BABEŞ BOLYAI UNIVERSITY
FACULTY OF ENVIRONMENTAL SCIENCES AND ENGINEERING

Quantitative and Qualitative Risk Analyses in the Chemical Industry

- summary -

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INTRODUCTION

Major technological accidents are extremely important from the point of view of their risk and impact on human health and the environment. The main regulation used in the EU for the prevention of technological accidents is the Seveso III Directive, which was implemented in Romania through the Government Decision no. 804 of 2007 [1] and amended through the Government Decision no 79 of 2009 [2]. These Seveso Directives establish the measures regarding the prevention and control of major accidents involving hazardous substances. The development of process industries lead to the increase of technologic and chemical incidents and accidents. The Seveso Directives were developed in the EU following the historical technological accidents from Flixborough (1974) [3], Seveso (1976) [3], Bhopal (1984) [3], Baia Mare (2000) [4], Toulouse

(2001) [5] etc. These accidents emphasized the need of a more rigorous control of chemical processes, in order to prevent technological disasters.

This paper studies a highly concern issue at national and international level, due to the fact that many industries use hazardous substances in large quantities and dangerous process parameters (high pressure, temperature etc.). The Seveso III Directive implemented in the EU regulates the activities which use hazardous substances in quantities large enough to generate major accidents. Therefore, risk assessment plays an important role in all industrial activities subjected to the Seveso Directive.

According to the regulations of GD no. 804/2007, local authorities responsible with land-use planning, in cooperation with the competent authorities at regional and national level must include in the land development policy the major accident prevention and consequences mitigation objectives. In several EU countries there are well developed methodologies for risk assessment within land-use planning. In Romania, in 2007 there were 202 Seveso sites identified [6], but three years later there is still no unique and accepted methodology to be used by risk planners for land-use planning.

The main goal of this PhD thesis is to find efficient solutions for technological risk assessment for land-use planning, emergency planning and to propose a methodology to be used with this purpose.

The PhD study provides a new approach of the issues regarding technological accidents modelling and simulations and a comparative approach of older and newer modelling techniques.

The general objectives of the paper are:

- Describing the technological risk assessment procedure, by presenting methods and techniques used in the field;
- Investigating several types of technologic accidents involving dangerous substances storage: propane, chlorine and ammonium nitrate;
- Comparing several land-use planning methodologies used in the EU, depending on the limits established within, using case studies;
- Finding practical and efficient solutions for technologic risk reduction, chemical emergencies planning and land-use planning, using the results of the elaborated simulations.

Among the specific objectives of the paper there can be mentioned:

- Comparison of the results obtained through modelling and computer simulation, for the studied accidents, using the risk analysis method based on accidents consequences;
- Comparison of the models developed for BLEVE (Boiling Liquid Expanding Vapour Explosion) type events;
- Comparison of the results of toxic dispersion modelling developed using the bi-dimensional and tri-dimensional models.

The paper is structured in two parts: the first part, of theoretical substantiation (Chapters 1-3), which presents the basic concepts used in technological disasters management, the structure of the technological risk assessment and the qualitative and quantitative analysis methods; the second part, the practical one (Chapters 4-9) emphasizes the need of a risk assessment methodology for land-use planning and presents three case studies on propane, chlorine and ammonium nitrate storage, which represent the basis for risk analysis, and the results are compared in order to propose the most efficient assessment methodology.

The results of the risk analyses obtained in the case studies reflect the importance of efficient land-use planning and the need of developing a risk assessment methodology in this field.

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Chapter 1
Introduction in the Technological Disasters Management

Technological disasters management represents the sum of activities taken for technological risk reduction, technological disasters prevention and of the measures developed for emergency response management, in order to protect the population, environment and economy against anthropic disasters.

1.1. Seveso Directives

These directives regulate the measures regarding the prevention and control of major accidents involving dangerous substances, as well as the reduction of consequences impact on human health and environment, to assure a high level of protection, in a high-performance, efficient and coherent manner. Within this framework, the activities associated to production, storage, transport, usage or discharge of dangerous substances are regulated, in order to reduce the consequences for the human population and the environment [1].

The activities categories subject to Seveso III Directive are listed in the Annex 1 of the thesis.

1.2. Technological disasters management

Technological disasters management can be divided into two main parts: *Chemical Risks Management and Emergency Situations Management.*

Risk management is defined as the sum of all activities and measures developed for risk reduction. Risk management aims at balancing the conflicts emerging at opportunities exploitation, on the one hand, and losses, accidents and disasters reduction, on the other hand [2].

1.3. Basic definitions used in technological risk assessment and management

Hazard in the chemical industry is defined as a chemical or physical property which has the potential to generate human losses, material or environmental damages; for example, an explosive substance or a tank under pressure containing a toxic substance [3].

Risk is the *probability* for the existing hazard to become an incident/accident [3].

Risk in chemical industry is defined as probable annual production damages or human accidents, resulted from unexpected technical events. Risk is a combination of incertitude and damages, the ratio between hazard and safety [4].

A new approach in the technological risk calculation proposes the inclusion of vulnerability in the risk formulae [3]:

$$R = F \times C \times V \qquad (1.1)$$

where: F – event frequency (number of events/year); C – consequences (tons/event or deceases/event); V – vulnerability of the population in the area or the site personnel.

Chemical accident can be defined as a loss of material or energy containment.

Risk analysis: quantitative risk assessment, based on engineering and mathematical methods for combining consequences and accidents frequency assessment.

Risk assessment: process in which the risk analysis results are used to make decisions by using risk reduction strategies [4].

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Chapter 2
Technological risk assessment

Technological risk assessment is a complex study, based on several qualitative and quantitative analyses methods, which estimates the technological accidents probability and magnitude and establishes the accidents prevention measures necessity. The technological risk assessment process can be divided into four major phases, namely: hazards identification, hazards assessment, risk analysis, risk assessment.

Each of these phases includes several acknowledged methods, successfully used at international level, which can be applied in the identification of existing hazards and in the technological risk assessment.

2.1. Structure of the technological risk analysis

Technological risk analysis and assessment can be divided into several major phases. Figure 2.1 shows the risk assessment procedure and the used methods.

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 will turn into an accident.

For determining 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.

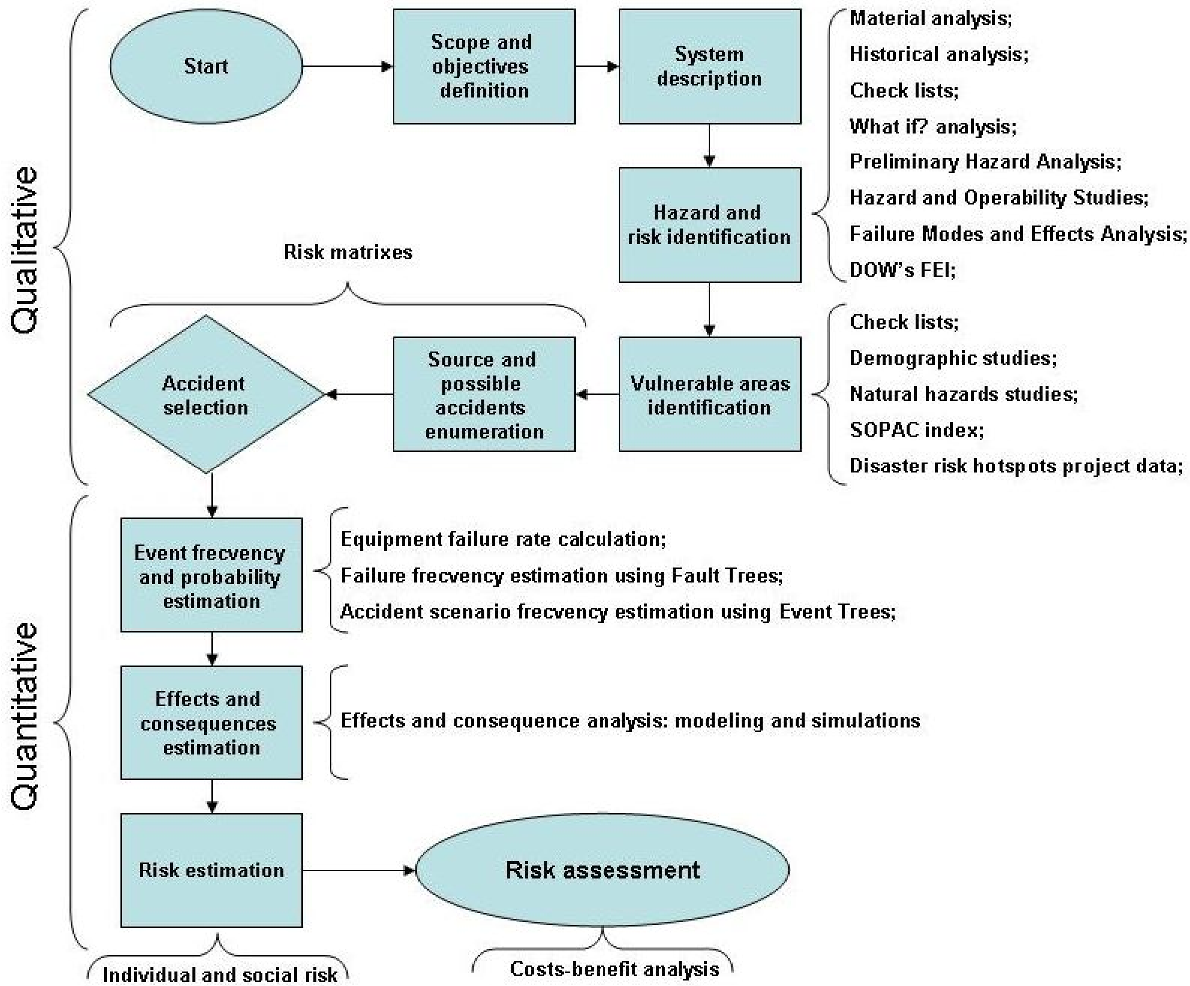

Figure 2.1: Technological risk assessment [1, 2]

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 analysis includes the use of numerical or quantitative data and provides 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 methods and techniques of technological hazards identification and risk analysis presented within the thesis are listed below:

a) Qualitative methods of hazards identification and risk assessment:

- Analysis of hazardous substances properties;
- Check list method;
- "What if?" analysis method;
- "Preliminary Hazard Analysis" (PHA) method;
- "Failure Mode and Effects Analysis" (FMEA) method;
- "Hazard and Operability" HAZOP Study method;
- Risk assessment method using the DOW index;

- Probability determination through Historical Analysis;

b) Quantitative risk assessment methods:

- Top events frequency assessment. Failure trees;
- Accidental scenarios frequency assessment. Event trees;
- Effects and consequences analysis through mathematical modelling and technological accident simulation.

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Chapter 3
Technological risk presentation and assessment

There are several methods for the presentation of the results obtained from the hazard and risk analysis. Risk can be presented as risk tables or it can be represented on maps, as the areas with different accident impact. Risk refers to the number of deceases, injured persons or material damages.

When representing risk, the expert must decide the presentation form and the terms of the results, either deceased, injured persons or material damages.

Quantitative risk analysis includes the determination of Individual Risk (IR) and Social Risk (SR).

Individual Risk represents the individual decease frequency caused by an accidental event occurred in a system with contamination potential. The person is supposed to be unprotected and present in the area during the entire exposure period [1].

Social Risk represents the accidental events frequency at which N number of deceases is expected. Social risk is graphically represented by the F-N curve, on a logarithmic scale, where F is the accidental events cumulative frequency, and N is the deceases number [2, 3].

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Chapter 4
Land-use planning in the Seveso Directives context

Risk assessment is a structured procedure of qualitative and/or quantitative assessment of the risk level generated by danger sources identified in the installations. The aim of the risk assessment is to provide the necessary information for decision making. Among these decisions, the ones related to land-use planning are extremely important, and risk, as a main factor, is one of the basic parameters.

According to GD no. 804 of 25th July 2005 regarding the control of major accidents involving dangerous substances (art. 13) the local authorities responsible with land-use planning, in cooperation with the competent public authorities at regional and county level, must include in the regional development policy the major accidents prevention and consequences reduction objectives [1]. In order to achieve this aim, the competent public authorities at regional and county level verify the location of new sites and (in cooperation with the public authorities responsible with the land-use planning) take the necessary measures for the regional development policies and their implementation procedures to consider the need of maintaining adequate distances, established based on the danger level, between the sites falling under the above mentioned regulations and residential and public utilities areas, main roads, recreation areas, natural protected areas, with the purpose of reducing population risk.

According to the final report of the F-Seveso study (Study regarding the efficiency of Seveso II Directive) published on 29th August 2008, in Romania there are 202 industrial sites, of which 131 are classified with major risk and 71 with lower risk, placing Romania on the tenth place within the EU countries regarding Seveso sites [2].

4.3. Risk assessment within land-use planning

Risk management in the context of land-use planning deals with the below mentioned issues:

- Natural disasters (floods, avalanches, earthquakes etc.);
- Long-term or permanent impacts (industrial or urban emissions etc.);
- Anthropic disasters (accidental discharges);
- NATECH disasters (natural disasters trigger technological accidents).

The risk assessment methods existing in the field of land-use planning can be considered as being part of the methods used in the risk assessment in the case of industrial operators. Experience demonstrates that in most cases there is a close connection between risk assessment in order to establish safety of industrial activities and risk assessment in the context of land-use planning.

The risk assessment methods categories recommended in the *„Land Use Planning Guidelines”* [3] edited in September 2006 by the European Commission to support the member states in choosing an adequate system, are described in the following subchapters.

4.3.1. Consequence – based methods: The “consequence based” approach assesses the consequences of potential accidents, without quantifying their probability of occurrence. Thus, the quantification of the potential accidents occurrence frequency and its associated uncertainties is avoided. The basic concept is the existence of one or more “extremely severe” scenarios, which are defined based on previous experiences, historical data, expert judgment and qualitative information obtained from the hazards identification.

4.3.2. Risk – based methods: the aim is the assessment of potential accidents magnitude and occurrence probability. For assessing the accident occurrence probability, several methods are used, starting with the simple selection of scenarios and frequency from a database and ending with the usage of sophisticated tools, like Logical trees. Generally, the risk-based approach defines risk as a combination between the consequences of several probable accidents and their occurrence probabilities.

4.3.3. Deterministic approach: it is not a risk assessment method for land-use planning in a strict manner. This approach is based on the concept that enough population protection measures must be implemented in case of an accident, considered the worst. Therefore, it is considered that the worst accident consequences were assessed. This approach is trying to maintain the installation operating without imposing a possible risk to the population in the site vicinity (*zero – risk principle*). In order to achieve this aim, state-of-the-art technology and additional safety measures are implemented in the installation, to reduce the consequences of a possible accident on site.

4.3.4. Combined methods: semi-quantitative methods can be seen as a specific category of risk or consequence-based methods. In this case, an explicitly quantitative element (probability analysis) is completed by a qualitative one (consequence assessment) or vice-versa.

There are well grounded reasons for which the worst case scenarios are not always selected in risk assessment for land-use planning, even if they must be assessed according to Seveso Directives, especially when elaborating the off-site emergency plans.

The selection of accident scenarios, either for land-use planning or for emergency response planning is based on the difference between the intervention time of the response teams and the accident's complete development time.

In other words, all scenarios referring to explosions (mechanical or chemical) must be considered a priority in land-use planning, due to the lack of time for the site intervention [3].

4.4. Current practices for land-use planning in the EU

Every attempt to establish regulations for land-use planning must take into account the significant differences between the national legislation of member states and the implemented practices. Thus, a clear distinction between the legislation from several countries can be made:

- Countries which have already established well structured procedures for considering major accidents in land-use planning;
- Countries in which these procedures are developing and in which there are not explicit regulations for land-use planning in the vicinity of dangerous installations.

Countries such as Holland, Great Britain, France and Germany have already elaborated a complete procedure for land-use planning. South-European countries, Italy, Greece, Spain, Portugal can be included in the second category, while Denmark is very close to establishing these procedures. The countries included in the second category pay attention to major accidents, but the control of land-use planning in the vicinity of dangerous sites is assured by the legislation regarding the "physical" planning and consists of procedures in which accident probability are not explicitly considered in land-use planning policies. Therefore, in these countries new and clear regulations are being developed, according to Seveso III Directive.

In May 2004 the "*Guide for major accidents calculation*" developed by PhD. H. Joachim Uth (Twinning Project RO/2002/IB/EN/02) was published, reflecting the German experience in this field [4].

4.6. Conclusions

In Romania there is no coherent legislation regarding land-use planning in the context of the art. 12 from the Seveso Directive, except the regulations regarding explosives and location of main pipelines for the transport of natural gases.

Therefore, this paper proposes the development of a risk assessment methodology for land-use planning in the case of inflammable, explosive or toxic substances storage. For the elaboration of methodology three case studies are considered: technological accident scenarios at the storage of the following dangerous substances: propane, chlorine and ammonium nitrate.

Each case study deals with a technological accident involving one of the above mentioned substances. The accidents consequences are assessed and the distances for land-use planning are calculated, considering several methodologies used in the EU member states.

The final proposed methodology is based on several documents:

- „*Guide for major accidents calculation*" developed by PhD. H. Joachim Uth [4];

- The French methodology for land-use planning developed by the Ministry of Ecology, Energy, Sustainable Development and Sea in France [5];
- The Italian methodology for land-use planning developed by the Ministry of Public Works in Italy [6];
- The Austrian methodology for land-use planning developed by the "Permanent Seveso Working Team" in Austria [7].

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Chapter 5
Consequences analysis and land-use planning in case of propane and liquefied petroleum gas storage accidents

In the last 50 years numerous technological accidents occurred in the petroleum refining and petrochemical industry, accidents involving very inflammable substances, like LPG (liquefied petroleum gas) and other petroleum products, generating BLEVE (Boiling Liquid Expanding Vapour Explosion).

The case study's objective is finding practical and efficient solutions for land-use planning and chemical emergencies planning. Therefore, a comparative study between the results obtained from BLEVE phenomenon modelling and the consequences recorded for the Feyzin accident (1966), in France [1] was performed, in order to offer proposals for a risk assessment methodology for land-use planning in case of LPG storage facility.

5.1. Substance characteristics: Propane and LPG (liquefied petroleum gas)

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 inflammable and explosive substances.

5.4. BLEVE explosion

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) [10]. 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 and which are contained: "hot BLEVE"; due to the heat, the material weakens, the containment becomes over pressurised, generating the failure of the building material.

During explosions, the personnel and the valuable goods will be affected by the pressures generated by the explosion (the shock wave), the energy (FB - fireball) or by mechanical impact generated by the remains projected by the explosion's blast.

5.4.1. BLEVE mathematical modelling

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 [12].

5.5. Case study: Feyzin accident

The Feyzin (France) chemical accident occurred on 4th January 1996 at a liquefied gases deposit, LPG type (liquefied petroleum gas: propane-butane). The accident was caused by a human error during a sampling from a spherical liquefied propane tank and it is considered the most severe industrial catastrophe in the France recent history.

The tank was located at a 22.5 m distance from the A7 highway. The site included 10 vessels, out of which 8 were spherical and 2 cylindrical, equally divided for propane and butane, as in Figure 5.1, [1].

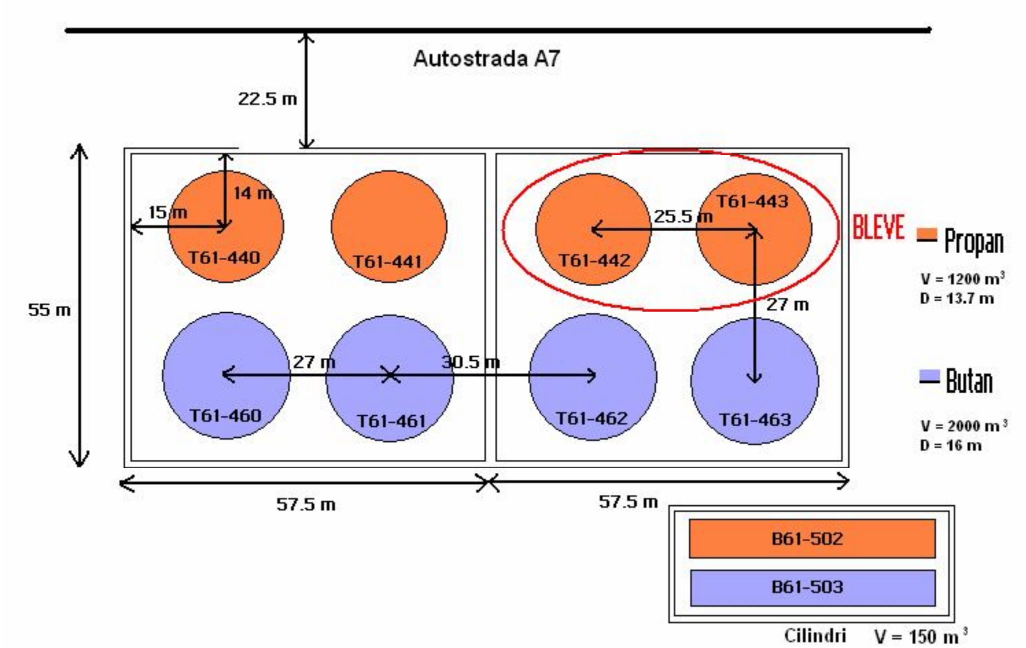

Figure 5.1. LPG vessels location [1]

5.5.2. Accident causes and development

During water purging and sampling from the T61-443 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 shut down, 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 vessels caught fire. The firemen arrived and intervened using water jets and cooled down the tank, in vain. The T61-443 sphere BLEVE'd (the first explosion), a 250 m diameter fire ball (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).

5.5.4. Human and material loses

Human loses [1]:

- 18 people were killed: 11 fire workers (7 from Lyon and 4 from Vienne), 3 subcontractors, 1 employee of the nearby company, the driver of the car who entered the gas cloud died 4 days later;
- 84 wounded, out of which 49 were hospitalized.

Damages [1]:

- LPG and hydrocarbons tanks site: 11 tanks with 5 spheres, 2 cylinders and 4 vessels with floating cap.
- Pumping installations;
- fuels: 2000 m^3 propane, 4000 m^3 butane, 2000 m^3 hydrocarbons;
- 6 fire trucks.

The thermal effect caused the death of everybody on a 50 m radius, and till 150 m those exposed were severely wounded.

5.5.5. Recorder errors and lessons learnt

Based on the investigations, the experts recorded the following errors causing the accident [1, 2]:

- *fault handling of the valves at the bottom of the sphere;*
- *22.5 m from the highway;*
- *the sphere was not cooled in the upper part;*
- *only one of the tow safety valve was found open;*
- *wrong design for the safety valves;*
- *the lack of fixed cooling equipments;*
- *the lack of a unique command centre for activities coordination;*
- *the dangerous areas were not defined;*
- *failure in complying with the location and safety regulations;*
- *wrong dimensions of the retention vat;*
- *the general safety regulations in case of accidents;*
- *fire fighting plan.*

5.6. Comparative analysis of BLEVE phenomenon consequences

The analysis of the Feyzin accident consequences 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, in this paper two propane quantities left in the tank before the explosion were calculated. The third quantity was calculated using the propane flow simulation, with the TPDIS (Two Phase Bottom Discharge Model) model, within the EFFECTS 7 software, developed by the TNO Dutch Company [15].

Thus, these approximations are:

Case no 1: based on the propane tank technical data, a flow of 8 kg/s was calculated [1]. 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: 125 min = 7,500 s; 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^3, with a 46 m^3 (23 t) difference from the 693 m^3 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 [1], according to the calculations: 23,000 kg / 3,600 s = 6.38 kg/s ≈ 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 [16].

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 5.7.

Table 5.7. Simulation results and recorded values

<table>
<tr><th>Case number</th><th>static BLEVE</th><th>dynamic BLEVE</th><th>BLEVE tank failure</th><th>Recorded values</th></tr>
<tr><td>No 1.
217 t propane</td><td>FB duration = 20.793 s
FB diameter = 351.5 m
H_{max} FB = 527.25 m</td><td>FB duration = 19.425 s
FB diameter = 348.54 m
H_{max} FB = 522.8 m</td><td>79 t fragment thrown at 394.11 m
Overpressure distance 30 mbar = 359.2 m</td><td rowspan="3">FB diameter = 250 m

H_{max} FB = 400 m

79 t fragment thrown at 248 m

Overpressure distance 30 mbar = 4,000 m</td></tr>
<tr><td>No 2.
231 t propane</td><td>FB duration = 21.13 s
FB diameter = 358.72 m
H_{max} FB = 538.08 m</td><td>FB duration = 19.73 s
FB diameter = 355.88 m
H_{max} FB = 533.81 m</td><td>79 t fragment thrown at 416.98 m
Overpressure distance 30 mbar = 367.9 m</td></tr>
<tr><td>No 3.
181 t propane</td><td>FB duration = 19.83 s
FB diameter = 331.36 m
H_{max} FB = 497.04 m</td><td>FB duration = 18.563 s
FB diameter = 328.07 m
H_{max} FB = 492.11m</td><td>79 t fragment thrown at 335.92 m
Overpressure distance 30 mbar = 335.5 m</td></tr>
</table>

As one can see, the differences between the results of the two models, static and dynamic, regarding the FB diameters are smaller then 1%. By contrast, 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, as it is represented in figure 5.22 and 5.23.

The differences between the results of the physical effects and the consequences of the three cases simulations are reduced, considering 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 [1], and based on the simulations performed within this paper, the obtained values ranged between 335 and 368 m, as in figure 5.26.

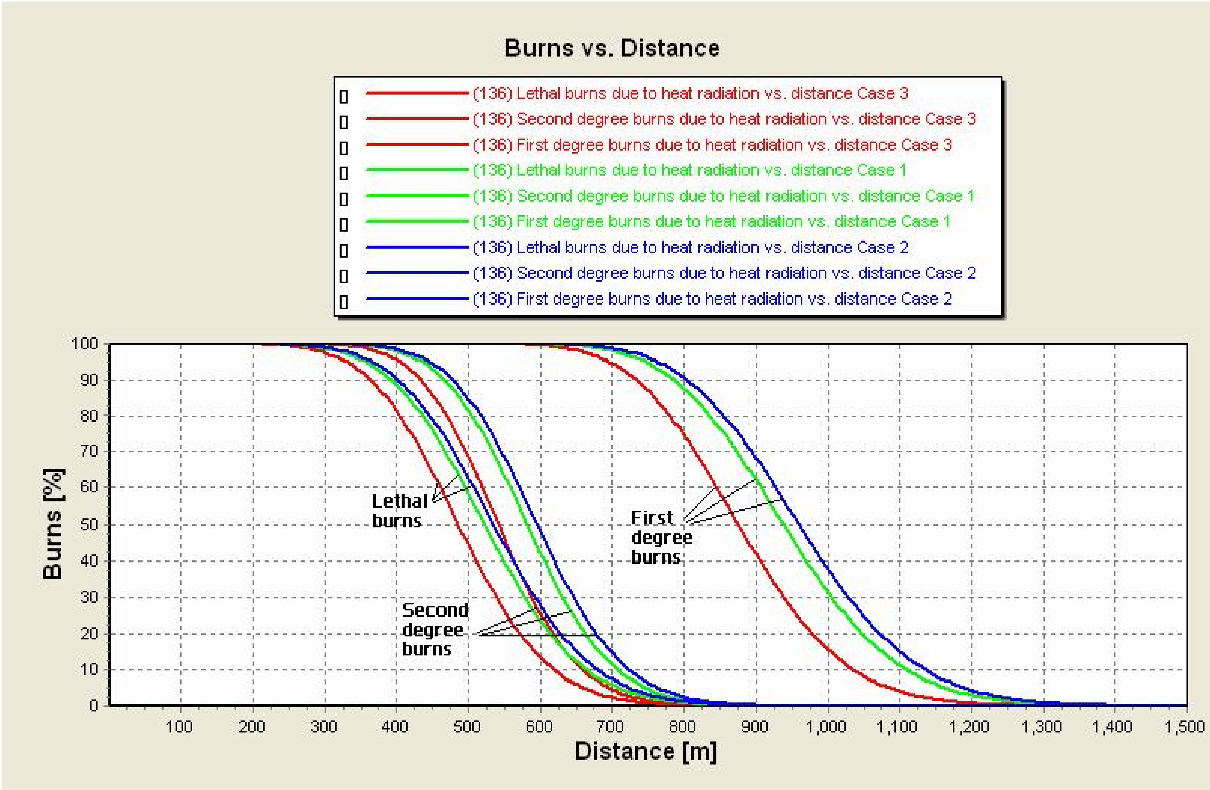

Figure 5.22. Burns depending on distance – static BLEVE model (green – case 1, blue – case 2, red – case 3)

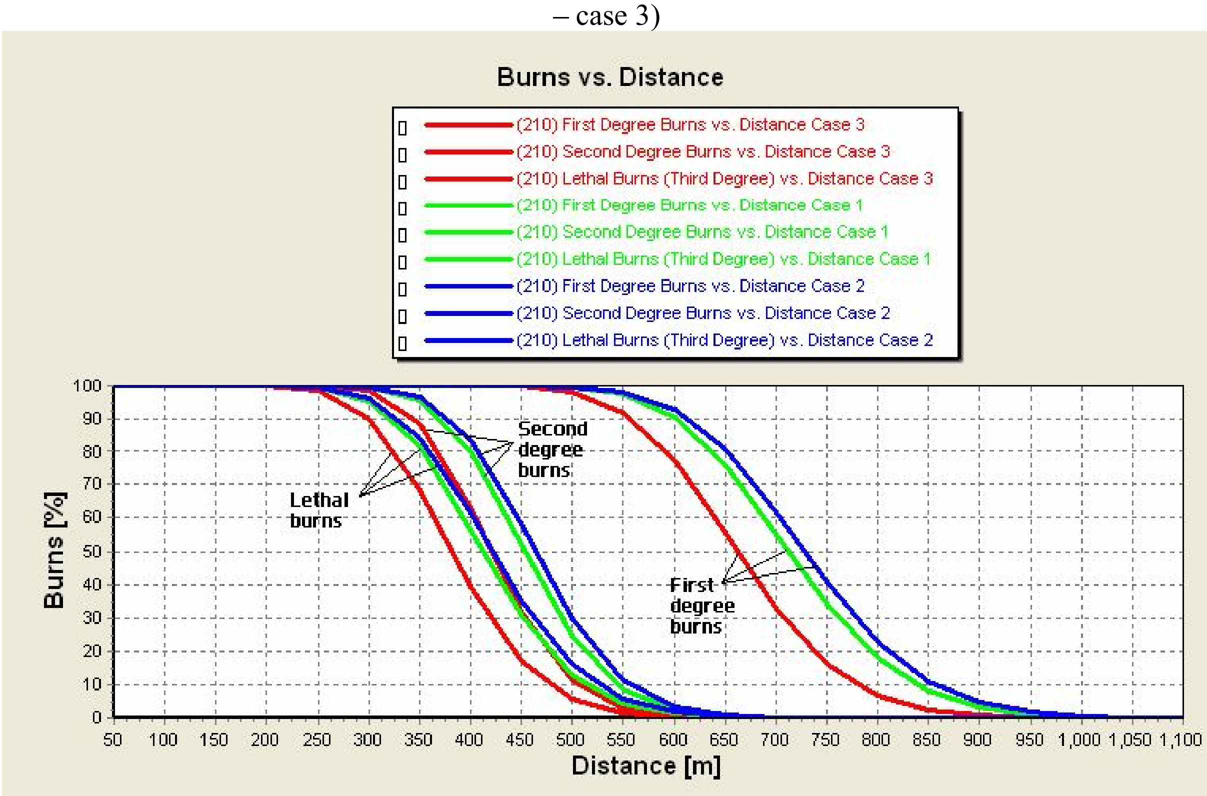

Figure 5.23. Burns depending on distance – dynamic BLEVE model (green – case 1, blue – case 2, red – case 3)

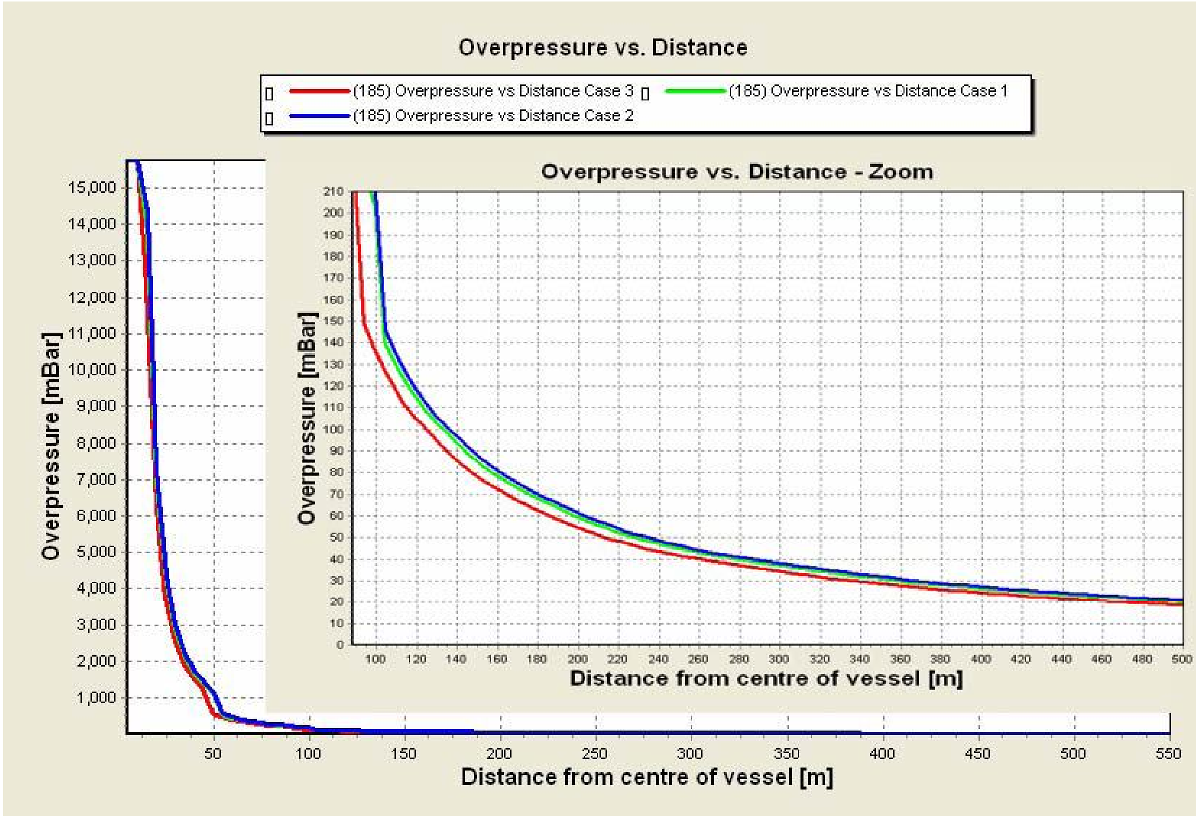

Figure 5.26. Overpressure depending on distance – “tank failure” model (green – case 1, blue – case 2, red – case 3)

The most similar simulation results to the results obtained after the Feyzin accident investigation regarding the FB maximum diameter, FB maximum high and thrown fragments distances (considering the B4 fragment weighting 79 t) were calculated 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.***

5.6.2. Effects and consequences analysis in land-use planning using the French methodology

The French land-use planning methodology aims at estimating magnitude and accidental scenarios probability, using the following limit values in representing the physical effects [18]:

a) Stationary heat radiation effects:

1. High lethality: 8 kW/m^2 (III degree burns at 20 s exposure 20 s [17]); *2. Beginning of lethality:* 5 kW/m^2; *3. Irreversible effects:* 3 kW/m^2 (IInd degree burns at 20 s exposure 20 s [17]);

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

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

c) Overpressure effects [18, 19]:

1. High lethality: 200 mbar (concrete buildings and metallic structures are destroyed [2]);

2. Beginning of lethality: 140 mbar (partial collapse of buildings walls [2]); *3. Irreversible effects:* 50 mbar (minor damages in buildings, windows break [2]); *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 adequate method.

The calculated distances are presented in table 5.8.

Table 5.8. Calculated distances for land-use planning

Case no 3 (181 t)	static BLEVE model (kW/m²)	dynamic BLEVE model ([s*(kW/m²)^4/3])	"tank failure" model (mbar)
High lethality distance (m)	834	295	92
Beginning of lethality distance (m)	1,069	391	97,5
Irreversible effects distance (m)	1,386	488	214
Indirect effects distance (m)	-	-	472

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 that heat radiation from the FB is considered constant throughout the FB.

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

5.6.3. Effects and consequences analysis in land-use planning using the Italian methodology

According to the Italian land-use planning guide [20], the below mentioned limit values are considered in BLEVE:

a) Effects of stationary heat radiation [19, 20]:

1. High lethality: 12.5 kW/m²; *2. Beginning of lethality:* 7 kW/m²; *3. Irreversible effects:* 5 kW/m²; *4. Reversible effects:* 3 kW/m²; *5. Domino effects:* 12.5 kW/m²;

b) Effects of heat radiations variable in time [20] :

1. High lethality: FB radius (100% mortality according to [11]); *2. Beginning of lethality:* 350 kJ/m²; *3. Irreversible effects:* 200 kJ/m²; *4. Reversible effects:* 125 kJ/m²;

c) Overpressure effects [19]:

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

The Italian land-use planning methodology uses the heat radiation limits (kW/m²) in case of long-term fires and radiation doses (kJ/m²) in cases of short-term FB phenomenon.

The calculated distances are presented in table 5.9.

Table 5.9. Calculated distances for land-use planning

Case 3 (181 t)	static BLEVE model (kW/m²)	static BLEVE model (results expressed in kJ/m²)	"tank failure" model (mbar)
High lethality distances (m)	647	169	72
Beginning of lethality distance (m)	896.5	521.5	97.5
Irreversible effects distances (m)	1,070	733.5	164
Reversible effects distances (m)	1,386	948	335.5

5.6.4. Effects and consequences analysis in land-use planning using the Austrian methodology

The Austrian Permanent Seveso Working Group establishes the following limit values for BLEVE phenomenon involving LPG [11]:

a) heat radiation effects:

1. Land-use planning: 2 kW/m^2 (generates discomfort at a exposure longer than 20 s [10]); *2. Domino Effects*: 12.5 kW/m^2;

c) Overpressure effects:

1. Land-use planning: 25 mbar (windows break [10]); *2. Domino effects:* 100 mbar (corresponding to severe building damages and deceases probability equal to 0.025 [10]).

Simulation results are presented in table 5.10

Table 5.10. Calculated distances for land-use planning

Case no 3 (181 t)	**Static BLEVE model (kW/m^2)**	**"Tank failure" model (mbar)**
Land-use planning distances (m)	1,500	392.5

The Austrian methodology is more restrictive regarding land-use planning. It uses only the stationary heat radiation equal to 2 kW/m^2 and 25 mbar overpressure. Thus, the obtained distances are long, assuring the population and infrastructure protection.

5.6.5. Comparative analysis of results obtained using the three methodologies

Regarding population protection, the Austrian methodology is more restrictive, using very low limits for heat radiation and overpressure.

Comparing the French methodology with the Italian one, it can be concluded that in case of stationary heat radiations (surfaces fires with medium or long period of time), the French methodology is more restrictive, using low values for the performed studies. 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, 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. The French methodology is less restrictive regarding the overpressure formed in explosions.

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Chapter 6
Consequence analysis and land-use planning in chlorine storage accidents

Chlorine is a highly used substance in chemical industry, in organic and inorganic syntheses. There were several accidents involving chlorine release, generating human loses and affecting human health, due to its toxic and irritating properties.

Chlorine is stored in large volume tanks, containing thousands of tons of liquefied chlorine. The study's objectives are the estimation of risks associated to chlorine storage, calculation of dangerous areas for the populations and finding practical, efficient solutions for land-use planning and chemical emergencies 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. Comparing the obtained results, conclusion regarding the risk assessment methodology for land-use planning and emergency planning for toxic gaseous substances storage can be drawn.

6.1. Substance description: chlorine

Chlorine is a dense gas, yellow-green and with an unpleasant, suffocating odour. Liquid gas 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.

6.2. Toxicological, eco-toxicological characteristics and threats to human and environment

Chlorine is the subject of Seveso Directive, in case the site quantity is equal or higher than 10 t [1], as it is a toxic and irritating substance.

6.2.1. Aspects regarding the human exposure to chlorine

Liquid chlorine generates burns of different severity degrees in contact to every part of the human body. Gaseous chlorine is a respiratory irritant. Concentrations higher than 5 ppm are irritating for the nasal and pharynx mucous membrane and eyes. At concentrations varying between 1 and 3 ppm, a few hours after the exposure, chlorine causes a slightly ocular and respiratory irritation.

The below list represents a compilation of limit exposure values and their effects, related to human subjects [2, 3]:

- 0.2-0.4 ppm: olfactory perception limit with considerable variations from one subject to another (olfactory perception is reduced in time);
- 1-3 ppm: slight irritation of nasal membrane, tolerated for approximately an hour;
- 5-15 ppm: moderate irritation of respiratory membrane;
- 10 ppm: IDLH concentration for 30 minutes exposure;
- 30 ppm: thoracic pains, nausea, cough, dyspnoea;
- 40-60 ppm: toxic pneumonia and pulmonary oedema;
- 430 ppm: lethal level in 30 minutes;
- 1,000 ppm: lethal level in a few minutes.

For the exposure to be lethal, a person should stand in the release air, inside the chlorine cloud, without respiratory protection.

6.5. Case study: Chlorine storehouse in Turda

This case study identifies hazards and risks associated to chlorine storage and use. Possible major accidents are analyzed by using toxic dispersions simulations and the dangerous areas are estimated, in order to offer solutions for land-use planning and emergency planning in case of liquefied toxic substances storage.

The simulations were performed using two soft wares, namely:

1. SEVEX View – major chemical accidents simulation software, using a complex meteorological model, terrain topography and 3D Lagrangian dispersion model [4].
2. SLAB View – toxic dispersion simulation software, using the bi-dimensional SLAB model [5].

Using these two simulation software, the obtained results can be compared, in order to emphasize the significant differences, to use the best results in land-use planning and emergency planning.

6.5.1. General data

The studied site is located in Turda town, in the industrial area, at an altitude of approximately 330 m above sea level [6]. The facility consists of the liquid chlorine bottling machine and the liquid chlorine storehouse. The liquid chlorine storehouse included two 50 t tanks each, situated in a contained room, semi-buried.

6.7. Critical points identification at the studied facility

Based on the study of the tank, the critical points of chlorine accidental releases were identified [7]. These critical points are presented below, in table 6.5.

Table 6.5. List of critical points of chlorine accidental releases [7]

No	Accidental pollution occurrence	Pollution possible causes	Name
	Liquid chlorine storage, handling		
a.	- rail road tank	- defect valves (closing inadequately).	Chlorine
b.	- chlorine containers barrel or cylinder type	- unsealed taps, - defect fitting taps.	Chlorine

c.	- chlorine handling path ways	- unsealed elastic coupling at the rail road tank or primary tanks, - pipe rupture, - defect gland seal connection, - couplings with unsealed flanges - inadequate fittings, - incorrect montage, - damages.	Chlorine
d.	- storage tanks	- valves with defect glands, - unsealed flanges couplings, - level bottle breaking, - cracks in the tank walls.	Chlorine

6.8. Qualitative risk estimation

Qualitative analysis aims at establishing the possible hazards and supports the events ranking according to risk level. Risk is assessed according to equation 1.1 from the first chapter and is represented by the risk matrix. Risk assessment matrixes are used for many years to rank risk depending on their significance. This fact allows prioritisation in control measures implementation.

6.8.1. Accidental scenario selection

According to table 6.5, 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 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*.

The following installation failure frequencies were considered: for failure of flanges at coupling a frequency of $3.1*10^{-3}$ ev./year was considered (according to probabilistic calculations [7]) and $3*10^{-6}$ ev./year for the total failure of the under pressure storage tank [8]. There were many accidents of chlorine release from the cylinders on site, thus a high frequency for this scenario was considered.

The risk assessment matrix for the relevant accident scenarios is presented in table 6.8:

Table 6.8. Risk associated to studied accident scenarios

No.	Danger	*Probability*	*Gravity*	Risk
A. Accident at the storage tank				
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 from a cylinder	4	2	**8**

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. As a consequence, these scenarios must be analyzed in detail, because their consequences can be catastrophic.

6.8.2. Conclusions regarding the qualitative risk assessment

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.

6.9. Comparative analysis of effects and consequences of the chlorine dispersion phenomenon

The effects and consequences assessment was elaborated by simulating the chlorine release, followed by the simulation of the chlorine dispersion. The input data depended on 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.

6.9.2. Chlorine simulation using SEVEX View software

The SEVEX View software considers the complex terrain topography from the GTOPO30 database for a surface of 37 km^2, 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.

Based on the frequent meteorological conditions in the studied area the following synoptic wind speeds are considered: 2m/s (SE) and 5m/s (NV) [6]. 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 favourable 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, day-time; 36 maps for 2 m/s synoptic wind, night-time.

6.9.2.1. Work methodology for land-use planning

In order to provide a land-use planning methodology for toxic dispersion, several parameters and factors influencing the results were taken into account, namely: for day-time: air temperature = 20 ^{o}C, relative humidity = 70%, nebulosity = 100%, stability class D (neutral); for night-time: air temperature = 10 ^{o}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 for the Austrian land-use planning methodology [9].

Concern concentrations:

The French land-use planning methodology uses three levels of concentrations, namely [10]:

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 concentration is usually considered for this level.

The Italian methodology uses the 30 minutes LC50 and IDLH concentrations for representation of dangerous areas [11].

The Austrian methodology recommends the use of IDLH values in land-use planning 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 [9].

Considering the discussed methodologies, the use of the LC50, IDLH and 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 [2];
- IDLH = 10 ppm, for 30 minutes exposure [3];
- ERPG2 = 3 ppm, 1 hour exposure[12];

It is considered that the areas affected by concentration equal or higher than LC50 must be immediately evacuated after the accident, because there is mortality 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.

6.9.2.2. Results obtained using SEVEX View simulations

In scenario A2, the total chlorine quantity released in 60 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 were performed;
- Distinct simulations for 2 m/s and 5 m/s wind speeds were performed.

Table 6.8 lists the results regarding the areas affected by the concern concentrations: LC50, IDLH, ERPG2.

Table 6.8. Areas affected by concern concentrations

Scenario name	Accident time	Wind sector	Validity (min)	S0 Unaffected area (km^2)	S1 Area affected by ERPG2 conc. (km^2)	S2 Area affected by IDLH conc. (km^2)	S3 Area affected by LC50 conc. (km^2)
A.1 – 2 m/s	Day	All	30	368.54	12.47	57.30	2.69
	Night	All	30	388.19	7.34	37.25	8.22
	Day	All	60	218.08	97.55	122.68	2.69

Scenario name	Accident time	Wind sector	Validity (min)	S0 Unaffected area (km^2)	S1 Area affected by ERPG2 conc. (km^2)	S2 Area affected by IDLH conc. (km^2)	S3 Area affected by LC50 conc. (km^2)
	Night	All	60	239.05	35.87	157.09	8.99
	Day	SE	240	359.10	48.88	32.13	0.89
	Night	SE	240	284.76	95.54	56.93	3.77
	Day	NV	240	401.45	23.97	14.73	0.85
	Night	NV	240	368.85	16.72	52.57	2.86
A.1 – 5 m/s	Day	SE	240	379.29	33.28	27.36	1.07
	Night	SE	240	354.10	29.96	54.16	2.78
	Day	NV	240	371.22	33.34	34.20	2.24
	Night	NV	240	370.38	43.98	25.08	1.16
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
B.1 – 2 m/s	Day	All	30	437.11	2.70	1.13	0.06
	Night	All	30	421.13	13.11	6.63	0.13
	Day	All	60	439.54	0.98	0.42	0.06
	Night	All	60	415.79	18.23	6.85	0.13
	Day	SE	240	439.37	1.01	0.56	0.06
	Night	SE	240	434.20	4.18	2.49	0.13
	Day	NV	240	439.58	0.84	0.51	0.07
	Night	NV	240	429.07	9.85	2.01	0.07
B.1 – 5 m/s	Day	SE	240	439.04	1.21	0.69	0.06
	Night	SE	240	434.93	4.33	1.63	0.11
	Day	NV	240	437.13	2.37	1.45	0.05
	Night	NV	240	439.07	1.24	0.69	0.00

The results listed in table 6.8 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 synoptic wind speed, 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 map.

- 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 land-use planning:

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

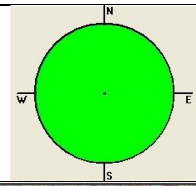
In this case, the 30 and 60 minutes maps are not available, because the 5 m/s wind speed can not be detectable from the accident starting point. Therefore, the 240 minutes maps are used from the beginning of the emergency situation.

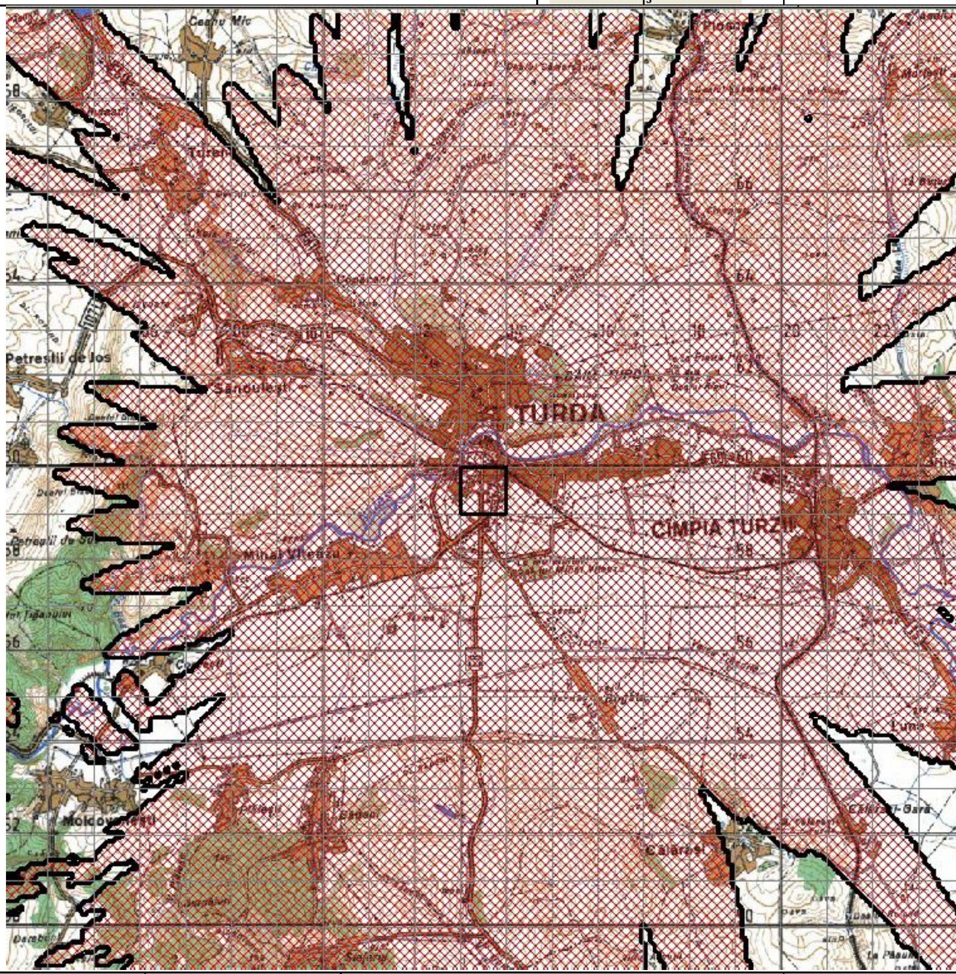
3) The described maps are built of a discrete data set (36 synoptic directions). Thus, the area represented on maps is not the total area. For a more complete representation of affected areas, the peaks of the iso-concentrations curves should be connected.

4) In the risk maps considering the NV or SE wind directions, three distinct directions are represented and the results are overlapped. In this case, a possible fluctuation of 30^o in wind direction is taken into account.

Risk maps recommended for land-use planning are represented in figures 6.12 – 6.14.

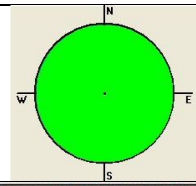
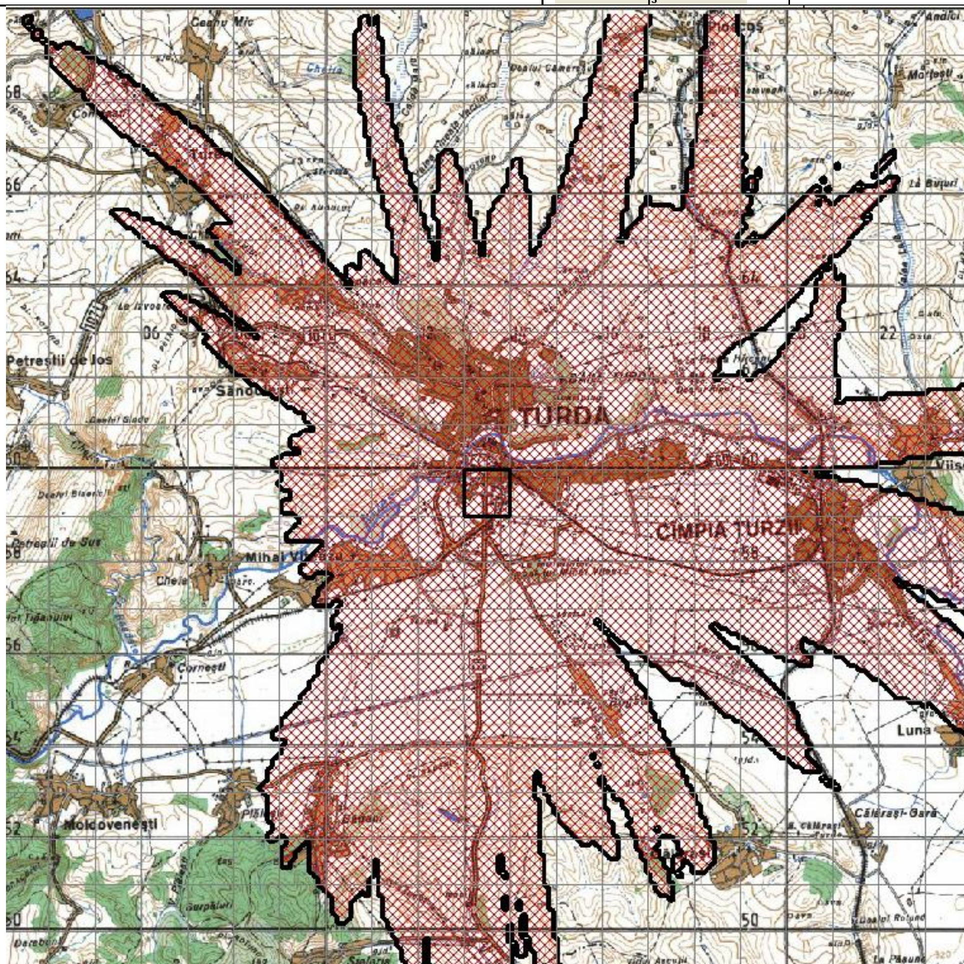
Figure 6.12. Risk map: Total possibly affected area by dangerous concentrations outside of buildings – scenario A.1.

<table>
<tr>
<td rowspan="2">SCENARIO A.1. – 56 tons chlorine, catastrophic release
Wind speed = [2 – 5] m/s
Wind sector: all directions</td>
<td rowspan="2"></td>
<td>Period:
Day and night</td>
</tr>
<tr>
<td>Scale:
0 4 km</td>
</tr>
</table>



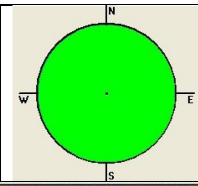
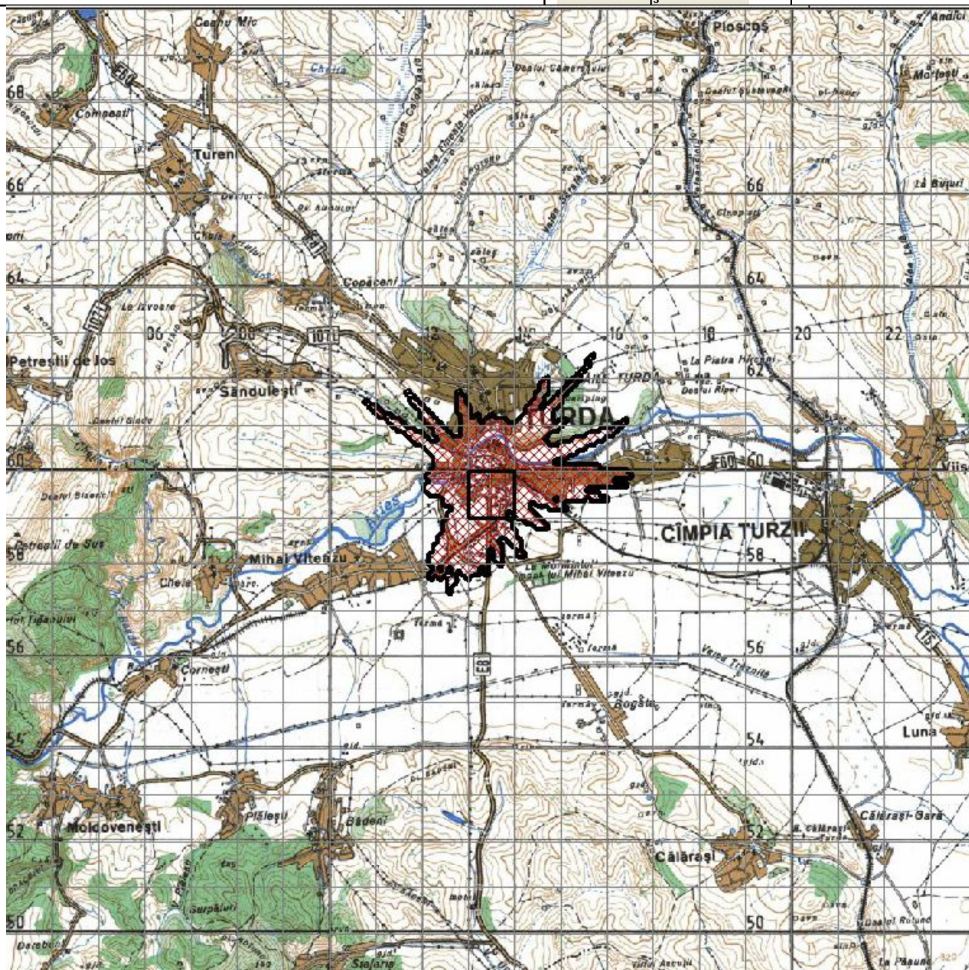
Irreversible effects outside buildings	(red)	Area evacuation or self-sheltering	10,0 < C < 430,0 ppm

Figure 6.13. Risk map: total possible area affected by dangerous concentrations outside buildings – Scenario A.2.

<table>
<tr>
<td rowspan="2">SCENARIO A.2 - 19,76 tons chlorine, continuous release for 10 minutes
Wind speed = [2 – 5] m/s
Wind sector: all directions</td>
<td rowspan="2"></td>
<td>Period:
Day and night</td>
</tr>
<tr>
<td>Scale:
0 4 km</td>
</tr>
<tr>
<td colspan="3"></td>
</tr>
</table>

Irreversible effects outside buildings	(red)	Area evacuation or self-sheltering	10,0 < C < 430,0 ppm

Figure 6.14. Risk map: Total possible area affected by dangerous concentrations outside buildings– Scenario B.1.

<table>
<tr><td colspan="2" rowspan="2">SCENARIO B.1. – 1 tons chlorine, catastrophic release from a cylinder
Wind speed = [2 – 5] m/s
Wind sector: all directions</td><td rowspan="2">
</td><td>Period:
Day and night</td></tr>
<tr><td>Scale:
0 4 km</td></tr>
<tr><td colspan="4">
</td></tr>
<tr><td>Irreversible effects outside buildings</td><td>(red)</td><td>Area evacuation or self-sheltering</td><td>10,0 < C < 430,0 ppm</td></tr>
</table>

These maps were performed by overlapping the maps elaborated using simulated weather conditions (2 m/s and 5 m/s wind speeds) for day time and night time. Therefore, these maps were obtained representing the dangerous areas, namely where the gas concentrations range between IDLH and LC50 limits and outside buildings the person is exposed to irreversible effects or even death, if the exposure lasts for a long period of time. The 36 synoptic wind directions are considered. The maps are built of a discrete data set and for obtaining the complete affected area; the peaks of the iso-concentrations curves should be connected.

6.9.3. The simulation of chlorine dispersion 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 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 showing the areas where concentrations of interest can appear, but does not consider the exposure time, as the SLAB maps do.

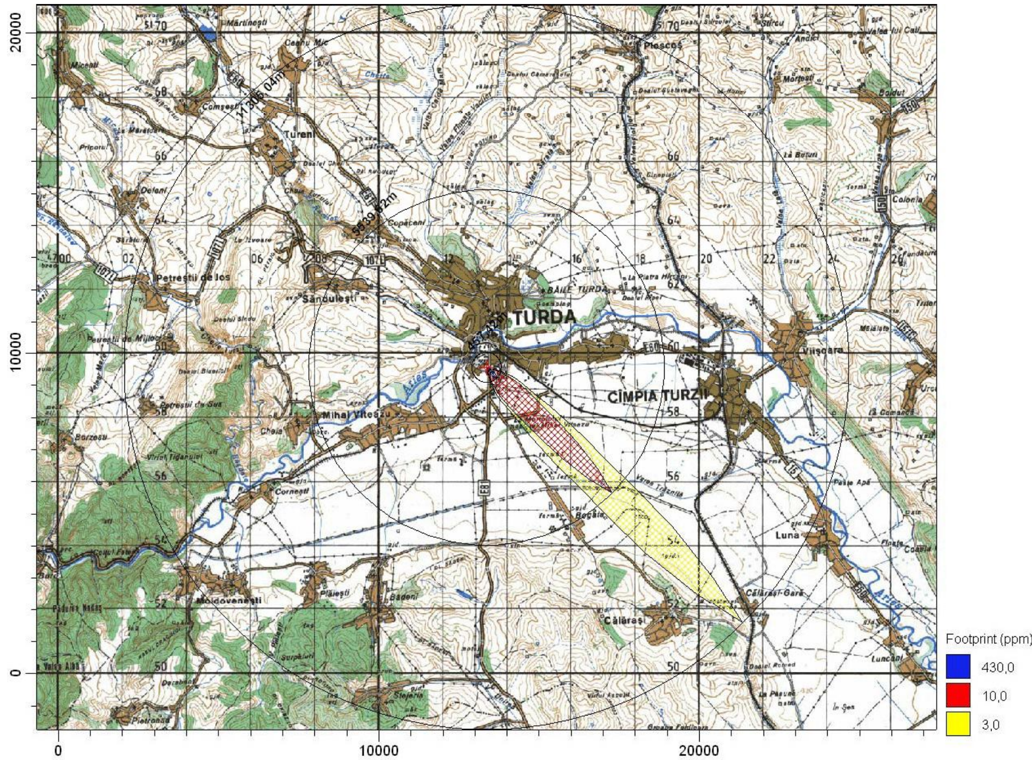


Figure 6.15. *SLAB. Scenario A.2.* – Potentially affected areas by concentrations: LC50 (blue), IDLH (red), ERPG2 (yellow), 30 minutes exposure – daytime, wind speed = 2 m/s

Table 6.9. Distances and areas calculated for concentrations of interest using SLAB model

	LC50		IDLH		ERPG2	
	Radius (km)	**Surface S3 (km^2)**	**Radius (km)**	**Surface S2 (km^2)**	**Radius (km)**	**Surface S1 (km^2)**
Daytime – wind speed = 2 m/s	0.457	0.657	5.539	96.385	11.306	401.576
Nighttime – 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
Nighttime – wind speed = 5 m/s	0.821	2.118	12.791	513.994	26.296	2172.347

Analyzing the results obtained using SLAB View can be observed 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 forms due to the present obstacles.

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 are presented in table 6.10. The values are representing the surface of the areas for 30 minutes exposure, from the beginning of the accident.

Table 6.10. Potentially affected surfaces calculated by SEVEX and SLAB for Scenario A.2.

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

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 different 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.

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Chapter 7
Consequence analysis and land use planning in case of accident at storage of ammonium nitrate

Ammonium nitrate (AN) is a substance often used as fertilizer in agriculture. The use of AN in agriculture presents the following disadvantages: highly emphasized hygroscopic, oxidizing and explosive character. Despite these dangerous properties the AN is widely used as explosive in the mining industry. After the Toulouse (2001) accident [1] AN was included in the list of dangerous substances of Seveso directive. In this context, the storage, handling and transportation of AN is regulated in Romania by the Governmental Decision 804/2007 for quantities equal or higher than provided in the Annex 1 of this decision [2].

The objective of the case study is to find practical and efficient solutions for land use and emergency planning in the case of AN storage, handling and transportation.

7.1. Presentation of the substance: ammonium nitrate

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.) [3].

7.6. Potential hazards and risks associated to ammonium nitrate

Three main hazards can be associated to AN:

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

7.6.1. Estimation of the risk of instability

AN in pure state can be subjected to thermal decomposition if sufficient caloric energy is obtained. During these reactions toxic gases like nitrogen oxides and ammonia are emitted. Adequate ventilation can stop the decomposition, if the heat source is stopped. The rate of decomposition is not too dangerous at moderate temperatures and the total thermal effects are not significant when the exothermic reaction is accompanied by endothermic dissociation.

Heated between 170 - 250^{o}C it decomposes in nitrogen dioxide and water vapour following the exothermic reaction:

$$NH_4NO_3 \rightarrow NO_2 + 2H_2O + 37\ kJ/mol \quad (7.1)$$

From the decomposition above 250 ^{o}C ammonia and nitric acid result:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 - 174\ kJ/mol \quad (7.2)$$

Because reaction (7.2) is endothermic, the decomposition temperature can be auto-limited by the process, if the produced gases are evacuated free in the air. At atmospheric pressure this temperature limit is 292 °C. If the nitrogen dioxide remains in the reaction environment the reversible dissociation is stopped together with the endothermic effects. The exothermic effect will start to dominate the reaction which will lead to the acceleration of the decomposition and explosive behaviour. The following very violent exothermic reaction will take place:

$$NH_4NO_3 + 2NO_2 \rightarrow N_2 + 2\ HNO_3 + H_2O + 232\ kJ/mol \quad (7.3).$$

At higher temperatures a detonation will take place according to the following reaction:

$$2NH_4NO_3 \rightarrow 2\ N_2 + 4H_2O + O_2 + 118\ kJ/mol \quad (7.4)$$

This phenomena explains the explosion of AN in closed spaced when heated.

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) [3].

1. Calculation of C_1 criteria: decomposition enthalpy - ΔH_d

C_1 = -1.47 kJ/g → medium risk.

2. Calculation of C_2 criteria: combustion tendency

For the C_2 criteria AN obtained **medium risk** level because it becomes explosive when heated [3].

2. Calculation of C_3 criteria: internal redox measures; oxygen balance

In case of AN: z = 0.5, M = 80; C_3 = 3,200/80 * 0.5 = 20 → **high risk.**

4. Calculation of C_4 criteria: the effect of mass

In case of AN: n = 9, M = 80; $C_4 = 10 * (-1.47)^2 * 80/9$ = 192,08 → **minor risk**

This criterion is underestimating the risk in case of AN [3].

Considering these four risk criteria calculated for AN results a final **medium risk regarding the instability of the substance.**

7.6.2. Fires

AN is not flammable or combustible. As an oxidizing agent, it can maintain the combustion and can amplify a fire even in the lack of oxygen, but only if combustible or flammable material is present. During combustion it decomposes in toxic gases as nitrogen oxides and ammonia.

Fires involving AN can not be extinguished by smothering, because AN can produce the necessary oxygen for maintaining the combustion. Water is the best extinguishing agent for fires involving AN and the best method is flooding the area with water [4, 5].

From the estimation of the risk of instability results that AN poses a **minor risk of fires.**

Dangerous substances resulting from decomposition of AN:

The main hazardous substances emitted at the decomposition of AN based fertilizers can be the following [6]:

a) the first version, after the classification of Perbal: water vapour (H_2O): 45-65 %; nitrogen (N_2): 19-26 %; nitrous oxide (N_2O): 7-20%; hydrochloric acid (HCl): 0.5-10%; nitrogen oxides (NO_x): 0-9%; ammonium chloride (NH_4Cl): 0-7%; chlorine (Cl_2): 0-2%;

b) the second version, after the classification of Kiiski: water vapor (H_2O): 56 %; nitrogen (N_2): 20 %; nitrous oxide (N_2O): 11 %; chlorine (Cl_2) and hydrochloric acid (HCl): 6 %; nitrogen oxides (NO_x), ammonia (NH_3) and hydrofluoric acid (HF): 7 %.

7.6.3. Explosion

AN can produce an explosion based on one of the following causes:

- heating in closed spaces;
- accelerated decomposition reactions – self heating from the thermal decomposition;
- detonation – initiation from mechanical shock or from other explosion.

There is a confusion in literature and safety reports regarding the explosive power of the AN based fertilizers. The general opinion regarding the hazards of AN in case of a fire at a warehouse is that a liquid pool will form at the end of the pile close to the fire. If this pool is hit by a fragment with high speed (a falling object) than a local explosion will occur. This explosion will send a shock wave to piles which are not melted. If this pile is easier than 300 t it will not detonate but will deflagrate liberating energy equal to the explosion of 41 t of TNT. This values was estimated based on a TNT equivalency on AN with 55 % explosive power and 25 % efficiency. The overpressure distance of $6.9 \cdot 10^3$ Pa (= 1 psi = 0,069 bar) for such an explosion is approximately 600 m [1, 5].

Application of TNT model for calculating the explosive power

Because an explosion of AN is a rapid conversion of solid in gas phase at a high temperature the essential parameters characterizing the explosive field are the gas quantity produced and the liberated energy from the reaction, which determines the reached maximum temperature.

The liberated energy from an explosion is the product of explosive mass – M (kg), explosive energy – E_S (J) for 1 kg substance and the efficiency of the explosion. The specific energy of the explosion is measured in terms of detonation energy of TNT and it is considered to be the explosive power:

$$Explosive\ Power = E_S / E_{TNT}$$

where: E_S – decomposition energy of 1 kg substance (J)

E_{TNT} – detonation energy of 1 kg TNT (J).

Because the consequences of explosion are documented in terms of TNT mass, it is convenient to determine the consequences of explosions of other materials using equivalent TNT mass. This is defined as: *Eq. TNT = M x (Explosive power) x (efficiency).*

In table 7.4 the values determined by HSE (Health and Safety Executive) for TNT equivalency are presented:

Table 7.4. Power, efficiency and TNT equivalency of AN based explosions [7]

Substance name	**Explosive power**	**Efficiency**	**TNT equivalency**	**Reference**
Ammonium nitrate	55 %	25 %	14 %	HSE, UK
FGAN (fertilizer grade AN)	30 %	10 %	3 %	varied
TGAN (technical grade AN)	40 %	25 %	10 %	varied

For AN stored in piles some of the experts accept 0.32 for TNT equivalency.

7.8. Case study: Risk assessment of ammonium nitrate storage at a harbour

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

7.8.2. Identification of hazards and vulnerable areas

The storage, handling and transportation of hazardous substances in large quantities, in this case of AN, 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 7.5.

Table 7.5. Hazards and identified risk factors

Hazard	**Potential risk factor**
Chemical	- storage and handling of potentially dangerous oxidizing substances, - emission of toxic gases (nitrogen oxides and ammonia), resulted from the thermal decomposition in case of an accident;
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.

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

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

To have an explosion in the AN mass, the mixing of a part AN with combustible material or the detonation of a significant quantity of explosive is necessary. This is possible under the following situations:

- military attack with explosive projectiles;
- terrorist attack and detonation of AN with explosive material or mixing a part of AN with combustible material and detonation;
- the production of a series of human errors leading to the detonation of AN in the warehouse;
- leakage and mixing of combustible material with AN; fire in the area where AN is mixed with combustible material.

Population and vulnerable areas

In the yard of the site there are 12 workers permanently. In addition, delegated persons, collaborators, beneficiary owners, firm representatives, visitors, control personnel can be present.

At 500 m from the warehouse is the supervisory office and restroom of workers from the harbour. At approximately 1.6 km from the warehouse in W direction are the first buildings of the residential area of the city. At approximately 2.1 km from the warehouse in N direction are also buildings from the residential area of the city.

The workers of the warehouse are the most susceptible to be affected in case of an accident.

7.8.3. Selection of accident scenarios

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 rout conveyor-elevator

Scenario C.1. Fire at the conveyor-elevator
Scenario C.2. Leakage of AN at the conveyor-elevator

7.8.4. Qualitative risk assessment of the identified major accidents

The quantitative assessment is performed using the identified consequences and probabilities. The risk is quantified using the formula of risk presented in chapter 1 and presented in the risk matrix.

7.8.4.2. Risk Matrix

All the failures and events with magnitude level 4 and 5 pose a major accident hazard. The other events are classified as potential hazards with the possibility of extension to other areas, aggravating the situations.

In the estimation of probability and magnitude levels it was considered the existence of safety measures implemented at the warehouse and the results of other previously performed studies.

Table 7.8. Risk matrix of the identified accident scenarios

No. scn.	Scenario	Probability	Magnitude	Risk
A. Warehouse 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 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 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**

7.8.4.3. Conclusions regarding the qualitative risk assessment

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.

7.8.5. Effect and consequence analysis of storage and handling of ammonium nitrate

For the assessment of magnitude of accidents in the case of explosion scenarios computer simulations using the EFFECTS 7 software from TNO 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 medium daily handled quantity;
  1,500 t being the medium minimum existing quantity in the warehouse;
  10,000 t being the medium 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.

TNT equivalents used in simulations for the above mentioned quantities:

- 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 [7];
- 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 [8].

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 [7, 8].

7.8.6. Effect and consequence analysis in the context of land use planning using the French, Italian and Austrian methodologies

The French land use planning methodology considers the following limits for the estimation of consequences [9]:

1. High lethality: 200 mbar (destruction of concrete buildings and metal structures [1]); *2. Beginning of lethality:* 140 mbar (partial collapse of walls in buildings [1]); *3. Irreversible effects:* 50 mbar (minor damage of buildings, breakage of windows [1]); *4. Indirect effects:* 20 mbar (breakage of windows).

The Italian land use planning methodology considers the following limits for the estimation of consequences [10]:

1. High lethality: 300 mbar (total destruction of buildings [1]); *2. Beginning of lethality:* 140 mbar; *3. Irreversible effects:* 70 mbar (partial destruction of houses [2]); *4. Reversible effects:* 30 mbar.

The Austrian LUP methodology [11] uses only one level of concern for overpressure: *1. Land use planning level:* 25 mbar (breakage of windows [12]).

According to these levels established by the three methodologies the distances for overpressures were calculated for the following quantities of AN: 1, 10, 100, 300, 1,500, 10,000, 14,000 t. The calculated distances are presented in table 7.11.

Table 7.11. Calculated distances (m) for LUP

Met.	Levels of concern	1 t	10 t	100 t	300 t	1,500 t	10,000 t	14,000 t
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
	Irreversible effects (70 mbar)	93	200	432	623	1,405	2,644	2,958
	Reversible effects (30 mbar)	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

The toxic dispersion effects in case of fires and NA decomposition were not studied due to the lack of dispersion models. The toxic gases obtaining phenomenon is very complex. Due to high temperatures, the gases will have a high ascensional speed and the dispersion will occur at high altitudes in the troposphere.

The use of all safety measures discussed above is recommended, to prevent technological accidents at ammonium nitrate storage and handling.

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Chapter 8
Land-use methodology proposal

The PhD thesis studies the major issues related to safety distances calculation, in order to create a risk assessment methodology which can be used in land-use planning.

The previous chapters analyzed three different case studies, involving inflammable, explosive or toxic substances, used in the chemical industry. In industry, they are stored in large quantities, generating a higher threat for the human population. The Seveso Directive regulates the risk studies elaboration for land-use planning for the sites subjected to this law, but it does not establish a methodology which can be equally applied by the UE member states. The Romanian legislation does not establish a methodology for calculating safety distances, used in land-use planning. This paper proposes a methodology for calculating these safety distances, by summarizing the existing methodologies used by other UE member states and the *"Guide for calculating major accidents"*, developed by PhD H. Joachim Uth.

8.1. Recommended methodology

The *"Guide for calculating major accidents"* has some disadvantages, namely:

1) for the industrial studied area, this guide considers the current security technology state; in Romania many facilities have not implemented security technologies;

2) it does not consider the stationary heat radiations;

3) it does not take into account the complex terrains in case of toxic dispersion etc. Therefore, the danger areas can be under or over estimated in case of BLEVE technological accidents or toxic dispersions involving large quantities of substances;

4) the recommended overpressure threshold for LUP (0.1 bar) is too high.

This paper recommends the use of a semi-quantitative methodology for land-use planning, based on expert judgment and including the following analyses:

- Analyses of hazards associated to dangerous substances present on site;
- Technological hazards identification and analysis, using the HAZOP, FMEA methods and the FEI – DOW risk indexes, depending on the problem's complexity and assessment team;
- Accidental scenario development depending on the identified hazards;
- Risk qualitative assessment, using risk matrix, frequencies and consequences estimation based on assessors experience;
- Selection of accidental scenarios based on several criteria: maximum possible scenario; maximum credible scenario; scenarios with a moderate or high risk;
- Quantitative analysis of physical effects and consequences, by accidents modelling and simulations;
- Use of the state-of-the-art models;
- Use of average and extreme weather conditions;

For calculating the planning distances, the compliance with the following concepts is recommended:

Heat radiation

In BLEVE accidents the victims died because of the heat radiation generated by the FB. Therefore, this paper proposes the use of dynamic models for calculating heat radiation's physical effects and distances for land-use planning. The physical effects can be expressed by heat load, in a more adequate manner than in the case of dynamic heat radiation.

The 1.6 kW/m^2 value used for heat radiation in the *"Guide for calculating major accidents"* overestimates the danger areas in case of fires and especially in case of fires with BLEVE stationary heat radiation.

For calculating the effects of the stationary and dynamic heat radiations, the use of limits established within the French methodology is recommended.

The distances calculated for land-use planning emphasize the fact that the LPG storage facilities should be built away from the process sites, refineries, hydrocarbons storage facilities, public roads and residential areas.

Toxic dispersions

For land-use planning in case of toxic dispersions, the use of LC50, IDLH and ERPG2 limit concentrations is recommended, in order to establish dangerous areas according to the following reasons:

1) these concentrations can be easily found in literature;

2) they represent different situations, which require different response actions: $C > LC50$ – immediate evacuation of the area; $IDLH \leq C < LC50$ – evacuation of the area with high concentrations and self-sheltering; $ERPG2 \leq C < IDLH$ – self-sheltering and exposure avoidance; $C < ERPG2$ – exposure avoidance, no danger.

3) it offers sufficient data for selecting safety distances in land-use planning, for several areas (urban, industrial, protected etc.).

For calculating safety distances in land-use planning for residential areas the ERPG2 concentration limit is recommended.

The use of tri-dimensional models is more adequate for calculating toxic dispersions, considering the complexity of fluids flow and the influence of topography on wind currents.

Based on the consequence analysis, according to simulations performed with SEVEX View and SLAB View software, the chlorine storehouse should not be located in Turda town, because it induces a major risk for the population in Turda, Câmpia Turzii and nearby villages.

Overpressure

For land-use planning in accidental explosions the use of the 20 mbar threshold is recommended, being the overpressure at which windows break. It is considered that because of the windows breaking, the population is indirectly affected, the persons being hurt by broken glass fragments.

The estimation of overpressures consequences formed in case of explosions using the French methodology is recommended. Using the Italian methodology, the distances are too short.

Ammonium nitrate storage poses a moderate risk, considering the catastrophic consequences and low occurrence probability. The accidental explosions occurrence probability is lower, if the safety measures indicated in the paper are implemented.

Chapter 9
Conclusions

The development of the process industries lead to a significant increase of the technological accidents number, generating the severe environmental pollutions and many human losses. 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 land-use planning in the context of the art. 12 from the Seveso Directive, except the regulations regarding explosives and the location of main pipes for natural gas transport.

In Romania there are currently more then 200 economic operators, classified as Seveso sites, most of them top-tier sites. 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, land-use planning and emergency planning. 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 land-use planning and emergency planning in case of Seveso sites, where inflammable, explosives and toxic substances in large quantities are stored, transported or processed.

The first part, theoretical, adds major contributions to the Romanian field literature, presenting in a logical order, the main aspects of hazards and risk in the chemical industry, the most used methods and techniques in the field of risk assessment, emphasizing their differences, advantages, disadvantages and limitations. This first part represents the basis of the methodology elaborated in the thesis last chapter.

For the methodology elaboration three case studies are considered: technological accident scenarios at the storage of the following dangerous substances: propane, chlorine and ammonium nitrate. These substances were selected due to several reasons: they are highly used in the chemical, petrochemical, mining industry and agriculture; they can generate almost all chemical or uncontrolled energy development accident types; they are stored in very large quantities; they are stored in the vicinity of vulnerable areas (for example, the chlorine storehouse in Turda).

Each case study deals with a technological accident involving one of the above mentioned substances. The accidents' consequences are assessed and the distances for land-use planning are calculated, considering several methodologies used in the EU member states.

The final proposed methodology is based on several theoretical considerations and methodologies:

- The risk assessment methods and techniques described in the first part of the thesis: HAZOP, FMEA, DOW index, historical analysis, quantitative risk analyses through effects and consequences modelling and simulations etc.;
- *"Guide for calculating major accidents*" developed by PhD. H. Joachim Uth, which describes the LUP experience used in Germany;
- The French methodology for land-use planning developed by the Ministry of Ecology, Energy, Sustainable Development and Sea in France;
- The Italian methodology for land-use planning developed by the Ministry of Public Works in Italy;
- The Austrian methodology for land-use planning developed by the "Permanent Seveso Working Team" in Austria.

Analyzing the three case studies and the obtained results, it can be concluded that the *Guide for calculating major accidents* methodology, which reflects the land-use planning experience in Germany has some weak points: 1) it does not take into account the non-stationary heat radiations case; 2) it does not consider the complex terrains in case of toxic dispersions; 3) it is too general and it can not be used for any accident; 4) for the studied industrial area, this guide considers the current status of security technology, which is not applied in many Romanian Seveso sites.

The Italian and Austrian land-use planning methodology is still being developed. 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 radiations ones.

The French methodology is based on consequences estimation. The limits are stricter than in the Italian methodology, thus the population's 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.

The methodology proposed in this paper uses the consequence-based method, using 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 ERPG2 limits are recommended, based on the following considerations:

1) these concentrations can be found in the literature;

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

3) they represent different situations, where different intervention actions are required: $C > LC50$ – immediate evacuation of the area; $IDLH \leq C < LC50$ – evacuation of the area with high concentration and sheltering in other area; $ERPG2 \leq C < IDLH$ – sheltering and exposure avoidance; $C < ERPG2$ – exposure avoidance, no danger.

4) they provide enough data for selecting safety distances in land-use planning, for different type areas (urban, industrial, protected etc.).

The ERPG2 concentration is recommended for land-use planning 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 land-use planning 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 or residential areas. All these aspects are clearly stated in the conclusions drawn after each case study.

A) 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 land-use planning should be greater than 488 m, this being the distance at which irreversible effects occur, due to the heat radiation.

B) Considering a chemical accident involving the entire chlorine quantity spilling at the Turda storehouse, in the worst meteorological conditions, an area equal or larger than 56.93 km^2 should be evacuated. This area partially affects Turda, Câmpia Turzii towns and Mihai Viteazu and Sănduleşti 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.

C) In case of ammonium nitrate (AN), the obtained distances for different physical effects and consequences increase significantly, dependent 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 medium 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 medium quantity of 300 t, the overpressure level used in land-use planning (20, 30 and 50 mbar) in the three methodologies does not affect the residential areas, only the industrial ones. If an explosion involving a larger quantity then the residential areas will be affected.

Taking into account the risk estimated in the qualitative and 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 storage facility's vicinity. 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.

In land-use planning, the 20 mbar level is recommended, as being the overpressure at which windows break. The use of all safety measures listed within this paper is recommended in order to prevent technological accidents in case of ammonium nitrate storing and handling.

Another important aspect to consider in risk assessment studies is the domino effect.

The domino effect in the Feyzin accident was mainly caused by two major errors: 1. the fault design of the LPG storage facility: small distances between spheres; small distance to the highway; lack of fixed equipments, used in fire fighting; inadequate and defect safety valves; and 2. human errors: sampling mistakes; lack of coordination between intervention teams; the T61-443 sphere stopped cooling when the safety valve opened. All these errors contributed to the technological safety development at LPG storage facilities.

In an ammonium nitrate storage facility, a fire can generate domino effects, leading to the explosion of the entire stored AN quantity.

The use of the following limits is recommended for calculating the distances at which domino effects can occur:

- 12.5 kW/m^2 heat radiation in case of stationary heat radiations;

- 100 mbar overpressure in case of explosion – it corresponds to severe damages to buildings;
- 300 mbar overpressure in case of explosion – it corresponds to severe damages to process installations;
- 400 m distance in case of air-born missiles.

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 problem's complexity; the used models validity; and the availability of the software.

The results obtained for the chlorine dispersion using the SEVEX View and SLAB View software are different as to the surface of the affected areas.

Analyzing the results obtained using the two programs it can be observed that in the case of the results obtained using the SLAB model, the areas with concentrations higher than LC50 are smaller, and the areas with concentrations between LC50-IDLH and IDLH-ERPG2 are over-estimated. The use of the SLAB results in an emergency plan means the under-estimation of the most dangerous area (where lethal concentrations occur) and over-estimation of the intoxications areas.

The results obtained using the SEVEX View software are more realistic than those obtained with SLBA View, as it consider two major elements: the topography and land-use, both having a significant influence on gas dispersion phenomena.

The resolution of the 1 km^2 evaluation grid of the SEVEX View software, regarding the terrain topography and land-use, is considered to be sufficient for its use in risk studies for off-site chemical emergency planning and for land-use planning in Seveso sites.

There is a future perspective that the software will be improved, to use a better resolution for topography and land-use. The improvement of the computer systems reduces the calculation time, compensating for the higher complexity.

This paper contributes to developing new future perspectives, namely the combination of the SEVEX model with the calculation model for individual and social risk. The elaboration of individual risk curves, depending on topography and land-use, would have a major advantage in case of complex areas (mountains, coast, urban and mixed areas) where gas dispersion is significantly influenced by the terrain's complex topography, land-use and specific meteorological phenomena.

The use of the risk assessment methodology for land-use planning and emergency planning facilitates the assessors and competent authorities' expertise, 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.

9.1. Original contributions

Based on the researches in this paper, the following original contributions can be listed:

- synthesis of risk assessment literature and description of examples for the case studies in the theoretical part of the paper;
- elaboration of a literature synthesis regarding the land-use planning methodologies in the context of the Seveso Directives;
- identification of hazards and risk associated to propane storage facilities;
- comparative analysis of the models used in BLEVE simulations;
- estimation of the propane quantities spilled in the Feyzin accident;
- assessment of effects and consequences in the technologic accident with BLEVE at propane storing;

- comparative analysis of the limits established within the land-use planning methodologies (French, Italian and Austrian) by performing BLEVE simulations and comparison of distances obtained using different models: static, dynamic and tank failure;
- identification of hazards and risks associated to chlorine storehouses;
- comparative analysis of models used in heavy gases dispersion simulation;
- qualitative and quantitative assessment of risks associated to chlorine storehouses;
- comparative analysis of the limits established within the land-use planning methodologies (French, Italian and Austrian) using dispersion simulations and comparison of surfaces using SEVEX and SLAB models;
- elaboration of consequence maps for several weather situations, considering several accident scenarios for a chlorine release in Turda;
- identification of hazards and risks associated to ammonium nitrate storage facilities;
- estimation of ammonium nitrate instability risk;
- qualitative and quantitative assessment of risks associated to ammonium nitrate storage facilities;
- calculation of distances for shock wave effects on objectives and personnel (according to Annex 3b of the Technical Standards approved by HG 536/2002) for several accidents involving ammonium nitrate explosion;
- comparative analysis of limits established within the land-use planning methodologies (French, Italian, Austrian) by performing explosion simulations and comparison of distances obtained for different ammonium nitrate quantities;
- comparative analysis of land-use planning methodologies and establishment of limits for developing a new methodology;
- proposal of a risk assessment methodology for calculating safety distances used in land-use planning.