Nep J Environ Sci (2022), 10(2), 59-66
https://doi.org/10.3126/njes.v10i2.43449
ISSN 2350-8647 (Print) 2542-2901 (Online)

Review Article

Physical and chemical analysis of Beirut Ammonium Nitrate Blast: A concern of status of particulate matter in atmosphere

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(***Received***: 26 February 2022; ***Revised***: 30 December 2022; ***Accepted***: 31 December 2022)

Abstract
Chemical disasters are caused by improper management, handling, transportation, and sudden accidents. The massive explosion of ammonium nitrate silo in the port of Beirut on August 4, 2020, has threatened the world with the loss of 220 people, about 6500 injuries, huge property loss, and environmental contamination. This paper aims to summarize the major ammonium nitrate accidents in the past 100 years in the world. We analyzed the accidents in terms of frequency, causes, property loss, and deaths. We reported 43 accidents in which 7 accidents triggered more than 100 casualties. Altogether seven terrorist attacks with ammonium nitrate are reported leading to the death of 411 people and huge loss of assets. The explosion releases a large amount of energy and produces a variety of gases along with nitrogen oxides, ammonia, and a lot of particulate matter (PM), which significantly contributes to air pollution. The size and amount of PM imposes negative impact on environment like low visibility, decreased solar radiation and adverse health impacts like chronic respiratory, pulmonary, cardiovascular, and other human diseases. Proper management and safety measures with stringent regulations at national and international level is warranted for the safe and sustainable use of industrial chemicals.

Keywords: Ammonium nitrate (AN), atmospheric degradation, explosion, particulate matter(PM)

Introduction
One of the most tragic and devastating explosions in history took place in the capital city of Lebanon, Beirut on August 4, 2020 (Fig. 1). The uncontrolled blast of about 2750 tons of Ammonium Nitrate (AN) caused a death of 220 people and more than 6500 injuries instantaneously (Al-Hajj et al., 2021). The massive explosion in the Beirut port, which was followed by the COVID-19 pandemic, was one of the main causes of the collapse of the Lebanese economy. The damage of the port hampered the proper import/export of commodities and constrained access to and sales of goods leading to an economic crisis (Hajjar et al., 2021). The accidental explosion was analyzed on the basis of seismological, hydroacoustic, infrasonic, and radar remote sensing data to estimate and characterize the explosion yield (Pilger et al., 2021). The explosion produced a large amount of particulate matter (PM) that remains suspended for long in the atmosphere. The major composition of those PM may contain a complex mixture of organic as well as inorganic particles suspended in air. Besides this, a large amount of SOx, NOx, NH_4^+ and COx compounds and black carbon emission can be expected to be deposited in the air due to the explosion .

The particles released from combustion basically contain fine particles in the size range of 2.5 micron or less and are called PM 2.5 particles. Higher exposure to ammonium (NH_4^+) ions from PM 2.5 particulate matter during pregnancy is associated with decreased maternal serum free thyroxin (fT4) levels and reduced birth weight Z score ($p < 0.05$) (Wang et al., 2019).They can easily spread into the alveolar region of the lung which causes different health hazards related to respiration like chronic respiratory, pulmonary, cardiovascular, and other human diseases (Li et al., 2020). It also affects the climate system due to the formation of haze which not only reduces the visibility but also affects the economic activities.

Ammonium nitrate [CAS 6484-52-2], NH_4NO_3 (AN), is one of the important chemicals widely used in propellants, fertilizer, and civil explosives (Babrauskas & Leggett, 2020). The challenges of safety for the handling of AN and its derivatives in production, storage, and transportation has attracted global concerns many years ago (Xu et al., 2019). It can commence spontaneous explosion due to minor pitfalls in the handling of whether in the storage, workplace, transportation, and disposal, leading to serious risk to the life, environment, and property. Ammonium nitrate undergoes spontaneous explosions when it gets in contact with pyrites ($Fe^{II}S_2$) or high temperatures referred to as "reactive ground" and "hot ground" respectively (Djerdjev et al., 2018). The practice of anodyne management and deliberate detonation of this chemical is necessary for the viable development of chemical industries.

Pure AN (molecular weight = 80.6) is a colorless, crystalline, and hygroscopic salt that does not form hydrates. It is soluble in water, alcohol, acetic acid, nitric acid, and ammonia. Although AN is relatively stable (melting point = 169.6℃), the presence of contaminants like organic acids, oils, pyrites, salts, etc. which are mixed

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in the process of its production, storage transport catalyzes the auto-ignition, decomposition, and explosion (Chaturvedi & Dave, 2013). Because of the limited experimental evidence and robust validation, there is no data in the literature on the mechanism of the reaction and intermediate products formed during combustion as well as thermal decomposition of the compound (Babrauskas & Leggett, 2020). Decomposition of AN liberates a large quantity of heat with toxic gases like ammonia and oxides of nitrogen. These oxides of nitrogen support combustion even in the absence of other sources of oxygen. The gases confined at high pressure and temperature increase the rate of decomposition and cause explosions. When the stockpile of AN gets a fire or over heated, it may melt and produce more shock-sensitive materials. A large quantity of AN at high temperature and pressure may be at confined in small volumes can start gigantic explosions (US EPA, 2015).

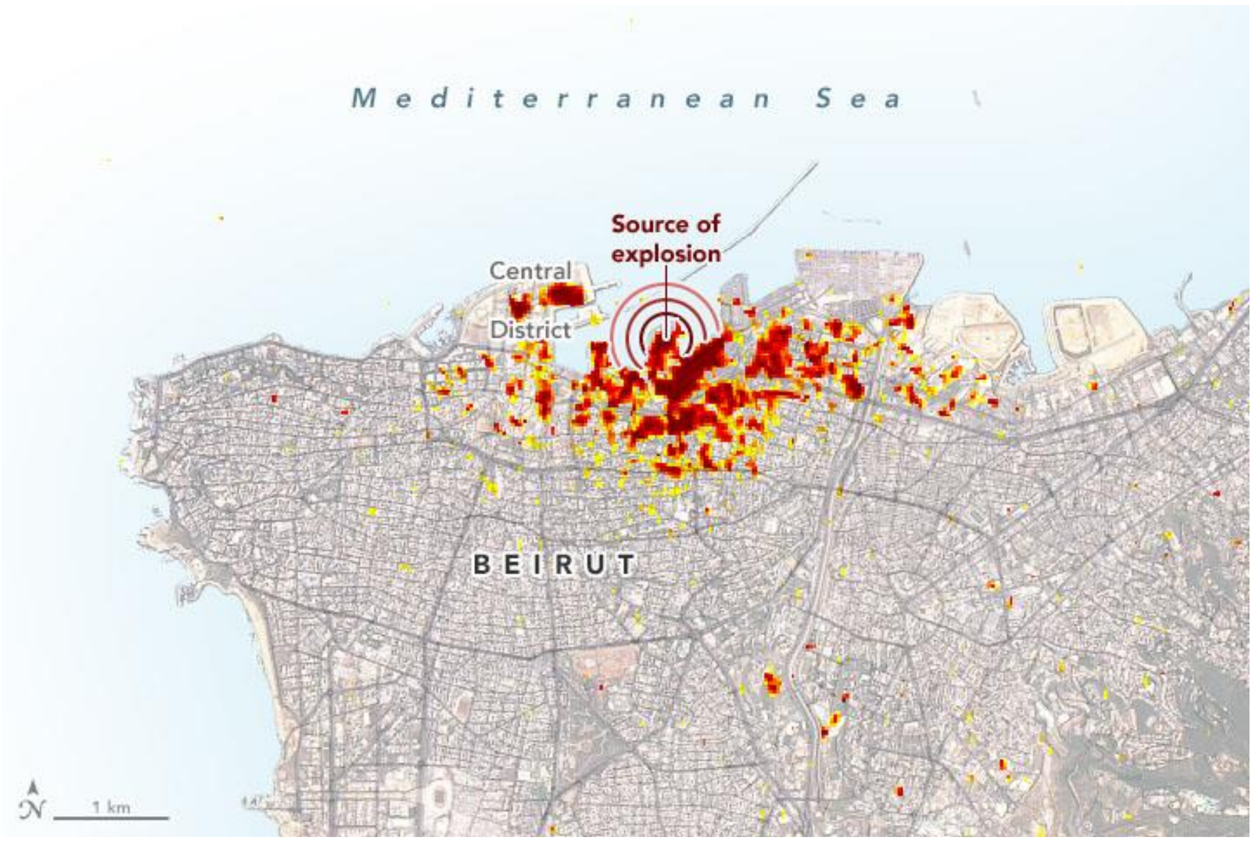

Figure 1 A proxy map created by scientists affiliated with NASA's Advanced Rapid Imaging and Analysis (ARIA) team and the Earth Observatory of Singapore (EOS). Dark red pixels represent the most severe damage, while orange and yellow areas are moderately or partially damaged. Each colored pixel represents an area of 30 meters by 30 meters *(Source: https://eoimages.gsfc.nasa.gov/images/imagerecords/147000/147098/beirut_aria_2020218.jpg)*

The thermolysis of AN greatly depends on the different factors like pressure, temperature, sample size, state, heating rate, presence of contaminants, etc. The reaction is so greatly influenced by circumstances that an endothermic reaction may convert into exothermic and vice versa. On gradual heating, the reversible decomposition of melted AN occurs as:

$$\underset{(l)}{NH_4NO_3} \longleftrightarrow \underset{(g)}{NH_3} + \underset{(g)}{HNO_3} \quad (\Delta H = 176\ kJmol^{-1}) \text{ ------1}$$

As the temperature rises above 170℃, it starts to decompose irreversibly,

$$\underset{(l)}{NH_4NO_3} \longrightarrow \underset{(g)}{N_2O} + \underset{(g)}{2H_2O} \quad (\Delta H = -59\ kJmol^{-1}) \text{ ---------2}$$

The above reactions occur simultaneously, and the detailed mechanism of the reactions has been the subject of extensive research. The thermal stability of pure AN is quite high (170°C) but in presence of pyrites, spontaneous decomposition occurs at about 25- 50°C before the usual temperature (Gunawan & Zhang, 2009).

Decomposition of solid ammonium nitrate into nitrous oxide and water results in an evolution of 36 kJ/mol of heat (equation 3). In the presence of some additives, more heat can be generated by the reaction (equation 4).

$$NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)} \quad (\Delta H = -36\ kJmol^{-1}) \text{ --------3}$$

$$2NH_4NO_{3(s)} + C_{(s)} \rightarrow 2N_{2(g)} + 4H_2O_{(g)} + CO_{2(g)} \quad (\Delta H = -280\ kJmol^{-1}) \text{ --------4}$$

The presence of moisture, pyrites, urea, or variation of pH also facilitates the reactive ground for the detonation of AN (Djerdjev et al., 2018).

Fused AN above 170°C is likely to react rapidly with any organic materials in contact with it. Many of the explosions with fire and melted AN are likely due to the explosive-decomposition reaction.

$$5NH_4NO_3 \rightarrow 3N_2 + N_2O + 2NO_2 + 10\ H_2O \quad \text{………………..5}$$

The heat of the explosion of this reaction is 1443.48 Joules/g, which is about 25% of the heat of the explosion of trinitrotoluene (TNT). Scientists have presumed to occur this reaction based on red gas reported in the Beirut explosion (Prugh, 2020; Willey, 2020).

In most explosions, a large amount of infrastructure, buildings, or materials are vaporized. The atmosphere is often filled with unknown levels of constituents like heavy metals, asbestos, chemicals, combustible material silica, etc. Exposure to different chemical pollutants leads to a serious impact on the health of people and other organisms. It causes immediate symptoms and diseases to the late effects within weeks or months after exposure. Some chemicals pose serious long-term threats to the ecosystem, mild or fatal effects on lives. The gases like nitrogen oxides (NO_x), ammonia, oxides of carbon, hydrocarbons, etc. often released in AN explosion are noxious to the human respiratory system. In the presence of sunlight and other different chemicals in the atmosphere, they can break down, undergo a chain of chemical reactions to produce more harmful secondary compounds. For example, the oxides of nitrogen and other particles in the atmosphere in the daylight can cause ground-level ozone that leads to the formation of poisonous photochemical smog (ur Rehman et al., 2021). In the latest explosion at Beirut, a sharp rise in the concentration of particulate matter in the atmosphere containing toxic chemicals, asbestos, silica, etc. was noticed that could reduce lung functioning, exacerbation in people with asthma (Devi, 2020).

The objective of this article is to analyze the chemical, technological and physical aspects of major accidental AN explosion within the past 100 years in the world. It also surveys some of the significant terrorist attacks using AN in the past 25 years in different parts of the world. It aims to provide an insight to the concerned authorities for the safe, legitimate, and sustainable production, storage, transportation, and application of this commodity in the days to come.

Materials and Methods

An extensive literature survey was conducted using search engines like Google and Google Scholar to find relevant articles, news, reports, etc. The details of the accidents were obtained from the Wikipedia article "List of Ammonium Nitrate Disasters". The search was conducted using the keywords like ammonium nitrate, Beirut explosion, terrorist attacks, etc. Only the articles written in the English language were taken for the study. A total of 43 accidents and 7 terrorist attacks involving ammonium nitrate were assessed. The results were evaluated and depicted using charts, tables, and histograms.

Result and Discussions

Accidental detonation of AN

The explosions of AN have caused a few of the most notorious and disastrous accidents in the 20th century. The accidents had brought about big explosions, fires, and the discharge of toxic fumes into the atmosphere. These events triggered many fatalities, severe damage to the infrastructure and the environment. Most of the accidents were triggered by crossing the safety barriers or triggering some anonymous preventive measures. Altogether 43 accidents involving AN were reported of which 17 accidents did not result in human casualty. There were 21 accidents in the USA alone with a total loss of more than 650 people in this time. In 1947, there were four accidents of AN with a major accident in Texas (USA) killing more than 600 people, Brest (France) killing 30 people and two accidents in the USA and Canada did not result in the loss

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of human life. Similarly, in 2004 4 accidents included the Neyshabur (Iran) with 300 deaths, Ryongchon (North Korea) with more than 161 deaths, Mihailesti (Romania) with 20 deaths, and Castellon (Spain) with 2 deaths. (See supplementary file).

Terrorist Attacks using AN

Ammonium nitrate is a very useful chemical for agriculture and explosives. It is manufactured and commercially available in many countries. The widespread availability has led to its use by criminals, terrorists, and other armed groups for the manufacture of an invasive explosive device (IED). When stringent regulations are not enforced, armed groups and terrorists around the globe can find legitimate access to AN. Several kinds of research have disclosed the use homemade explosives used in Iraq and Syria were produced from ammonium nitrate, and urea mixed with other chemical precursors. It has created a tough security challenge around the globe on the exploitation of AN. In May 2015, Cyprus police had raided a stockpile of over eight tons of ammonium nitrate from the suspects (https://cyprus-mail.com/2020/08/05/ammonium-nitrate-found-in-cyprus-in-2015-destroyed-police-say/).

Table 1 List of terrorist attacks using AN in the past 25 years (see supplementary materials)

Date	Place/country	Deaths	Injuries	Explosive used
April 19, 1995	Oklahoma/USA	168	591	A truck carrying explosives was detonated by a homemade bomb in a rented truck on Alfred P. Murrah Federal building in a **terrorist** attack (Teague, 2004).
June 15, 1996	Manchester/UK	-	212	A vehicle borne IED was detonated by about 1.5 tons of AN as the main charge (https://www.manchestereveningnews.co.uk/news/greater-manchester-news/manchester-ira-bomb-20-years-11425324).
October 12, 2002	Bali/Indonesia	202	-	Series of explosions at nightclubs by bombs containing AN as main charge (2002 Bali bombings - Wikipedia).
April 28, 2011	Marrakech/Morocco	17	23	The blast was made by an IED bag containing AN and triacetone triperoxide (TATP) (Marrakesh blast was remote-controlled bomb: France | Reuters)
July 22, 2011	Oslo/Norway	8	dozens	A car bomb exploded with a strong IED with AN and fuel oil. The assassin disguised police shot many people before he was arrested (https://en.wikipedia.org/wiki/2011_Norway_attacks).
February 23, 2013	Hyderabad/India	16	100+	Two serial explosions were done by using AN, and trinitrotoluene (TNT) in a bicycle (Hyderabad blasts: six detained for questioning (ndtv.com)).
October 2017	Mogadishu/Somalia	500	300	A truck loaded with an explosive of AN exploded and ignited a fuel tanker (Grantham, 2020).

Classification of AN Accidents

Ammonium nitrate undergoes deflagration when it gains a favorable physical and chemical condition. It may acquire this situation during its manufacture, transportation, or application stages. Figure 2 shows that out of fifty events reported, maximum of the accidents was come about during transportation (42%), followed by storage period (36%), terrorist attack (14%) and least of the cases was during the application (8%) of AN.

Nature of Accidents

The detonation of AN might be triggered by diverse means. When AN is ignited, it burns and produces different conditions which lead to devastating possessions. This study shows that 58% of the events initiate with fire and lead to explosions, 30% of the accidents were ferocious explosions, and 12 % of the incidents were reported smooth burning of ammonium nitrates (Fig. 3).

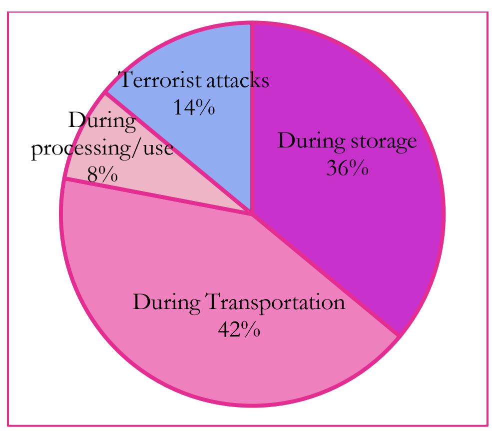

Figure 2 Distribution of accidents based on the analysis of 43 major accidents (see supplementary materials) in the past 25 years of the explosion

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Figure 3 Types of accidents of AN using the analysis of 43 major accidents (see supplementary materials) in the past 25 years

Distribution of Accidents at Different Decades

Afterward every incident, some lessons are learned, and preventive measures are implemented. Once some faults are recovered, another type of pitfall brings about other accidents. In this study, we found that the maximum number of accidents (8) were observed in 2001-2011, followed by seven accidents in 1941-1951 and 1991-2001, and only one/one accidents were observed during 1931-1941 and 1981-1991 decades (Fig. 4). It shows that the frequency of accidents was not minimized from the lessons from previous accidents. The results demonstrate that nothing has been improved to reduce the accidents of AN in the world.

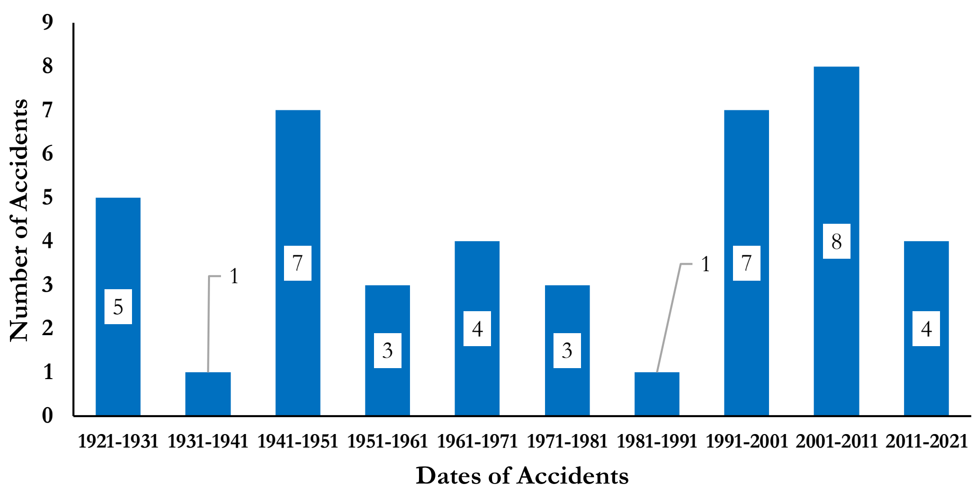

Figure 4 Distribution of accidents in different decades in 100 years (Data in Supplementary file)

Major Accidents Involving a Large Mass of AN, and Fatalities

The results show that eight accidents caused more than 100 deaths in the past 100 years. In Oppau in 1921, and Texas in 1947 caused the highest fatalities of 561 and 600 respectively (Table 1; Fig. 5). After the serious accidents, necessary accommodations and adjustments minimizing possible accidents have been implemented. While in the period before 1950, many serious explosions bringing a large number of fatalities (Oppau, 1921, over 500 deaths, Texas, 1947, over 600 deaths), new anti-caking techniques, and better controls measures, the accidents with 100 fatalities were reduced. Despite awareness measures, Neyshabur-2004 (300 death), Ryongchon-2004 (161 death) during transportation, and Tianjin-2015 (165 death) and Beirut-2020 (220 death) in the storage sites happened. Almost seven accidents were found to cause more than 100 fatalities in the past 100 years. The terrorist attacks of Oklahoma-1995 (168 death), Bali-2002 (202 death), and Mogadishu-2017(500+ deaths) (shown in table 2 in supplementary file) also posed serious challenges to the exploitation of AN. This scenario indicates the obligation of appropriate safety, preventive and legal amendments over the production, transportation, trading, and application of AN.

Climatic impact of chemical accidents

The explosion released a large amount of energy along with large quantities of greenhouse gases including carbon dioxide and methane into the atmosphere. All these emissions are responsible for the significant climatic impact by trapping heat in the atmosphere that raises the temperature of the region and alters the weather pattern. We could not find significant data related to the Beirut explosion to measure the concentration of particulate matter. One of the model-based trajectories of pollution after 72 hours of explosion (Fig. 6) shows that the toxic plumes were dispersed into atmosphere and traversed towards the sea reducing the level of damage to the area of accident.

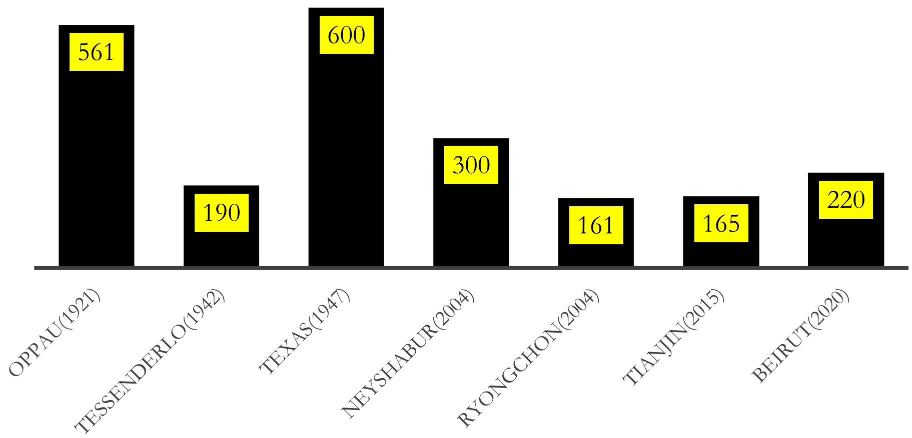

Figure 5 Accidents with more than 100 casualties in the past 100 years (see supplementary materials)

Based on weather conditions, it is supposed that the toxic dust was deposited on surfaces and settled on the ground in areas downwind of the port (Al-Hajj et al., 2021). Since AN is highly biodegradable, the chance of accumulating is slim. It was reported that there was rainfall after 5 days of the explosion, which might have washed out the suspended particles from air that ultimately might have dispersed into soil and water sources.

Safety principles

Regulating body

The implementation of safety measures is necessary to prevent accidents, control severity, and mitigation of domino effects. The safe handling of AN requires stringent regulations to ensure safe production, transportation, and application. Certain legal formalities must be fulfilled before getting the regulatory permit for the production, application, transportation, and storage license. Any suspicious transaction or attempt intended for malicious purposes must be judged and barred.

Selection of land

The site that produces, uses, stores, or receives AN must be located at a safe distance from the urban area. Guidance should be followed from government legislation for the construction planning. Various aspects of the land should be assessed to prevent accidents, getting easy access to transportation, and rescue operations.

Storage in Silo

The storage area must be cleaned with a periodic schedule. Combustible materials and organic substances such as packing materials, dust, seed, oil, waxes, etc. must be at a safe distance from AN in the warehouse. Forklift trucks, conveyor belts, or other easier equipment can be used as transfer vehicles. Gasoline vehicles must be properly inspected and kept in good condition. All the vehicles should be parked at a safe distance when not in use to minimize the spilling of diesel, oil, and grease. A one-story building made of non-combustible materials and flooring is preferred. It should be in a safe place, spacious, and provided with proper ventilation, enough stowage structures and a temperature controlling system. Power, water, drainage, waste management should be standard. AN should be stored in clean bins free from contaminants. Instead of using metal containers, paper or plastic bags are safe. The piling of the stacks should be at a safe distance from the roof, walls, and pile to pile. Very big piling results in caking and a rise in temperature and pressure. Dynamites, explosives, or blasting agents should not be used to break up the cakes, and absorbing moisture should be avoided. A clear warning board with daily updates of the material should be provided.

Fire protection

Fire is one of the important factors that bring about the accidents of AN. To avoid this combustible materials and fire-producing materials should be kept at a safe distance from AN at any time. The automated water sprinkler and fire detection system with audible and visible alarm should be installed for the detection of fire hazards. Suitable firefighting devices like hosepipes, water pipes, portable firefighting cans should be available at the storage, loading-unloading sections. Fire from AN is not extinguished by depriving oxygen, chemical carbon dioxide, or foam. It can only be controlled by using a water sprinkler (Grantham, 2020). An immediate response system and coordination mechanism are necessary to fight against fire and explosion.

Employee competency

All the laborers and the employees should be trained in the nature and hazards of AN. Employees must know the correct use of safety equipment, the potential danger of AN, emergency response, etc. They should have proper

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guidance for the inspection, repair, packaging, as well as instant response in case of accidents.

Safe transportation

The company involved in the transportation of AN and AN-based fertilizers is classified as dangerous goods of the oxidizer category. They have to be conveyed with the provision of the specified security plan. The container or the vehicle carrying AN should be clean and regularly checked for any spillage at loading, unloading as well as the carriage. Fire extinguishers and emergency plans should be efficient. Display banners of no smoking, amount of material, its category, etc. might develop awareness about the potential danger (Grantham, 2020).

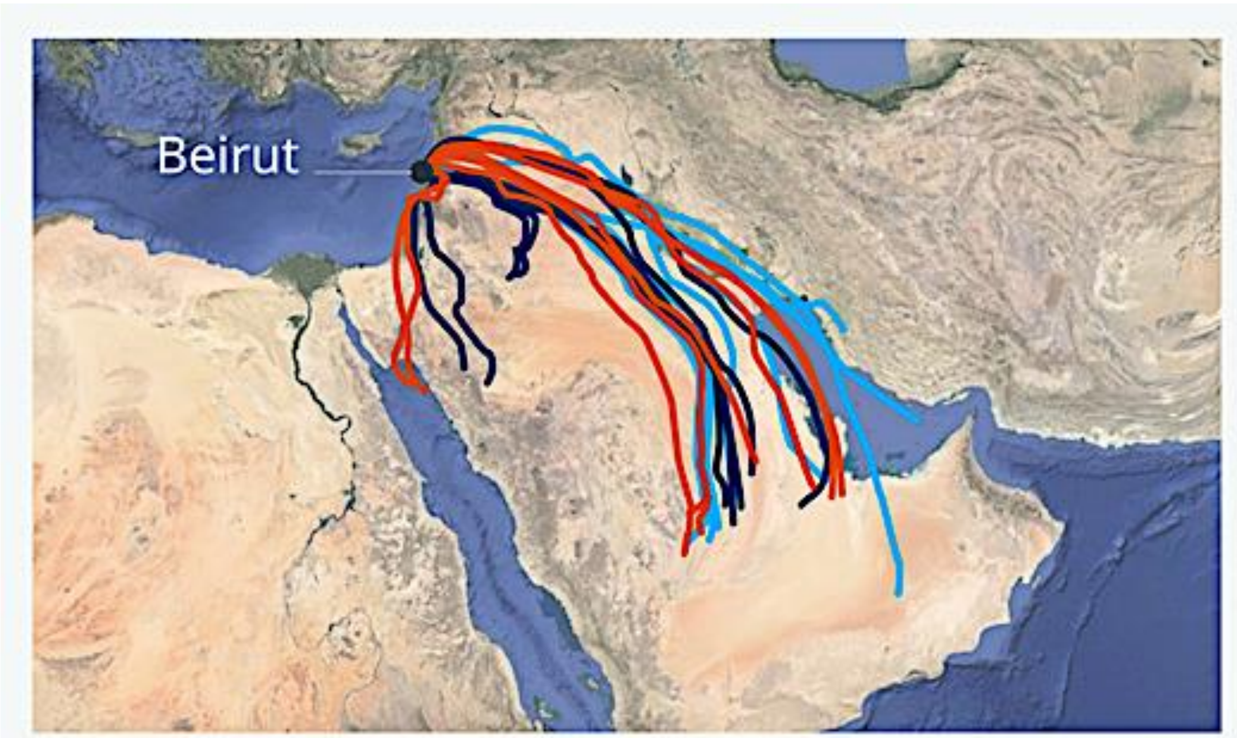

Figure 6 Trajectory of pollution after 72 hours of Beirut explosion(model based on weather conditions) (*Source: T.Christoudias, The Cyprus Institute / Google Maps; Terra Metrics)*

Operational safety

AN must be handled safely in the production and manufacture site. Precise care must be taken during heating, processing, packaging, housekeeping, and dispatching. It should not be heated in confinements, metal canes, with impurities, which may lead to self-sustained detonation. Employers should be provided with adequate safety equipment, security, subsidizations, and motivation to work with this dangerous chemical.

Conclusions

In this paper, we have presented different dimensions of the AN explosion, resulting socio-economic loss along-with environmental degradation and possible safety measurements. AN has a great potential of causing catastrophic events with a big loss of life and property. Accidental as well as deliberate mishaps of detonation of AN in the past have significantly lessened. But still such incidents take place due to improper chemical storage, irregularity in the risk assessments and observations. The concerned governments and regulatory bodies require the implementation of appropriate preventive and safety measures to mitigate accidents in the future. Guidance and legal compulsions for the regulation and management of hazards associated with AN should be incorporated into national and international legislation.

Acknowledgements

Authors are thankful to NASA's Advanced Rapid Imaging and Analysis (ARIA) team and the Earth Observatory of Singapore (EOS) for the proxy map of Beirut accident site.

Author Contributions: LNK: conceptualized, prepared the manuscript, and made chemical and graphical analysis. JR: conceptualized, prepared the manuscript, and carried

out physical and atmospheric analysis. Both are involved in final reviewing of the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

Data Availability Statement: The data that support the finding of this study are available from the corresponding author, upon reasonable request.

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