levels:

- 1-3: Very low risk – the operator is following normal operational procedures and maintenance;
- 4-6: Low risk – normal operational procedures and maintenance;
- 8-12: Moderate risk – specific operational and maintenance procedures to follow in order to maintain the risk at this level;
- 15-16: High risk – Prompt risk reduction measures to be taken in order to mitigate the risk;
- 20-25: Extreme risk – Immediate risk reduction measures are necessary to mitigate the risk.

The hazard identification and risk analysis process applied for the selected case study, a HW management plant in Ploiești city, Romania, starts with a PHA of the waste treatment process. The main results of this analysis consist in the list of potential accident scenarios and their level of risk. Based on expert judgement, some of these scenarios were selected for quantitative consequence analysis, by using EFFECTS modelling and simulation software v.11, developed by Gexcon.

In order to construct the model, publicly available documents, such as the Site Report (ANPM, 2023a) and the Integrated Environmental Authorization (ANPM, 2023b), have been used as data sources.

In addition to ArcGIS (ESRI-Canada) for spatial analysis was used. The location of the HW management plant is presented in figure 1.

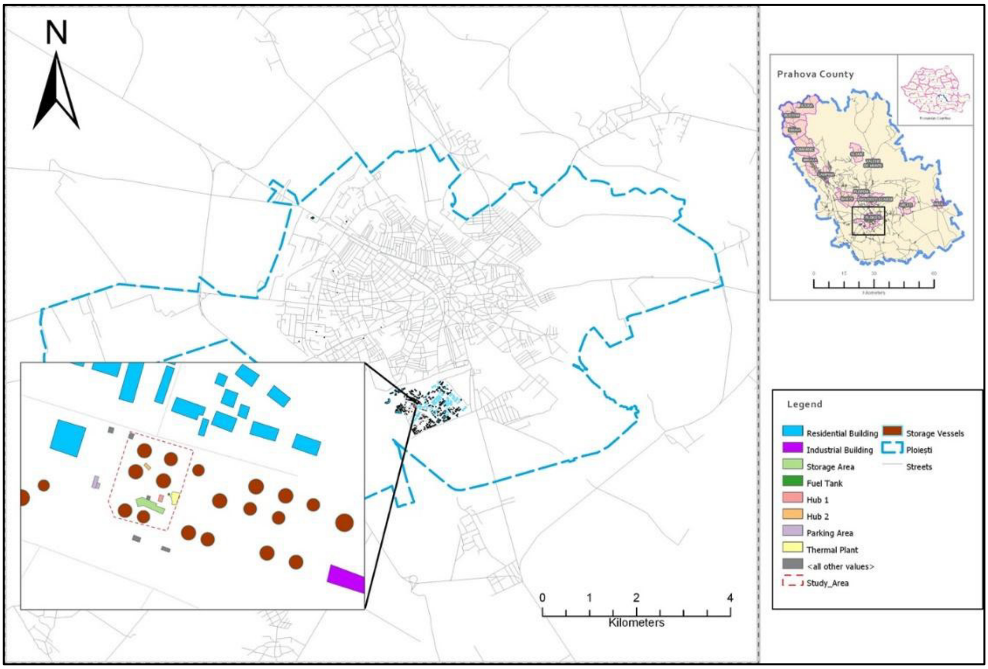

Fig. 1. *Study area location*

Figure 2 presents the HW treatment process flow diagram. The diagram was built up by the authors of this paper, based on the information available in the Site Report (ANPM, 2023a) and the Integrated Environmental Authorization (ANPM, 2023b). Since the information in these two documents is limited and no details on safety systems for accident prevention and consequence mitigation could be found, in the PHA a two-level risk analysis was applied, firstly by considering the absence of such systems and secondly by taking into account possible risk mitigation measures.

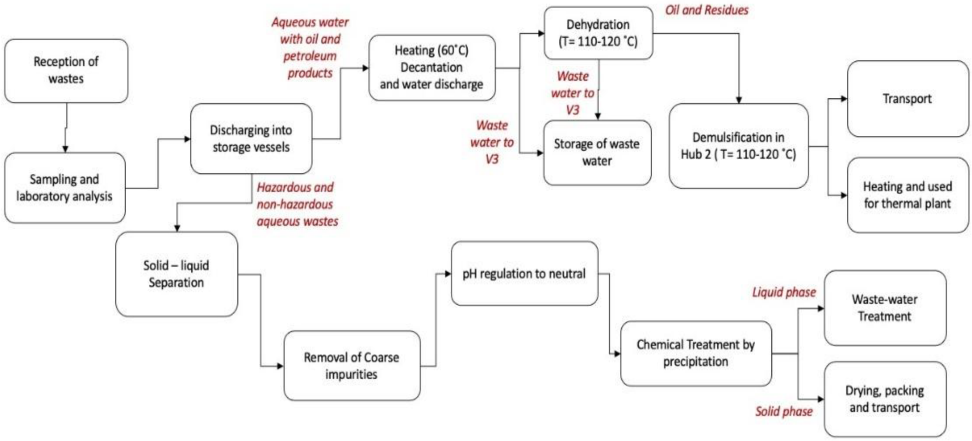

Fig. 2. *Hazardous wastes treatment process flow diagram*

The analysis is focusing on the identification of potential accident scenarios, involving fires and explosion due to HW accidental release or inappropriate process conditions. From this reason, only the HW containing flammable materials, such as oil and petroleum products, were considered in further analyses.

In order to identify the potential hazards of the HW treatment process, the flow diagram was divided into the most important stages as follows:

I. Transfer and discharge of HW into storage vessels: high waste water content, normal temperature;

II. Decantation of oil and petroleum products: high waste water content, temperature: 60 ^{o}C;

III. Dehydration: medium waste water content, temperature: 110-120 ^{o}C;

IV. Demulsification in Hub2: low waste water content, temperature: 110-120 ^{o}C.

RESULTS

An extract with the most important hazards and potential accident scenarios identified during the qualitative PHA is presented in Table 2. The risk are presented in Table 3, where the risk values with “red” text present the situation before applying mitigation measures and with “black” text the situation after the mitigation measures are implemented.

Table 2. *PHA developed for the waste treatment process (Probability - P, Consequences - C and Risk - R)*

No.	Possible Hazard*	Cause	Consequence	Risk before mitigation measures			Possible risk mitigation measures	Risk after mitigation measure		
				P	C	R		P	C	R
I.	**Transfer and discharge of HW into storage vessels**									
A	**Continuous loss of hazardous wastes due to mechanical failure**									
A1	Exceeding the permissible pressure during transfer	- Failure in pump's controlling system - Blockage inside the pipelines or pumps	- An increase in the pressure which might lead to an elimination of hazardous waste - Contamination of soil and emission of toxic wastes into the ecosystem - Potential source of fire or explosion hazard	3	3	9	- Periodic maintenance of equipment and instrumentation - Leakage detecting and collecting systems - High pressure valve to avoid failure due to pressure increase - Pressure indicator, alarm and controller system	2	2	4
A2	Degradation due to corrosion, aging of equipment or vibrations	- Advanced corrosion of the storage vessels - Corrosion of the pipelines - Corrosion of the pumps - Aging of sealing at joints	- Leakage of hazardous liquid wastes - Elimination of hazardous wastes inside the emplacement with possible contamination of the environment	4	3	12	- Periodical maintenance of the vessels and corrosion protection by painting; cathodic protection of vessels and pipelines; - Leakage detecting and collecting systems	2	2	4
II.	**Decantation of oil and petroleum products: high waste water content, temperature: 60 °C**									
B	**Continuous loss of hazardous wastes due to mechanical failure**									
B1	Exceeding the permissible capacity of the decantation unit	- High flow rate of the hazardous liquid wastes into the decantation unit - Blockage at the exit point of liquid wastes from the decantation unit	- Continuous release of hazardous liquid wastes next to the decantation unit and contamination of the environment	3	3	9	- High flow rate indicator, alarm and control - Removal of course parts of the waste by mechanical filters; - Leakage collecting system; - Periodical supervision of the decantation process by operator;	1	2	2

No.	Possible Hazard*	Cause	Conse-quence	Risk before mitigation measures			Possible risk mitigation measures	Risk after mitigation measure		
				P	C	R		P	C	R
B2	Exceeding the per-missible tempera-ture of the liquid waste	- Excess heating of liquid waste and increase of temperature above 60 ºC	- Volatilization of organic components from the petroleum waste; - Potential formation of explosive atmosphere	3	4	12	- Temperature sensor, indicator and alarm;	2	2	4
III. Dehydration: medium waste water content, temperature 110-120 ºC										
C	**Fire or toxic emissions from inside the equipment**									
C1	Exceeding the per-missible tempera-ture in de-hydration processes	- Failure in the functioning of the temperature control system	- Reaching the flash point of one of the petro-leum waste components, leading to a fire inside the dehydration equipment	3	5	15	- Temperature sensor, indicator and alarm; - Installation of fire extinguishing systems; - Ventilation of the building to avoid accumulation of explosive athmospheres.	2	4	8
IV. Demulsification in Hub2: low waste water content, temperature: 110-120 ºC										
D	**Fire or toxic emissions from inside the equipment**									
D1	Exceeding the per-missible tempera-ture in de-mulsifica-tion pro-cesses	- Failure in the function-ing of the temperature control system	- Reaching the flash point of one of the petro-leum waste components, leading to a fire inside the demulsification Hub2	3	5	15	- Temperature sensor, indicator and alarm; - Installation of fire extinguishing systems; - Ventilation of the building to avoid accumulation of explosive athmospheres.	2	4	8
D2	Failure in flammable vapor or fire detecting system	- Failure of flammable gas or vapor senzors - Failure of fire detection system	- Accumula-tion of flammable vapors in Hub2 and increase of pressure - Fire spreading to other equipment	3	5	15	- Periodic maintenance and testing of the sensors	2	4	8

No.	Possible Hazard*	Cause	Conse-quence	Risk before mitigation measures			Possible risk mitigation measures	Risk after mitigation measure		
				P	C	R		P	C	R
E	Vapor cloud explosion inside demulsification Hub2									
E1	Failure in flammable vapor detecting system	- Failure of flammable gas or vapor senzors	- Accumulation of high concentra-tions of flammable vapors - Explosion of vapors	3	5	15	- Periodic maintenance and testing of the sensors - Ventilation of the building to avoid accumulation of explosive athmospheres.	2	4	8
E2	Insufficient protection against earth-quakes	- Bad design of building or equipment	- Elimination of flammable hazardous wastes into the surround-ings in uncontrolled quantities - Collapse of installations - Potential fire and explosion	2	5	10	- Applying earthquake resistant design; - Protection of utilities against earthquakes; - Specific emergency planning for Natech situations;	1	4	4

Table 3. *Risk matrix of the HW treatment process – without mitigation measures (red text); with mitigation measures (black text)*

			Consequences				
			Insignificant	Minor	Moderate	Major	Catastrophic
			1	**2**	**3**	**4**	**5**
Likelihood	Improbable	**1**	*1*	*2: B1*	*3*	*4: E2*	*5*
	Isolated	**2**	*2*	*4: A1, A2, B2*	*6*	*8: C1, D1, D2, E1*	*10: E2*
	Occasional	**3**	*3*	*6*	*9: A1, B1*	*12: B2*	*15: C1, D1, D2, E1*
	Probable	**4**	*4*	*8*	*12: A2*	*16*	*20*
	Frequent	**5**	*5*	*10*	*15*	*20*	*25*

As it can be noted from the risk matrix, without mitigation measures the risk of the HW treatment process ranges between 9 and 15, representing potential threats that need to be immediately dealt with, by applying prevention measures, stringent operating procedures, periodic maintenance and consequence mitigation measures in case of accidental release of hazardous liquids or vapours.

After introducing mitigation measures, it is evident that the risks have been significantly reduced and are now within permissible levels, categorized as either low or moderate. This indicates that normal or specific operational and maintenance procedures should be followed.

However, the most hazardous stage was identified being the Demulsification in Hub 2, where hazardous wastes are heated up to 120˚C. Therefore, hazards such as flammable vapor release and explosion were identified with the highest risk level and computer simulation via software EFFECTS were carried out in order to quantify the potential consequences on human health (figure 3). The explosion scenario considers the release of

Fig. 3. *Vapor-Cloud Explosion consequence areas from Computer Simulation –Effects*

flammable vapours in the Hub 2 building and ignition of the cloud when it reaches the Lower Explosion Limit. The estimated quantity of Fuel Oil vapours (the material used in the simulations) is 5.6 kg.

The effects of the Vapor-Cloud Explosion are presented in Fig. 3 in terms of buffer zones that differ in their pressure intensity. The overpressure levels have been set based on the provisions of Ministerial Order 156/2017 on the development and testing of emergency plans (MIA, 2017).

Within the zone marked by the orange circle, the overpressure generated by the explosion can reach or exceed 140 mbars, potentially leading to severe consequences for human health, including the risk of fatalities. In the area between the orange and yellow circles, where overpressure falls within the 70-140 mbar range, irreversible effects on human health are anticipated, such as hearing loss due to eardrum rupture and mild lung impairment. In the area between the yellow and blue circles, which extends beyond the site's boundaries, overpressure in the 30-70 mbar range is expected, causing effects such as the breakage of windows and mild health impacts on humans.

In the risk analysis other types of hazards for human health and environment were identified, such as odour levels, noise pollution, potential leakages of petroleum product and oily water leading to groundwater and environmental pollution.

Protective measures for containing the consequences of these hazards have been recommended in the PHA report. The presence of the concrete walls around Hub 2 and the site boundaries are reducing some of the effects of potential accidents and noise pollution.

CONCLUSIONS

Urban activities are the primary drivers of the increasing quantities of hazardous waste generated each year, resulting in significant environmental and health consequences. Hazardous waste possesses specific harmful properties that necessitate specialized management. In this study, it was demonstrated that the analysed process does not pose a significant risk. Furthermore, the site does not fall under the provisions of the Seveso Directive, and the hazardous waste contains a high-water content, exceeding 70%. However, some stages of the treatment process may present accident risks.

Nevertheless, uncertainties in the study are still associated with the hazardous wastes content and its flammability, as well as the precise dimensions of the hub where an explosion could occur. The presence of concrete walls serves as a protective layer in the event of a Vapor-Cloud Explosion, potentially containing the consequences within the site area and ensuring that the nearby population remains unaffected by this type of accident.

The results of such risk assessment studies can facilitate decision making in land-use and emergency planning procedures.

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