THE SELF-SUSTAINING DECOMPOSITION OF AMMONIUM NITRATE FERTILISER: CASE STUDY, VALLE DE ESCOMBRERAS, CARTAGENA, SPAIN

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ABSTRACT

Fertilizers containing ammonium nitrate have caused several accidents over time, including toxic clouds, fires and explosions. Therefore, in this work we have studied the accident produced in Escombreras (Spain) related to the decomposition of fertilizer NPK 15-15-15 composed basically of monoammonium phosphate, ammonium nitrate and potassium chloride. The fertilizer was stored in a silo and its decomposition produced a toxic cloud formed by nitrogen oxides. Calculations have been made to determine the amount of heat released in the accident and the temperature gradient in the stored pile. The causes of the accident are not clear but could be related to the presence of decomposing organic matter. The fault tree has revealed several weak points in the storage conditions. The dispersion of the gases produced has been simulated to evaluate the distance to which dangerous concentrations of gases would reach. The consequences of the accident are met with almost 4000 people affected although most of them only with minor irritations and episodes of confinement of the nearby population. To conclude, a series of lessons have been extracted that can help avoid similar accidents in the future.

Keywords: decomposition; ammonium nitrate; fertiliser; accident; temperature gradient.

1. Introduction

Ammonium nitrate (AN) is a commercially important product around the world, with an annual global consumption of more than 20 million tonnes. Its two main uses are as a nutrient in agricultural fertilisers (NPK-type fertilisers) and as a component in explosives (in the manufacture of ANFO – Ammonium Nitrate Fuel Oil, for example). During its lifecycle, AN and its derivatives need special attention in safety aspects, due to its complex properties and the product's specific risk profile **[1]**. In recent years, it has also been used by terrorists as a raw material for explosives, mixed with petroleum **[2]**.

Industry now has more than a century's experience in the manufacture of ammonium nitrate and the product's intrinsic safety has substantially improved. However, AN-related accidents still occur today, in both its storage and its transportation, justifying the special attention paid to safety, particularly in terms of regulation by the authorities **[1,3]**. For example, ammonium nitrate is considered as hazardous substance in Annex I of Directive 2012/18/EU, known as 'Seveso III' (Table 1) **[4]**.

Table 1. Classification of ammonium nitrate and qualifying quantities according to Directive 2012/18/EU

Hazardous substances	CAS number	Qualifying quantity (tonnes) for the application of	
		Lower-tier requirements	Upper-tier requirements
1. Ammonium nitrate (see note 13)	---	5,000	10,000
2. Ammonium nitrate (see note 14)	---	1,250	5,000
3. Ammonium nitrate (see note 15)	---	350	2,500
4. Ammonium nitrate (see note 16)	---	10	50
(Note 13) fertilisers capable of self-sustaining decomposition. (Note 14) fertiliser grade. (Note 15) technical grade. (Note 16) 'off-specs' material and fertilisers not fulfilling the detonation test.			

The most significant reported accident, related to ammonium nitrate, occurred in Oppau, Germany, in 1921, resulting in 561 victims, but there have been many more: West (Texas, USA) in 2013 **[5]**, Toulouse (France) in 2001 **[6,7]**, etc.

This article analyses the accident happened between 26 and 31 January 2002 in Escombreras (Cartagena, Spain) in a silo storing ammonium nitrate-based NPK fertiliser, where the phenomenon of self-sustaining decomposition occurred.

2. The intrinsic hazardous properties of ammonium nitrate

AN, with a chemical formula NH_4NO_3, is a colourless salt formed by hygroscopic rhombic crystals. It can appear in five different crystalline forms in a solid state. The density of solid AN is 1.725 g/cm^3 at room temperature. It does not have a true boiling point, as decomposition begins before boiling point is reached. Its melting point is 169.6 °C. It has good solubility (194 g of NA at 20 °C or 405 g of AN at 60 °C in 100 g of water) **[8]**.

AN is stable at room temperature and pressure. In terms of fire hazard, the following information should be kept in mind **[9]**:

- AN does not in itself burn, but acts as an oxidant, enhancing and improving the combustion of combustible material.
- AN melts at a very low temperature (169.6 °C), initiating a complex decomposition, although this occurs with higher intensity from 200 °C. Decomposition initially occurs endothermically and, finally, progresses into exothermic reactions. Decomposition is likely to release significant amounts of toxic fumes containing ammonia and nitrogen oxides. In extreme conditions, the occurrence of explosive reactions, caused thermally or mechanically, cannot be completely ruled out **[10]**.
- AN has a number of incompatibilities that may significantly increase the risk of fire and explosion, and even, in many cases, reduce the temperature at which decomposition occurs **[11]**.

Given these properties, the accident scenarios involving AN and AN-based products can be **[10]**:

- Although the probability of occurrence is very low, there is a risk of detonation for technical-grade ammonium nitrate (more than 28% AN), simple fertilisers and, possibly, compounds containing significant amounts of ammonium nitrate **[12,13]**.
- The process of simple decomposition associated with, for example, a situation of exposure to external fire **[14]**.
- In the case of some AN-based fertilisers (for example NPK-type fertilisers), situations of self-sustaining decomposition have been identified in storage facilities and sea freight **[15,16]**.

3. Ammonium nitrate-related accidents

There have been many ammonium nitrate-related accidents over the last hundred years **[5,17]**, since that of Oppau, Germany in 1921. This one, although not the first, was the most important to date, causing 561 deaths, 1,952 injured and more than 7,500 people to be evacuated **[18]**.

In terms of seriousness, noteworthy are accidents such as those occurred in Tessenderlo (Belgium, 1942, 189 dead and more than 900 injured), Texas City (USA, 1947, 581 dead and more than 4,000 injured), Ryongchŏng (North Korea, 2004, 162 dead and more than 3,000 injured) and Monclova (Mexico, 2007, 37 dead and around 150 injured) **[1,3,5,17,19]**.

Accidents have been identified in which ammonium nitrate was being used for fertilisers **[8,20,21,22]**, making it possible to analyse the seriousness of the consequences based on this use of AN. Two clearly differentiated types of accidents have been identified for fertiliser ammonium nitrate: explosions and self-sustaining decomposition creating a toxic cloud **[10,15,23]**.

In terms of fertiliser use, particularly worthy of note are the explosion-type accidents of Port Neal (USA, 1994, 4 dead and 18 injured) **[24]**, Toulouse (France, 2001, 32 dead and 2442 injured) **[6,7]** and West (Texas, USA, 2013, 15 dead and 200 injured) **[25]**.

Important accidents involving self-sustaining decomposition **[1,21,26]** include, in addition to that of Cartagena (the object of this article), those of Nantes (France, 1987, 24 injured and more than 20,000 evacuated) and Estaca de Bares **[15]** (Spain, aboard the ship Ostedijk, 2007, no reported victims). All these cases involved ammonium nitrate forming part of fertilisers. Table 2 shows other self-sustaining decomposition accidents in recent years **[3,5,21,27]**.

Table 2. Accidents involving the self-sustaining decomposition of ammonium nitrate

Accident	Product	Description	Cause	Damage
The Netherlands (November 1963)	NPK 12-12-12 (4,000 tonnes)	Self-sustaining decomposition with toxic fumes and small fire.	Not established.	Warehouse. No victims.
South Africa (February 1965)	NPK 5-13-5 (450 tonnes)	Decomposition in warehouse containing NPK and ammonium sulphate.	Not established.	Warehouse.
M.V. Sophocles, Atlantic Ocean near the Azores (February 1965)	NPK (5,300 tonnes)	Decomposition of the fertiliser.	Buried electric lamp.	Ship sank. 3 dead.
Norway (April 1965)	NPK 15-4-12 with 2.5% Mg, 0.3% Cu, 3.3%S (100 tonnes)	Self-sustaining decomposition in warehouse with toxic fumes.	Welding work carried out in warehouse.	Warehouse. 2 people affected by smoke.

Austria (December 1966)	NPK 13-13-19	Decomposition in warehouse with toxic fumes.	Overheating due to mechanical fault.	7 dead. 22 affected by smoke.
Germany (December 1966)	NPK 16-11-14 (7,200 tonnes)	Decomposition in warehouse with cloud of nitrous gases.	Not established.	No victims
Norway (July 1968)	NPK	Decomposition due to fire in wooden warehouse, with nitrous gases.	Fire.	Warehouse.
Rhodesia (October 1968)	NPK 9-12-15	Spontaneous decomposition.	Self heating due to low pH.	One person affected by gas inhalation.
France (January 1970)	NPK in sacks	Self-sustaining decomposition with gases.	Chimney in adjoining building.	Children and adults in nearby school affected by gases.
United States (January 1975)	NPK 12-12-12	Decomposition with toxic gases.	Fire caused by machinery in warehouse.	1.000 evacuees. 28 hospitalised. Irritation of eyes.
Germany (June 1975)	NPK (15 tonnes)	Decomposition in warehouse with fumes.	Welding work carried out in warehouse.	1,000 evacuees. 67 people placed under hospital observation.
Finland (March 1978)	Material prone to self-decomposition (70 tonnes)	Decomposition and 100 m-wide cloud of gas that travelled 3–4 km over the sea. Duration of 2 hours.	During the cleaning of drying equipment, decomposition of material close to hot oven.	No victims.
Salzburg, Austria	Fertilisers and	Decomposition	Welding sparks.	No victims

(February 1982)	pesticides (450 tonnes)	due to fire and dispersion of toxic cloud.		(favourable weather conditions).
Ipswich, Suffolk, United Kingdom (October 1982)	Fertilisers (1,380 tonnes) including 35 tonnes of NPK and 150 tonnes of coal.	Toxic cloud of nitrogen oxides and nearby buildings affected by corrosion.	Welding sparks due to safety measures failure in maintenance work.	1,000 evacuees.
Nantes, France (October 1987)	NPK 15-8-22 (1,450 tonnes), NA (750 tonnes) and urea (150 tonnes)	Decomposition of all fertiliser materials with toxic cloud.	Unclear: burning material or electrical fault.	20,000 evacuees. No injuries.
Yugoslavia (September 1988)	NPK (17,000 tonnes)	Decomposition in warehouse with toxic smoke.	Lamp falling from ceiling.	12,000 evacuees.
Lithuania (May 1989)	NPK (20,000 tonnes)	Accident in tank with 7,000 tonnes of ammonia, which caused a fire and decomposition in the warehouses.	Fire in ammonia tank.	7 dead.
Humberside coast, United Kingdom, (October 1993)	NPK (3,000 tonnes)	Slight decomposition, quickly extinguished.	Buried halogen lamp.	No victims.
Valle de Escombreras, Cartagena, Spain **[26]** (January 2002)	NPK 15-15-15 (15,000 tonnes)	Product decomposition in silo. Toxic cloud.	Organic matter in storage silo.	170,000 people confined indoors. Shutdown of industrial activities.

The Netherlands (March 2002)	NPK 12-12-17 (2,500 tonnes)	Decomposition and toxic cloud.	Fire in ship hold due to welding work.	Confinement indoors of population in 1 km radius.
Nazaire, France (September 2002)	NPK 15-12-24 (2,500 tonnes)	Decomposition and toxic cloud.	Fire in ship hold due to a hotspot of unknown origin.	1,000 people confined indoors.
Northwest Coast, Spain (February 2007) **[15]**	NPK (2,627 tonnes)	Decomposition and toxic cloud.	Fire in ship hold due to a hotspot of unknown origin.	No victims.

It can be seen that self-sustaining decomposition-type accidents occur infrequently with, on average, one accident every three years **[21]**.

4. The process of self-sustaining decomposition of ammonium nitrate-based fertilisers

Decomposition processes in NPK-type ammonium nitrate-based fertilisers are possible with the existence of NO_3^-, NH_4^+, H^+ and Cl^- ions, irrespective of their chemical composition **[28]**.

Self-sustaining decomposition is a situation that arises at one point and spreads throughout all the mass of substance. The self-sustaining decomposition mechanism includes two steps: an initial endothermic induction followed by exothermic decomposition **[28]**.

The increase in decomposition temperature and the overcoming of the endothermic step require an external heat source or the exothermic decomposition of surrounding material. In the case of the AN contained in the fertiliser, melting of the material occurs followed by exothermic decomposition into gaseous products **[29]**.

The decomposition mechanism of this type of fertilisers is complex, with endothermic decomposition and material melting beginning at around 190 °C and exothermic decomposition starting at 200-230 °C **[10]**.

Two decomposition mechanisms can be distinguished: catalysed and non-catalysed **[21]**. In the case of non-catalysed decomposition, the reaction steps are the separation of ammonium nitrate into nitric acid and ammonia and the decomposition of the nitric acid into N_2O and N_2.

The catalysed decomposition requires the presence of chloride ions that are not directly consumed in the reaction. If enough heat is released to progress beyond the endothermic phase, the steps of catalysed decomposition are: 1) the formation of nitric acid and hydrochloric acid; 2) a chain reaction producing ions and free radicals; 3) the conversion of potassium nitrate into potassium chloride. The temperature during decomposition must be above 300 °C.

The catalysed reaction is more common in fertilisers, because they contain the chloride ion, which acts as a catalyst in the form of potassium chloride. The catalysed decomposition reaction is as follows:

$$NH_4NO_3 \xrightarrow{Cl^-} NH_3 + HNO_3 \longrightarrow N_2 + H_2O + HNO_3 + NO_x$$

The self-sustaining decomposition begins by spontaneous heating or by an external heat source. In large amounts of fertiliser (remaining unmoved for long time periods), in bulk storage or when transported, the heat accumulates in the entire mass of the substance. The situation gets worse by hot surroundings and by the contaminating presence of organic substances. Examples of external heat sources include hot work, hot surfaces or embers in contact with the material. In some cases, where the fertiliser is highly reactive, only a spark is needed to start the process of self-sustaining decomposition **[28]**. Table 2 shows the initial cause of reported accidents involving this phenomenon.

5. The accident: Valle de Escombreras, Cartagena 2002

During 26 to 31 January 2002, a serious exothermic decomposition-related accident occurred in an NPK fertiliser storage silo of a fertilisers plant operated by the company Fertiberia and located in the "Valle de Escombreras", Murcia, Spain **[26,30,31]**. The press reported the accident and its development over the period in which the decomposition reaction remained active **[32,33]**.

The "Valle de Escombreras" industrial estate is located few kilometres to the east of the city of Cartagena. It is the leading chemical-industrial complex in the Murcia Region (Figure 1), and one of the most important in Spain, alongside those of Tarragona and Huelva. Its activities are focused on oil refining, the storage and distribution of energy products and other products, such as fuel, fertilisers, etc. **[34]**.

Figure 1. Accident location

In the early hours of Saturday, 26 January 2002, an initial-phase fire was identified in one of the company's storage silos, affecting more than 15,000 tonnes of NPK 15-15-15, a fertiliser for direct agricultural use. This is a complex mixture of ammonium nitrate (NH_4NO_3), potassium chloride (KCl) and ammonium phosphate ($NH_4H_2PO_4$) providing equal proportions of the three main nutrients: 15% nitrogen, 15% potassium and 15% phosphorus. Table 3 shows the substances involved in NPK 15-15-15 fertiliser **[26]** and Table 4 its main specifications **[26]**.

Table 3. Substances contained in the composition of NPK 15-15-15 fertiliser

Contained substances	Amount (kg/t)
Anhydrous ammonia	21.60
Potassium chloride	252.50
Monoammonium phosphate	276.10
Ammonium nitrate liquor	299.70
Clay	165.60
Talc (anticaking agent)	8.00
Fuel oil (anticaking agent)	3.00

Table 4. NPK 15-15-15 specifications

Total nitrogen (N)	15%
Nitric nitrogen (N)	5.2%
Ammoniacal nitrogen (N)	9.8%
Total phosphate (P_2O_5)	15%
Phosphorus soluble in neutral ammonium citrate (P_2O_5)	15%
Water-soluble phosphorus (P_2O_5)	13.5%
Total potassium (K_2O)	15%
Particle size	
> 5 mm (maximum)	1.0%
5 to 2 mm (maximum)	93%
2 to 1 mm (maximum)	5.0%
< 1 mm (maximum)	1.0%
Other characteristics	
Maximum moisture	1.5%
Density	1,020 kg/m^3

At the time of the accident, the substance in decomposition (the NPK 15-15-15 fertiliser) had no assigned hazard classification. It was not included in the list of hazardous substances for the transport (IMDG by sea, ADR by road and RID by rail) or in the legislation on the labelling and use of hazardous substances.

The silo (named E-2), where the fertiliser was stored, had a maximum storage capacity of 25,000 tonnes of solid product and dimensions of 130 m long by 33.5 m wide, with a height of 14 m at its tallest point (Figure 2). The ceiling was vaulted and the structure was of concrete **[26]**. The volume occupied by fertiliser was 70 m long, 20 m wide and 10 m high, equivalent to 15,000 tonnes, information consistent with the estimated density of 1,020 kg/m^3 **[31]**.

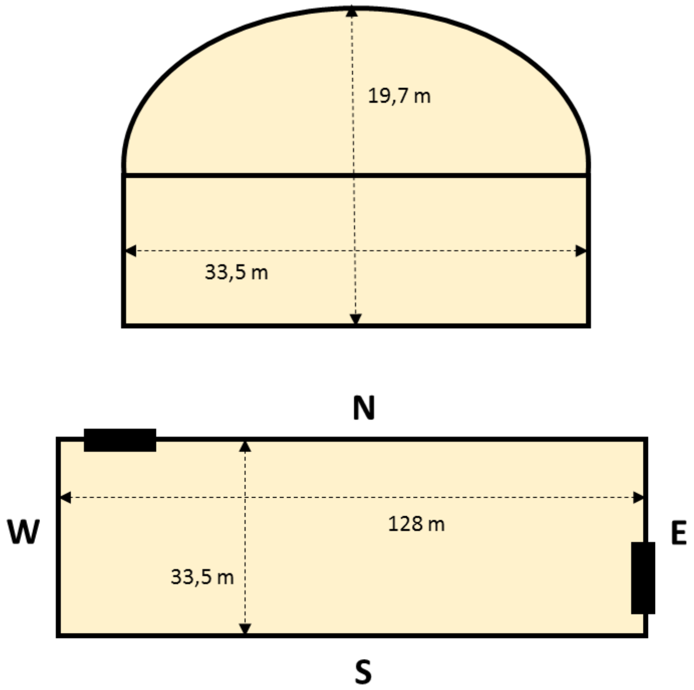

Figure 2. Floor plan and elevation of E-2 silo

Around 9:30 am, the company alerted the Cartagena Fire Brigade and several fire units flocked to the area. The extinction work was focused on cooling the product with abundant water and reducing the smoke inside the silo by opening up holes in the walls and using electric fans. In this way, they attempted to access inside the silo to remove the fertiliser, but it was not possible due to an increase in the smoke volume (Figure 3). A thermal imaging camera showed that the entire mass of fertiliser was at a high temperature: in other words, the combustion was not zonal but generalised to the entire mass of fertiliser **[30]**.

Figure 3. Production of fumes during the accident

Studying a similar accident occurred in Nantes, France, involving NPK 15-8-22-complex fertiliser and other substances such as ammonium nitrate and urea, it can be concluded that the best extinction procedure is to project large amounts of water onto the substance in decomposition, improving the water action with the addition of a small amount of surfactant **[31,36]**.

At the same time, drainages were built to collect the product mixed with water exiting the silo, to prevent its discharge into the sea. The access points to the building were blocked with land dams and metal sheets to ensure that all the product was wetted.

The whitish appearance of the gases emitted was due, fundamentally, to the emission of water vapour and suspended particles of the fertiliser itself and of ammonium chloride **[10,26,27]**.

In the early morning of 27 January, the lack of wind implied that the cloud expanded entirely, covering the “Valle de Escombreras” and reaching Cartagena city centre (Figure 4). This led to the order for the evacuation of the companies staff and the implementation of measures to safeguard their premises **[35,37]**.

In the morning, the wind direction swung 180°, moving towards the sea. The situation remained until the evening, when it again turned 180°. No changes in direction occurred during the early morning, and the formation of mist and banks of fog diluted a large part of the cloud.

During 27 January, holes were opened up in the walls of the silo, allowing the release of the gases. Removal of the material begun (200 tonnes) but was suspended due to the lack of visibility. It was decided to continue with the strategy of wetting with large amounts of water (up to 30,000 L/min), leading to the outflow of large amounts of sludge to the exterior, which was contained in the different drainages built for this purpose.

On 28 January watering and sludge containment operations were continued, whilst particularly important neighbouring companies were granted access **[35,37]**.

The wind direction during 28 January remained north-northwestern, carrying the cloud to the sea until the early hours of the afternoon, when it was once again blown inland. At this time, some reduction in the cloud's intensity was observed, which, combined with the absence of northern winds, meant that neighbouring towns and villages were not further affected.

From 6:00 pm onwards on 29 January, a significant decrease was observed in the amount, intensity and pressure of the column of fumes coming from the silo. In these conditions, holes were made to inject directly water and to provide access for heavy machinery to remove product from inside the silo.

From 12:00 noon on 30 January, heavy machinery could gain access to remove the material, supported by water jets. Later, a number of wheel loaders and 10 trucks began to remove product from the silo. The amount of fumes coming from the combustion was greatly reduced, and the decomposition process was deemed ended at around 5:30 pm **[35,37]**.

Once the accident was under control, it was noted that the amount of product stored had been significantly reduced (from a height of around 10 m to less than 2.5 m). The resulting product was mostly sludge, with some balls of matter arising from the decomposition and some melted product **[26]**.

6. The causes of the accident

Ammonium nitrate, the main constituent of NPK 15-15-15 fertiliser, is an oxidant that shows accelerated exothermic decomposition from certain temperature. This behaviour may even be explosive when the nitrogen concentration exceeds 28%. Studies on the pure substance show that the temperature required for the occurrence of this phenomenon is around 175–200 °C **[38]**.

From this temperature, in a few months, localised ammonium nitrate decomposition can develop, increasing the temperature and producing the phenomenon of self-sustaining decomposition of the rest of the stored fertiliser, up to the point the accident was detected on 26 January 2002.

The studies of the accident have pointed to an external heat source as the trigger, although it was not possible to establish a conclusive cause-effect relationship. From the analysed situations (fire, lamp buried in the pile of fertiliser, radiation of any kind, electrical faults, etc.), there is only some evidence of the possible presence of decomposing organic matter (such as a dead animal) that could have acted as a trigger **[8]**, something that would have been fostered by the pressure of the stacked product **[26]**. Self-sustaining decomposition caused by a hypothetical heat source was not expected given the inherent characteristics of the fertiliser in question. However, looking at the ternary diagram for self-sustaining decomposition for fertilisers with a mix of ammonium nitrate, ammonium phosphate and potassium chloride (Figure 5) **[39]**, it can be seen that NPK 15-15-15 fertiliser appears at the outer limit of the decomposition area (the point close to 1-1-1). This fact would mean that any small variation in the proportions of ammonium phosphate or potassium chloride would bring it to an area of possible self-sustaining decomposition.

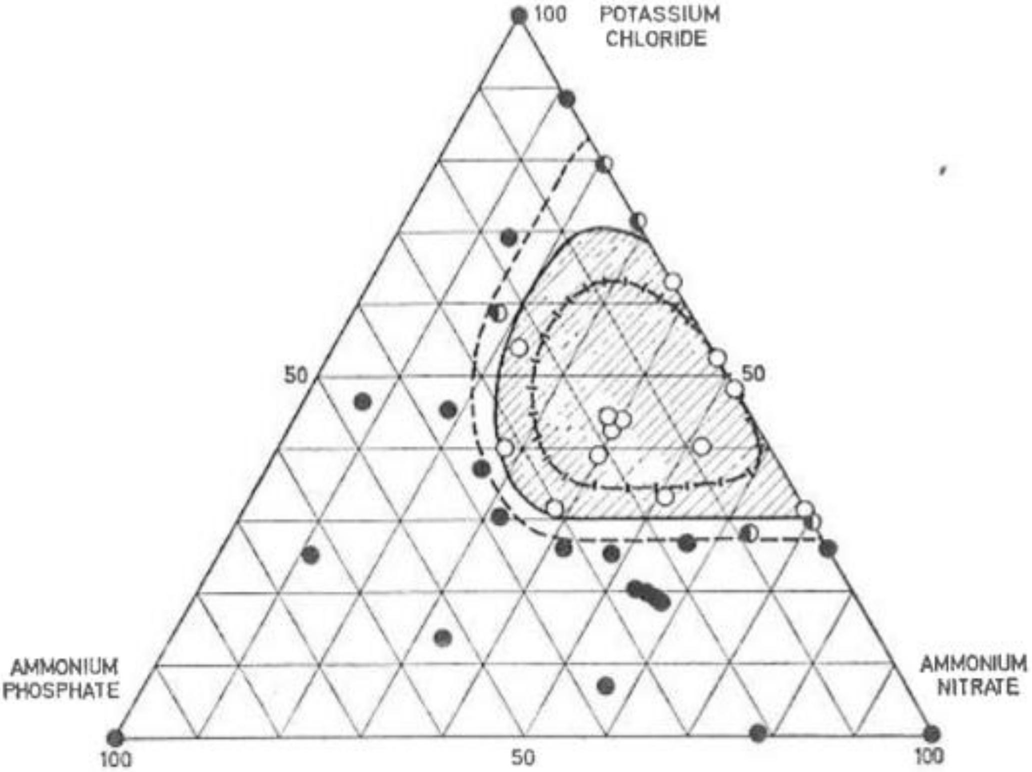

Figure 5. Ternary diagram of self-sustaining decomposition for ammonium nitrate, ammonium phosphate and potassium chloride-mix fertilisers **[39]**.

There are also other factors that, whilst not the direct cause of the accident, could favour its occurrence **[26,31]**. Figure 6 shows a fault tree diagram of the accident, with the possible events occurring from the beginning to the final accident, including the propagation ways.

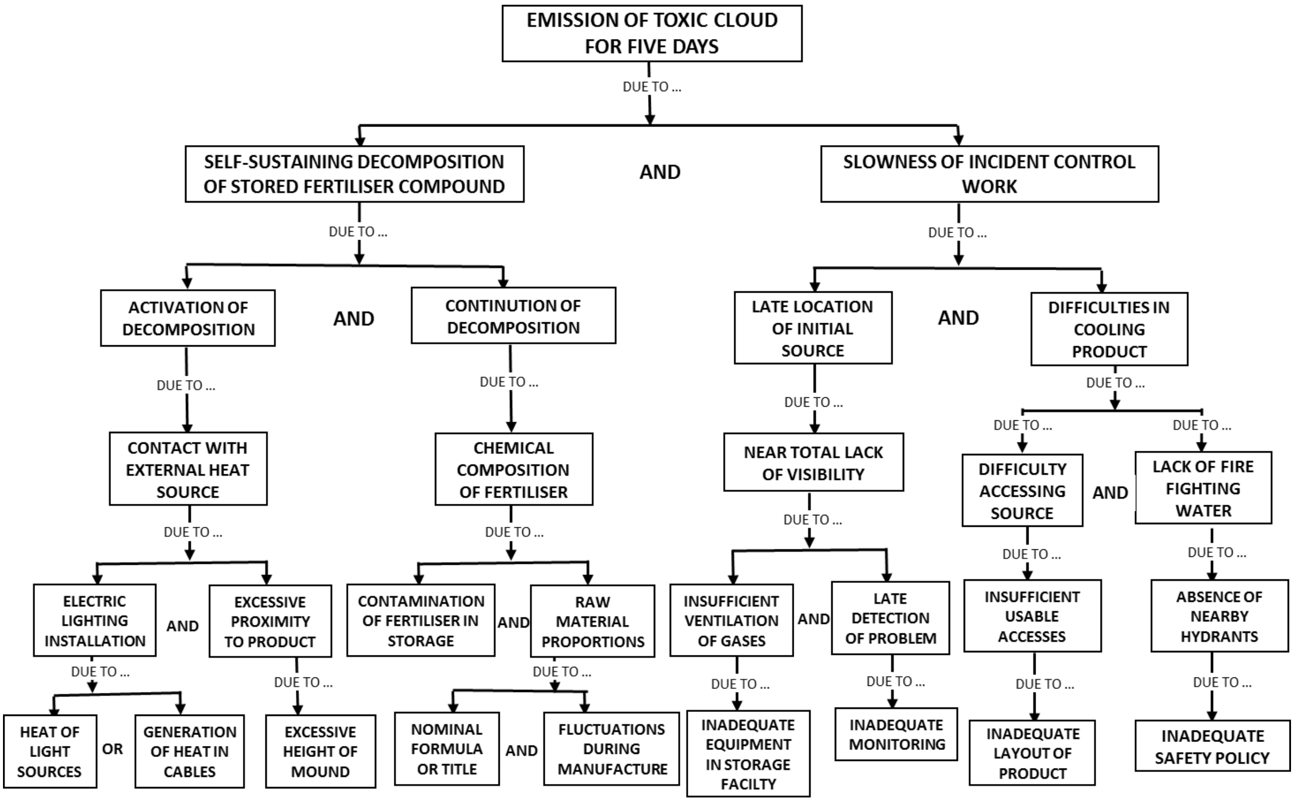

Figure 6. Accident fault tree.

The storage, in a single pile, of around 15,000 tonnes of product is a figure greatly in excess of the amounts normally collected in a single pile at industrial level (4,000 tonnes at most) **[8]**. With such a volume, any self-sustaining exothermic reaction behaves adiabatically, accumulating heat at the point where it takes place and therefore increasing the temperature at this point **[40]**.

Additionally, the estimated height of the pile, around 10 metres, was much higher than the recommended values for this type of products **[8]**. This situation significantly diminishes the system's ability to dissipate heat by conduction and convection, favouring a localised increase of temperature. Furthermore, it seems that the product remained piled in place for months, with no movement or turnover due to additions or removals **[26,35]**. This meant that there was sufficient time for any exothermic reaction to take place **[40]**.

It is important to note that the listed aspects (large volume and height and low turnover) are identified as risk factors by different manuals and technical guides on the handling of unstable or oxidising substances, which include fertilisers **[8, 27, 40, 41]**.

In this way, it must be added that the large amount of fertilizer masks a possible decomposition reaction and this is not detected until the gases start to come out. In addition, since the thermal conductivity of the fertilizer is very low, an increase in temperature relatively far from the decomposition point and in the air is not detected either. With all these conditions, an attempt has been made to model the transmission of the heat generated by decomposition through the fertilizer bulk.

As far as we have been able to ascertain, there are no exact and concrete data on the conditions and reasons why the decomposition of the fertilizer occurred. In addition, some physical and chemical properties of the fertilizer are unknown and also the data concerning many of the decomposition reactions. Therefore, it is not easy to model how heat transmission occurred from the point where the decomposition began to the rest of the fertilizer. However, we will try to do some approach to explain the temperature gradient and the relatively low air temperature.

Assuming that all the nitrogen contained in the fertilizer has been transformed into NO_2, the amount of decomposed fertilizer can be calculated. As discussed in section 7, it can be estimated that the rate of generation of NO_2 was 2.16 kg/s. With this data and the molecular weight of NO_2, the rate of disappearance of nitrogen from the fertilizer can be calculated and, knowing that the fertilizer has a total of 15% nitrogen (Table 4), the rate of decomposition of the fertilizer can be calculated, according to equation (1).

$$2.16\frac{kg\ NO_2}{s} \times \frac{14\ kg\ N}{46\ kg\ NO_2} \times \frac{100\ kg\ F}{15\ kg\ N} = 4.38\frac{kg\ F}{s} \qquad (1)$$

Taking into account that the accident lasted practically 5 days (120 h), the total amount of decomposed fertilizer is estimted from equation 2.

$$4.38\frac{kg\ F}{s} \times 120\ h \times \frac{3600\ s}{1\ h} = 1892160\ kg\ F \qquad (2)$$

Therefore, approximately 1,900 t of fertilizer were decomposed, representing 13% of the total (15,000 t) of fertilizer stored.

Of all the compounds that constitute the fertilizer, as far as we have been able to find out, only decomposition data of NH_4NO_3 (AN) have been found, according to the reaction:

$$NH_4NO_3 \rightarrow N_2O + 2\ H_2O \qquad (3)$$

This reaction occurs from 200 °C and is accompanied by a heat release of 122 kJ / mol.

As only data of this type have been found for the AN, calculations have been made from that component. Keep in mind that the objective is not to obtain a totally quantitative result, which is not possible from the data available, but to have an estimate of how heat is transmitted and how the low thermal conductivity of the fertilizer makes it the transmission of heat through it is not very effective. Hence, no high temperatures in the air were detected.

As in the fertilizer, according to Table 3, there are 299.7 kg of AN per 1000 kg of fertilizer, if 4.38 kg F/s are decomposed, the amount of decomposed AN will be 1.31 kg/s. Therefore, the heat evolved, taking into account the reaction (2), the heat of reaction and the molecular weight of the AN (80 g/mol), will be 2003 kJ/s. This would correspond only to the decomposition of the AN to give N_2O but, in turn, it is very possible that the N_2O will continue oxidizing to give NO_2. Also the other components of the fertilizer would be decomposing, or at least a large part of them. Therefore, and in a very simple first approximation, it could be said that, if the AN only represents 30% of the fertilizer, the total heat given off by the decomposition of all the fertilizer could be 3.3 times greater, that is, it would be approximately 7000 kJ/s.

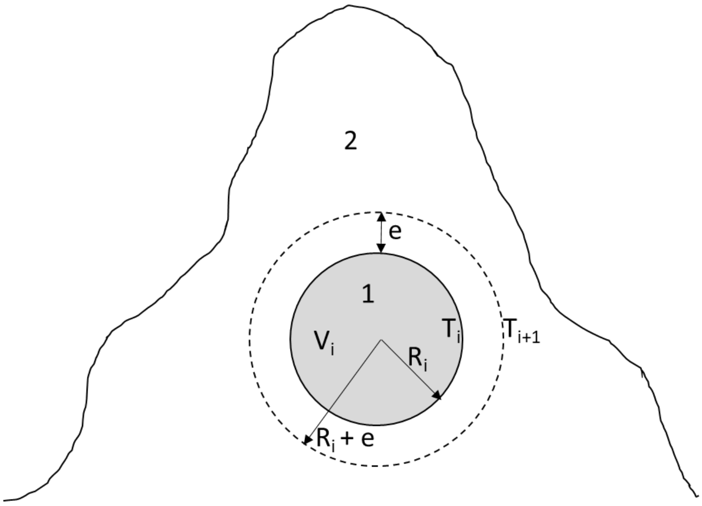

Figure 7. Evolution of the decomposed volume of fertilizer. 1 = Decomposed fertilizer. 2 = Bulk of fertilizer. e = Distance from the external area of decomposed fertilizer. R_i = Radius of the sphere corresponding to decomposed fertilizer. T_i = Temperature of reaction (200 °C). T_{i+1} = Temperature at distance e from the external area of decomposed fertilizer. V_i = volume of decomposed fertilizer.

From here, it is possible to relate heat transmitted through the fertilizer bulk with the gradient of temperature and thickness or distance to the point where the decomposition reaction originated. As logical, it is assumed that heat transfer through the fertilizer bulk occurs by conduction. The mathematical and theoretical basis on heat transfer by conduction can be found in any book on fundamentals in Chemical Engineering [49,50]. To do this, a type of geometry is supposed and, in this case, spherical geometry has been chosen. A spherical model has been used to explain the heat transfer because it is assumed that the decomposition reaction begins at a point and, from that point focus, the heat is transferred radially. It is the assumption that seemed more logical, given that the reaction occurs within the fertilizer. That is, it is assumed that the reaction zone has a spherical shape and that this sphere increases as the fertilizer decomposes (see Figure 7). The volume (V_i) of the sphere corresponding to the amount of decomposed fertilizer can be calculated from the rate of disappearance of the fertilizer (4.38 kg/s), divided by the density of fertilizer (1020 kg/m^3) and multiplied by the time of reaction. Obviously, it is assumed that the spherical shape is maintained. As an example, some values are shown in Table 5.

Table 5. Results for the estimation of volume reacted and gradients of temperature. Nomenclature is the same than in Figure 7. Some aparametrshave been added: A_i = External area of the sphere of volume V_i. A_{i+1} = External area of the sphere of radius R_i + e. A_m = Average of the areas A_i and A_{i+1}. I = Average radiation intensity for the areas A_i and A_{i+1}.

t (min)	V_i (m^3)	e (m)	R_i (m)	R_i + e (m)	A_i (m^2)	A_{i+1} (m^2)	A_m (m^2)	I (J/(s.m^2))	T_i (ºC)	T_{i+1} (ºC)
60	15.5	1.84E-04	1.55	1.55	30.02	30.03	30.03	233134	200	20
120	30.9	2.92E-04	1.95	1.95	47.66	47.67	47.66	146861	200	20
600	155	8.52E-04	3.33	3.33	139.35	139.42	139.39	50220	200	20
1440	371	1.53E-03	4.46	4.46	249.79	249.97	249.88	28013	200	20
2880	742	2.43E-03	5.62	5.62	396.52	396.87	396.69	17646	200	20
4320	1114	3.18E-03	6.43	6.43	519.59	520.11	519.85	13465	200	20
5760	1485	3.85E-03	7.08	7.08	629.44	630.13	629.78	11115	200	20
7200	1856	4.47E-03	7.62	7.63	730.40	731.26	730.83	9578	200	20

From a certain volume of decomposition, the temperature gradient can be calculated knowing the intensity of radiation that is transmitted through the fertilizer bulk, coming from the area that is reacting, and which is given by equation (4).

$$I = (T_i - T_{i+1}) \cdot \frac{k}{e} \qquad (4)$$

The parameters of eq. (4) are the indicated in Figure 7 andd Table 5. k is the thermal conductivity of the fertilizer. As there are no other data of this parameter, the thermal conductivity of the AN has been taken, which, according to the International Fertilizer Industry Association, is 0.238 J/(s.m.°C). From a volume of decomposed fertilizer V_i, the temperature gradient can be calculated according to equation (4). Thus, T_i is the decomposition temperature (200 °C) and the temperature at which the volume V_i is. It is assumed that T_i remains constant. The temperature gradient is calculated from the surface of V_i. Therefore, assuming a thickness e, by means of the equation (4) T_{i+1} can be calculated or vice versa, assuming T_{i+1}, e can be calculated, that is, the distance necessary for the temperature decrease from T_i to T_{i+1}. The obtained values are shown in Table 5. The calculation process is now detailed. For a value of Vi, the radius Ri of that sphere is calculated ($V = 4/3\pi R^3$) and, known Ri, the external area Ai ($Ai = 4\pi R_i^2$) is calculated. The temperature inside the sphere of radius R_i is the reaction temperature (200 °C) and we want to know at what distance the temperature will have dropped to 20 °C. Then we assume a value of e and we have $R_{i+1} = R_i + e$. Thus, we can calculate A_{i+1} ($A_{i+1} = 4\pi(R_i+e)^2$). Since the flow rate of heat released by the reaction (7000 kJ/s) is known, the radiation intensity can be calculated as $I = Q/A_m$.

This mean value of I is replaced in equation (4), along with T_i (200 °C) and k, and then values of e are assumed and iterated until T_{i+1} equals 20 °C, which was the fixed temperature. This gives the distance to V_i for which the temperature will have dropped to 20 °C. As can be seen, the temperature drops rapidly from 200 to 20 °C in a very small distance (e), which in most cases is lowere than 5 mm. This is due to the fact that the thermal conductivity of the fertilizer is very small and, therefore, the transmission of heat by conduction is not good. It would also explain that the temperatures detected in the air were not high, also due to that bad transmission of heat that causes the outermost layers of the fertilizer to be at temperatures very close to the ambient temperature.

7. Dispersion modelling

With the aim of reproducing the facts observed consequence estimation models have been used. It needs to be stressed the fact that the event lasted for several days, therefore, the conditions of the source term as well as those from the environment have surely changed during this time. For this reason, the final aim of this simulation is not to fully reproduce the event from a dynamic point of view, but to define the scenario which could reasonably helped to anticipate the necessary emergency response.

The first factor to determine is the release rate of NOx. Considering the decomposition model mentioned above and the facts observed during the event in terms of amount involved and duration, it has been estimated that a reasonable average release rate would be 2.16 kg/s of NOx and for calculation purposes, all NOx has been considered as NO_2.

Even if the release rate is clearly a very important parameter, from the observed facts it is also clear that the gases released had a clear buoyant behaviour due to their temperature. For this reason, a plume rise model has been used to determine the maximum height that dispersion would achieve as a function of its temperature.

$$z = z_o + C_o Q_h^{C_1} x^{C_2} {U_w}^{C_3} \qquad (5)$$

Where:

- z is the effective release height (m)
- z_0 is the physical release height (m)
- Δz is the plume rise (m)
- C_0, C_1, C_2 and C_3 are constants obtained based on experimental data and theoretical considerations. In this case the values given by Briggs [45], [46], [47] have been used
- $C_0 = 1.6$
- $C_1 = 1/3$
- $C_2 = 2/3$
- $C_3 = -1$
- Q_h is the rate at which buoyancy is added
- x is the downwind distance and
- U_w is the wind speed

The results on the application of this model and the detailed calculations related with equations of state and properties of the substances considered have been obtained as implemented in the in the Process Safety Office 8.1 package from ioMosaic Corporation [44].

Results are shown in Figure 8. It can be seen how for values below 160ºC in terms of gas temperature, there is no significant plume rise effect, above this temperature a leap is observed in results and a calculations have been done at smaller temperature increase values. In this case, model input parameters are shown in Table PY1. As can be seen in the referenced table, the input parameters are defined to minimise the momentum effect so that the plume rise is almost exclusively influenced by the buoyancy factor.

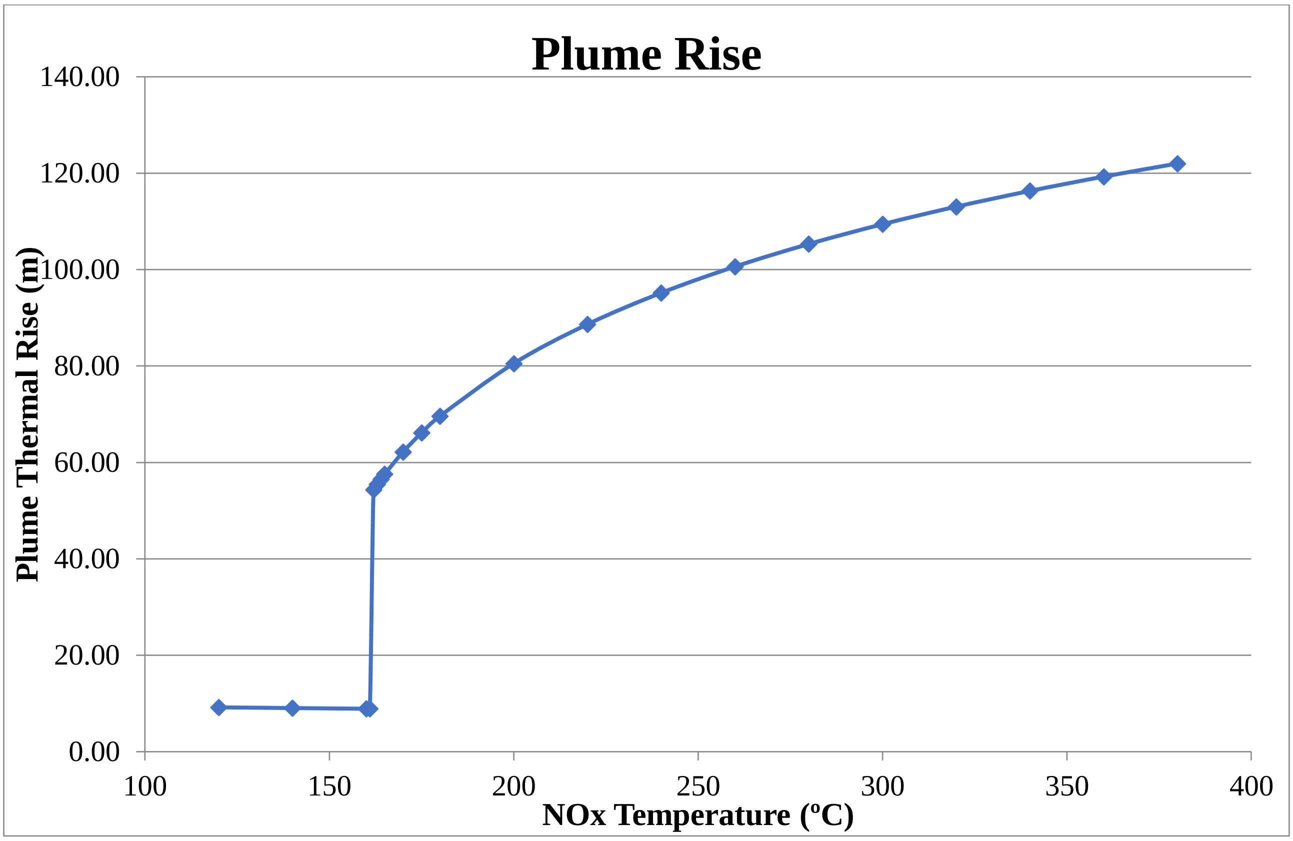

Figure 8. Plume thermal rise as a function of gas temperature.

Considering the result of the plume rise modelling, the dispersion has been simulated assuming a source height between 20 and 70 m. All other relevant parameters have are shown in Table PY02. Concentrations as a function of distance and source term height are summarised in the figure 9.

The dispersion has been modelled by a Gaussian Puff implemented in the in the Process Safety Office 8.1 package from ioMosaic Corporation [44]. This model has been selected since the release duration in this case is much longer than the downwind travel time and considers the integration defined by Petersen [46] to the Gaussian dispersion which is summarised in the following equation:

$$C(x,y,z,t) = \int_0^t G(x,y,z,t-t^*)dt^* \qquad (6)$$

The Gaussian puff considers the effect of all smaller Gaussian puffs defined by the traditional Gaussian equation:

$$G(x,y,z,t-t^*) = \frac{M(t^*)}{2\Pi^{3/2}\sigma_x\sigma_y\sigma_z} \cdot exp\left[-\frac{1}{2}\left(\frac{x-u(t-t^*)}{\sigma_x}\right)^2\right] \cdot exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \cdot \left[exp\left(-\frac{1}{2}\left[\frac{z-H}{\sigma_z}\right]^2\right) + exp\left(-\frac{1}{2}\left[\frac{z+H}{\sigma_z}\right]^2\right)\right] \qquad (7)$$

Next figure shows the dispersion concentration results in a receptor position in the centre axis downwind of the source term as a function of distance and effective dispersion height.

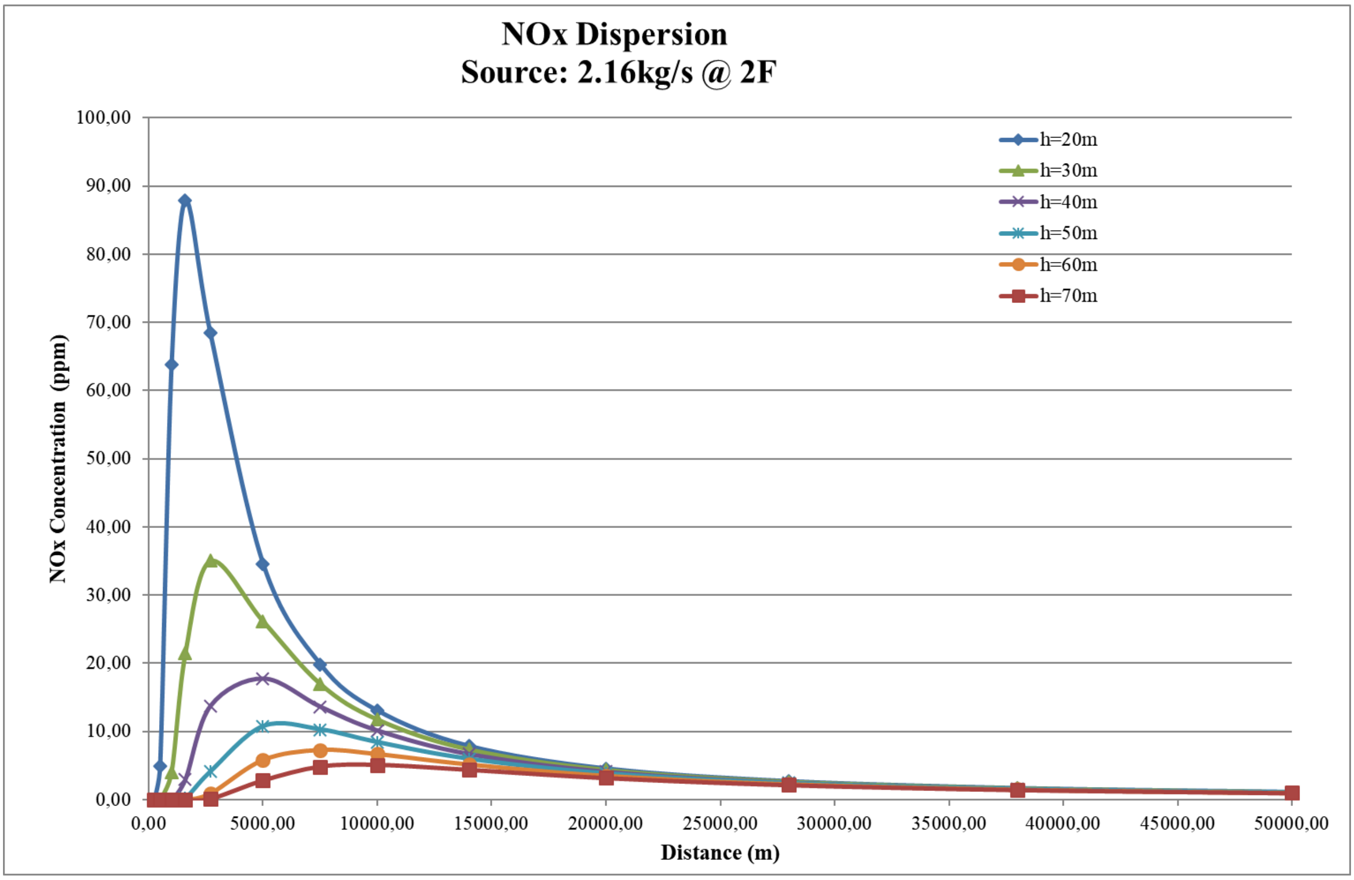

Figure 9. NOx dispersion results.

As it can be seen, the source height has a clear effect in distances close to the release point, but as far distances are considered the concentrations are almost the same. As well, as the height of the source increases, the distance from the release at which no NOx concentration is expected increases.

If the buoyancy caused by the temperature of the gases is high enough, no high concentrations are expected at ground level and they are low enough to prevent acute effects, but still high enough to cause discomfort or other reversible non-disabling effects.

The purpose of consequence modelling in accidents is basically aimed to check if, with reasonable justified, assumptions, the models available can reproduce the consequences observed. In this case this is considered to be proven, since, taking the worst reasonable conditions and considering the application of a sequence of dispersion model defined by the Plume Rise and Gaussian Puff, the results obtained help to justify the fact that no significant toxic effects were observed in the population nearby.

Calculation under other atmospheric conditions is not shown as it has not been systematically assessed, but results were in line with the fact that higher wind speeds and less stable atmospheric conditions were leading to even lower concentrations as a function of distance.

8. The consequences of the accident

According to Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances (SEVESO III), after an accident, the operators (*Article 16. Information to be supplied by the operator and actions to be taken following a major accident*) and the Member States (*Article 18. Information to be supplied by the Member States following a major accident*) shall inform the European Commission **[42]**. All this information is collated in the MARS (Major Accident Reporting System) database **[43]**.

The following information has been extracted from the consultation on the accident according to the consequences reported to the competent authority **[43]**: five members of the local population were affected by eyes irritation, conjunctivitis or allergic skin reaction; 24 members of the response team received hospital treatment for minor complaints and employees in the area suffered eyes irritation and throat. It was also registered that they were affected approximately 50 people from the establishment itself, 130 people from the different emergency services and 3,500 people from the population.

The cloud produced by the decomposition affected Cartagena, a city of around 200,000 inhabitants, compelling the confinement of the susceptible population. Additionally, activities at the Valle de Escombreras industrial estate were paralysed and all the companies were ordered to evacuate. This situation remained in place for more than 24 hours, from the early morning of 27 January until the afternoon/evening of 28 January, when the situation was normalised **[37]**.

No noteworthy environmental impact occurred, despite an increase in the concentration percentages of the gasses emitted from the fertiliser's decomposition **[26,30]**. The water containment drainages, containing rests of fertiliser and products of its chemical decomposition, prevented their uncontrolled discharge and therefore any contamination of the marine environment. The earth used to contain the runoff water was treated as waste by an authorised waste management agency, together with the sludge retained and that formed by the drying of the water, as well as the product removed from the silo and transported by truck. Figure 10 shows the residual product remaining after the accident inside the silo.

Figure 10. The silo after the accident.

9. Learned lessons: Prevention, control and mitigation measures

Analysis of the accident concludes that it probably occurred due to contamination of the fertiliser stored in the silo, facilitated by some industrial malpractice in caring for this kind of stored material. Based on this analysis, a series of prevention measures can be established avoiding incidents of this kind. The following generic measures are specified for ammonium nitrate and derivatives such as fertilisers **[4,5,8,20,26,41]**:

- Store ammonium nitrate in a space that is not shared with other products.
- Warehouses and buildings must be well ventilated and built with fireproof materials.
- It is very important to clean the spaces before storing the ammonium nitrate.
- Any possible spillages must be quickly removed and cleaned to prevent the ammonium nitrate compacting on the floor and coming into contact with oils or other spilled liquids.
- Bulk storage facilities (silos) must be protected with tarpaulins to prevent humidity.

- Avoid holes, gratings, drains, conduits, etc., where ammonium nitrate can be retained. If they exist, the ammonium nitrate entering into them must be prevented and they must be regularly cleaned.
- Storage must be located away from any possible sources of heat, fire or explosion, such as fuel stores or gas pipes.
- Electrical installations must not be in contact with the stored material. Electrical panels must be located outside of the storage area.
- Regular inspections of the installations must be performed, including control of animals and pests that may affect the product.
- The no smoking rule must be followed.
- The competent authority must be informed that ammonium nitrate is being stored.
- Water has to be guaranteed to deal with an incident.
- Staff must receive training on the risks of the material and the procedures to follow in the case of an incident, including those risks associated with the high toxicity of the fumes produced,.
- Consider the possibility of installing a fire detection system and sprinklers.
- Handling equipment must be made of fireproof material and must be regularly checked for oil and fuel leaks.
- Clean loading and unloading equipment before and after use with other products.
- Loading and unloading material is not recommended on rainy days.

Additionally, in the case of an ammonium nitrate decomposition accident scenario, the protection and mitigation measures to take would be the following **[4,5,8,34,37]**:

- Immediately inform the fire brigade of the accident, indicating its characteristics, the substances involved and their quantities, all those possibly affected by the incident and the affected establishment’s own resources.
- Avoid breathing in any gases or fumes generated, due to their toxic and irritant nature. Use breathing apparatus if you have inhaled fumes.
- Keep the staff of the establishment itself and/or neighbouring establishments confined.
- Access to the accident area must be restricted and the proper measures have to be taken with regard to the possible affected population, based on the forecast movement of the contaminant cloud.
- Use abundant water. If the decomposing fertiliser is bulk stored, spray pressurised water onto the decomposition point.
- Prevent contamination of the fertiliser by any combustible, oxidising or highly reactive material.

10. Conclusions

The analysis of the accident shows that its root causes are related to human errors. These focus basically on four aspects:

- Excessive amount stored and without removing.
- Late detection of the problem.
- Not optimal storage conditions.
- Insufficient and / or inadequate means of protection.

In addition, radiation studies indicate that, given the low thermal conductivity of the fertilizer, the temperature drops rapidly, in less than 5 mm, from 200 to 20 ºC.

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Table PY1. Input variables for Plume Rise model

Variable	Units	Value(s)	Comments
Release temperature	ºC	120, 140, 160, 161, 162, 163, 164, 165, 170, 175, 180, 200, 220, 240, 260, 280, 300, 320, 340, 360, 380	A range of values has been considered due to uncertainty on current conditions during the accident.
Release velocity	m/s	0.5	Low value considered due to natural release considitions
Release diameter	m	12	Value defined by considering the large opening on the incedent location

Table PY2. Input variables for Gaussian Puff model

Variable	Units	Value(s)	Comments

Receptor height	m	1.5	
Source height	m	20, 30, 40, 50, 60, 70	
Wind speed	m/s	2	most of the time the atmosphere was stable and the windspeed low
Pasquill stability class		F	
Release rate	kg/s	2.16	
Release duration	h	24	The duration is not relevant once the dispersion achieves stationary state
Composition	-	NO_2	