QUANTITATIVE RISK ANALYSIS OF AN AGROCHEMICAL PROCESSING PLANT

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Abstract. *This article describes a quantitative risk analysis of an agrochemical processing plant. The methodology followed international standards aimed at evaluating what risks the facility posed for the population living in the surrounding area. Accident scenarios that could be generated by the highest risk materials such as ammonia, chlorine, hydrochloric acid and nitrogen contained in the plant were analyzed. The main effects that were analyzed were the continuous and sudden release of these substances at different product processing stages, that lead to the forming of toxic clouds. Quantification of the consequences was achieved by applying discharge, sparking and evaporation models, followed by atmospheric dispersion coupled with distributions of concentration and population by using vulnerability models. The possible consequences of each scenario were evaluated for eight main wind directions, resulting in death probability curves in the region around the plant. Expected event frequency of each scenario were also calculated and through this it was possible to obtain the average societal risk and isorisk curves of the assessed facility.*

Key words: *quantitative risk analysis*

1. Introduction

Product processing in agrochemical processing plants requires the use of a great variety of chemical products which could potentially harm human beings and the environment. If there is accidental release of these substances into the atmosphere, company workers could be harmed or the effects could go beyond the facility's boundaries, affecting the neighboring population.

In such cases, it is said that the plant poses a risk for the neighboring population. Quantitatively estimating the risk that a facility of this type poses for the population has become an important tool in the licensing process and safe operation of industrial plants. Without quantifying the risk, how can it be defined as a high or low, acceptable or unacceptable risk?

This paper will present the Quantitative Risk Analysis (QRA) technique applied to identifying possible accident scenarios and a quantitative evaluation of the consequences outside the boundaries of the facility.

The article will describe each phase of the analysis separately, from the identification of a possible accident scenario to obtaining the average societal risk that the facility poses for the population living near the plant.

2. Goals

This work aims at presenting the use of the QRA technique at an agrochemical processing plant that uses several hazardous substances in its production process.

According to Brandsæter (2002) the goals of quantitative risk analysis may include the following items:

- Estimate risk levels and analyze what they represent;
- Identify main contributing events of the risk;
- Define project accident scenarios;
- Compare project options;
- Evaluate measures to mitigate risk;
- Show risk acceptability of regulating bodies and employees;
- Identify equipment and critical procedures for safety and
- Identify causes of accidents.

The motivation for elaborating the quantitative risk analysis was the requirement made by the State environmental regulating body.

3. QRA Phases

A QRA study is a long and, many times, complex work, therefore, it is recommended to be carried out in phases.

The present work has been shaped into the following phases:

- Characterizing the substances involved: the main substances involved in the production process are identified in this phase, assessing their physical-chemical properties and their hazard provoking potential for both toxicity and flammability/explosiveness;
- Identifying and characterizing accident scenarios: in this phase, possible accident scenarios are listed and characterized for modeling, to evaluate both frequency and consequences;
- Evaluate scenario occurrence frequency: expected occurrence frequency of each accident scenario are calculated in this phase.
- Evaluate consequences: physical effects are calculated in this phase, (release, atmospheric distribution, spatial distribution of concentrations, overpressure areas so that these may be coupled with data regarding population in the vicinity of the facility, by using vulnerability models, seeking to quantify the probable number of victims at main accident scenarios;
- Risk assessment: using the results obtained from the evaluation of frequency and consequences phases it is possible to couple them and obtain the average societal risk and individual risk;
- Proposals for risk mitigating measures: in this phase, several proposals which contribute to mitigating risks at the facility under study are listed;
- Reassess risks: in this phase, scenario frequency and consequences are re-calculated and new risk results are obtained, using the risk reduction proposals and
- Conclusions: study findings are presented.

4. Characteristics of Substances Involved

An analysis of the properties of all the substances used in the facility's production process was carried out. After this analysis, it was verified that among all the substances, only ten of them could pose a risk for the population in case of accidental release. Substances are presented in Tab (1).

Table 1 - Substances used in the QRA

Substances
Ammonia
Chlorine
Hydrogen fluoride
Hydrochloric acid
Fuming sulfuric acid
Nitric Acid
Sulfuric Acid
Oxirane, Dimetilacetamida and Methylcyclohexane

It may be noted that all the substances in Tab (1) are potentially toxic and because of this in the scenario identification and characterization phase only the toxic effects of these products were assessed. Ammonia, besides being toxic is also flammable, but the reach of flammable clouds did not show potential to cause damage outside the plant boundaries and, therefore, were not taken into account.

5. Identification and Characterization of Accident Scenarios

Identification of possible accident scenarios was done through meetings with company members and the team responsible for carrying out the QRA, based on documents from the assessed units, visits and a PRA that had been previously carried out.

The definitions of which ways of containment losses to take into account and carrying out simulations, were made based on the Purple Book (1999) which prescribes several ways according to equipment or pipeline being studied.

Regarding leaks in stationary tanks, three types of scenarios were taken into account:

- Catastrophic tank rupture and consequent sudden release of total inventory;
- Continuous total leakage of inventory in ten minutes with a constant release rate and
- Continuous release of material through a ten millimeter diameter hole.
- Simulations were carried out by taking into account full storage tank capacity and 50% of its capacity.
- For pipelines, two loss of containment scenarios were simulated:
- Total pipeline rupture and
- Leakage through a 10% diameter hole in the pipeline up to a maximum of 50 mm.

Regarding the position of the leak for pipelines that are longer than 20 meters, leaks near the tank with the highest pressure, leaks near the one with the lowest pressure and the distance between these were taken into account.

In cases of leaks from fuel trucks, concerning cases within which the truck is not connected to the unit, the catastrophic rupture of the tank with total release of inventory and spillage through the biggest connection were taken into account. For cases within which the fuel truck is connected to the unit, total rupture with leaks at both ends of the pipeline and also, through a 10% hole in diameter of the pipeline were considered.

Concerning cases within which the PSV (Pressure Safety Valve) is opened and then cannot be closed, it was considered that the valve would discharge total vapor (leak through the full valve connection pipeline section), in case of over-filling the tank and causing internal pressure build-up of the tank resulting in opening the PSV.

Lethal Concentrations (LC) were determined for each accident scenario depending on the time taken to get the situation under control and therefore exposure time to the concentration. That is, exposure time was considered as being equal to the time taken for release of material to form a toxic cloud. This means that an escape possibility (conservative hypothesis) was not taken into account. Regarding sudden release with toxic puff formation, the time that was analyzed was how long the puff took to pass through the interest point. The assessed lethal concentrations were calculated by using the Probit equation from the Eisenberg vulnerability model, which will be explained further on.

After an in-depth analysis, 76 possible initiating event scenarios were identified and atmospheric dispersion was estimated for all of them; after analyzing the reach and width of the plumes, the number of initiating events with the potential of generating scenarios that could affect the population outside the plant were reduced to 26. As 8 wind directions were used, 208 accident scenarios were in fact generated.

All calculations referring to the reach and width of the plume were made by using internationally used models and, partly, with the VULNER program developed by "*Principia Engenharia de Confiabilidade e Informática Ltda*".

6. Evaluating the Frequency Occurrence of each Scenario

The evaluation of accident frequency was done through a logical process where the frequency of the initiating event with several probabilities regarding possible outcomes that logically make up the scenario were combined. To assess the frequency of the initiating event, the frequency associated to the basic cause of loss of containment was used (catastrophic tank rupture or leak, pipeline rupture or leak, in this case taking into account its diameter and length) and the probability of failure of safety systems, when they are present. Due to this, it was unnecessary to build error trees, except for one scenario where an error tree was used to calculate the unavailability of the safety system. Event trees were used to identify and evaluate different accidental sequences triggered off by each initiating event. The frequency of the initiating event for each accident scenario was determined by using the Red Book (1997) as a base. Frequency occurrence was calculated for the 26 main accident scenarios.

The frequency of each accident scenario was determined through the use of event trees. The event tree is a probabilistic analysis method that represents possible outcomes of a given initiating event in various possible accident scenarios. For the case under study the scenarios were all toxic cloud and puff ones. This method starts from an initiating event and covers the different accident scenarios. Once the event tree framework has been determined, probabilities of each of the tree's branches are determined and, then the resulting frequency is calculated by multiplying each one of the tree's sequences.

The necessary data to calculate the frequency of a given accident scenario through the events tree method are: the frequency of the initiating event weighted by the time fraction in which the event could occur (explanation follows), the probability of safety system failure (when present), relative frequency of wind direction, relative frequency of wind speed and the relative frequency of atmospheric stability classes.

In Fig (1), there is an example of the events tree for an accident scenario involving ammonia release. Likewise events trees were drawn up for the other scenarios.

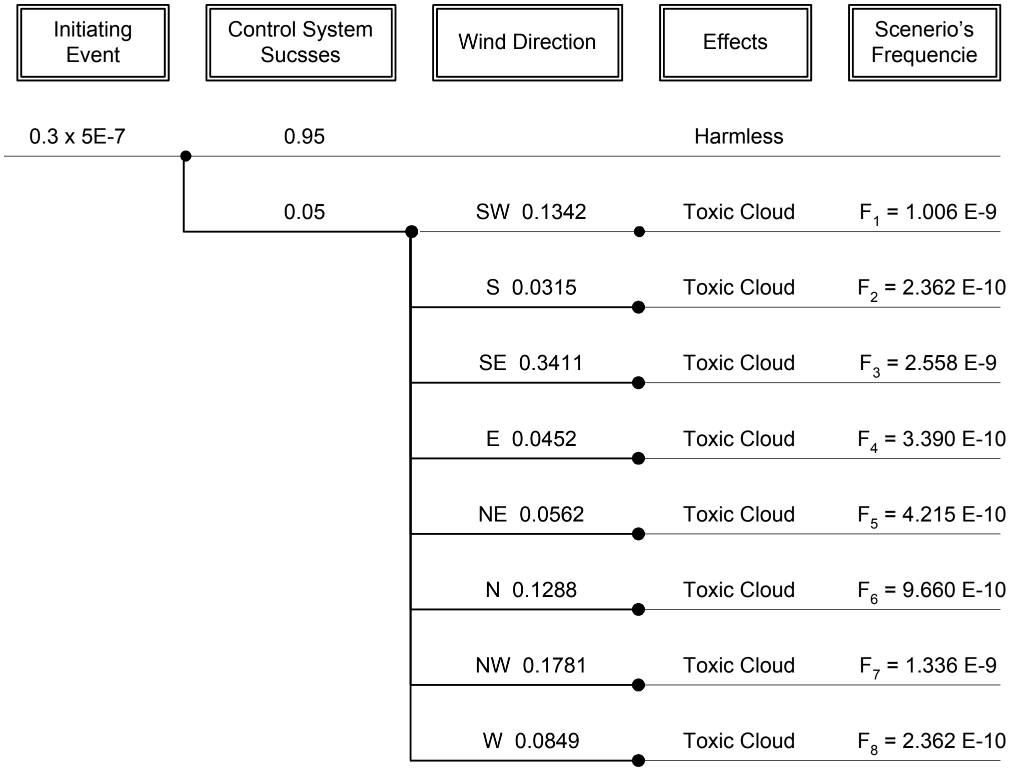

Figure 1 - Example of events tree

Given that only one wind speed and only one stability class were used in this work as previously explained, the frequency occurrence of an accident scenario has been simplified, as can be seen in the following equation:

$$F = F_t \cdot F_{EI} \cdot Pf_{SP} \cdot P_v \qquad (1)$$

where F is the scenario occurrence frequency per year, F_t is the fraction that was used (fraction of time that the system was used per year) F_{EI} is the initiating event frequency, Pf_{SP} is the probability of safety system failure and P_v is the relative wind direction frequency.

7. Evaluating Consequences

The extent of damage caused by the accident scenario was evaluated in the vulnerability analysis, caused by the 26 initiating events, which are potentially capable of harming the population in the vicinity of the assessed facility. In the specific case of this work, the harm is directly related to the exposure of people to toxic clouds.

From the number of people in each house who could be affected by accidents initiated in the facility, numbers obtained from a house to house field survey, a population distribution grid, represented by a matrix whose inputs corresponds to the number of people in each 50x50 m^2 cell, was generated, following this procedure, the study is carried out as if the number of people in each cell were subject to the physical effects that can be observed in the center of the cell. Next, a matrix, whose inputs correspond to death probabilities as a function of the two variables: distance to the release point and the distance to the plume or puff centerline, measuring meter by meter in both aforementioned mentioned examples, was estimated for each initiating event. These probabilities were computed by combining the concentration levels and duration of the accident, in cases of continuous releases and puffs path, in cases of sudden releases and by using the Eisenberg vulnerability model with corresponding PROBIT equations.

Concentration levels for ammonia and hydrogen fluoride were calculated with the spatial gas dispersion model and, levels for other substances were calculated with the DEGADIS program, which is appropriate for dense gas dispersion calculations.

The vulnerability analysis, in this work, is based on the Eisenberg vulnerability model (Eisenberg, 1975) which through using the PROBIT equation makes it possible to determine the probability of death of a person exposed to a given concentration of a toxic substance for a given time. The PROBIT equation shown below

$$y = k_1 + k_2 \cdot \ln(\text{Dose}) \tag{2}$$

has parameters k_1 e k_2, which are specified for each substance. The variable y is the Probit (Probability Unit) which is related to the death probability, the Dose or D is the result of exposure to a concentration C in ppm (1 part of the substance for 1 million parts of mixture) to the power of n, during exposure time t (in minutes) at that concentration.

When the concentration varies throughout exposure time, the dose or toxic discharge received by a person from a toxic cloud or puff is worked out by using the formula in Eq. 3 (Purple Book, 1999):

$$D = \int_0^t C^n \cdot dt \tag{3}$$

where D is the dose received by a person, C is the cloud's toxic concentration and t is the exposure time. After the dose has been obtained, it is possible to calculate the Probit number (y) and consequentially the death probability P, using the equation below (Lees, 1996).

$$P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{y-5} e^{\frac{-u^2}{2}} \cdot du \tag{4}$$

Table 2 lists the parameters of the PROBIT equations that were used in this study.

Table 2 - Parameters of the PROBIT equations

Substance	**k_1**	**k_2**	**n**
Ammonia	-9.82	0.71	2
Chlorine	-5.3	0.5	2.75
Hydrogen fluoride	-26.4	3.35	1
Nitric acid	-13.79	1.4	2

Source: World Bank (1998) - Technical Report N° 55: Techniques for Assessing Industrial Hazards, Washington DC: The World Bank

Therefore, with the spatial distribution of the concentration and its time variation, in a given region, it is possible to calculate the dose a person would receive by being exposed for either a given time or puff, at any interest point. The results from the estimated concentration resulting from accidental releases of the different toxic substances for each of the scenarios under survey were combined with the vulnerability model, generating a spatial distribution of death probability, throughout the region that could be affected by the cloud. Or rather, "a death probability plume" was generated from the plume or puff. An example of the results supplied by the program of half-plume probabilities for a dense gas in the wind direction presented in figure 2. follows. In the upper part of the figure, there is a bi-dimensional view (upper view) of the half-plume and in the lower part an illustration with a spatial view (3D). As there is axial symmetry in relation to the plume axis, the other half of the plume can be automatically generated by symmetry.

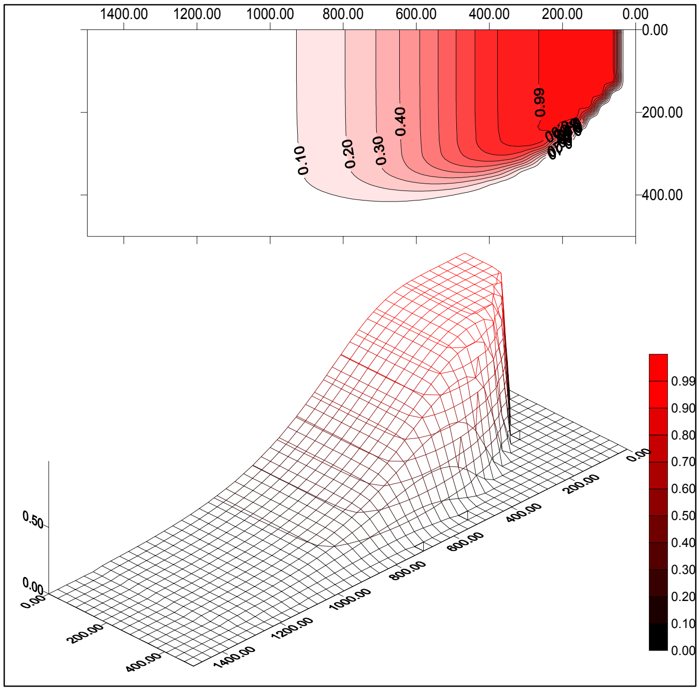

Figure 2 - Spatial view of the distribution of probabilities corresponding to "half-plume" release of dense gas.

This method can be used to generate both isorisk curves as well as the results of the consequence calculations at each point in the grid, in a simple and direct way.

Figure 2 shows that death probability would be 100% on a plateau that ranges from the release point, in the wind direction and laterally to the plume axis, for distances of some hundreds of meters and tends to go down as distances increased to the source and plume axis, becoming negligible for very distant points, as would be expected. Calculations were made until death probability of 1% was reached.

The composition or superimposition of this death probability grid or matrix with the population distribution grid allows one to calculate the number of deaths associated to each of the accident scenarios. The procedure consists of positioning a system of coordinates originated at the release point (source) with the axis of the ordinates aligned with the wind direction making a determined angle with the system of general positioning coordinates and that contain the population distribution at the central points in the grid cells. After obtaining the relative frequency of one wind direction, the wind direction can be varied in the sector, in this case, one of eight, computing the contribution in terms of scenario probability for each position, at each point in the grid affected by the probability cloud in that position. Upon completing the total of positions used, contributions for the individual risk are obtained and, by multiplying the probability result in each cell by the number of people associated to it, the number of deaths associated to the scenario that corresponds to the wind in a given direction can be obtained.

To apply the evaluation method, FORTRAN 90 programs were developed to calculate the individual risk and the consequences of each scenario.

8. Risk Calculation

The risk calculation is a coupling of the results obtained in the evaluation phase of frequencies and consequences of each scenario. Risk was presented in two ways, individual risk, represented by isorisk curves, and the societal risk, presented through F-N curves.

The individual risk represents the death probability of a person, who resides permanently for a year, at a given point, due to the presence of the facility.

The societal risk calculation is a combination of the results obtained in the evaluation phase of frequencies and consequences, resulting in the number of expected deaths per year:

$$R_s = \sum_{i=1}^{N} f_i \cdot C_i \tag{5}$$

where f_i and C_i are, respectively the expected frequency and consequence of the scenario and N is the number of scenarios. It is also possible to represent the risk through F-N curves with these results.

The F-N curves, also known as the complementary accumulated distribution function, measured in terms of N or more fatalities, are plotted in the accumulated frequency of N or more deaths. Or rather, the curve is built up by a determined number N of deaths and adding the frequency of all scenarios that caused N or more deaths. Doing this with a series of N values enables one to draw the F-N curve.

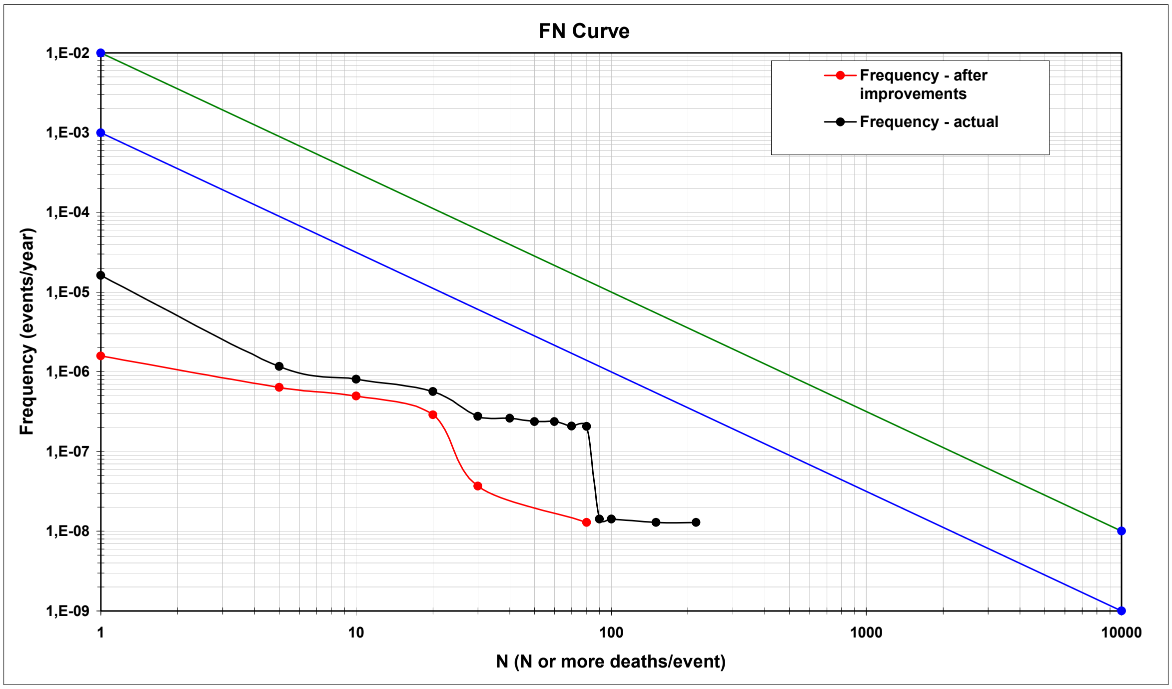

Figure 3 - F-N Curves used to study the case presented

Figure 3 shows the F-N curve obtained from the initial situation, that is, before implementing the risk mitigating measures and the situation afterwards. The same figure presents the curves that define the completely tolerable, intolerable range and an intermediary range between the two known as the ALARA (As Low as Reasonably Achievable) range. As can be observed, the plant's curve is within the tolerable risk range and the implementation of suggested risk mitigating measures led to a reduction of risks.

9.Conclusions

The use of tools that are available nowadays to evaluate the risks that industrial facilities pose for the population are vitally important for decision making concerning licensing processes. The licensing of facilities that handle considerable quantities of hazardous products, when there is a population in the vicinity of the proposed site for the facility, require quantitative risk analysis to ground decisions of approval or refusal.

Besides supplying information that enables technicians from environmental bodies make their decisions, a company that undergoes a quantitative risk evaluation has a series of very important gains that impact on plant safety, through the identification of measures that can mitigate or eliminate risks, increases knowledge/awareness of safety for company technicians involved in the evaluation process, democratizing information, the clear definition of possible accident scenarios and their potential consequences which allows for better planning to deal with these emergency situations. From a risk management point of view, if one has the contribution of each risk scenario, it is possible to establish an accident scenario hierarchy and also define where investments in safety are most cost effective for risk reduction in the facility.

This work presented the framework and summarized description of the phases in a quantitative risk analysis, followed by the presentation of the main results obtained through applying the method at an agrochemical processing plant where there is storing and processing of considerable quantities of various toxic substances.

10. References

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