



### BABES – BOLYAI UNIVERSITY FACULTY OF ENVIRONMENTAL SCIENCE AND ENGINEERING

DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCE

### CONTRIBUTIONS REGARDING THE TECHNOLOGICAL RISK ASSESSMENT ON SEVESO SITES WITH A PRODUCTION AND STORAGE PROFILE OF AMMONIUM NITRATE FERTILIZER IN THE CONTEXT OF TERRITORIAL PLANNING

SUMMARY OF PHD THESIS

Coordinating teacher, Prof. Univ. dr. eng. OZUNU Alexander

> Phd student Eng. SABĂU (Leordean) Olimpia Ramona

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### CONTRIBUTIONS ON TECHNOLOGICAL RISK ASSESSMENT ON SEVESO PRODUCTION AND STORAGE SITES AMMONIUM NITRATE FERTILIZER IN THE CONTEXT OF TERRITORIAL PLANNING

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Keywords

major accidents, qualitative risk analysis, ammonium nitrate, chemical fertilizers, explosions, dangerous substances, technological risk, risk perception, territorial planning, preventive maintenance, predictive maintenance

The abstract contains part of the thesis results, general conclusions and selective bibliography, pagination for the table of contents, as well as the numbering of chapters, subchapters, figures, tables and mathematical relationships, being the same as those in the thesis for easier identification.

#### **1 INTRODUCTION**

#### 1.1 Thesis summary

It is known that the development of process industries in recent decades has caused chemical and technological incidents and accidents to increase. In order to gain new knowledge, studies show more and more often that the "learning by doing" technique is a very effective one. Unfortunately, this requires, among other things, learning from the mistakes or unfortunate happenings of others in order to prevent or reduce potential unwanted effects or resulting from the occurrence of a risk, be it in the form of an incident or an accident (*Eckhoff, 2005*). The growing interest in improving operational safety actions regarding the storage, transport and handling of hazardous substances, such as ammonium nitrate, stemmed from a series of catastrophic events that occurred around the world.

Ammonium nitrate has been involved in recent years in a lot of well-known and publicized accidents and disasters, such as the one in Toulouse (France) in 2001, Mihăileşti, in Buzau County, Romania, on May 24, 2004, Texas City, on April 16, 1947, and most recently, the accident in Beirut in 2020. All these are described in more detail in subchapter 2.4.2 Brief history – major accidents.

Of course, in order to outline a clearer idea around this topic, itwas taken into account to describe in a special chapter dedicated to this purpose, the legislative and methodological context regarding the management of dangerous chemical substances and preparations existing in fertilizer factories. Thus, inChapter 3 of this paper, there is a synthesis of extensive literature, which brings together all regulatory acts on dangerous chemical substances and preparations, specifically fertilizers and ammonium nitrate. Also in this chapter, the main Seveso sites with a production / storage profile of ammonium nitrate fertilizer in Romania and their proximity to vulnerable areas were identified.

In accordance with the objectives set and treated in thefollowing chapters, significant steps have been taken in creating a general framework for treating the technological risks existing in fertilizer factories at conceptual level, by defining key terms in this context (e.g. hazard, risk, vulnerability, major accident, risk analysis, etc.). Specifically, within C of Epitole 4, the risk of explosion of ammonium nitrate during the production/storage process is analysed comparatively, by applying two different methods of analysis, from the point of view of the compatibility of these sites (Seveso) on which these processes take place, with vulnerable activities carried out in close proximity, topic for which it was considered appropriate to write an article in this regard, approved for publication *Comparative study on land-use planning methodologies based on physical effects, consequence and risk analysis for ammonium nitrate fertilizer production facilities (Torok et al., 2023).* 

In this context, it should be noted that continuous analysis and the growing interest of authorities and legislators in relation to accidents and disasters are essential in raising awareness and learning lessons for process safety, especially in generating programs to prevent them. This is visible in Capitol 5 of this thesis, in which practically with the help of preliminary hazard analysis one of the key equipment involved in the production process and specifically, granulation, of ammonium nitrate fertilizer is subjected to analysis. As a result of the PHA analysis, the main causes that can lead to malfunctions in the installation, respectively that can affect the process, generating major material consequences, on the environment and on the safety of the population, were identified.Preventive and predictive maintenance measures will therefore be proposed to avoid and properly manage such risks in the future.

Chapter 6 proposed future research directions on technology risk assessment in the context of territorial planning.

#### **1.2** Motivation for choosing the theme

The topic chosen to be treated in the doctoral thesis represents a particularity in the direction initially established, due to the fact that chemical fertilizers are mostly dangerous substances, classified as such by numerous legislative acts, both nationally and internationally. In order to choose the theme, it was taken into account the prior identification of aspects that can lead to the conclusion that the process of manufacturing chemical fertilizers is a really dangerous one.

As a result of numerous accidents involving chemical fertilisers, especially ammonium nitrate, which have occurred throughout the world, the conditions for the production, use, handling, storage and transport of ammonium nitrate have become increasingly stringent and clearly regulated in numerous pieces of legislation.

#### 1.3 Purpose

Undoubtedly, one of the most important goals envisaged in the work was to increase the safety of the population, industrial and process, through the objectives clearly established and pursued during the development of the work.

The protection of the environment andtheir future developments were also some of the most impactful aims of this work, in the context in which SEVESO sites at risk of major accidents should exist and operate only to the extent that they verifyand confirm compatibility with spatial planning. Thus, another purpose defined in this workwas to identify appropriate measures to prevent and reduce risks in the production and storage process of ammonium nitrate fertilizer, in order to streamline the response to emergency situations, in the context of territorial planning.

#### **1.4 Objectives**

The **major** objective of this work was to make significant contributions to increasing the safety of the population and industry by improving the Territorial Planning methodology for Seveso sites with ammonium nitrate production / storage profile in Romania.

More specifically, through this paper, the aim was to point out the most important aspects regarding the shortcomings of the methodology applicable at national level regarding territorial planning and to propose suggestions for improving this methodology, in order to properly manage accidents with explosions involving ammonium nitrate fertilizer in Romania.

In this respect, one of the main objectives of this paper was to qualitatively assess the technological risks present on the above-mentioned sites, with the help of preliminary risk analysis – PHA, the identification of risks being carried out depending on the degree of hazardousness of the substances and raw / auxiliary materials used in the process, as well as taking into account the hazard character of installations / equipment handling substances and those materials. Thus, through the PHA-type analysis, those events that may occur when essential aspects related to the physico-chemical characteristics of dangerous substances / preparations involved in the production / storage process of fertilizers, specifically ammonium nitrate, will be identified, treated and inventoried. The scenarios for possible explosions involving ammonium nitrate were then analysed in a separate chapter, in terms of physical effects/consequences, in the context of compatibility with existing territorial planning at national level.

In this context, another important objective pursued in this paper is to increase industrial safety by establishing appropriate preventive and predictive maintenance measures, in the case of Seveso sites with ammonium nitrate fertilizer production / storage profile, measures that will generate by themselves increased safety and health of the population and the environment.

### 2 THEORETICAL CONSIDERATIONS REGARDING THE QUALITATIVE ASSESSMENT OF TECHNOLOGICAL RISKS IN AMMONIUM NITRATE – FERTILIZER PLANTS

#### 2.1Technological hazards - concept, definitions, prioritization

#### 2.1.1 Concept

The three main components of hazard form what is known in system safety as the hazard triangle, and if any part of the hazard triangle is eliminated by design techniques, the hazard and associated risk are also eliminated (*A. Ericson II, 2015*).

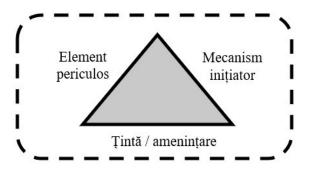


Fig. 1 Triangle of Chance (adapted from A. Ericson II, 2015)

Currently, the concept of hazard does not have a unitary meaning. In most available concepts, highlighting the essential attributes of hazards is omitted. So the concept is an unclear one, often confused with accident potential, accident-causing factor, etc., when literally chance is a source of danger. However, the safety of systems takes hazards into account as a precondition for an accident to occur (*Yuebing et al., 2011*).

#### 2.1.2 Definitions

Hazard can be defined, according to UNISDR, as a process, phenomenon or human activity that can cause effects on health, as well as injuries or even deaths, material losses, with social and economic implications or damage to the environment (*UNISDR, 2009*).

According to Baldea (2007), a very important aspect regarding hazards is the perception of their nature and evolution. Thus, hazards are perceived as an integral part of our lives, being often influenced by factors related to education, personal and professional experience, social and political context, etc.

Technology hazards address the potential threat that a technology, or its products, will produce harmful effects on people, nature, capital or man-made facilities. In public perception, the two terms, hazard and risk, are often interchangeable, which creates real challenges in the field of their communication (*Scheer et al., 2010*).

#### 2.1.3 Prioritising technological hazards

The correct identification of hazards is one of the major tasks of system safety and requires, among other things, hazard recognition. In order to prioritize hazards as accurately as possible, checklists are often drawn up, which can be satisfactory and sufficient when we talk about an old technology, with few innovations and previously encountered hazards, but which are certainly insufficient when we talk about new technologies and designs. Precisely for this reason, methods of qualitative analysis of hazards have appeared, which help to prioritize them as realistically as possible (*Kletz, 1999*).

Thus, within the thesis were the hierarchy of hazards related to the production and storage process of ammonium nitrate fertilizer and were evaluated from a quantitative point of view, the hazards responsible for a potential major impact on society, in terms of infrastructure, economy, health and environment. The prioritization was carried out taking into account several aspects, correlated or taken independently of each other, such as the cause or triggering event, the context in which the event occurred and / or the resulting consequences.

# 2.2. Technological risks on Seveso sites with ammonium nitrate fertilizer production and storage profile – concept, definitions, risk assessment and management

#### 2.2.1 Concept

Basically, in any decision made vis-à-vis a new technology or an existing one, it involves an acceptable level of risk, which involves a balance between potential risks and benefits associated with the technology itself. Risk, as a concept, from a technical point of view, focuses around the probability of events occurring, respectively the magnitude of any specific consequences.

Risk is often defined, mathematically, by multiplying variable ones, assuming that society should be indifferent to a risk with low consequences and high probability of occurrence on the one hand and a risk with high consequences and low probability on the other (*Kasperson et al., 1988*).

#### 2.2.2 Definitions

According to the SEVESO III Directive, 'risk' is 'the probability that a specific effect will occur within a certain period or under certain circumstances'.

The term "risk" has a number of definitions, which of course differ from each other, depending on the meaning. For example, risk is the probability that the existing hazard will turn into an incident/accident. Risk in the chemical industry is defined as probable annual production losses or human accidents as a result of unforeseen technical events.

If hazard considers only the trigger for risk and focuses on its potential to cause damage, risk also takes into account the probability of exposure and its impact (*Scheer et al. b., 2010*).

## 2.2.3 Risk assessment and management on Seveso sites with ammonium nitrate fertilizer production and storage profile

More and more often, concerns about technological risks have grown. In this context, risk assessment has become a genuine industry, involving a complex and controversial process of assessing technological hazards, communicating information on potential risks and developing appropriate control measures (*Nelkin*, 1989).

Risk assessment and risk management, as areas of research, are relatively recent, appearing 30-40 years ago. Throughout this period, numerous scientific journals in the field, papers, conferences have made their presence felt, all of which try to cover the fundamental ideas and principles best suited to proper risk assessment and management (*Aven, 2016*).

### 2.2.4 Risk perception of Seveso sites with ammonium nitrate fertiliser production and storage profile

A look at the perception of rare random events shows that human beings are more comfortable with threats they can foresee and plan for, rather than threats that could materialize at any time, no matter how unlikely that may be *(Ozunu etal., 2008)*.

According to Slovic (1987), perceived risk is multidimensional, caused by triggers varying depending on the person and context. Risks are always created or exist within social systems. Therefore, it is important to take into account the social context in which risks arise and, above all, the fact that people do not share the same perceptions of risks and their generating causes (*Aven, 2012*).

Of course, it is important to note that sometimes the perception of risk is different depending on the stakeholders who take part in its assessment. In the context of this paper, we can mentionenvironmental specialists or experts, certification and regulatory bodies / public

authorities, mass-media, as well as industry and economic operators carrying out activities in the immediate vicinity, the role of stakeholders being that of building a solid basis in the decisionmaking process of risk management, in terms of its assessment and communication.

### 2.2.5 Classification of major accident hazards by Seveso sites with ammonium nitrate fertiliser production and storage profile

Risk classification is that stage of the risk management process, in which all identified risks are evaluated either quantitatively or qualitatively, depending on the probability of occurrence and the possible consequences produced.

On the other hand, another classification proposed in the literature is that of *dynamic* risks and *static risks*. Dynamic risks are those involved in the possibility of dynamic change. They are basically the result of changes in economic conditions, such as price levels, consumer tastes and preferences, and technology. They are those risks that the whole society may encounter over time.

In other words, static risks involve losses that would occur even if there were no change in the economy, including the risks of accidents, fires or natural disasters. These losses are also caused by irregular actions or human error.

### 2.3 The concept of vulnerability in the context of territorial planning for Seveso sites with ammonium nitrate fertilizer production and storage profile

Vulnerability can be defined as the potential of an individual (individual or part of a group) to manage an event with a dangerous impact. Vulnerability involves a combination of factors that basically determine the level of danger to health, life and property. Quantitatively, vulnability can be expressed as a percentage, 0 % - 100 %. Vulnerability depends on both infrastructure and socio-economic conditions of the area.

As Marin Bîldea points out in his paper (2007), vulnerability is defined by losses incurred at individual or group level, as a result of their exposure to a certain risk. In the same paper, Marin Bîldea describes that certain people/groups are more vulnerable than others, depending on several factors, such as age, experience, different socio-economic conditions, etc. Specifically, each new technology seems to generate new vulnerabilities for its users, vulnerability to accidents, diseases, environmental degradation or social disruption. The usual approach in this case is done through the concept of risk, which deals with the chance that the adverse effects specified above may occur due to malfunction or failure of the respective technology (*Martin*, 1996).

#### 2.4 Major accidents involving dangerous substances on Seveso sites

#### 2.4.1 Concept. Definitions

The complexity of industrial sites, the type and characteristics, variety of substances and preparations used, stored, handled and produced within sites within given technological processes undoubtedly make it necessary to adopt and use risk assessment and management methods that are as realistic as possible.

As regards "major accident", it is defined in the Seveso III Directive and transposed into national law by Law nr. 59/2016, as a result of an action that evolves uncontrollably, generating a fire, explosion or significant pollution of one or more environmental factors due to accidental emissions, generating negative consequences for humans or the environment and involving dangerous chemical substances or preparations.

Regarding spatial planning, the Seveso III Directive and implicitly Law nr. 59/2016, draws some guidelines, so that the approach of having spatial planning as a legislative requirement at national level, comes as a reasonable and necessary requirement, since most industrial installations are capable of causing major accidents in certain circumstances, with far-reaching consequences beyond borders and can cause significant damage to man and the environment.

One of the most pressing problems related to LUPs is the "domino effect", in which there is the problem of interaction between neighboring process units, which is largely related to the severity of the risk of major hazards present in those units, which can be avoided and adequately managed by positioning and planning the use of territory in their vicinity, in an appropriate way. In general, the aim and objective of LUPs in the vicinity of hazardous installations is to ensure that the consequences of potential accidents are taken into account when deciding on the siting of new installations (*Török et al., 2010*).

#### 2.4.3 Brief history – major accidents involving dangerous substances

Process safety, as well as storage and transport of dangerous chemical substances/preparations has become a topic of great importance in recent decades. The increased interest in improving safety actions regarding the storage, transport and handling of hazardous substances stemmed from numerous incidents / accidents that occurred around the world, ammonium nitrate being involved in many of them (*Kirchsteiger, 1999*), some of the most significant of which are presented chronologically in this distinct subchapter of the thesis,

among which we mention the following: Oppau, Germany (1921), Texas City, USA (1947), Toulouse, France (2001), Mihăilești, Buzău, Romania (2004), Beirut, Lebanon (2020), Ryongchon, North Korea (2004).

#### 2.5 Riskassessment of major accidents involving dangerous substances

#### 2.5.1 General description

Risk analysis is an estimation of risk, either qualitatively or quantitatively, based on different methods that take into account the frequency and potential consequences to be produced, in order to quantify them and subsequently establish appropriate prevention and reduction measures (*Török et al., 2011*).

In the context of territorial planning, it should be noted that damage and damage arising from the materialization of the risk will not in itself generate a disaster unless the return to the baseline state or to a state close to normal is achieved within a reasonable period of time (*Blaikie et al., 1994; Etkin et al., 2012*).

In this respect, a risk assessment based on the identification and chronological quantification of the data that led to its production is necessary for planning and adopting appropriate response strategies (*Scrădeanu*, 2014).

## 2.5.2 Qualitative risk analyses applicable to Seveso sites with ammonium nitrate production and storage profile fertilizer

In this subchapter were described enumeratively, but not limitatively, the most used methods of assessing technological risk in particular. Among them, we mention: PHL (Preliminary Hazard List), PHA (Preliminary Hazard Analysis), HAZOP (Hazard and Operability Studies), FMEA (Failure Mode and Effects Analysis), WHAT IF ANALYSIS.

Specifically for assessing the explosion risk of ammonium nitrate fertilizer on Seveso production and storage sites, the PHA analysis method was used to assess hazards from a qualitative point of view, and then they were subjected to quantitative analysis methods, in the context of territorial planning. PHA analysis is often used to identify hazards and potential associated triggers from the early stages of a project, in order to prepare in advance a security plan with risk prevention and reduction measures (*Török et al., 2011*). Regarding the steps to be taken in this method of analysis, the first step was to identify all potential hazards within the installation/system under assessment. Subsequently, each hazard was assigned a score on 5 levels, from 1 to 5 for the probability of occurrence, respectively for the consequences generated

(according to a risk matrix), following that based on the equation  $R = P \times G$ , each risk identified and subjected to analysis, having calculated a score with which it was classified in a certain level of risk, Level which practically indicates the size of riski, with related prevention and mitigation actions.

All these aspects are detailed and concretely exemplified, under chapter 4.2.1.1 Preliminary hazard analysis (PHA) for the production / storage process of ammonium nitrate fertilizer, chapter in which the risks of explosion are practically analyzed on a Seveso site of higher level in Romania, with ammonium nitrate production and storage profile. This analysis forms the basis for the subsequent explosion risk assessment involving an fertiliser in terms of physical effects (overpressure) produced, using quantitative risk calculation methods, all in the context of spatial planning.

### 2.5.3 Quantitative risk analyses applicable to Seveso sites with ammonium nitrate production and storage profile fertilizer

A. Fault Tree Analysis (FTA)\_Arborele Mistakes (AG)

The "Mistake Tree" is a technique for analyzing a system, often used to determine the causes of possible unwanted events at the root and the probability that they will occur. The method is required in evaluating systems with a more complex dynamic, in order to understand and prevent potential problems as early as possible.

#### B. Event Tree Analysis (ETA)\_Arborele Events (AE)

Event tree analysis is an analysis technique used to identify and evaluate a sequence of events in a potential accident scenario after an initiating event occurs. The purpose of the AE is to evaluate all possible outcomes that may result from an initiating event and provides a probabilistic assessment of the risk associated with each potential outcome.

#### C. Root Cause Analysis (RCA)\_Analiza Root Causes

Root cause analysis is a process designed to be used in investigating and classifying root causes of occurrences concerning safety, health, environment, quality, reliability and production impact. Simply put, it is a tool designed to help identify not only "what happened" and "how the event happened," but most importantly "why it happened." Identifying underlying causes is key to preventing similar relapses.

The best-known diagram applied in root cause analysis is the cause and effect diagram, a tool that highlights the relationship between a quality characteristic (effect) and possible sources of variation (causes).

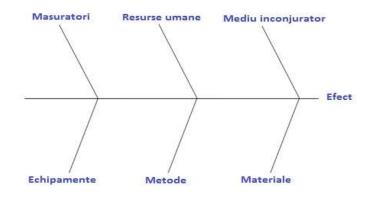


Fig. 7 Cause-effect diagram / Ishikawa

### 3 KNOWLEDGE IN THE FIELD AT NATIONAL AND INTERNATIONAL LEVEL REGARDING TERRITORIAL PLANNING IN THE CASE OF SEVESO SITES WITH AMMONIUM NITRATE PRODUCTION / STORAGE PROFILE FERTILIZER

#### **3.1 Chemical fertilizers**

#### 3.1.1 General

According to *BASF Agricultural Solutions Romania, for proper plant development, plants* need nutrients that they get from the soil. Just as humans need minerals and nutrients essential for strong and healthy growth, so do crops around the world. Fertilizers replace nutrients that crops remove from the soil. Without the addition of fertilisers, crop yields and agricultural productivity would be significantly reduced.

Fertilizers contain variable proportions of major essential plant elements (N, P, K, etc.) and minor (Zn, Mn, Fe, etc.), as well as impurities and other non-essential elements (*Chandini et al.*, 2019).



Fig. 8 Representation of the process soil mineralization, with the help of fertilizers (Source: fertilizerseurope.com, 2021, accessed on 06.06.2021)

Given the increasing global demand for food, this land could be used efficiently and much more intensively to support local food needs. Agricultural policy at European Union level promotes the decisive role to be played in ensuring that the agricultural sector is strong and diversified. European farmers must be encouraged to optimise production, but also to reduce their environmental impact.

#### 1.1.2 Fertilizer classification

Although farmers sometimes choose certain types of fertilizers over others, in reality organic fertilizers will certainly have greater advantages in the medium and long term. Of course, each category of fertilizers comes with a number of disadvantages, all these aspects being necessary to be balanced when choosing a certain type of fertilizer, before application.

# 3.1.3 Hazardous properties of chemical fertilisers — specific ammonium nitrate for explosiveness

The manufacture of chemical fertilizers is characterized by the presence of large amounts of hazardous substances, both as raw materials (methane gas) and as intermediates (ammonia, nitrogen dioxide) or finished products (ammonium nitrate). In turn, chemical fertilizers are classified as follows:

#### A. NITROGEN FERTILISERS

Nitrate fertilizers are the most widely used simple fertilizers, especially fertilizers such as ammonium nitrate (AN) and calcium ammonium nitrate (CAN), suitable for most soils and climatic conditions.

#### A.1 Ammonium nitrate\_AN

Ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), an inorganic, oxidising and irritant substance for eyes, mono-constituent, to which the provisions relating to the marketing and use of explosives precursors, as regulated by Regulation No 1148 of 20 June 2019 on the marketing and use of explosives precursors, amending Regulation (EC) no. Regulation (EU) No 1907/2006 and repealing Regulation (EU) No 1907/2006 98/2013. It is also a hazardous substance in storage and transport, regardless of the means of transport used, with clear specific requirements to be complied with, in accordance with the provisions of ADR, RID and IMDG.

Ammonium nitrate fertilizer is not a combustible substance, however, and can maintain combustion even in the absence of air. At temperatures above 170 °C it melts, undergoing a slow decomposition process into ammonia and nitric acid, and at temperatures above 200 °C it decomposes rapidly, requiring immediate intervention measures. In case of contact with incompatible materials, the decomposition reaction of AN can turn into an explosion at any time.

From a physico-chemical point of view, AN has a very complex behavior, which is why among its main characteristics, the following should be mentioned:

- instability during decomposition, with the formation of toxic gases;

- source of generating a fire, due to strong oxidizing property;
- source of explosion.

Of course, the hazards mentioned above are often influenced by the presence of specific parameters, such as: contamination, porosity and particle density (*Török et al., 2016*). Pure AN begins decomposition only after heating to a certain temperature, releasing toxic substances, gases such as nitrogen oxides and ammonia. If the heat source is removed and the space is properly ventilated, the decomposition process stops.

During decomposition, several chemical reactions may occur, the most important of which would be:

- between the temperature range 170 and 250 °C:

NH<sub>4</sub> NO  $_3 \rightarrow$  NO 2 + 2H<sub>2</sub>O + 37 kJ/mol;

- between the temperature range 250 and 292 °C:

NH<sub>4</sub>NO 3 NH $\rightarrow$ <sub>3</sub>+ HNO<sub>3</sub> - 174 kJ/mol;

- at higher temperatures:

NH<sub>4</sub> NO 3 + 2NO 2 N 2 + 2HNO<sub>3</sub> + → H <sub>2</sub>O + 232 kJ/mol; 2NH<sub>4</sub>NO<sub>3</sub>→ 2N2 +4H 2 O + O<sub>2</sub> + 118 kJ/mol. 3.1.4 Identification and inventory of the main SEVESO sites with production / storage profile of ammonium nitrate fertilizer in Romania and Europe and their proximity to vulnerable areas

In this subchapter, the identification and description of the main SEVESO sites with production / storage profile of ammonium nitrate fertilizer in Romania was considered, in terms of proximity and proximity to buildings and economic operators.

Their identification was made on the basis of the *Inventory of sites covered by Law* 59/2016 of 11 April 2016 on the control of major-accident hazards involving dangerous substances (SEVESO) on 31 December 2022, published on the ANPM website and made available to the interested public, section Risk Management –SEVESO (ANPM, 2022). As will be seen below, the vast majority of SEVESO sites with ammonium nitrate fertilizer storage profile are found in the South of the country (Agrii Romania, Azochim, Borealis LAT Romania with several higher level locations in the Center (Targu – Mures: Azomures SA and Dafcochim SRL) and West (Archim Fertil SRL Arad), the only location with a production profile being Azomures SA (Targu – Mures).

Therefore, SEVESO top-level locations were written punctually, due to the increased interest in their location / positioning in relation to neighbors / neighboring activities. The review and inventory, in other words of the locations below, was made precisely to reinforce the idea of the need to increase the safety of the population, industrial and process, which is also one of the main goals considered in the work.

The protection of the environment and future developments will be adequately ensured only to the extent that SEVESO sites involving major-accident hazards (in this paper we are talking about sites with ammonium nitrate fertilizer production/storage activities) will be built in the context of appropriate territorial planning. This chapter was conceived and conceived precisely as a support chapter for achieving the major objective of this work, namely that of bringing significant contributions to increasing the safety of the population and industry by improving the Territorial Planning methodology in the case of Seveso sites with ammonium nitrate fertilizer production / storage profile in Romania.

#### **3.2 Literature summary**

# 3.2.1 Knowledge in the field at national level regarding dangerous chemical substances and preparations – specifically fertilizers – legislative and methodological context

One of the most important pieces of legislation regarding environmental protection in general and specifically regarding chemical fertilizers is Emergency Ordinance nr. Regulation (EC) No 195/2005 on Environmental Protection which, inter alia, in Article 34, provides that 'chemical fertilisers and plant protection products shall be subject to a special regulatory regime established by specific chemicals legislation'.

Another important normative act in the context of the thesis is Government Decision no. 557/2016 on the management of risk types that regulates at national level what is the management of different types of risk.

At EU level and subsequently transposed at national level, different risk assessment methodologies have been developed transposed into national legislation in order to improve risk response capacity by putting in place measures to prevent, prepare for and mitigate major-accident risks. The Unitary Risk Assessment Methodology was practically the first attempt of the Romanian state to align with the requirements of the European Commission and to promote a unitary approach for sectoral risk assessment (*European Commission, 2010* 

Another applicable legislative act in the field of production, handling, storage of chemical fertilizers (for hazardous ones) is Law nr. 360/2003 on the regime of dangerous chemical substances and preparations. The object of this law is to establish a general framework regarding the control and monitoring of the regime of dangerous chemical substances and preparations, in order to ensure the health of the population and the environment. According to Article 7, certain dangerous chemical substances and preparations are restricted from placing on the market and using in order to ensure the protection of the environment and human health. Also in order to protect the environment and the health of the population, at national level there is a special restrictive regime for those dangerous chemical substances and preparations prohibited in production and use, when imported or exported by Romania.

At European level, some of the most important regulatory acts are undoubtedly the CLP and REACH Regulations, which were also the basis for identifying the physico-chemical characteristics of ammonium nitrate. Over the years, ammonium nitrate fertilizers have been involved in several accidents that have influenced transport, storage and handling legislation. Europe adapted the European version of the GHS and issued Regulation 1272/2008 (CLP) on classification, labelling and packaging of chemical substances and mixtures. The regulation

introduces an EU-wide classification and labelling system for chemicals, building on a UN Global System (GHS), all with a view to enhancing the protection of human health and the environment during activities on the handling, transport and use of hazardous substances.

Regarding the best practice guides for the safe storage and use of fertilizers on farms, prepared and developed by IGSU (2021) in collaboration with Azomures SA, the largest producer of chemical fertilizers in Romania , measures and practices are proposed regarding the storage and use of fertilizers, for the proper management of fertilizers on farms , and not only. Thus, it is important to consider the following:

- Ensuring the health of personnel involved in fertilizer handling;
- ➢ Good practices for fertilizer storage both indoors and outdoors;
- Ensuring storage security of fertilizers;
- Reducing as much as possible the environmental impact during storage, use and handling;
- Making safety data sheets available to persons directly involved in handling, storage and transport activities;
- Training of personnel involved in the management of the above-mentioned activities, in order to know the physico-chemical characteristics of fertilizers and the potential risks associated with them.

These practices regarding the proper management of fertilizers during storage and related activities are important primarily from the point of view of creating a safe working environment for the personnel directly involved, but also for growth to ensure a safe workplace, as well as to maintain products in optimal quality parameters, thus avoiding risks of degradation.

Another standard considered in this paper isInternational Standard 31000:2009, Risk Management – Principles and Guidelines, updated in 2018, which also underlies many organizations in various fields of activity, regardless of their size, by drawing clear and effective guidelines regarding risk management of any kind.

The standard sets out some basic elements in terms of building a robust risk management system at the level of an organization/activity:

- communication and consultation;
- defining the context;
- risk estimation (composed of hazard identification, risk analysis and assessment);
- risk treatment;
- monitoring and review.

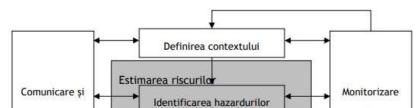


Fig. 17 Representation of the basic elements of a management system

# 3.2.4 Knowledge in the field at national and international level regarding the territorial planning of major accident risk objectives involving the production and storage of fertilizer nitrate – legislative and methodological context

Directive 2012/18/EU, known as the Seveso III Directive, appeared at EU level from the desire to create a unitary regulatory and management framework for everything that means production, storage, transport, use or discharge of dangerous substances, in order to align with the new applicable legislative provisions (*Török et al., 2011*).

Seveso directives were developed as a result of major accidents, with catastrophic effects on humans and the environment, among which the following should be mentioned: Flixborough, Germany (1974) - explosion (Lees, 2012), Seveso, Italy (1976) - dioxin emission (Lees, 2012), Bhopal, India (1984) - methylisocyanate emission (Lees, 2012, *Chouhan, 2004*), Dakar, Senegal (1992) – liquid ammonia emission (UNEP, 2016), Baia Mare, Romania (2000) – cyanide spill (UNEP, 2016), Toulouse, France (2001) – explosion (*Lees, 2012*), etc. These accidents have been the basis of numerous regulations in the field, in order to prevent and manage chemical processes as adequately as possible, in order to avoid technological disasters.

The object and scope of the Seveso III Directive concerns the establishment of specific measures to prevent major accidents involving dangerous substances, but also in order to generate an increased level of protection, by reducing the consequences of these accidents on human health and the environment.

In the context of the production and storage of chemical fertilizers, aspects dealt with in this paper, it is also necessary to remember Article 11. It refers to the fact that any changes occurring on SEVESO sites / installations and which could produce considerable negative effects through the major accidents they could generate, must be notified to the competent authorities, before such change takes place, in order to draw up / update the defining documents of the safety management system implemented at site level.

One of the most addressed aspects of the Seveso legislation is undoubtedly that of spatial planning, because in this case the situation is much more complex as regards its transposition by Member States into national law, as there is no clearly defined link between Seveso and town planning regulations. However, existing guidelines for territorial planning at both EU and national level indicate that scenarios with the worst consequences but at the same time credible should be considered for territorial planning, i.e. with a certain degree of probability of occurrence, with planning areas resulting in this way generally being smaller than emergency planning areas.

Law nr. 59.2016 represents a transposition into national law, of Directive 2012/18/EU of the European Parliament and of the Council of 4 July 2012 on the control of major-accident hazards involving dangerous substances.

Regarding territorial planning, Law nr. 59/2016, treats it as dependent on what technological progress means, so it can also be regarded as an unplanned spontaneous component of territorial planning, but most often as a time- and space-oriented component.

According to Iațu (2015), spatial planning is a set of actions and interventions meant to provide, over time, a clear and fair distribution of the population and economic and industrial activities in a given territory (*Iațu, 2015*).

When constructing new sites, making modifications to existing sites, constructing new facilities close to sites whose activity presents a potential major-accident hazard, the operator must take care to respect appropriate distances from them, being considered sources of risk. The determination of these distances is made according to the methodology established at national level and approved by Order no. 3710/2017 on the approval of the Methodology for establishing appropriate distances from potential sources of risk within locations falling under the provisions of Law no. 59/2016 on the control of major-accident hazards involving dangerous substances in town and country planning activities, which, moreover, only give guidelines as regards town and country plans.

In the alternative, the methodology takes into account the establishment and maintenance of appropriate distances taken over in the spatial planning and planning plans, between different areas, constructions (existing or future) and sources of risk established in the context of the provisions of Law no. 59/2016.

In order to achieve the aforementioned objectives, the Methodology proposes to go through the following steps, as follows:

*a)* First of all, it is necessary to determine and graphically represent the impact areas in the immediate vicinity of SEVESO sites

b) The next step is to identify the territorial vulnerability in the previously determined areas

For this stage, the Methodology proposes 4 impact areas, depending on the specific effects felt by the population in case of a major accident, as follows:

- high mortality;
- mortality threshold;
- irreversible damage;
- reversible harm to the affected population.

*c) After determining the impact zones, territorial compatibility shall be established in those areas* 

At this stage, it is necessary to identify those major-accident scenarios likely to have significant effects on human health and/or the environment, based on the risk analysis previously carried out.

*d) After determining the appropriate distances, they will be taken over in the spatial and urban planning plans for the areas in the vicinity of the site.* 

Basically, the methodology regulated at national level by Order 3710/2017 does not propose any methods, techniques, databases to be taken into account, which is why, for a more realistic territorial planning, it is necessary to apply the indications from the methodology proposed at national level, in parallel with a quantitative risk-based (hybrid) risk analysis approach developed on the basis of existing and applicable literature.*see next point in Chapter 3, Subchapter 3.2.4, point D*).

Yellow Book (Van den Bosch and Weterings, 2005), Green Book (Instituut voor Milieu -TNO, 1992) and Purple Book (Uijt de Haag, Ale & Post, 2001) are the basic books in carrying out modelling of major accidents at international level, in order to determine the physical effects on the population and structures and their associated consequences, in case of accidents involving dangerous substances.

In order to achieve a very important objective of this paper, in the following I will carry out modeling of the scenarios regarding the explosion of ammonium nitrate present on one of the most important SEVESO top-level sites in Romania (Azomures SA), modeling based on the methodology adopted at national level, respectively used internationally, in order to propose an appropriate methodology, taking into account as many relevant factors as possible. To this end, the Purple Book proposes some clear guidelines on risk determination by means of quantitative risk analyses, both for stationary installations containing hazardous substances (as is the case with this paper) and for risks associated with transport activities and related to them.

For crash simulations involving explosive substances, such as ammonium nitrate explosions, it is important to note that Purple Book proposes using the TNT equivalent method. In addition, another extremely important thing is that the program used to calculate physical effects in the next chapter, namely Effects, was also developed based on these books / guides.

### 4 RISK ANALYSIS IN THE CONTEXT OF TERRITORIAL PLANNING (LUP) FOR SEVESO SITES WITH AMMONIUM NITRATE PRODUCTION/STORAGE PROFILE USING DIFFERENT ANALYSIS METHODS

### 4.1 Manufacturing process of ammonium nitrate fertilizer – description, technological flow scheme

In order to determine the territorial compatibility of Seveso sites on which ammonium nitrate fertilizer is produced and / or stored, in the following, comparative analyzes will be carried out to assess the risk, for a specific location, namely Azomures SA, located in the central-northern area of Romania, based on official data made available in official documents by the competent authorities, data that formed the basis for the elaboration of the article published in the EEMJ journal, by Leordean et al. (2023), with the prior consent of the operator, for which special thanks are given.

Azomures SA, is a company producing mineral fertilizers (chemical fertilizers) based on nitrogen, of which, of interest in this work, we mention ammonium nitrate. In the Environmental Permit in force and the Safety Report prepared at company level, the process of obtaining ammonium nitrate is described as a manufacturing process licensed by KALTENBACH - THÜRING, ammonium nitrate being obtained by neutralizing ammonia with nitric acid, followed by concentration of the obtained solution, obtaining ammonium nitrate melt, granulation, conditioning and treatment of granules and packaging.

In terms of storage, ANC should be stored in enclosed, dry, clean and well-ventilated spaces, away from heat and fire sources. The existing international best practice guidelines regarding the storage of AN, fertilizer, indicate that the maximum height in a space where it is stored must be at least 1 m away from the roof, eaves, beams, walls and lighting sources. Moreover, transport and storage operations of ammonium nitrate must be carried out by ensuring temperatures of at least -10 o C, maximum 30 ° C, in order to avoid agglomeration of the product in the form of lumps, because in the absence of optimal temperatures the transformation of AN into dust occurs due to its transition from one crystalline phase to another.

More extensive aspects related to good practices regarding the storage of an fertilizer are described in more detail in subchapter 3.2.3 Standards and good practices for fertilizer storage at national and international level, letter A of the paper.

### 4.2 Application of different risk analysis concepts to sites with ammonium nitrate production/storage profile

As regards territorial planning, it should be noted that it can only be done adequately following the application and use of risk analyses, in order to create a favourable context for managing risks associated with industrial activities.

Thus, in order to outline the context we discussed earlier, in a comprehensive and punctual way regarding territorial planning, two very important steps will be taken: the first of them involves the analysis of hazards and risks related to explosions involving ammonium nitrate fertilizer, and the second determining territorial compatibility using the GIS technique (Geographic Information System) that will integrate different categories of data, organizing them in the form of overlapping layers. Finally, with the help of GIS, maps will be built based on the results of modeling of different explosion scenarios involving AN fertilizer, on the site of Azomures SA, to exemplify as clearly as possible the areas regarding the effects felt among the affected population.

Regarding the first stage, namely the analysis of hazards and risks related to the explosion of AN, 2 methods of determination were considered. The first of these, namely the use of the PHA method for the preliminary analysis of risks associated with the production/storage process, was a very important starting point for choosing modeled scenarios using the Effects program, for selecting those modeled scenarios in order to calculate their associated physical effects.

### 4.2.1. Preliminary hazard analysis (PHA) for the ammonium nitrate fertiliser production/storage process

As stated in Chapter 2.6.2 of the sentence, a preliminary hazard analysis (PHA) being generally a qualitative method of risk analysis, it is easy to apply for all types of operations and functions, and can be performed on a system, subsystem, unit or even on an integrated set of systems (*Martel, 2004*).

PHA nalysis was performed for the production/storage stages of fertilizer ammonium nitrate, in granulated form, specifically analyzingcenariums on possible explosions involving ammonium nitrate. Subsequently, these scenarios were analyzed in more detail, in 2 separate chapterse 4.2.2 and 4.2.3, in terms of physical effects and consequences produced, in the context of compatibility with functional areas (territorial planning) regulated by the methodology established at national level, approved by Order no. 3710/2017.

In order to perform the PHA analysis, official information contained in the operator's Safety Report, made available to the interested public by the competent authorities (SRAPM Mures, CJ – GNM Mures and ISU Mures), respectively in the Environmental Authorization in force, was used as input data, in order to obtain results as close to reality as possible and to propose appropriate risk prevention / mitigation measures.

Each hazard thus identified was assigned a specific score, depending on the consequences generated and the probability of occurrence and occurrence of that event over time, these scores being assigned using the risk matrix below (Table 2), matrix that for each scenario thus inventoried, will have a score calculated, based on the equation  $R = P \times G$ , where P is the probability of the event and G is the severity of the consequences.

The installations in which these scenarios will be analyzed are:

- Ammonium nitrate plant I + II;
- Ammonium nitrate plant III;
- Packaging, storage facility and ADEX II shipping platform;
- Packaging, storage facility and ADEX III shipping platform.

#### **Results and discussion**

Theoremal priority is the moderate risk level, with a calculated score between 10-12. The probability that such explosions occur on site is an occasional one, a score assigned based on the history of such events that have occurred in recent decades around the world, expertise in the field, literature and personal experience, but with major consequences on the population and structures.

Theactions that need to be established and implemented at this level of risk are largely procedural, it is necessary to manage events of this kind at preventive and predictive level, in a much more responsible and thorough way, precisely because the main causes of occurrence of the events identified above, are due to human error, process conditions (high temperatures) or fires in installations.

# 4.2.2 Analyses based on effects / consequences associated with them for the production / storage process of ammonium nitrate fertilizer in order to determine territorial compatibility

The frequencies used to perform modeling were chosen taking into account the impact zones, according to the indications regulated by Order no. 3710/1212/99/2017 on the approval of the Methodology for establishing appropriate distances from potential sources of risk within sites falling under the provisions of Law no. 59/2016 on the control of major-accident hazards involving dangerous substances, in spatial planning and urban planning activities. These are described punctually, for each scenario, in the following (*Order 3710, 2017*).

The impact areas, four in number, regulated in the methodology, are established according to the effects felt at population level, where the smallest area corresponds to a high level of mortality (expressed as probability of death) and the largest area, to a level of reversible damage.

# 4.2.3 Risk-based analyses (individual) for ammonium nitrate fertilizer production/storage process

With regard to assessment analyses based on individual and/or social risk. A limit of the thesis in this regard is precisely the fact that for determining the territorial compatibility in terms of territorial planning of Seveso sites with a profile of production and storage of ammonium nitrate fertilizer, it is precisely the fact that for the risk assessment, only the analysis based on the determination of individual risk was used. This was partly due to a lack of data needed to carry out the analysis (population density in that area, capacity of objectives of interest in neighbouring areas – e.g. the shopping complex in the immediate vicinity), as well as due to the lack of a specific software program for calculating social risk.

4.2.3.1. Calculation of associated physical effects/consequences by TNT equivalent for ammonium nitrate fertilizer depending on the quantities produced/stored – results and discussions.

Known for its explosive properties, ammonium nitrate can produce serious consequences in the event of resulting accidents, such as explosions. The main method of determining the effects of an explosion (*Baker et al., 1983*) is the TNT equivalent model. This model may generate a certain degree of uncertainty in the estimation of explosive power. The problem arises due to the fact that TNT equivalent can be determined by different tests, each of which empirically measures the effects produced, compared to an equivalent amount of TNT that could produce the same effects, but these tests are not always as relevant, as TNT equivalent is strongly influenced by the conditions under which the tests take place. and possible system errors (*Cooper, 1994; Locking, 2011*).

In order to achieve the objectives set at the writing, accident modelling involving ammonium nitrate explosions was carried out on a top-tier SEVESO site with a fertiliser ammonium nitrate production and storage profile, using the assessment method based on the use of probit functions.

In order to simulate the physical effects felt on the affected population as a result of the resulting explosions, the Effects software, version 11.5.2, developed by GEXCON, was used, starting from the application of different analysis models described in the literature, specifically the Yellow book (*Van den Bosch, 2005*) and an e14% TNT chivalent. The program defines risk as the annual probability that people in the vicinity of an accident involving dangerous chemical substances/preparations will suffer life-incompatible consequences.

The maximum pressure caused by the pressure wave never occurs at the location of the wave generation. So, in addition to the shock wave overpressure, it is also characterized by the so-called positive "impulse", defined as the area under shock waves in a certain period of time, as follows:

 $i_s = \int t_p P_s(t) x dt$ , where

 $P_s$  - represents the peak of overpressure;

T<sub>p</sub> - represents positive duration.

In order to determine the consequences associated with the overpressure effect resulting from the explosion of ammonium nitrate on persons and structures, specific probit functions from the literature have been selected in this paper (*Lees, 2005; TNO, 1992*), with the mention

that the modelling took into account threshold values representing only the effects felt by people outside buildings, for damage to the lungs and ears, the organs most sensitive to overpressure caused by explosions. It is important to mention that death was not taken into account due to fragments resulting during the explosion or due to the impact of the body with various types of fragments.

As will be seen in the modeling that follows, P functions were chosen from different bibliographic sources, as follows:

• For irreversible damage (eardrum damage):

 $Y = -12.6 + 1.524 \text{ x} \ln (P_s) (TNO, 1992)$ 

 $Y = -15.6 + 1.93 \text{ x ln} (P_s) (Lees, 2012)$ 

• For death (destruction of the lungs – long damage):

 $Y = -77.1 + 6.91 \text{ x} \ln (P_s) (Less, 2012).$ 

After calculating the physical effects, the next step is to calculate the consequences associated with it using specific probit functions identified in the literature, after which, by association with the frequency of the event, the individual risk will be determined.

### 4.2.3.2 Comparative analysis of major accident modelling and simulation results involving ammonium nitrate stored or handled on the Azomures site from a territorial planning perspective - CASE STUDY

I address special thanks to the operator AZOMURES S.A. formaking possible the carrying out of this case study, through the agreement offered to use the scenarios involving the explosion of ammonium nitrate, as input data in the process of comparative risk analysis from the perspective of territorial planning. The data and information used were the basis for writing and publishing an article (Leordean et al., 2023) in EEMJ (Environmental Engineering and Management Journal), under the direct and careful coordination of Prof. Ozunu Alexandru.

#### Description of the methodology applied

In order to perform simulations on the calculation of physical effects by TNT equivalent for ammonium nitrate fertilizer depending on the quantities produced / stored, data were used and information contained in the Security Report of Azomures SA, SEVESO site of superior level, located in Targu – Mures, Mures County, with a production / storage profile of ammonium nitrate fertilizer were used.



Fig. 19 Location of Azomures SA on the geographical map of Romania

In order to carry out this case study, it was considered to go through several stages, described and defined punctually below. These steps were pre-empt in previous chapters where the legislative context in terms of territorial planning and applicable methodology at national and international level was described. What needs to be mentioned is that the scenarios were identified and taken over, with the operator's agreement, from the Security Report, using the coding assigned in the Report, as follows:

Coding according to the Security Report	Scenario description
I.15	Explosion of 10 tons of ammonium nitrate at the base of the
	granulation tower, ammonium nitrate I + II plant
J.17	Explosion of 2 tons of ammonium nitrate at the base of the
5.17	granulation tower, Ammonium nitrate III plant
N.3.1	Explosion of 25 tons of ammonium nitrate from bunker,
11.3.1	ADEX 2 plant
N.3a	Explosion of all ammonium nitrate during handling activities
IN.3a	- (800 tonnes) worst-case scenario
	Explosion of the entire quantity in a stack during handling
N.3b	operations of ammonium nitrate - maximum possible
	scenario (300 t)
N.9	Explosion of the entire quantity in a storage box (300 t) within
11.2	the AN/CAN warehouse

Table 4 – Coding ammonium nitrate explosion scenarios fertilizer

N.12	Explosion of a stack of 300 tons of ammonium nitrate on the ADEX II platform
O.5	Explosion of 300 tons of ammonium nitrate from bunker – maximum possible scenario

## I. Stage of identification of major accident scenarios involving ammonium nitrate stored or handled on site

At this stage, all scenarios involving ammonium nitrate explosions except transport were identified. As far as the transport activity is concerned, I mention that the representation of the consequences, respectively of the risk of explosion, involves modelling on different transport routes within the site, which is why, due to technical reasons, in the absence of specific software, this could not be done.

## II. The stage of identifying and grouping scenarios into different frequency categories to determine the probability of occurrence

For modelled scenarios, three frequency categories were identified and used:

- $^{10-4} > F > 10-5$  events/year
- $^{10-5} > F > 10-6$  events/year
- $F < {}^{10-6}$  events/an

#### III. Modelling and simulation of accident scenarios

One of the most elaborate steps taken in this case study, in order to achieve the objectives set to be delivered in the context of this paper, was the modeling and simulation of major accident scenarios. This stage, in turn, involves going through several steps, including:

- a. Estimation of impact zones determined by overpressure thresholds, according to the requirements of Order 3710/2017, Annex 2, and elaboration of individual impact maps in the form of raster image (JPG) and vector.
- b. Estimation of areas of damage inflicted on humans, by using the Probit function for lung damage and developing individual risk maps for each scenario in the form of raster image (JPG) and vector.

At this stage, 8 ammonium nitrate explosion scenarios were identified, during production, storage and handling activities, subjected to modeling and simulation. In the following, the results obtained will be presented, which are discussed and debated punctually, in the context of territorial planning, in the doctoral thesis.

## IV. Uniting the contours of impact and individual risk, considering scenarios in the same frequency category, by using GIS

Following this stage, a total of 6 maps resulted, of which:

i. three impact representation with the consequence approach (one for each frequency category) *outlined above in point III*

ii. three other individual risk representation with the risk-based approach (one for each frequency category);

At this stage, it was chosen to present the 6 maps on the determined impact areas, compared to the two methods used, in order to have an overview and as clear as possible of the significant impact that the application of one methodology can have, to the detriment of another.

In order to determine and assess the vulnerability around the site, the functional areas proposed in the Methodology approved by Order no. 3710/2017, by taking into account the use of land and buildings in the vicinity, as follows:

- type A: associated with industrial and storage areas;
- type B<sub>a</sub>: associated with type A functional areas and green spaces, as well as short transport routes;
- **type B**<sub>b</sub>: associated with the activity of public transport with a flow of less than 100 persons / hour;
- type C<sub>a</sub>: associated with type A and B functional areas, as well as residential areas with 2 floors;
- type C<sub>b</sub>: associated with commercial areas with a capacity of maximum 1000 people, schools, health institutions with less than 1000 people, as well as public transport activity of no more than 1000 persons / hour;
- type D: assigned to all categories of functional areas, to all categories of constructions, protected areas and natural areas;

# V. Reclassification of the categories of land use in the site area, extracted from Urban Atlas into those described in Order 3710/2017 (functional area categories A, B, C, D), using the methodology developed by Torok et al. (2020)

The GIS analysis phase is based on data identified from the European Environment Agency 2012 (2021), a database built on the basis of multiple geographical indications, as well as data on land use and cover for approximately 700 different functional urban areas belonging to 31 European countries.

The Urban Atlas inventory was used to have a more detailed picture of the areas in the vicinity of the site under analysis and to obtain relevant details regarding the possibility of underestimating the potential consequences of major accidents involving the explosion of ammonium nitrate.

#### VI. Overlapping vector maps of impact and risk on the map of functional areas

VII. Analysis of territorial compatibility by applying the provisions of Order 3710/2017, respectively the method proposed by Torok et al. (2020)

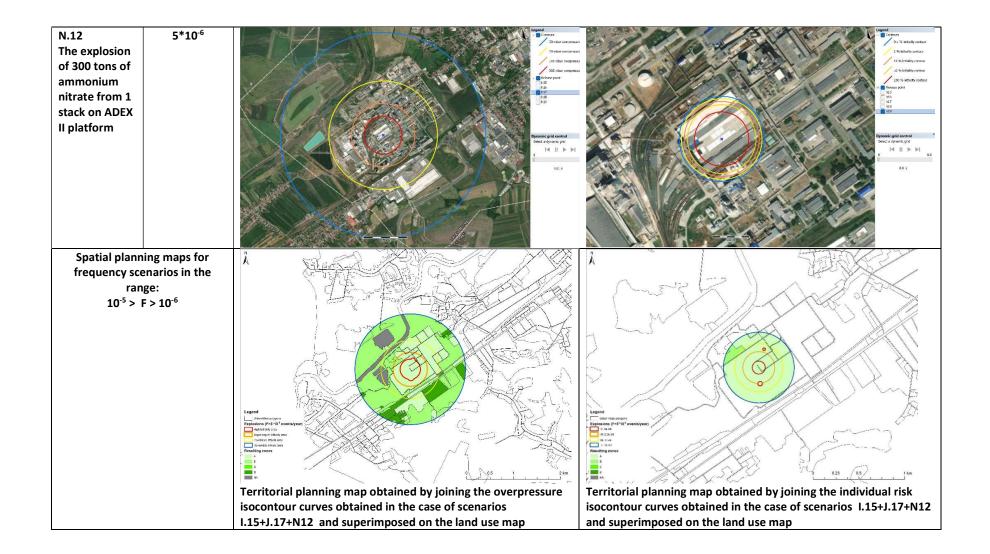
Scenario description	Scenario frequency (events /year)	Consequence based/ hybrid method based on Order no. 3710/2017	Risk based method (individual risk)
O.5 300 tons ammonium nitrate explosion from the bunker – the maximum possible scenario	5*10 <sup>-5</sup>		Image: Section of the section of th
N.9 The entire amount of ammonium nitrate from a storage box (300 tons)	5*10 <sup>-5</sup>		

N.3b The explosion of the entire amount of ammonium nitrate from one stack during its manipulation – maximum possible scenario	5*10 <sup>-5</sup>	
N.3.1 The explosion of 25 tons ammonium nitrate from the bunker	5*10 <sup>-5</sup>	

Spatial planning maps for frequency scenarios in the range: 10 <sup>-4</sup> > F > 10 <sup>-5</sup>	Territorial planning map obtained by joining the overpressure isocontour curves obtained in the case of scenarios 0.5 + N.9 + N.3b + N.3.1 and superimposed on the land use map	Territorial planning map obtained by joining the individual risk isocontour curves obtained in the case of scenarios 0.5 + N.9 + N.3k + N.3.1 and superimposed on the land use map				
The analysis of territorial compatibility	<ul> <li>Taking into account the frequency of the analyzed scenarios (10-4 &gt; F &gt; 10-5), according to the territorial compatibility matrix with the constructed alternative (Order 3710/2017, Annex 3):</li> <li>the radius of the high-mortality zone and the mortality-threshold zone may intersect only type A areas;</li> <li>the radius of the area with irreversible damage can only intersect areas type A and B;</li> </ul>	Based on the methodology developed by Torok et al. (202 territorial compatibility limits based on individual risk will be used comparing those obtained through modelling. Table: territorial compatibility matrix for existing Seveso sit proposed by Torok et al. (2020) PROPOSED TERRITORIAL COMPATIBILITY MATRIX FOR EXISTING SEVESO FACILITIES				
	- the radius of areas with reversible damage can only intersect areas type A, B and C;	$\begin{tabular}{ c c c c c c c } \hline Individual & IR < & 10^{-5} > IR & 10^{-4} > IR \\ \hline risk & 10^{-6} & \geq 10^{-6} & > 10^{-5} \\ \hline \end{tabular} IR \ge 10^{-4} \end{tabular}$				
	According to these provisions, the incompatibilities obtained for these scenarios are analyzed in the following table, using the	Functiona l areasA, B, Ca,b, DOnly within the site, at its boundaries				
	consequence method (representation of overpressure isocontour curves following possible explosions). The surfaces of					

	npatibility assessment Order no. 3710/2017:	tabe based on the	Functional area	Risk zone	Area of functional area intersected with the risk		
Functional	Impact zone	Functial area intersected with the			zone (km²)		
area	inipact zone	impact zone (km <sup>2</sup> )	A	1 - IR: 5E-05	0.037864		
A	1 – High mortality	0.215427	A	2 - IR: 2.5E-05 3 - IR:1E-05	0.115805 0.140572		
	2 - Mortality	0.215427		4 - IR:1E-06	0.240866		
A	threshold	0.276767	A B	1 - IR: 1E-05	0.001511		
	3 – Ireversibile		B	2 - IR: 2.5E-05	0.001511		
A	damages	0.432332	B	3 - IR:1E-05	0.018044		
	4 – Reversibile		B	4 - IR:1E-06	0.059014		
A	damages	0.349271	NA	4 - IR:1E-06	0.000386		
В	1 - High mortality	0.016444		4 - IN.12-00	0.000388		
В	2 – Mortality threshold	0.052685	Sum of incompation	tible areas: type B: 0.02747 km <sup>2</sup>			
В	3 - Ireversibile damages	0.326474					
В	4 - Reversibile damages	2.432119					
С	4 - Reversibile damages	0.005798					
D	3 – Ireversibile damages	0.015281					
D	4 – Reversibile damages	0.366761					
NA	3 – Ireversibile damages	0.132433					
NA	4 – Reversibile damages	0.20699					
	tible areas: type B: 0.06913 km <sup>2</sup> type D: 0.38204 km <sup>2</sup>						





The analysis of territorial	U U	e analyzed scenarios (10-				• ·	• •	/ Torok et al. (2020),		
compatibility							•		dual risk will be used by	
	the constructed alte	•	· · ·		omparing tho		-			
	<ul> <li>the radius of the h</li> </ul>	high-mortality zone	may intersect only type A		Table: territorial compatibility matrix for existing Seveso sites,					
	areas;				proposed by Torok et al. (2020)					
		mortality threshold	area may intersect only		PROPOS			-	ITY MATRIX FOR	
	type A and B areas;							ESO FACILI	TIES	
			ersible damage can only		Individual	IR <	10 <sup>-5</sup> > IR	10 <sup>-4</sup> > IR	IR ≥ 10 <sup>-4</sup>	
	intersect areas type		· · · · · ·		risk	10 <sup>-6</sup>	≥ 10 <sup>-6</sup>	> 10 <sup>-5</sup>	_	
		eversible damage m	ay intersect areas type A,		Functiona	А, В,			Only within the	
	B, C, D;	provisions the inco	mnatibilities obtained for		l areas	C <sub>a,b</sub> ,	A, B, C <sub>a</sub>	A	site, at its	
	_		mpatibilities obtained for blowing table, using the			D			boundaries	
			foverpressure isocontour		<b>6</b>				. 1	
			ns). The surfaces of		ne surfaces of	rincom	incompatible areas are marked in red.			
	incompatible areas a		Functional	Risk areas			Area of functional area intersected with risk zone (km <sup>2</sup> )			
	Territorial compatibility assessment table based on the requirements of Order no. 3710/2017				area				RISK areas	Inte
					Α		1 - IR: 5E-06 0.017293		, ,	
		Impact zone Function Impact zone the imp	Functional area		A		- IR: 2.5E-00		0.077662	
	Functional area				A		3 - IR:1E-06		0.114124	
					A	4 - IR:1E-07			0.218761	
			(km²)		B	_	- IR: 5E-06		0.000928	
	А	1 – High	0.14805		B		- IR: 2.5E-06		0.001714	
	A	mortality	0.14805		B		3 - IR:1E-06		0.00547	
	А	2 – Mortality	0.238712		B		- IR:1E-07		0.031974	
	^	threshold	0.238/12		0		F III.IL 07		0.031374	
	A	3 – Ireversibile 0.43606		N	o incompatib	mpatibilities were found for these scenarios.				
		damages	damages		omeompatio	incles n				
	A 4 – Reversibile		0.445191							
		damages	0.110101							
	В	1 – High	0.003219							
		mortality								
	В	2 – Mortality	0.026117							
	threshold									

	В	3 – Ireversibile damages	0.268313	
	В	4 – Reversibile damages	2.110931	
	С	4 – Reversibile damagesa	0.005798	
	D	3 – Ireversibile damages	0.035558	
	D	4 – Reversibile damages	0.318529	
	NA	3 – Ireversibile damages	0.063056	
	NA	4 - Reversibile damages	0.259516	
	Sum of incompatible	e areas:		
	Functional area type	e B: 0.003219 km <sup>2</sup>		
	Functional area type	2 D: 0.035558 km <sup>2</sup>		
N.3a 5*10 <sup>-7</sup> Explosion of the entire quantity during handling operations of ammonium nitrate – worst case scenario (800 t)	CIDENT		Fundamental and the second se Second second seco	ar and it marks in a star in a sta

Spatial planning maps for frequency scenarios in the range: F < 10 <sup>-6</sup>	A Constrained in scenario N.3a and superimposed on the land use map	Sp	ential plannir tenario N.3a				sk curves obtained for use map
The analysis of territorial	Taking into account the frequency of the analyzed scenarios (F <						/ Torok et al. (2020),
compatibility	10-6), according to the territorial compatibility matrix with the constructed alternative (Order no. 3710/2017, Annex 3):	territorial compatibility limits based on individual risk will be used by comparing those obtained through modelling.					
	- the radius of the high-mortality zone may intersect only type A	Table: territorial compatibility matrix for existing Seveso sites,					
	areas ;I B;	proposed by Torok et al. (2020)					
	- the radius of the mortality threshold area may intersect only	PROPOSED TERRITORIAL COMPATIBILITY MATRIX FOR					
	areas of type A, B and C;	EXISTING SEVESO FACILITIES					TIES
	- the radius of the area with irreversible damage may intersect		Individual	RI <	10 <sup>-5</sup> > RI	10 <sup>-4</sup> > RI	IR ≥ 10 <sup>-4</sup>
	areas type A, B, C and D;		risk	10 <sup>-6</sup>	≥ 10 <sup>-6</sup>	> 10 <sup>-5</sup>	_
	- the radius of areas with reversible damage may intersect areas		Funcționa	А, В,			Only within the
	type A, B, C and D; According to these provisions, the incompatibilities obtained for		lareas	C <sub>a,b,</sub> D	A, B, C <sub>a</sub>	A	site, at its boundaries
	these scenarios are analyzed in the following table, using the consequence method (representation of overpressure isocontour curves following possible explosions). The surfaces of incompatible areas are marked in red.	Tł	ne surfaces of	fincom	oatible area	is are marke	ed in red.

	compatibility assessm nts of Order no. 3710/20		Functional area	Risk area	Area of functional area intersected with risk zone (km <sup>2</sup> )		
Functio	nal	Area of functional area	aiea				
area	Impact zone	intersected with impact	A	1 - RI: 5E-07	0.031992		
		zone (km²)	A	2 - RI: 2.5E-07	0.019171		
A	1 – High	0.260217	A	3 - RI:1E-07	0.010051		
	mortality	0.200217	A	4 - RI:1E-08	0.010018		
A	2 – Mortalitaty	0.364801	В	1 - RI: 5E-07	0.001295		
A	threshold	0.504001	В	2 - RI: 2.5E-07	0.000582		
A	3 – Ireversibile	0.495002	В	3 - RI:1E-07	0.000197		
	damages	0.433002	В	4 - RI:1E-08	0.000172		
A	4 – Reversibile damages	0.545004		lities were found for			
В	1 – High mortality	0.0224					
В	2 – Mortality threshold	0.145558					
В	3 – Ireversibile damages	0.657123					
В	4 – Reversibile damages	4.577654					
C	4 – Reversibile damages	0.028059					
D	3 – Ireversibile damages	0.158132					
D	4 – Reversibile damages	0.724011					
NA	2 – Mortalitaty	0.004829					
NA	3 – Ireversibile damages	0.236767					
NA	4 – Reversibile damages	0.157412					

#### 4.2.3.3 Study limitations and uncertainties

One of the reasons why it was considered opportune to elaborate this paper was precisely from the perspective of the challenges that the methodology itself implies. Thus, if, on the one hand, there are shortcomings in terms of a clear direction in determining the appropriate distances from Seveso sites, in the context of territorial planning, on the other hand, they can lead to a series of limitations generating uncertainties regarding the results obtained.

So, in view of the above, I mention the following:

• The study does not represent the complete risk situation of the study site, as only scenarios involving the explosion of ammonium nitrate during production, handling and storage were considered.

• The Urban Atlas database necessary for the representation of risk maps contains over 20 land use categories, which is why it was necessary to reclassify them and classify them in the 4 categories described in Order 3710/2017. In this situation, differences may arise from the urban planning requirements applied at national level.

A major problem identified in this case was that of the reclassification of the land use category: *Industrial, commercial, public, military and private units,* which basically contains both type A (industrial) and type D functional areas (commercial and public with a capacity of more than 1000 people). Thus, certain areas in the vicinity of the studied site can be represented on the maps obtained as type A areas, in reality they correspond to other functional areas, which is why this uncertainty significantly influences the accuracy of the areas calculated for the analysis of territorial compatibility.

 in the risk-based method used in ammonium nitrate explosion scenarios, only the effect of the explosion on humans by damaging the lungs and therefore causing death was considered (using the probit function presented by Lees, 2012).

Other consequences caused by the explosion, such as death from collapse of damaged buildings, injuries due to projectiles, etc. were not taken into account. Thus, the individual risk areas, determined below, represent only those areas where deaths are expected as a result of causing serious damage to the population, which clearly underestimates the total area associated with the risk of death.

• Them odel based on the TNT equivalent itself represents a certain degree of uncertainty, as has already been discussed. The 14% TNT equivalent chosen for AN is at the upper limit of the values determined for the fertiliser grade AN. Normally, TNT equivalence depends on

several factors such as nitrogen content, porosity, density, presence of contaminants, space closure (leading to accumulation of heat and gases from the decomposition reaction), pressure, etc.

As a conservative approach, using a higher TNT equivalent value to determine the consequences of the explosion will result in larger impact zones, leading to more restrictive territorial planning and greater protection of the population. In the case of newly designed layouts, a more conservative approach is widely accepted.

However, in the case of existing sites, where, for various reasons, residential houses and commercial premises have been built in areas with potentially major consequences, a conservative approach can lead to incompatibilities and many other legal consequences.

In other words, usingProbit functions is a widely accepted method for estimating consequences, and combining it with the frequency of events can determine individual risk. However, only lethality caused by lung injury was considered in this study. Therefore, risk-based results may underestimate areas of lethality without considering indirect effects of explosions, such as collapse of buildings and impact of the corsp with other moving objects.

Another category of uncertainty that directly influences the results of territorial compatibility was identified in the process of reclassification (phase V of the proposed methodology) of the land use categories from the European Map of Settlements (Copernicus Land Monitoring Service, 2019) in the four functional areas defined in Order no. 3710/2017. For example, in the European Map of Settlements the category "Industrial or commercial establishments" covers both industrial and commercial areas. Thus, during the testing of the methodology, inconsistencies were found, a concrete case being the commercial complex located in the immediate vicinity of the site under analysis being classified in "functional area A – industrial area" according to the European Map, while according to the Officialno. 3710/2017 falls within "functional area D – large population flow, with a capacity of over 1000 people".

### 4.2.3.4 Results and discussion

**I.** The territorial compatibility analysis was carried out by distributing the scenarios subject to modelling into 3 groups (one for each frequency range considered) and representing the affected areas for each of the scenarios treated in the previous point, according to the territorial compatibility matrix with the built alternative, as established by Order 3710/2017, Annex 3. The representation was made by overlapping in parallel, the spatial planning maps,

over the land use maps. As for the spatial planning maps, they were obtained on the one hand by joining the overpressure contours, resulting from the modelling carried out in point **III. Modelling and simulation of accident scenarios and**, on the other hand, by joining individual risk curves obtained from modelling carried out for each of the 8 scenarios.

Thus, for the first frequency interval allocated, with a frequency of occurrence of events of 5 x 10-5, between 10-4 > F > 10-5, from the maps obtained from comparative modeling, it can be concluded that the territorial incompatibilities identified as a result of applying the consequence / hybrid methodology proposed at national level, resulted in type B functional areas, where the presence of a high mortality (calculated for an area of 0.016444 km 2), respectively the mortality threshold (calculated for an area of 0.052685 km 2), respectively type D, with a sum of incompatible areas of 0.38204 km<sup>2</sup>, will be felt .

In other news, for this frequency category between  $10^{-4}$  and  $10^{-5}$  events per year, the territorial compatibility analysis was made using the methodology proposed and developed by Torok et al. (2020), by using risk-based compatibility limits for existing Seveso sites. In this situation, following the inclusion of the frequency range in the proposed territorial compatibility matrix, the results indicate that the area affected by the effects felt on the population following the occurrence of an explosion involving fertilizer AN, is identified with the type B functional area, totaling an area of only  $0.02747^{\text{km}^2}$ .

The difference between the two approaches, in terms of potentially incompatible areas, is significant, thus raising the question: which approach is more efficient and suitable for territorial planning? Given the uncertainties given by the reclassification of land use categories in Urban Atlas, there may be errors in the calculation, for example: the land in the immediate vicinity of the site on the west side of the site was classified in category B – green spaces, but in reality it may also be classified in class A – industrial area, This would virtually eliminate the incompatibility achieved with the risk-based approach.

**II.** In the second frequency range, scenarios with a probability of occurrence of 5 x 10-6 ranging from 10-5 > F > 10-6 events / year were compared, a category into which scenarios I.15, J.17 and N12 fall. As in the previous case, the representation of the areas where the effects of the explosion will be felt was made by superimposing the spatial planning maps on the territory use maps. Thus, for this frequency range, from the maps obtained from comparative modeling, it can be concluded that the radius of the area with high mortality can intersect only type A areas, while the radius of the mortality threshold area can intersect both type A and B areas. it can be noted that it can intersect areas of type A, B and C. Territorial incompatibilities identified as a result of applying the methodology adopted at national level by Order no. 3710/2017, based on consequences / hybrid, were determined at the level of functional areas generally associated with transport activities on short routes and with a small number of people (functional area type B), respectively at the level of zone D, assigned to all categories of constructions and protected areas. For incompatibility with type B functional areas, a distance of 0.003219 km 2 and 0.035558 km<sup>2</sup> with type D areas was determined.

As regards the risk-based approach, no territorial incompatibilities were found in this case, which favours the operation of the site.

**III.** In the third frequency range, corresponding to a probability of occurrence < 10-6, i.e. 10-7 attributed to the explosion of the entire quantity of ammonium nitrate (800 tonnes) during handling, being also the worst scenario chosen, it was found that the radius of the area with high mortality will intersect areas of type A and B, the radius of the area with mortality threshold type A, B and C areas, and the radius of the area related to irreversible and reversible injuries, respectively, will concern all functional areas (A, B, C and D).

In this scenario, no territorial incompatibilities were identified, the results being fully superimposed on the territorial compatibility limits proposed in each of the two methodologies applied, whether it is the consequence / hybrid methodology or the effects-based one. The reason for this is obvious, namely because of the low frequency in this scenario of the probability of an explosioninvolving such a large amount of ammonium nitrate.

As can be seen from the above, the compatibility analysis was carried out precisely from this perspective, namely that of grouping scenarios in which the same amounts of ammonium nitrate were involved, which is why, implicitly, the same frequencies of occurrence of explosions were chosen. This is also apparent from the modelling carried out under point **III**. **Modeling and simulation of accident** scenarios in this chapter, regarding the estimation of impact zones, where for the same quantities of AN modeled within different explosion scenarios, the same distances of physical effects and overpressure were calculated.

In view of the above, it can be concluded that defining for determining territorial compatibility, v to be the frequency of occurrence of the identified scenarios. This is practically

why, although some scenarios involve large amounts of ammonium nitrate, due to the low frequency of explosions, no territorial compatibility has been identified, while at smaller quantities, but with higher probability of occurrence, the risk will also be higher, with previously identified incompatibilities.

Thus, it can be concluded that, in the case of higher frequency scenarios, territorial incompatibilities for type B and D functionalities are obtained for larger areas compared to lower frequency ranges. This is achieved due to the stricter compatibility conditions, defined in the matrix regulated by Order No. 3710/2017, for scenarios of higher frequency and implicitly of more significant consequences. Also, due to differences between the two approaches, deviations were obtained in the areas of incompatibilities for the two cases. For the scenario involving the explosion of the maximum possible quantity that may be present inside the packaging unit (800 tonnes), no incompatibilities were found, due to the low frequency associated with this scenario.

### 5 RISK AND PROCESS SAFETY MANAGEMENT ON SEVESO SITES WITH AMMONIUM NITRATE – FERTILIZER PRODUCTION AND STORAGE PROFILE

## 5.1 Preventive and predictive maintenance in the granulation process of ammonium nitrate fertilizer. Concept

The maintenance of a technological system is becoming increasingly critical due to technical advances, legislative changes and operational variations (*Söderholm, 2007*). Complex systems increase the likelihood of hazards occurring, requiring effective risk analysis and management (*Swanson, 2001*). The production process of chemical fertilizers, as well as other chemicals, relies on several key equipment to maintain efficient production rates. Granularit, incidentally, is one of the most common processes used to produce solid AN, with improved qualities of handling, bulk storage and packaging. Fertiliser production processes and systems are often very complex, which is why they contain a significant number of hazards, which can often lead to technological accidents on the site where they occur.

Preliminary hazard analysis (PHA), being generally a qualitative method of risk analysis, is easy to apply for all types of operations and functions, and can be performed on a system, subsystem, unit or even on an integrated set of systems (*Martel, 2004*).

The analysis carried out considered only part of the entire production process of AN fertilizer, namely the granulation stage, with the main critical equipment involved, the rotary drum granulator and its components. Some of the safety measures and actions proposed in the PHA analysis that are commonly used include:

- compliance with work procedures and parameters;
- periodic updating of working procedures, according to legal requirements;
- good practices and specific guidelines;
- regular staff training;
- laboratory tests, where necessary;
- accessibility and maintenance of intervention equipment;
- wearing personal protective equipment in compliance with applicable legal requirements in the field of safety and health at work.

The results of the analysis show that most of the hazards identified in the granulation process fall between low and moderate risk levels. The highest level of risk obtained is 12 - moderate risk, generated by potential leaks in the technological process, due to excessive vibration of the equipment. The probability of identified hazards ranges from Unlikely to Occasional, while their consequences range from minor to catastrophic.

By applying the PHA method, several important preventive and predictive maintenance measures and actions have been identified. These include: visual inspections, routine realignments, jet running-in, lubrication and periodic operator training. For predictive measures, techniques such as vibration analysis, noise monitoring, fluid analysis, oil monitoring, tribology and thermography were considered relevant (*Endevco an amphenol company*).

## 5.2 Methodology used in preliminary hazard analysis (PHA) for establishing preventive and predictive maintenance measures in the fertiliser granulation process

According to US EPA AP 42, ammonium nitrate manufacturing – Technical Paper (1981), "rotary drum granulators produce granules by spraying a concentrated melt of ammonium nitrate (99.0 to 99.8 percent) onto small, seed-sized ammonium nitrate particles in a rotating cylindrical drum" (*United States Environmental Agency, 1981*). In the performed PHA analysis, all hazards and potential failures that can lead to an accident during the granulation of the AN process were identified, especially due to the hazardous properties of AN (*Török and Ozunu, 2015*).

The risk matrix used (Table 7) in PHA aims to classify risks, based on their probability level (P) and consequences (C), where risk (R) is the product of both ( $R = P \ge C$ ). The qualitative values assigned to these risks were chosen (on a scale from 1 to 5, described in detail in (*Török et al., 2011*) based on working procedures and instructions for the granulation process of AN fertilizer, maintenance plans, HAZOP, scientific literature, as well as on the experience of the analysis team.

			Consequences					
			Insignificant	Minor	Moderate	Major	Catastrophic	
			1	2	3	4	5	
	Improbable	1	1	2	3: 8a, 13b, 13c	4	5	
ility	Lonely	2	2	4:3b	6: 11a, 11b, 11c, 12a, 13a	8: 12b	10: 4a, 4b, 4c, 5a	
Probability	Occasional	3	3	6: 1a, 2a, 3rd	9: 9a, 10a, 10b	12: 7th	15	
	Probable	4	4	8	12	16	20	
	Frequently	5	5	10	15	20	25	

**Table 21** Risk matrix used in PHA analysis regarding the establishment of preventive and predictive maintenance measures in the granulation process of ammonium nitrate fertilizer

 Table 2 2 Risk levels for framing the analyzed scenarios within the PHA regarding the establishment of preventive and predictive maintenance measures in the granulation process of ammonium nitrate fertilizer

Level of risk	Definition
1 – 3	Very low risk
4 – 6	Low risk
7 – 12	Moderate risk
13 – 19	High risk
20 - 25	Extreme risk

# 5.3 Preventive maintenance measures proposed for SEVESO sites with ammonium nitrate fertilizer production profile

In this subchapter preventive maintenance measures such asvisual inspections, routine realignments, belt and spindle running, lubrication and operator training, described in more detail in the paper were proposed.

### 5.4 Predictive maintenance measures proposed for SEVESO sites with ammonium nitrate fertilizer production profile

In this subchapter were proposed predictive maintenance measures such as vibration analysis, noise monitoring, fluid analysis, oil monitoring and tribology and thermography actions, described in more detail in the paper.

### 5.5 Conclusions regarding the implementation of preventive and predictive maintenance programs in ammonium nitrate fertilizer production plants

The results of the study show that the scenarios with the highest degree of danger in terms of consequences are potential explosions of AN due to friction and melting in case of danger 4. Rupture of the screw feed shaft, danger 5. Overheating or self-decomposition of the screw feed shaft belt. and AN explosion due to danger 6. Contamination with organic substances.

A potential research objective for the future might involve examining the influence of maintenance on a fertilizer manufacturing company's profitability and product quality, using data from a particular company, and considering variables that provide insight into the impact of maintenance on quality.

### **6** CONCLUSIONS AND PROSPECTS FOR THE FUTURE

### 2.5 Concluding Remarks

The writing of this paper had as starting point the desire to carry out a study in order to increase the safety of the population, industrial and process, which was also one of the main goals of the thesis. Also in this respect, it was pursued the development and proposal of guidelines in terms of ensuring a high level of environmental protection, while ensuring the protection of future developments, from the point of view of spatial planning.

In another context, through this paper, it was intended to establish adequate measures to prevent and reduce potential risks existing on Seveso sites, with a production and storage profile of ammonium nitrate fertilizer, in order to streamline the response to emergency situations, in the context of territorial planning.

In order to make it possible to achieve all aspects set as a goal and starting point in the elaboration of this work, several clear goals were established, which were dealt with throughout the thesis, each of which was placed in a specific methodological context.

Thus, the general objective of the thesis was to bring significant contributions in terms of increasing population and industrial safety, by improving the Territorial Planning methodology proposed at national level, for Seveso sites with production / storage profile of ammonium nitrate fertilizer in Romania.

In this respect, three other major objectives were pursued in the alternative:

1) qualitative assessment of technological risks present on the above sites by means of preliminary risk analysis – PHA;

2) territorial compatibility analysis for risks identified by PHA analysis, using the effects/consequences method in the context of LUP;

**3)** territorial compatibility analysis for risks identified by PHA analysis, using the riskbased approach in the context of LUP;

The first objective of the three, that of qualitative risk assessment, emerged from the need to identify those scenarios significant in terms of the level of risk, in terms of probability of occurrence and consequences generated, in order to subsequently undergo analyses in order to establish territorial compatibility. For this objective, the PHA method was used, in which the potential causes of major accidents involving the explosion of ammonium nitrate, the probability of occurrence of these events, the associated level of severity, respectively some existing and/or proposed (preventive) safety measures were identified.

Regarding the territorial compatibility analysis, I mention that for this purpose modeling / simulations were made with the help of specially dedicated software.

Regarding the territorial compatibility analysis using the risk-based method (individual risk), I mention that the presentation was made by overlapping in parallel, the spatial planning maps (obtained on the one hand by joining the overpressure contours, resulting from the modeling previously carried out for effects, respectively by joining individual risk curves obtained from modelling carried out for each identified scenario) over land use maps.

I would like to emphasize that the analysis of territorial compatibility through the two methods, applied and treated comparatively, was considered appropriate primarily in light of the shortcomings of the Romanian methodology in terms of indicating clear guidelines for planning and spatial planning in terms of determining adequate distances from Seveso sites. The purpose of the paper was to apply the territorial planning criteria defined in Order nr. 3710/2017, compared to a risk-based RE approach, for an existing Romanian ammonium nitrate fertiliser production facility located in the vicinity of vulnerable areas and to recommend improvements for risk assessment and territorial planning analysis. The analysis followed a well-established

methodology, starting with hazard identification, scenario analysis in terms of physical effects, consequences and associated risk, continuing with territorial compatibility analysis using a version using a GIS algorithm, which can be proposed as a useful tool for competent authorities in establishing territorial compatibility.

By applying the two approaches for the production and storage site of ammonium nitrate fertilizer under analysis, large differences in results were found. The Romanian method gave greater areas of territorial incompatibility compared to the risk-based approach. These differences were investigated for uncertainties and limitations of methods.

Specific conclusions on the application of different methods and techniques of analysis, together with their results and interpretation, were presented punctually within each chapter.

#### **2.6 Prospects for the future**

Starting from those presented in the previous subchapter, a future perspective could be to propose the method of territorial compatibility analysis used in this paper, for use at national level, as an integral part of the political and legislative strategies established at national level regarding risk management in the context of spatial planning and planning, by obtaining validation from the authorities involved in risk management decision-making, in terms of risk assessment. Specifically, it is proposed to use an analysis carried out on several levelsand taking into account a hybrid form of determining territorial compatibility regarding existing Seveso locations, while for newly designed Seveso sites the method regulated by the Romanian methodology shall be considered sufficient.

#### SELECTED BIBLIOGRAPHY

Anh D. T., Dąbrowski K., Skrzypek K., (2018), The predictive maintenance concept in the maintenance department of the "industry 4.0" production enterprise, Foundations of Management, **10**, pp. 283 – 292.

Arunraj N.S., Maiti J., (2007), Risk-based maintenance - Techniques and applications, Journal of Hazardous Materials, Volume 142, Issue 3, pp. 653-661, 2007, ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2006.06.069, B. Al-Najjar; Internation Journal of Production Economics, **107**(1), pp. 260–273.

Aven T., (2016), Risk Assessment and Risk Management: Review of Recent Advances on Their Foundation, *European Journal of Operational Research*, **253**, pp. 1 - 13, https://doi.org/10.1016/j.ejor.2015.12.023. Aven T., (2012), The risk concept - historical and recent development trends, Reliability Engineering and System Safety, University of Stavanger, Ullandhaug, Stavanger, Norway, pp 33–44.

Băbuț M. C., (2011), Risk analysis and assessment methods applicable for Seveso industrial sites, Focus Publishing House, Petroșani, ISBN : 978-973-677-252-8

Blaikie P., Cannon T., Davies I., Wisner B., (1994), At Risk: Natural Hazards, People's Vulnerability and Disasters, https://doi.org/10.4324/9780203714775

Bîldea M., (2007), Community and vulnerability: perception, communication, disaster risk reduction, M.I.R.A. Publishing House, Bucharest.

Azomures product catalog, updated 2021\_www.azomures.com – Produse\_Download, https://www.azomures.com/download/, accessed on 25.09.2021.

Siwar C., Islam R., (2012), Characterization of Hazards, Vulnerability and Risk of Disaster Management, Institute for Environment and Development (LESTARI), Universiti Kebangsaan Malaysia (UKM), Kedah Darul Aman, Malaysia, Characterization of Hazards, Vulnerability and Risk of Disaster Management, *Advances in Environmental Biology*, **6**(3): 955-966, ISSN 1995-0756, pp. 955-964.

Kirchsteiger C., (1999), Trends in accidents, disasters and risk sources in Europe, *Journal* of Loss Prevention in the Process Industries, **12**, 7–17, European Commission, DG JRC, ISIS-SMA, 21020 Ispra (Va), Italy.

Cooper P.W., (1994), Comments on TNT Equivalence, Proc. 20th Pyrotechnic Seminar, Colorado Sprinds, Colorado, USA,

European Commission, (2016), Communication from the Commission to the European Parliament, the European Council and the Council, Delivering on the European Agenda on Security to fight against terrorism and pave the way towards an effective and genuine Security Union, COM(2016) 230 final,

https://eur-lex.europa.eu/legal-content/RO/TXT/?uri=celex%3A52016DC0230.

Directive 2012/18/EU of the European Parliament and of the Council, (2012), on the control of major-accident hazards involving dangerous substances, amending and subsequently repealing Council Directive 96/82/EC.

Duffuaa S. O., Raouf A., Campbell J., (1999), *Planning and Control of Maintenance Systems: Modelling and Analysis*, In John Wiley & Sons Inc., New York, USA, pp. 59-66.

Eckhoff R., (2005), *Explosion Hazards in the Process Industries*, In *Gulf Professional Publishing*, 1st Edition, ISBN 978-0-12-803273-2, https://doi.org/10.1016/C2014-0-03887-7.

European Environment Agency, (2021), Urban Atlas — Copernicus Land Monitoring Service, https://land.copernicus.eu/local/urban-atlas, accessed 20.06.2023.

EN 13306 Standard – Maintenance – Maintenance terminology. .

Ericson Clifton A., (2005), Hazard analysis techniques for system safety, In John Wiley & Sons. Inc., ISBN 0-471-72019-4 (cloth).

Etkin D., Medalye J., Higuchi K., (2012), *Climate warming and natural disaster management: An exploration of the issues*, Climatic Change, **112**, pp. 585–599, https://doi.org/10.1007/s10584-011-0259-6.

Fertilizers Europe, https://www.fertilizerseurope.com/fertilizers-in-europe/types-of-fertilizer/, accessed on 06.06.2019.

ISO Guide 73:2009, Risk management. Vocabulary.

Goyal D., Chaudhary A., Kumar D.A., Pabla B. S., Dhami S. S., (2018), Condition Monitoring of Rotating Machines: A Review, *World Scientific News*, 113, pp. 98 - 108, EISSN 2392-219.

Iațu C., (2015), Spatial planning and planning, GEOGRAPHY AND SPATIAL PLANNING, Alexandru Ioan Cuza University, Iasi.

IGSU, Azomures SA, (2021), Good practice guide for storage and use of fertilizers in order to minimize environmental impact.

ISO 31000:2009 Risk management – Principles and guidelines, updated 2018.

ISO 31010:2009 Risk management – Risk assessment techniques.

Kasperson R.E., Renn O., Slovic P., Brown H.S., Emel J., Goble R., Kasperson J.X., Ratick S., (1988), The Social Amplification of Risk: A Conceptual Framework, *Risk Analysis*, 8, pp. 177-187, https://doi.org/10.1111/j.1539-6924.1988.tb01168.

Khudbiddin M., Rashid Z., Mohd S.Y., Farhanah A., Azil A., Fuad F. I., Fuad M., Hayati H., (2018), Prevention of Major Accident Hazards (MAHs) in major Hazard Installation (MHI) premises via land use planning (LUP): a review, *IOP Conference Series: Materials Science and Engineering*, 334, 012033. 10.1088/1757-899X/334/1/012033.

Kletz T., (1999), What Went Wrong. Case Histories of Process Plants Disasters, 4th ed., In Gulf Publishing Company, Houston TX, USA, pp. 370 - 371.

Locking P.M., (2011), The Trouble with TNT Equivalence, Proc. 26th International Symposium on Ballistics, Miami, USA, pp. 143 - 154.

Lees F.P., (2012), Loss Prevention in the Process Industries: Hazard Identification, Assessment, and Control, fourth edition, In Elsevier Inc., Oxford 2547, 2551, 2605-2623, 2624-2634, 2635-2640, 2641-2651, 2655-2700 pp. 70-96.

Law nr. 59 of 11 April 2016 on the control of major-accident hazards involving dangerous substances, published in Official Decision no. 290 of 18 April 2016.

Law nr. 360 of 2003 on the regime of dangerous chemical substances and preparations Methodology for risk assessment and integration of sectoral risk assessments in Romania, published in the Official Gazette no. 178 of 12 March 2014.

Lepesteur M., Wegner A., Moore S.A., McComb A., (2008), Importance of public information and perception for managing recreational activities in the Peel-Harvey estuary, Western Australia, *Journal of Environmental Management*, **87** (3), pp. 389–395.

Leordean R., Ozunu A., Török Z., (2023), Preventive and predictive maintenance of ammonium nitrate granulation process based on preliminary hazard analysis technique", *Studia Universitatis Babeş-Bolyai Chemia*, **68**, pp. 265-274, 10.24193/subbchem.2023.1.19

Leordean R., Ozunu A., (2023), Risk perception among the most interested parts in case of a fertilizers production company closure in the actual context of the energy crisis with focus on socio-economic aspects, *AES Bioflux*, 15, Issue 1, pp. 12-19.

Lindell M.K., Prater C.S., (2002), Risk area residents' perceptions and adoption of seismic hazard adjustments, *Journal of Applied Social Psychology*, **32** (11), 2377–2392

Mannan M. S., (2005), Lees' loss prevention in the process industries: Hazard identification, assessment and control (3rd ed.), Butterworth-Heinemann

Martel B., (2004), Chemical risk analysis: a practical handbook, Butterworth -Heinemann, United Kingdom, pp. 29-31

Merkt O., (2019), On the Use of Predictive Models for Improving the Quality of Industrial Maintenance: an Analytical Literature Review of Maintenance Strategies, *Proceedings of the Federated Conference on Computer Science and Information Systems*, **18**, pp. 693 – 704.

Methodology for risk assessment and integration of sectoral risk assessments, version 2, General Institute for Emergency Situations, 2018.

Mulilis J.P., Duval T.S., (1995), Negative threat appeals and earthquake preparedness: a person-relative-to-event (PrE) model of coping with threat, *Journal of Applied Social Psychology*, **25** (15), pp. 1319–1339.

Nelkin D., (1989), Communicating technological risk: the social construction of risk perception, Annu Rev Public Health, 10:95-113. doi: 10.1146/annurev.pu.10.050189.000523. PMID: 2655644.

Order no. 3710/2017 on the approval of the Methodology for establishing appropriate distances from potential sources of risk within sites falling under the provisions of Law no. 59/2016 on the control of major-accident hazards involving dangerous substances in spatial planning and urban planning activities, published in the Official Gazette no. 755 of 21 September 2017.

Renn O., (2004), Perception of Risks, *The Geneva Papers on Risk and Insurance*, **29** no. 1, pp 102–114.

Ozunu A., Torok Z., Cosara V., Cordos E., Dutrieux A., (2008), Vulnerability mitigation and risk assessment of technological disaster, *NATO Science for Peace and Security Series, E: Human and Societal Dynamics*, **35**, Risk Assessment as a Basis for the Forecast and Prevention of Catastrophies. Apostle I., Coldewey W. G., Barry D. L., Reimer D. (eds), Springer Netherlands, pp. 177-186.

Renn O., Burns W., Kasperson J., Kasperson R., Slovic P., (2010), The Social Amplification of Risk, 10.1017/CBO9780511550461.002.

Regulation (EC) No .../... Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

Regulation (EC) No .../... Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures (CLP).

Risk Assessment and Mapping Guidelines for Disaster Management, Series Title: European Commission, Risk Assessment and Mapping Guidelines for Disaster Management, Disaster Risk Reduction Program, Florida International University (DRR/FIU) (summary contributor), European Commission, SEC (2010), 1626 final.

Kasperson R.E., Renn O., Slovic P., Brown H.S., Emel J., Goble R., Kasperson J.X., Ratick S., (1988), The Social Amplification of Risk A Conceptual Framework, Risk *Analysis*, **8**, No. 2, p p. 177.

Rooney J., Hauvel L.N., (2004), Root Cause Analysis For Beginners, *Quality Progress*, **37**, pp. 45-53.

Scrădeanu D., (2014), Hazard and risk in the evaluation and management of natural resources, http://www.ahgr.ro/media/197003/mrn\_hazard\_si\_risc\_scradeanu\_2.pdf, accessed on 20.03.2019.

Slovic P., (1987), Perception of risk, Science, 236, pp 280–285.

Söderholm, P (2007), Review: A system view of the No Fault Found (NFF) phenomenon, *Reliability Engineering & System Safety*, **92**, pp. 1-14.

Swanson L. (2001), Linking maintenance strategies to performance, *International Journal of Production Economics*, **70**, No. 3, pp. 237-244.

TNO, (1992), Methods for the determination of possible damage - The Green Book - CPR 16E. The Hague (The Netherlands): CIP-data of the Royal Library., pp. 8-12.

TNO (2005), Methods for the calculation of physical effects: due to releases of hazardous materials (liquids and gases) – The Yellow Book -, pp. 82.

Török Z., Ajtai N., Turcu A.-T., Ozunu A., (2011), Comparative consequence analysis of the BLEVE phenomena in the context on Land Use Planning. Case study: The Feyzin accident, *Process Safety and Environmental Protection*, **89**, Issue 1, pp. 1-7, ISSN 0957-5820, https://doi.org/10.1016/j.psep.2010.08.003.

Török Z., Ozunu A., (2010), Chemical risk assessment for storage of hazardous materials in the context of Land Use Planning, *AES BIOFLUX Advances in Environmental Sciences* -*International Journal of the Bioflux Society*, 2, Issue 1, pp. 33-53.

Török Z., Ajtai N., Ozunu A., (2011), Applications for assessing the risk of major industrial accidents involving dangerous substances, *EFES*, Cluj-Napoca, Romania, pp. 27.

Török Z., Kovacs L.A., Ozunu A., (2016), Ammonium Nitrate Explosions. Case study: the Mihailesti accident (2004), *ECOTERRA - Journal of Environmental Research and Protection*, 2, pp. 56-60.

Török Z., Ozunu A., (2015), Hazardous properties of ammonium nitrate and modeling of explosions using TNT equivalency, *Environmental Engineering and Management Journal*, **14**(11), pp. 2671-2678.

Török Z., Leordean R., Maloş C-V, Ozunu A., Senzaconi F., (2023), Comparative study on Land-use planning methodologies based on physical effects, consequence and risk analysis for ammonium nitrate fertilizer production facilities, *Environmental Engineering and Management Journal, EEMJ* – approved for publication.

United Nations Office for Disaster Risk Reduction, (2020), International Science Council, Hazard definition & classification review technical report.

UNISDR, (2006), International Strategy for Disaster Reduction, Press Release, UNISDR, 06/11.

UNISDR, (2010), Climate change adaptation and disaster risk reduction institutional and policy landscape in Asia and Pacific Advances in Environmental Biology, **6**(3), pp. 955-966, 2012 ISSN 1995-0756.

Weinstein N.D., Rothman A.J., Sutton S.T., (1998), Stage theories of health behavior: conceptual and methodological issues, *Health Psychology*, **17**, pp. 290–299.

https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-greendeal en, accessed on 2021-10-21