# AES BIOFLUX

### Advances in Environmental Sciences -International Journal of the Bioflux Society

## Chemical risk assessment for storage of hazardous materials in the context of Land Use Planning

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**Abstract.** Historical technological accidents caused in numerous occasions the major environmental pollution and the loss of many human lives. Lessons learned from these accidents contributed significantly to the development of technological safety in two ways: technological and legislative. After three years from the adherence of Romania to EU, a coherent legislation for land-use planning is still missing in the context of Article 12 of Seveso Directive. Nowadays there are more than 200 Seveso-type economical operators in Romania, most of them with major risk, located close to areas highly vulnerable for population or environment. The elaboration of risk assessment studies for the technological accidents prevention, land-use planning and emergency planning is necessary and essential for these sites. Based on these studies the population can be informed, instructed and prepared for accidents, thus saving many lives. In this paper the development of a risk assessment methodology for land-use and emergency planning is proposed for Seveso-type sites, where large quantities of dangerous, explosive, flammable or toxic substances are stored, handled or processed. Three case studies were considered storage of common hazardous substances: propane, chlorine and ammonium nitrate. Several methodologies applied in the EU member states were approached and the proposed methodology is based on the results of this research.

Key Words: hazardous materials, risk assessment, land use planning, consequences.

Rezumat. Accidentele tehnologice istorice au cauzat de multe ori poluarea excesivă a mediului și pierderea multor vieți omenești. Lecțiile învățate în urma acestor accidente au contribuit în mod semnificativ la creșterea siguranței tehnologice, prin două căi: pe cale tehnologică și pe cale legislativă. După trei ani de la aderarea la UE, în România încă nu există o legislație coerentă privind planificarea utilizării terenurilor în contextul prevederilor art. 12 al Directivei Seveso. Momentan în România există peste 200 de operatori economici clasificați tip Seveso, majoritatea lor cu risc ridicat, localizați în apropierea zonelor cu vulnerabilitate crescută pentru populație sau mediu. În cazul acestor amplasamente necesitatea elaborării unor studii de risc este esențială în prevenirea accidentelor tehnologice, în planificarea utilizării teritoriului și în planificarea urgențelor. Pe baza acestor studii populația poate fi informată, instruită și pregătită pentru accidente, ceea ce poate să salveze multe vieți omenești. Articolul propune dezvoltarea unei metodologii de evaluare a riscului pentru planificarea utilizării terenurilor și planificarea urgențelor în cazul amplasamentelor de tip Seveso, unde sunt depozitate, transportate si procesate substante periculoase inflamabile, explozive sau toxice în cantități mari. Pentru elaborarea metodologiei au fost luate în considerare trei studii de caz cu scenarii accidentale tehnologice la depozitarea unor substanțe periculoase comune: propan, clor și azotat de amoniu. În studiile de caz au fost cercetate mai multe metodologii aplicate în statele membre ale UE, iar metodologia propusă se bazează pe rezultatele acestor cercetări.

Cuvinte cheie: materiale periculoase, evaluare de risc, planificarea utilizării terenurilor, consecințe.

**Introduction**. Technological accidents can have a major impact on human health and environment. The risk assessment process is the first step in the Technological Disasters Management process and it sets the basis for measures to be taken for prevention of technological accidents and reduction of risk.

Many industrial sites were built near highly populated residential areas or vice versa, ignoring the risks of the technological accidents. These accidents prompted the adoption of legislation aimed at the prevention and control of such accidents. The Seveso

II Directive amended by the Directive 2003/105/EC, applies in the European Union (EU) as the main Directive for major industrial accidents prevention and control to some thousands of industrial establishments where dangerous substances are present in quantities exceeding the thresholds in the directive. The Article 12 of the Directive reads as follows: "Member states shall ensure that the objectives of preventing major accidents and limiting the consequences of such accidents are taken into account in their land use policies and/or other relevant policies..." (MAHB 2006). The Directive does not contain a pre-established risk analysis methodology with threshold limits for Land Use Planning (LUP) and the EU Member States are using their own methodologies for LUP.

The F-Seveso effectiveness study indicated a number of 202 Seveso-type sites in Romania in 2007 (Salvi et al 2008), placing the country on the 10<sup>th</sup> position among the European countries. There is a gap in the Romanian legislation regarding a specific risk analysis methodology for the calculation of LUP distances in case of Seveso type industrial sites.

The aim of the paper is to find efficient solutions for technological risk assessment for LUP and Emergency Planning (EP) and the proposal of a methodology which can be used in Romania with this purpose for Seveso-type sites, where dangerous substances are stored, handled, transported and processed in large quantities.

The paper considers three case studies of potential technological accidents in the storage of propane, chlorine and ammonium nitrate. The hazards and risks are analyzed and the obtained results are compared with the purpose to propose the risk assessment methodology. These three substances were selected for the study from several reasons: 1. they are widely used in chemical, petrochemical, mining industries and agriculture; 2. they present almost all the chemical accident types, with release of uncontrolled energy; 3. they are stored in large quantities; 4. they can be found in many cases close to vulnerable areas.

The paper presents an innovative approach of modelling and simulation of technological accidents, a comparative analysis of newer and older modelling techniques. The results of the simulations are analyzed in the context of LUP using the threshold limits of the French, Italian and Austrian LUP methodologies, in order to establish the most adequate threshold limits for the Romanian legislation.

#### Material and Method

In the field of risk assessment there are differences of opinion regarding the use of qualitative or quantitative risk analysis methods. The qualitative-quantitative factor is the basic property of hazards analyses methods. Most of the analysis methods are developed in order to identify hazards and to determine the risk of that hazard to turn into an accident.

To determine the accident risk of the identified hazard, a methodology for the characterization of probability and magnitude parameters must be used. There were developed both qualitative and quantitative methods, which are successfully used, each methods having its specific advantages and disadvantages. Qualitative analysis implies the use of qualitative criteria, using different categories for parameters separation, with qualitative definition which establish the scale for each category. Also, qualitative decisions are made, based on the field experience, in order to assign elements into categories. This approach is subjective, but it allows a higher generalization degree, being less restrictive. Quantitative results. This approach is more objective and more precise. It must be mentioned that the quantitative results can be highly affected by the precision and validity of the input parameters. Therefore, the quantitative results within the risk analyses should not be taken into consideration as exact numbers, but as estimates, with a variable scale depending on data quality.

The combined use of qualitative and quantitative methods seems to be the most adequate way to estimate the technological risk in a complete manner, taking into account the experience of the assessor, the accumulated knowledge in this field and the sophisticated technology in computer based modelling and simulation. With the combined use of these methods and techniques the effects and consequences of the studied accidents were determined and the LUP and EP distances were calculated.

The proposed methodology in the paper is based on the following techniques and methodologies:

- qualitative hazard identification and risk assessment using techniques like HAZOP studies (Hazard and Operability), FMEA (Failure Modes and Effects Analysis), DOW's FEI (Fire and Explosion Index) analysis, risk matrices etc.;

- The French methodology for LUP developed by the Ministry of Ecology, Energy, Sustainable Development and Sea in France;

- The Italian methodology for LUP developed by the Ministry of Public Works in Italy;

- The Austrian methodology for LUP developed by the "Permanent Seveso Working Team" in Austria.

**Case study no 1: Accidents involving propane or liquefied petroleum gas (LPG).** During the last 50 years numerous technological accidents occurred in the petroleum refining and petrochemical industry, accidents involving very flammable substances, like LPG (liquefied petroleum gas) and other petroleum products, generating BLEVE (Boiling Liquid Expanding Vapour Explosion).

Propane is included in the gaseous hydrocarbons category, as it is a saturated acyclic alkane with a three carbon atoms chain, connected by simple covalent links. LPG is a mixture of gaseous hydrocarbons, usually containing propane-butane in higher percentage and propylene-butylene in lower percentage. Propane and LPG are stored in liquefied state and they are used as fuels for machinery and heating equipments, being classified as highly flammable and explosive substances.

A comparative study between the results obtained from BLEVE phenomenon modelling and the consequences recorded for the Feyzin accident (1966), in France (Mannan 2005) was performed, in order to offer proposals for a risk assessment methodology for LUP in case of LPG storage facility.

By definition, the BLEVE, a boiling liquid expanding vapour explosion, is typical for the liquids at a higher temperature then the boiling point (in normal atmospherically conditions), like the liquefied gases, in case of tank rupture (failure) (Van Doormaal & Van Wees 2005). BLEVE explosions can be generated by two mechanisms:

- tank failure caused by corrosions or strong mechanical pressures: "cold BLEVE";

- in case of fires involving equipments (tanks, vessels, pumps, pipes), containing LPG: "hot BLEVE"; due to the heat, the material weakens, the containment becomes over pressurised, generating the failure of the material and sudden explosion of the equipment.

During explosions, the personnel and the valuable goods will be affected by the overpressure generated by the explosion (the shock wave), by the thermal radiation resulted from the fireball (FB) or by mechanical impact of missiles projected by the explosion's blast.

In the speciality literature there are several models for describing BLEVE phenomenon. Some models describe the overpressure phenomenon in case of BLEVE explosions, while other models describe the phenomenon's dynamics and calculate the heat radiation depending on the distance from the explosion centre and time. Standard techniques use static models for assessing heat radiation in case of BLEVE. These techniques presume that the heat radiated by the FB is constant throughout the combustion time period. Based on the experimental researches, dynamic models were also built, which consider the evolution of the heat radiation from the FB, changes in the shock waves power and form, thus offering more realistic results in estimating dangerous areas for burns and overpressure effects (Roberts 2000).

**Accident causes and development.** The Feyzin accident occurred on 4<sup>th</sup> of January 1996 at a LPG deposit. The accident is considered the most severe industrial catastrophe in the France recent history. This case was selected for study because it was well

analysed and documented by experts and the data can be used for modelling and computer simulations.

The site was located at a 22.5 m distance from the A7 highway, near Feyzin city. The deposit included 10 vessels, out of which 8 were spherical and 2 cylindrical, equally divided for propane and butane. During water purging and sampling from the T61-443 propane storage tank, the operators fault the procedures and a major propane release took place. The propane cloud increased and spread over the nearby highway. The highway traffic was stopped, but a car entered the cloud and the cloud ignited from a hot spot of the car. The fire propagated towards the refinery and the sphere caught fire. The firemen arrived and responded using water jets and cooled down the tank, in vain. The T61-443 sphere BLEVE'd (the first explosion), a 250 m diameter FB rose rapidly 400 m high. The shock wave propagated 16 km on the Rhone Valley. The windows in the city broke on a distance of 8 km. In the moment of the explosion, heavy missiles blew up in the air, causing severe damages to other spheres, pipes and equipments in the area. The T61-442 sphere was severely damaged, caught fire and exploded BLEVE (the second explosion). The losses were catastrophic, 18 people were killed, 84 were seriously injured, all the tanks were destroyed containing 2000 m<sup>3</sup> propane, 4000 m<sup>3</sup> butane, 2000 m<sup>3</sup> hydrocarbons and 6 fire trucks were destroyed (French Ministry of Environment 2006).

**Case study no 2: Chemical accidents involving liquefied chlorine.** This case study identifies hazards and risks associated to chlorine storage and use. Chlorine is a highly used substance in chemical industry, in organic and inorganic syntheses. There were several accidents involving chlorine release, generating human losses and affecting human health, due to its toxic and irritating properties.

Chlorine is a dense gas, yellow-green and with an unpleasant, suffocating odour. Liquefied chlorine has the aspect of an oily liquid, green and with a chlorine content of min. 99.7 % vol. and a water content of max. 0.05 %. It is used in the chemical industry due to its high reactivity, as a strong oxidising agent or chlorination agent. Also, chlorine is used for water disinfection, being a toxic substance for micro organisms and aquatic species. Chlorine is stored in large volume tanks, containing tons of liquefied chlorine.

The objectives of the study are the estimation of risks associated to chlorine storage, calculation of dangerous areas for the populations and finding practical, efficient solutions for LUP and chemical emergency planning. Therefore, a comparative study between the results of the chlorine dispersion modelling, using a bi-dimensional and a tri-dimensional dispersion model was performed. The simulations were performed using two software, namely:

1. SEVEX View – major chemical accidents simulation software, using a complex meteorological model, terrain topography and 3D Lagrangian dispersion model (ATM-Pro 2009).

2. SLAB View – toxic dispersion simulation software, using the bi-dimensional SLAB model (Lakes Environmental 2009).

Possible major accidents are analyzed by using toxic dispersions simulations and the dangerous areas are estimated, in order to offer solutions for LUP and EP in case of liquefied toxic substances storage.

The studied site is located in Turda town, Romania, in the industrial area, at an altitude of approximately 330 m above sea level. The facility consists of the liquid chlorine bottling machine and the liquid chlorine storehouse. The liquid chlorine storehouse included two 56 t tanks each, one tank always empty for safety reasons.

Based on the study of the tank, the critical points of chlorine accidental releases were identified. According to these critical points, several accidental scenarios of chlorine release were elaborated, namely:

A. From the storage tank:

1. Catastrophic releases of the total stored chlorine (56 tons) – considered the *worst case scenario*;

2. Continuous chlorine release through the R7A flange coupling, in a 10 minutes period (considered the necessary period of time for stopping the release).

#### *B. From a 1000 kg cylinder:*

1. Catastrophic release scenario – considered the *worst case scenario* with cylinders.

**Case study no 3: Chemical accidents involving ammonium nitrate.** Ammonium nitrate (AN) is a substance often used as fertilizer in agriculture, but it presents the following disadvantages: highly hygroscopic, oxidizing and explosive character. Due to these dangerous properties the AN is widely used as explosive in the mining industry. After the Toulouse (2001) accident, AN was included in the list of dangerous substances of Seveso directive.

The objective of the case study is to find practical and efficient solutions for LUP and EP in the case of AN storage, handling and transportation.

Ammonium nitrate is a salt obtained from the neutralization reaction of nitric acid with ammonia. AN is an oxidizing agent that, when heated to high temperatures in confined spaces, forming pressure, can produce violent reactions and can explode, especially if it is contaminated with other substances (combustible materials, reduction agents, lubricants etc.) (Martel 2004).

Three main hazards can be associated to AN:

- Instability in decomposition process;
- Fires (due to its oxidizing nature);
- Explosions.

The studied site is a harbour, where AN is stored in warehouses in large quantities. The AN is loaded in ships and transported.

#### **Results and Discussion**

**Case study no 1: Accidents involving propane or liquiefied petroleum gas (LPG).** The analysis is focused on the BLEVE of the T61-443 sphere. The consequence analysis can be performed only if the propane quantity contained by the tank at the moment of explosion is estimated. Based on different information sources (operators, workers, technical data), the experts investigating the accident found two approximations for the propane flow rate from the purging system. Using these approximations, two propane quantities left in the tank before the explosion were calculated. A third quantity was calculated using the propane flow simulation, with the TPDIS (Two Phase Bottom Discharge Model) model (Van den Bosch & Duijm 2005), within the EFFECTS 7 software, developed by the TNO Dutch Company (TNO 2009). Thus, these approximations are:

*Case no 1:* based on the propane tank technical data, a flow of 8 kg/s was calculated (French Ministry of Environment 2006). Considering a discharge period of 125 minutes from the starting point until the BLEVE, this paper estimated the spilled propane quantity at 131 t, according to the calculations: 7,500 s x 8 kg/s = 60,000 kg = 60 t; 60 + 71 = 131 t; (60 t from the purging system and 71 t from safety valve). The propane quantity estimated in the tank at the BLEVE moment was **217 t** (348 – 131 = 217 t).

*Case no 2:* the T61-443 sphere volume counter was found blocked after the explosion at 647 m<sup>3</sup>, with a 46 m<sup>3</sup> (23 t) difference from the 693 m<sup>3</sup> initial volume of liquid propane (348 t). The sphere was loaded until the purging incident. Technicians declared that the counter blocking could have happened any time until the explosion moment (in the 125 minutes), but most likely the fire from the safety valve caused the blocking, so that the spilling was reduced to 60 minutes. The spilling flow from the purging system was estimated at 6.4 kg/s (French Ministry of Environment 2006), according to the calculations: 23,000 kg / 3,600 s = 6.38 kg/s  $\approx$  6.4 kg/s. Considering this flow, in this paper the propane quantity in the tank in the moment of explosion is estimated at **231 t**, according to the calculations:

6.4 kg/s x 7,200 s = 46,000 kg; 46 + 71 = 117 t (46 t from the purging system and 71 t from the safety valve); 348 - 117 = 231 t.

*Case no 3:* Propane spilling simulation using the TPDIS model

The simulation was performed considering the 125 minutes spilling from the 2'' pipe and the quantity spilled for 60 minutes from the safety valve (71 t).

The final quantity in the tank is estimated at **181 t**, according to the calculations: 96 + 71 = 167 t (spilled quantity); 348 - 167 = 181 t (quantity left in the tank). The average spilling flow estimated through simulation is 13.244 kg/s.

Considering these three different estimations for the propane quantity in the tank at BLEVE moment, in this paper simulations were performed, using the static, dynamic model and vessel rupture model, in order to estimate the accident's physical effects and consequences. These models are included in the "EFFECTS 7" simulation software (TNO 2009).

The static and dynamic model offers results on the FB's duration and diameters and the heat radiation effects and consequences. The "vessel rupture" model calculates the distances at which tank fragments are thrown and the effects of the overpressure formed after the explosion. The simulation results for the three models for the three estimated quantities and the recorded values of the accident are presented in Table 1.

Table 1

Model	Case no 1. – 217 t	Case no 2. – 231 t	Case no 3. – 181 t
<i>static BLEVE</i>	$t_{FB} = 20.793 \text{ s}$	$t_{FB} = 21.13 \text{ s}$	$t_{FB} = 19.83 \text{ s}$
	$D_{FB} = 351.5 \text{ m}$	$D_{FB} = 358.72 \text{ m}$	$D_{FB} = 331.36 \text{ m}$
	$H_{max} FB = 527.25 \text{ m}$	$H_{max} FB = 538.08 \text{ m}$	$H_{max} \text{ FB} = 497.04 \text{ m}$
dynamic BLEVE	$t_{FB} = 19.425 \text{ s}$	t <sub>FB</sub> = 19.73 s	$t_{FB} = 18.563 \text{ s}$
	$D_{FB} = 348.54 \text{ m}$	D <sub>FB</sub> = 355.88 m	$D_{FB} = 328.07 \text{ m}$
	$H_{max} \text{ FB} = 522.8 \text{ m}$	H <sub>max</sub> FB = 533.81 m	$H_{max} \text{ FB} = 492.11 \text{m}$
BLEVE – vessel	LF79 = 394.11 m	LF79 = 416.98 m	LF79 = 335.92 m
rupture	L30 = 359.2 m	L30 = 367.9 m	L30 = 335.5 m
Recorded values	$D_{FB} = 250 \text{ m}$ $H_{max} FB = 400 \text{ m}$ LF79 = 248  m L30 = 4000  m		

Simulation results of BLEVE and recorded values of Feyzin accident

 $t_{\mbox{\tiny FB}}$  – Duration of fireball;  $D_{\mbox{\tiny FB}}$  – maximum diameter of fireball;  $H_{\mbox{\tiny max}}$  FB – Fireball maximum lift height; LF79 – distance calculated for 79 tones fragment was thrown; L30 - 30 mbar overpressure contour distance.

As one can see, the differences between the results of the two models, static and dynamic, regarding the FB diameters are smaller then 1%. On the contrary, the differences between the results regarding the heat radiation consequences calculated using the static model and the dynamic model are significant. The dynamic model calculates smaller distances for consequences (I, II, III degree burns) considering the dependence of the fire ball on time (Martinsen & Marx 1999), as it is represented in Figs 1 and 2.



Figure 1. Burns depending on distance – static BLEVE model (green – case 1, blue – case 2, red – case 3)



Figure 2. Burns depending on distance – dynamic BLEVE model (green – case 1, blue – case 2, red – case 3)

The differences between the results of the physical effects and the consequences of the three cases simulations are small, despite the large differences between the propane quantities.

There is a significant difference between the results of the BLEVE overpressure simulations using the "vessel rupture" model and the overpressure values estimated by the experts in the accident's investigation. The 30 mbar overpressure contour was estimated by the experts at a maximum distance of 4 km along the Rhone valley (French Ministry of Environment 2006), and based on the simulations performed within this paper, the obtained values ranged between 335 and 368 m.

The most similar simulation results to the results estimated after the Feyzin accident investigation regarding the FB maximum diameter, FB maximum lift height and thrown fragments distances (considering the B4 fragment weighting 79 t) were obtained using the quantity estimated in Case no 3 (181 t), with propane spilling simulation. Thus, the distances for land-use planning were calculated using this quantity.

**Consequences analysis in LUP using the French, Italian and Austrian methodologies.** The French LUP methodology aims at estimating magnitude and accidental scenarios probability, using the following limit values in representing the physical effects (French Ministry of Ecology, Energy, Sustainable Development and the Sea 2009):

a) Stationary heat radiation effects:

1. High lethality: 8 kW/m<sup>2</sup> (III degree burns at 20 s exposure 20 s (Van den Bosch & Twilt 1989); 2. Beginning of lethality: 5 kW/m<sup>2</sup>; 3. Irreversible effects: 3 kW/m<sup>2</sup> (II<sup>nd</sup> degree burns at 20 s exposure 20 s (Van den Bosch & Twilt 1989);

b) Effects of heat radiation variable in time, expressed by heat load:

1. High lethality: 1,800  $[(kW/m^2)^{4/3}]$ ·s; 2. Beginning of lethality: 1000  $[(kW/m^2)^{4/3}]$ ·s; 3. Irreversible effects: 600  $[(kW/m^2)^{4/3}]$ ·s;

c) Overpressure effects (Federal Ministry of Environment, Nature Conservation and Reactor Safety, Germany 2010):

1. High lethality: 200 mbar (concrete buildings and metallic structures are destroyed (Uijt De Haag & Ale 2005)); 2. Beginning of lethality: 140 mbar (partial collapse of buildings walls (Van Doormaal & Van Wees 2005); 3. Irreversible effects: 50 mbar (minor damages in buildings, windows break (Van Doormaal & Van Wees 2005); 4. Indirect effects: 20 mbar (windows break);

Considering the limits imposed by the French methodology, BLEVE simulations were performed, using the three available models, in order to analyze the differences between the obtained distances to select the most adequate method and model.

The calculated distances are presented in Table 2.

Table 2

Calculated	distances	for LUP	usina	the	French	methodology
Calculated	uistances		using	the	THENCH	methodology

Case no 3 (181 t)	<i>static BLEVE model</i> ( <i>kW/m</i> <sup>2</sup> )	dynamic BLEVE model ([s*(kW/m²)^4/3])	"vessel rupture″ model (mbar)
			(111541)
High lethality	834	295	92
distance (m)			
Beginning of lethality	1069	391	97.5
distance (m)			
Irreversible effects	1386	488	214
distance (m)			
Indirect effects	-	-	472
distance (m)			

Comparing these results with those recorded after the Feyzin accident, it can be concluded that the results obtained by using the static model are overestimated, due to the fact that in the static model the heat radiation from the FB is considered constant during the FB evolution.

According to the Italian LUP guide (Italian Ministry of Public Works 2001), the below mentioned limit values are considered for BLEVE:

a) Effects of stationary heat radiation (Italian Ministry of Public Works 2001):

1. High lethality: 12.5 kW/m<sup>2</sup>; 2. Beginning of lethality: 7 kW/m<sup>2</sup>; 3. Irreversible effects: 5 kW/m<sup>2</sup>; 4. Reversible effects: 3 kW/m<sup>2</sup>; 5. Domino effects: 12.5 kW/m<sup>2</sup>;

b) Effects of heat radiations variable in time:

1. *High lethality:* FB radius (100% mortality according to (Uijt de Haag & Ale 2005); 2. *Beginning of lethality:* 350 kJ/m<sup>2</sup>; 3. *Irreversible effects:* 200 kJ/m<sup>2</sup>; 4. *Reversible effects:* 125 kJ/m<sup>2</sup>;

c) Overpressure effects (Federal Ministry of Environment, Nature Conservation and Reactor Safety, Germany, 2010):

1. *High lethality:* 300 mbar (buildings complete collapse (Mannan 2005)); 2. *Beginning of lethality:* 140 mbar; 3. *Irreversible effects:* 70 mbar (buildings partial collapse (Mannan 2005)); 4. *Reversible effects:* 30 mbar; 5. *Domino effects:* fragments to 200-800 m;

The Italian LUP methodology uses the heat radiation limits  $(kW/m^2)$  in case of long-term fires and radiation doses  $(kJ/m^2)$  in cases of short-term FB phenomenon. The calculated distances are presented in Table 3.

Table 3

Case 3 (181 t)	<i>static BLEVE</i> model (kW/m²)	static BLEVE model (results expressed in	"vessel rupture" model (mbar)
		$kJ/m^2$ )	· · ·
High lethality	647	169	72
distances (m)			
Beginning of lethality	896.5	521.5	97.5
distance (m)			
Irreversible effects	1070	733.5	164
distances (m)			
Reversible effects	1386	948	335.5
distances (m)			

Calculated distances for land-use planning

The use of heat dose  $(kJ/m^2)$  in the Italian LUP methodology is taking into consideration the duration of the FB, but without the variation of heat radiation during the FB evolution. It is a simple conversion of the heat radiation expressed in  $(kW/m^2)$  multiplied with the duration of FB.

The Austrian Permanent Seveso Working Group establishes the following limit values for BLEVE phenomenon (Austrian Permanent Seveso Working Group 2010): a) heat radiation effects:

1. Land-use planning: 2 kW/m<sup>2</sup> (generates discomfort at a exposure longer than 20 s (Uijt de Haag & Ale 2005)); 2. Domino Effects: 12.5 kW/m<sup>2</sup>;

c) Overpressure effects:

1. Land-use planning: 25 mbar (windows break (Uijt de Haag & Ale 2005)); 2. Domino effects: 100 mbar (corresponding to severe building damages and deceases probability equal to 0.025 (Uijt de Haag & Ale 2005)).

Simulation results are presented in Table 4.

Table 4

Calculated distances for land-use planning

Case no 3 (181 t)	Static BLEVE model (kW/m²)	"vessel rupture" model (mbar)
LUP distances (m)	1500	392.5

The Austrian methodology is more restrictive regarding LUP, using very low limits for heat radiation and overpressure. It uses only the stationary heat radiation equal to 2  $kW/m^2$  and 25 mbar overpressure. Thus, the obtained distances are long, providing the protection of population and infrastructure.

Comparing the French methodology with the Italian one, it can be concluded that in case of stationary heat radiations (medium or long-term surface fires), the French methodology is more restrictive, using lower values. The approach method for the dynamic heat radiation is different in the two methodologies. The French methodology uses heat load for estimating effects, and the Italian one uses the radiation dose. Therefore, using the French methodology, the calculated distances are shorter than those calculated using the Italian methodology (considering the time dependency of the FB), excepting the distance for high mortality, where the Italian methodology recommends the FB diameter for 100 % mortality rate. The overpressure levels used in the two methodologies are quite similar.

Taking into account that the FB duration in case of BLEVE is between 5 and 30 seconds (depending on the fuel quantity) (Roberts 1982) and that the heat radiation varies with time, in this paper the use of the heat load ( $[s*(kW/m^2)^4/3]$ ) is considered to be the most adequate in consequence estimation.

In the Feyzin accident, the propane cloud ignition source was a warm car engine, situated on the road in the vicinity of the storage facility. The distance used in LUP should be greater than 488 m, this being the distance at which irreversible effects occur, due to the heat radiation.

**Case study no 2: Chemical accidents involving liquefied chlorine.** Qualitative risk estimation aims at establishing the possible hazards and supports the events ranking according to risk level. Risk (R) is assessed according to the well known equation:  $R = F \times C$  (Ozunu & Anghel 2007), where F (events/year) represents the frequency of scenario and C (deaths/event) represents the consequences of the accident. The risk is represented by the risk matrix. Risk assessment matrices are used for many years to rank risk depending on their significance. This fact allows prioritisation in control measures implementation.

Considering the three identified scenarios, the following installation failure frequencies were estimated: for failure of flanges at coupling a frequency of  $3.1*10^{-3}$  events/year was considered (according to probabilistic calculations) and  $3*10^{-6}$  events/year for the total failure of the storage tank (Mannan 2005). There were several accidents of chlorine release from the cylinders on site, thus a high frequency for this scenario was considered (between  $10^{-2}$  and  $10^{-4}$  events/year).

The risk assessment matrix for the relevant accident scenarios is presented in Table 5.

Table 5

No.	Danger	Frequency	Consequences	Risk		
	<u>A. Accident at the s</u>	<u>storage tank</u>				
1	Instantaneous release of the total chlorine quantity from the storage tank	3	5	15		
2	Liquid chlorine release for 10 minutes from the input pipe	4	4	16		
B. Accident at the chlorine cylinders						
1	Instantaneous release of the total chlorine quantity (1 t) from a cylinder	4	2	8		

Risk Matrix: Risks associated to studied accident scenarios

Frequency ranking on scale 1-5, where 1 = Improbable (F  $\leq$  10<sup>-8</sup> events/year); 5 = Very frequent (F  $\geq$  10<sup>-2 8</sup> events/year); Consequence ranking on scale 1-5, where 1 = Insignificant (without health effects), 5 = Catastrophic (lethal effects, off-site toxic dispersions).

The results of the qualitative risk analyses indicate that the considered scenarios pose a **moderate to high risk**, on a risk scale of 1 to 25. Based on the performed qualitative risk analyses, the following conclusions can be drawn:

- Chlorine storage in large quantities pose high risks for the population in Turda town;
- the consequences of the studied accidents can be catastrophic, except the scenario of chlorine release from the cylinder;
- in case of a chlorine accident, the affected areas must be immediately evacuated;
- the three accidental scenarios must be analyzed in a quantitative manner, too, in order to quantify the accidents effects and consequences.

**Comparative analysis of effects and consequences of the chlorine dispersion phenomenon in LUP context.** The effects and consequences assessment was elaborated by simulating the chlorine release, followed by the simulation of the chlorine dispersion. The input data was obtained from the installations technical parameters.

The chlorine release simulation was performed using the SEVEX View software, which included a source model for substances release from different types of vessels. The results obtained from the release simulation were used in dispersion simulation using the SEVEX View software and the SLAB View software.

The SEVEX View software considers the complex terrain topography from the GTOPO30 database for a surface of 37 km<sup>2</sup>, and land-use from the "CORINE Land Cover" database. By combining topography and land-use, wind directions can be calculated, using the meso-meteorological model (ATM-Pro 2009).

Based on the frequent meteorological conditions in the studied area the following synoptic wind speeds are considered: 2m/s (SE) and 5m/s (NW). These two wind speeds can be considered to be representative for the unfavourable weather condition (when wind speed is low = 2 m/s) and also for the average weather condition (when wind speed = 5 m/s). The results of the weather conditions simulations represent a database comprising a total of 144 wind vectors maps (intensity, direction): 36 maps for 2 m/s synoptic wind, day-time; 36 maps for 2 m/s synoptic wind, night-time; 36 maps for 5 m/s synoptic wind, night-time.

In order to provide a LUP and EP methodology for toxic dispersions, several parameters and factors influencing the results were taken into account, namely: for day-time: air temperature = 20 °C, relative humidity = 70%, nebulosity = 100%, stability class D (neutral); for night-time: air temperature = 10 °C, relative humidity = 90%, nebulosity = 0%, stability class F (very stable).

These weather conditions fulfil the requirements for the "*worst possible"* and "*credible"* weather condition principle for day and night time. The weather conditions established for day-time overlap the conditions recommended in the Austrian LUP methodology (Austrian Permanent Seveso Working Group 2010).

**Concern concentrations (C).** The French LUP methodology uses three levels of concentrations, namely (French Ministry of Ecology, Energy, Sustainable Development and the Sea 2009):

1. Significant lethal effects: LC 5% (lethal concentration which causes the death of 5% of the exposed population);

2. Lethal effects beginning: LC 1% (lethal concentration which causes the death of 1 % of the exposed population);

3. *Irreversible effects:* concentration which causes irreversible effects in case of e 30 minutes exposure.

The methodology does not establish exactly the third level of concentration which causes irreversible effects, but the IDLH (Immediately Dangerous to Life and Health) concentration is usually considered for this level.

The Italian methodology uses the 30 minutes LC50 (Lethal Concentration which causes the death of 50% of the exposed population) and IDLH concentrations for representation of dangerous areas (Italian Ministry of Public Works 2001).

The Austrian methodology recommends the use of IDLH values in LUP and proposed the introduction of AEGL2 (Acute Exposure Guideline Level) values and ERPG2 (Emergency Response Planning Guidelines) in case the AEGL values is not available for the studied substance (Austrian Permanent Seveso Working Group, 2010).

Considering the discussed methodologies, the use of the LC50, IDLH and AEGL2 (or ERPG2) concentrations is proposed, for several reasons:

1) these concentrations can be easily found in literature;

2) their conversion for a certain exposure period is easy (for example, from a 1 hour exposure period to a 30 minutes exposure period);

3) they represent different situations, which require different intervention actions.

The concentrations used in this case study, for representing the dangerous areas affected by chlorine are:

- LC50 = 430 ppm, for 30 minutes exposure (Chlorine Institute 1999);
- IDLH = 10 ppm, for 30 minutes exposure (NIOSH 2010);
- ERPG2 = 3 ppm, 1 hour exposure (Cavender et al 2008);

It is considered that the areas affected by concentration equal or higher than LC50 must be immediately evacuated after the accident, because there is lethal threat inside buildings. In areas affected by concentrations between IDLH and LC50 the immediate evacuation or sheltering is needed, using protective equipments (gas masks, wet cloths etc). In areas affected by concentrations between ERPG and IDLH, sheltering and exposure avoidance are recommended.

**Results obtained using SEVEX View.** In scenario A2, the total chlorine quantity released in 600 seconds is 19,761 kg. This scenario is the most important from the risk point of view, because the accident occurrence probability is higher than in the case of tanks catastrophic failure (scenario A.1.) and the consequences can be extremely severe.

- The simulations were performed as follows:
- distinct simulations for day and night conditions;
- distinct simulations for 2 m/s and 5 m/s wind speeds.

The results obtained can be characterized:

1) For the 2 m/s wind speed (it is considered a low speed, which reflects the more dangerous situation, when chlorine dispersions is weaker and concentrations are higher for a long period of time):

- Risk map for a 30 minutes period (starting from the accident occurrence), which represents the dispersions for the 36 different synoptic wind, previously calculated.
- Risk map for a 60 minutes period similar to the 30 minutes situation.

These two map types (for 30 and 60 minute) are necessary in the first emergency phase, when the accident's and weather details are not entirely known, but safety measures must be taken and the most affected areas must be evacuated. In other words, the wind dominant direction is not known and the cloud can spread in any direction, graphically represented on the maps.

• Risk maps for a 240 minutes period (starting from the accident occurrence), which represent the areas affected by the concern concentrations, in wind predominant directions: NW and SE.

2) For a 5 m/s wind speed, considered as an average speed in the studied area and representative for LUP:

• Risk maps for a 240 minutes period, which represent the areas affected by the concern concentrations, in wind predominant directions: NW and SE.

In this case, the 30 and 60 minutes maps are not available, because the 5 m/s wind speed is detectable right from the start of the accident. Therefore, the 240 minutes maps are used from the beginning of the emergency situation.

3) The described maps are built of a discrete data set (36 synoptic directions). Thus, the area represented on maps is not the total area. For a more complete representation of affected areas, the peaks of the iso-concentrations curves should be connected.

4) In the risk maps considering the NW or SE wind directions, three distinct directions are represented (with a difference of  $10^{\circ}$ ) and the results are overlapped. In this case, a possible fluctuation of  $30^{\circ}$  in wind direction is taken into account.

The results of the simulations performed for Scenario A.2 are presented in the Table 6.

Scenario	Accident	Wind	Validity	S0 (km²)	S1 (km²)	S2 (km²)	<i>S3</i>
	time	sector	(min)	Unaffected	(ERPG2	(IDLH <	(km²)
				area	< C <	<i>C</i> <	(C >
					IDLH)	LC50)	LC50)
A.2 – 2 m/s	Day	All	30	387.39	17.05	34.67	1.89
	Night	All	30	402.34	6.52	28.81	3.33
	Day	All	60	297.42	98.67	43.02	1.89
	Night	All	60	283.65	56.02	97.95	3.38
	Day	SE	240	402.44	28.36	9.72	0.48
	Night	SE	240	362.81	45.51	30.06	2.62
	Day	NV	240	418.39	12.99	7.95	1.67
	Night	NV	240	384.32	12.48	43.26	0.94
A.2 – 5 m/s	Day	SE	240	411.54	20.49	8.70	0.27
	Night	SE	240	377.57	31.04	30.94	1.45
	Day	NV	240	407.32	20.56	12.70	0.42
	Night	NV	240	416.98	17.69	6.23	0.10

Affected areas calculated with SEVEX View - Scenario A.2

C - concentration

The overall affected area in case of Scenario A.1 is presented in Figure 3, in case of Scenario A.2 in figure 4 and in case of Scenario B.1 in figure 5. The risk maps are obtained from the overlap of all the simulations performed for the scenarios, containing day and night conditions, 2 and 5 m/s wind speeds for all of the 36 wind directions simulated.

**Results obtained using SLAB View.** To highlight the differences between results obtained using SEVEX View and SLAB View it was considered the Scenario A.2 with transient chlorine release during 10 minutes.

The SLAB View software does not include a release model. Therefore, the input data in the dispersion model, regarding source terms, were obtained with SEVEX View release simulations. The same synoptic weather conditions were used as for SEVEX simulations. The results for Scenario A.2 are presented in Table 7.

Table 7

Table 6

Distances and areas calculated for concentrations of interest using SLAB model

	(C > Radius (km)	LC50) Surface S3 (km²)	(IDLH < Radius (km)	C < LC50) Surface S2 (km²)	(ERPG2 < Radius (km)	C < IDLH) Surface S1 (km <sup>2</sup> )
Daytime – wind speed = 2 m/s	0.457	0.657	5.539	96.385	11.306	401.576
Night time – wind speed = 2 m/s	0.824	2.137	14.277	640.359	27.704	2411.208
Daytime – wind speed = 5 m/s	0.367	0.424	3.648	41.808	7.262	165.677
Night time – wind speed = 5 m/s	0.821	2.118	12.791	513.994	26.296	2172.347

C – concentration



Figure 3. Risk map: total possible area affected by dangerous concentrations (10.0 < C < 430.0 ppm) outside buildings – Scenario A.1.



Figure 4. Risk map: total possible area affected by dangerous concentrations (10.0 < C < 430.0 ppm) outside buildings – Scenario A.2.



Figure 5. Risk map: total possible area affected by dangerous concentrations (10.0 < C < 430.0 ppm) outside buildings – Scenario B.1.

Analyzing the results obtained using SLAB View, presented in Table 7, one can notice that there are no significant differences between distances obtained with 2 m/s and 5 m/s wind speeds. The SLAB model is bi-dimensional, it ignores the terrain topography and it uses just a single surface roughness type for the studied area. The effect of the wind on dispersion in case of a flat terrain is not as significant as in case of a complex terrain, where turbulence occurs due to the present obstacles.

The maps obtained with SLAB View represent the potentially affected areas by concentrations of interest for 30 minutes exposure time. There is a significant difference between maps obtained using SEVEX View and SLAB View. SEVEX maps show the areas where concentrations of interest can occur, but do not consider the exposure time. On the contrary, SLAB maps consider the 30 minutes exposure time.



Figure 6. SLAB View, Scenario A.2. – Potentially affected areas by concentrations: LC50 (blue), IDLH (red), ERPG2 (yellow), 30 minutes exposure – daytime, wind speed = 2 m/s

The iso-concentration circles on the SLAB maps represent the total area which can be potentially affected in case of an accidental release.

The results of SEVEX and SLAB simulations regarding the areas affected by concentrations of interest, for the same scenario, are presented in Table 8.

Table 8

Software	Time of day	S3 (km²) - LC50	S2 (km²) - IDLH	S1 (km²) - ERPG2
SEVEX	Daytime	1.89	34.67	17.05
	Night time	3.33	28.81	6.52
SLAB	Daytime	0.657	96.385	401.576
	Night time	2.137	640.359	2,411.208

Potentially affected surfaces calculated by SEVEX and SLAB for Scenario A.2.

Analyzing these results there can be observed that in the case of SLAB simulations the surfaces with concentrations higher than LC50 are reduced and the surfaces with concentrations between LC50-IDLH and IDLH-ERPG2 are overestimated.

Using the SLAB results for emergency planning could cause the underestimation of the most dangerous areas and overestimation of the areas where toxic effects can appear.

The results obtained using SEVEX View are much more realistic than the SLAB View results, because it considers two important factors: terrain topography and land cover, with significant influence on dispersion phenomena of gases.

Considering a chemical accident involving the entire chlorine quantity spilling at the Turda storehouse, in the worst meteorological conditions, an area equal to or larger than 56.93 km<sup>2</sup> should be evacuated. This area partially affects Turda, Câmpia Turzii towns and Mihai Viteazu and Săndulești villages, affecting more than 10,000 inhabitants.

Among the scenarios calculated with SEVEX software, the largest affected areas (in a period of 240 minutes) were obtained in cases A.1. and A.2., for night-time dispersion, when the wind is blowing from South-East, with a speed of 2 m/s. These results emphasize that the night-time scenarios are more dangerous, the atmosphere being stable and thus, the cloud dispersion is weaker. The situation is worsened by the fact that the population is more difficult to warn and evacuate during night-time. Scenario B.1 with 1 t chlorine release from a cylinder has a lower risk than the other two scenarios, but the simulations show that the affected areas are significant and evacuation measures from the neighbouring areas must be taken.

**Case study no 3: Chemical accidents involving ammonium nitrate.** AN is a hazardous substance from the point of view of instability of the  $NH_4NH_3$  molecule, which contains two atoms of N in different, extreme oxidation states: the N atom in the  $NO_3^-$  ion has the oxidation number V, in the maximum state of reduction, but the N atom in the  $NH_4^+$  ion has the oxidation number –III in the maximum state of oxidation.

The risk of instability of the molecule was estimated using the quantitative CHETAH method (Chemical Thermodynamic and Energy Release Programme) (Martel 2004). Considering the four risk criteria of the CHETAH method, a final **medium risk** results for AN, in terms of instability of the substance.

The storage, handling and transportation of AN in large quantities generate major risk situations in certain conditions, necessitating the chemical alarming. The major chemical accident hazard is determined by the coexistence of several risk factors, as presented in Table 9.

Table 9

Hazard	Potential risk factor
Chemical	<ul> <li>storage and handling of potentially dangerous oxidizing substances;</li> <li>emission of toxic gases (nitrogen oxides and ammonia), resulted from the thermal decomposition in case of an accident;</li> </ul>
Explosion	- AN can produce explosion if it is contaminated with organic substances or in case of thermal decomposition;
Fire	- AN is not flammable or combustible. As an oxidizing agent can maintain and intensify a fire in lack of oxygen, but only if combustible or flammable material is present.

Hazards and identified risk factors

The areas with potential major hazards at the storage and handling of AN at the studied warehouse are the followings:

- unloading ramp from carriage;
- warehouse;
- transport route of material with conveyor-elevator.

At approximately 1.6 km from the warehouse in W and 2.1 km in N directions are the first buildings of the residential area of a city, where the population could be affected in case of an explosion accident. The workers of the warehouse are the most susceptible to be affected.

Accident scenarios were developed depending on the three potentially hazardous areas identified above.

A) Warehouse of AN

Scenario A.1. Total destruction of warehouse by terrorist attack or air attack; Scenario A.2. Fire in the warehouse where AN is stored;

Scenario A.3. Decomposition of AN; Scenario A.4. Explosion of AN stored in the warehouse; B) Unloading ramp of carriage Scenario B.1. Fire at the unloading ramp; Scenario B.2. Explosion of AN at the unloading ramp; Scenario B.3. Leakage of AN at the unloading ramp; C) Transport route conveyor-elevator

Scenario C.1. Fire at the conveyor-elevator

Scenario C.2. Leakage of AN at the conveyor-elevator

The qualitative assessment was performed using the identified consequences and frequencies. The scale of the frequency and consequences is the same as in case of the chlorine accident assessment. In the estimation of frequency and consequence levels it was considered the existence of safety measures implemented at the warehouse and the results of other previously performed studies. The risk matrix is presented in Table 10.

Table 10

## Risk matrix of the identified accident scenarios

No.	Scenario	Frequency	Consequences	Risk
A. Wa	arehouse of AN			
A.1	Total destruction of warehouse by terrorist attack or air attack	1	5	5
A.2	Fire in the warehouse where AN is stored	2	3	6
A.3	Decomposition of AN	2	3	6
A.4	Explosion of AN stored in the warehouse	2	5	10
B. Fire	e at the unloading ramp			
B.1	Fire at the unloading ramp	2	3	6
B.2	Explosion of AN at the unloading ramp	2	5	10
B.3	Leakage of AN at the unloading ramp	3	1	3
C. Fire	e at the conveyor-elevator			
C.1	Fire at the conveyor-elevator	2	3	6
C.2	Leakage of AN at the conveyor-elevator	3	1	3

From the qualitative risk assessment it results that the risk of a major accident at the warehouse is acceptable, being necessary a periodical monitoring and a strict operational system. The biggest risk of a major accident belongs to the Scenario A.4. Explosion of AN stored in the warehouse. The terrorist or air attack scenario has a reduced risk because of the probability of occurrence, but the consequences can be significant and this scenario can not be ignored. Fires also induce low risks, but the consequences of such accidents can be very severe if they are not managed immediately by the operating personnel.

In conclusion, a major accident at the AN warehouse can have very severe consequences due to the large quantities stored in a single place.

**Consequence analysis of storage and handling of ammonium nitrate in LUP context**. For the assessment of accidents magnitude in the case of explosion scenarios computer simulations using the EFFECTS 7 software were performed.

For the assessment of consequences of the explosion the overpressure parameter in the front of the shockwave was used. In the simulation the following assumptions were used:

- I. Explosion of AN on the conveyor-elevator:
  - estimated quantity: 10 t of AN;
- II. Explosion of AN on the unloading ramp from carriage:
  - estimated quantity: 100 t;
- III. Explosion of AN in the warehouse:
  - estimated quantities:

• 300 t being the average daily handled quantity;

- 1,500 t being the average minimum existing quantity in the warehouse;
- 10,000 t being the average maximum existing quantity in the warehouse;
- 14,000 t being the maximum projected quantity in the warehouse;

IV. Explosion of 1 t AN for situations when in the warehouse AN can be found from leakages during loading/unloading operations.

For the above mentioned quantities the following TNT equivalents (EqTNT) were used in simulations:

- For quantities of 1 t, 10 t, 100 t and 300 t, EqTNT of 14 % (0.14) was considered, calculated with 55 % explosive power and 25 % efficiency (Kersten & Mak 2004);
- For quantities of 1,500 t, 10,000 t and 14,000 t, EqTNT of 32 % (0.32) was considered, calculated with 55 % explosive power and 58% efficiency (NTWorkSafe 2009).

The values are different due to the different way of the explosion process as function of the involved quantity, deflagration until 300 t and detonation above 300 t of AN (Kersten & Mak 2004; NTWorkSafe 2009).

According to the overpressure levels established by the French, Italian and Austrian methodologies, described in *case study no.* 1, distances for overpressures were calculated for the above mentioned quantities of AN. The calculated distances are presented in Table 11.

Table 11

	AN quantities(t)	1	10	100	300	1,500	10,000	14,000
Met.	Levels of concern			Calcu	ılated dis	tances(m	ı)	
FR.	High lethality (200 mbar)	45	97	208	300	676	1,272	1,423
	Beginning of lethality (140 mbar)	54	117	252	364	821	1,546	1,730
	Irreversible effects(50 mbar)	119	257	553	798	1,797	3,381	3,783
	Indirect effects (20 mbar)	237	511	1,102	1,589	3,579	6,737	7,636
IT.	High lethality (300 mbar)	34	74	161	232	523	985	1,102
	Beginning of lethality (140 mbar)	54	117	252	364	821	1,546	1,730
	(The mbar) Irreversible effects (70 mbar)	93	200	432	623	1,405	2,644	2,958
	Reversible effects (30	175	376	811	1,170	2,638	4,959	5,547
AUT.	LUP (25 mbar)	198	426	917	1,322	2,978	5,605	6,270

Calculated distances (m) for LUP

The obtained distances for different consequences increase significantly, depending on the exploded AN quantity.

In case of maximum quantity explosion (14,000 t) the 200 mbar overpressure (corresponding to the high mortality rate in the French methodology) affects the residential areas located at 1.6 km from the AN deposit.

In case of maximum quantities explosion (14,000 t) or the maximum average quantity in the deposit (10,000 t) the 140 mbar overpressure (corresponding to the beginning of lethality in the French and Italian methodology) affects the residential areas located at 1.6 km from the AN deposit.

Considering an explosion with a daily average quantity of 300 t, the overpressure levels used in LUP (20, 30 and 50 mbar) in the three methodologies does not affect the residential areas, only the industrial ones. If the AN quantity involved in the explosion exceeds 300 t, then the residential areas will be affected.

Taking into account the risk estimated in the qualitative analysis, the consequences estimated in the quantitative analysis and the low accident probabilities, it can be concluded that the AN storage facility does not induce a risk for the population of the town situated in the vicinity of the storage facility. The safety distances are sufficient, but the occurrence of extreme cases must be considered, with the explosion of larger quantities and with distances that exceed the town's boundaries. Therefore, the building of houses closer to the storage facility, at a smaller distance than the existing buildings is not recommended.

#### Conclusions

These historical technological accidents contributed to the technological safety improvement in two ways: through technologies, by developing new safety systems, processes automation or use of less dangerous technologies; through legislation, by implementing regulations at European and national level, regulating the industrial activities, in order to protect the population, environment and economy, in an efficient and coherent manner.

Three years after the adhesion to the EU, Romania still does not have a coherent legislation regarding LUP in the context of the art. 12 of the Seveso Directive. In Romania there are currently more then 200 economic operators, classified as Seveso sites, most of them with major risk. Moreover, these sites are located in the vicinity of high vulnerability areas. In these cases, the need of risk studies elaboration is essential in technological accident prevention, LUP and EP. Based on these studies, the population can be informed, trained and prepared for accidents, thus saving many human lives.

Therefore, this paper proposes the development of a risk assessment methodology for LUP and EP in case of Seveso sites, where flammable, explosive and toxic substances in large quantities are stored, transported or processed.

For the elaboration of the methodology, three case studies were considered. Each case study deals with a technological accident involving propane, chlorine or ammonium nitrate. The consequences of accidents were assessed and the distances or areas for LUP were calculated, considering several methodologies used in the EU member states.

The Italian and Austrian LUP methodologies are subjected to ongoing development. The Italian methodology is more complete than the Austrian one, but it does not deal in an adequate manner with all kinds of accidents, for example the non-stationary heat radiation ones.

The French methodology is based on consequences estimation. The limits are stricter than in the Italian methodology, thus the population protection level is higher. This methodology takes into account the dynamic heat radiations, therefore the dangerous areas estimations are more correct and the distances are not overestimated. In accidents where BLEVE phenomenon occurred, most victims were killed by the heat radiation from the fire ball. The physical effects can be expressed by heat load in a more adequate manner in case of dynamic heat radiation. In LUP, the 20 mbar overpressure level is recommended, as being the overpressure at which windows break.

The methodology proposed in this paper uses the consequence-based method, using mostly the limits established by the French methodology, to determine the dangerous areas in case of fires and explosions. In order to determine the areas affected by toxic concentrations, the French methodology does not establish exactly the third concentration level, which produces irreversible effects. Usually, the IDLH concentration is considered for this level. To conclude, the LC50, IDLH and AEGL2 (or ERPG2) limits are recommended.

The ERPG2 concentration is recommended for LUP limit, because it is a limit at which the population is not affected by severe consequences.

Scenarios frequency is qualitatively analyzed based on available databases and assessors expertise. In special decision-making cases, when the frequency is low, but the consequences are severe, and thus the risk is medium, the consequences magnitude factor must be more important than the occurrence frequency.

The distances calculated for LUP emphasize the fact that the LPG, chlorine or ammonium nitrate storage facilities should be located at a significant distance from the process installations, refineries, hydrocarbons storage facilities, public roads, residential or protected areas.

There is a wide range of software which can be used for technological accidents simulation, but their use requires the understanding of the basic models. The selection of the software depends on several factors: the investigated accident; the availability of the input data; the complexity of the problem; the validity of the models; and the availability of the corresponding software.

The results obtained for the chlorine dispersion using the SEVEX View and SLAB View software are presenting significant differences regarding the surface of the affected areas. The SLAB results are overestimated and it is not advised to be used for LUP and EP in case of major accidents with toxic dispersion.

The use of the risk assessment methodology for LUP and EP facilitates the expertise of the assessors and competent authorities, in decision making and project verification.

Based on the analyses performed using the proposed methodology for several Seveso sites, the population must be informed and trained for emergency situations.

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Submitted: 02 May 2010. Accepted: 10 June 2010. Published online: 10 June 2010.

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Török Z., Ozunu A., 2010 Chemical risk assessment for storage of hazardous materials in the context of Land Use Planning. AES Bioflux 2(1):33-56.