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The Effect of Storage Temperature on Threat Zone Caused by an Ammonia Release from a Storage Tank

Mustafa Serhat Ekinci **Abdurrahman Akman**
Republic of Turkey Ministry of Labour and Social Security, Ankara, Turkey

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***Correspondence to**: Mustafa Serhat Ekinci, Republic of Turkey Ministry of Labour and Social Security, Ankara, Turkey*
E-Mail: serhat.ekinci@csgb.gov.tr

ABSTRACT

In this study, the threat zone that may occur as a result of an accidental release of anhydrous ammonia, a flammable and highly toxic substance (Flammability:1, Health:3, NFPA 704), which has many uses, was investigated. A fire can be prevented by taking precautions such as not keeping ignition sources in the environment as a result of the accidental release of ammonia gas. However, although its ignition is prevented, it can cause harm to humans and the environment due to its highly toxic nature. Therefore, the toxicity of ammonia was taken into account in this study. A common type of storage of anhydrous ammonia is in a horizontal cylindrical tank at ambient temperature and its vapor pressure. Therefore, in this type of storage, storage is carried out at different temperatures in different seasons. This study aims to examine the effect of storage temperature on the size of the threat zone, taking into account the knowledge that the storage temperature will change in seasonal conditions. Areal Locations of Hazardous Atmosphere (ALOHA) and DOW's Chemical Exposure Index (DOW CEI) methods were used to determine the size of the threat zone, and the results obtained from these two methods were compared. The advantages and disadvantages of the two methods were presented. It is thought that this study will guide the relevant people such as operators who use these methods in calculating the hazard distances in the establishments that store ammonia and will provide awareness that the storage temperature affects the size of the threat zone.

Keywords:
Ammonia; ALOHA; DOW CEI; Threat zone.

INTRODUCTION

Chemicals are indispensable for our modern life. Besides many different chemicals being used today, this diversity is increasing day by day depending on the developing technology and need. Storage and handling of chemical substances involve high levels of risk. These risks vary depending on the nature and quantity of the chemical and also process conditions. If not properly managed, chemicals can threaten human health, the environment, and the economy.

Ammonia is one of the most used chemicals in various organic and inorganic chemical industries. It is generally used in the production of explosives, nitric acid, and fertilizers and used as a refrigerant agent in the industry and a corrosion inhibitor in the refinery. The most common use of ammonia is in the form of ammonium sulfate and ammonium nitrate for fertilizers and its anhydrous liquid. In addition, it is used in the production of some plastics and fibers such as nylon urea-formaldehyde resins, urethane, acrylonitrile, and melamine. Besides, ammonia is used in the production of hydrazine, amines, amides, nitriles, and dyestuff intermediates, and urea, sodium cyanide, and sodium carbonate [1]. Total ammonia production in the world is 144,000 in thousand metric tons of contained nitrogen [2].

Ammonia is a flammable and colorless gas. Its odor is pungent, suffocating, and is detectable even at a very small concentration of 4 ppm. With rising temperature ammonia expands rapidly, which causes to increase in internal pressure in vessels and pipes. Since the normal boiling point of ammonia is - 33.4°C, it is a gas at ambient temperature. Ammonia, with a vapor pressure of 8.6 bar at 20°C, is usually stored as a liquefied gas either under pressure or refrigerated. When pressurized liquefied ammonia is released into the atmosphere, it flashes [1]. Ammonia can cause significant toxic effects even at great distances from the source of release [3]. Because it is widely used in industry, ammonia plays a role in va-

Table 1. Summary information on major accidents involving ammonia.

Year	*Accident Title*	*Cause*	*Consequence*
2022		*No record*	
2021	*Release of ammonia from sphere tank*	*Tank overfilling due to valve failure*	*No injury, Economic loss*
2020	*Explosion and fire at a coking plant*	*Fire due to unknown cause at detarrer.*	*No injury, Material loss*
	Explosion of tank containing waste water from batch production plant and subsequent fire	*The use of an electric arc welder when sealing the previously cut pipe caused the flammable mixture within the tank (waste water vapor) to ignite.*	*2 injuries*
2019	*Ammonia release*	*Human error not following procedures during ammonia transfer*	*1 Fatality, 15 injuries*
2018		*No record*	
2017	*Leak from an ammonia sphere*	*Failure of the seal on the sectional valve for the pipe supplying the NH_3 sphere.*	*No injury, Material loss*
	Syngas compressor oil tank explosion	*An uncontrolled management of change on the air separation unit trip system that allowed enriched air to be sent in the nitrogen grid.*	*No injury*
2016		*No record*	
2015	*Ammonia leak at a chemical plant following a power shutdown*	*Loss of electrical energy*	*No injury*
2014	*Ammonia release*	*Failure to keep safety procedures by the staff.*	*1 fatality*
	Flame jet and fire at an ammonia production plant	*Corrosion under the lagging of the pipes connecting to the measuring instrument*	*No injury*
2013		*No record*	
2012	*Ammonia release from exchanger*	*Failure of the exchanger due to thinning of its sides/walls caused by corrosive impact*	*6 injuries*
2011	*Ammonia leak from high-pressure section of urea plant*	*Pipe corrosion*	*No injury*
2010	*Explosion and fire at ammonia production unit*	*Equipment failure at an ammonia synthesis reactor resulting increase pressure on the pipe*	*5 injuries*
	Explosion in a wastewater treatment unit in a pharmaceutical plant	*Cutting operation that causes sparks in the tank containing flammable gas*	*1 fatality, 4 injuries*

rious hazardous incidents. A total of 100 records related to ammonia was found in the e-Mars accident database between 1985-2022 years. Of these, 83 were reported as major accidents, 12 as other accidents, and 5 as near misses. All reported records were examined and it was determined that 342 people were injured and 49 people died due to these incidents. Summary information on major accidents involving ammonia that occurred between 2010-2022 years is given in Table 1 [4].

Ammonia leakage often occurs due to equipment failures such as piping systems, storage tanks, valves, pumps, compressors, and refrigeration systems, or unsafe handling during transportation [5]. According to the review report of the UK Health & Safety Executive in 2012, 73 of 139 accidents occurred during the refrigeration process, and 25 of them were stated to be caused by not being effectively isolated during maintenance and commissioning. It was stated that the main causes of 43 chemical process and transport accidents were corrosion, component failure, ineffective isolation, operator error, failure to comply with procedures, and pipeline clogging [6].

Today, the toxic dispersion of toxic chemicals in the atmosphere is analyzed using a software. Dispersion models deal with flow systems for various fluids that can be lighter than air or heavier than air. These models exist in a range from simple to complex, from those that can be solved using simple algebraic equations to those that require the solution of complex equations to try to find the most accurate results solving them. Among these models, the decision is made by considering the characteristics of the problem such as the requested accuracy, the available input data, and desired outputs [7]. ALOHA is software that can estimate threat zones associated with hazardous chemical releases. The model is capable of predicting the impacts of undesirable consequences such as fires, explosions, and toxic dispersions. It can also visualize the impacted area on GIS to gain a better understanding of the condition and the extent of the impacted area [8]. ALOHA is one of the widely accepted models used for simulating the dispersion of hazardous gases and implementation of ALOHA is successfully incorporated in several studies for risk assessment purposes [9]. DOW CEI is a simple method used to rate the toxic effects of a chemical release and it is published by the American Institute of Chemical Engineers (AIChE) in 1994. This index is a widely used method for calculating the exposure of individuals to chemicals and determining the distance in possible release events. DOW CEI is also used in Emergency Response Plans [10].

Rahman et al. [11] presented a systematic approach for layout optimization of an ammonia plant using ALOHA software. Prasun et al. [12] presented the results of the risk analysis for the accidental instantaneous release of ammonia under different prevalent weather conditions from a pressurized container using heavy gas dispersion model. Anjana et al. [9] showed the extent of hazard areas and the population likely to be affected in the event of accidental release of ammonia under different atmospheric conditions using ALOHA. They concluded that climatic conditions such as wind speed, humidity, atmospheric stability, etc. play a determinative role in deciding the areas that are more prone to hazardous effects. ALOHA software has been used in many studies for modeling atmospheric dispersion of various hazardous chemicals under different conditions, and these studies have revealed its usefulness in risk assessments and consequences analysis [13, 14]. Orozco et al. [15] determined the environmental and human effects of a fictitious ammonia release to analyze the risk and benefits of ammonia tanks in an industrial area and presented that the risk of toxic vapor cloud caused by ammonia release is less than the risk of fire and explosion using ALOHA software. Jabbari et al. [16] showed that CEI, ALOHA, and PHAST methods could be used in emergency response plans for Iran's road transport fleet in which chlorine, ammonia, benzene, toluene, and 1,3-butadiene were carried in a scenario with full bore rupture of the tankers. Tseng et al. [17] simulated the release of toxic substances such as chlorine, epichlorohydrin, and phosgene in storage tanks using ALOHA. They revealed that the simulations obtained from ALOHA could be the basis for impact analysis and risk assessment studies. Cheraghi et al. [18] used the CEI method to determine hazard distances caused by toxic release in a gas refinery as a case study. Consequence analysis was carried out with the PHAST software for the scenario with the highest airborne quantity. Kim and Byeon [19] determined the hazard distances from hydrofluoric acid leakage by using Korea Offsite Risk Assessment (KORA), Risk Management PlanComp (RMPComp^{TM}), and ALOHA methods. They compared the results and investigated the characteristics and limitations of these methods. Boppana et al. [3] used a dispersion model of an ammonia release from refrigerated liquid storage for an emergency plan for an ammonia storage terminal and presented a case study on the emergency exercise.

Our society needs chemicals in many ways. A world without chemicals is unrealistic and undesirable. Instead, we must learn to live safely in their presence. The occurrence of an event that would cause an emergency should be prevented. Despite all the measures taken, it is indispensable to eliminate the effect of them in case of an emergency situation, if not possible, to minimize it.

In this study, the size of the threat zone that would occur when ammonia released from the storage tank was determined using Areal Locations of Hazardous Atmospheres (ALOHA) and DOW Chemical Exposure Index (DOW CEI) methods. Corrosion was considered as the initiating event of the accident scenarios involving toxic release from the anhydrous ammonia storage tank, and the effect of storage temperature on the size of the threat zone caused by the release was investigated. The reasons for choosing corrosion as the initiating event are that ammonia is corrosive and corrosion has an important role among the accident causes in the e-Mars database and the UK Health and Safety Agency report mentioned above. There is no study in the literature examining the effect of storage temperature on hazard distances. It is thought that this study can help establishments with similar hazards to determine appropriate emergency strategies.

MATERIAL AND METHODS

Methods

The threat zone caused by a release of anhydrous NH3 to the atmosphere from a cylindrical tank was determined by using ALOHA 5.4.7 Modeling Program and DOW Chemical Exposure Index (CEI).

Definitions of The Threat Zones

The threat zone was defined in terms of three hazard distances according to ERPG (Emergency Response Planning Guidelines) values. Three ERPG values are defined. Nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects below the ERG-3, without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action below the ERPG-2, without experiencing other than mild transient adverse health effects or perceiving a clearly objectionable odor below the ERPG-1 [10,

Table 2. Accident scenarios that thought to be occurred in the storage tank. The fill level of the tank was % 85.

Scenario number	*Storage temperature (°C)*	*Vapor pressure [21]. (Absolute&gauge pressures in the tank, kPa)*	*Description of the scenario*
1	*5*	*514.54 & 413.19*	*A: Full rupture of the 2 inch diameter pipeline attached to the tank at the ground level.*
2	*5*	*514.54 & 413.19*	*B: 2 inch diameter rupture on the wall of the tank at the ground level.*
3	*15*	*726.24 & 624.89*	*A: Full rupture of the 2 inch diameter pipeline attached to the tank at the ground level.*
4	*15*	*726.24 & 624.89*	*B: 2 inch diameter rupture on the wall of the tank at the ground level.*
5	*30*	*1162.87 & 1061.52*	*A: Full rupture of the 2 inch diameter pipeline attached to the tank at the ground level.*
6	*30*	*1162.87 & 1061.52*	*B: 2 inch diameter rupture on the wall of the tank at the ground level.*
7	*40*	*1549.65 & 1448.30*	*A: Full rupture of the 2 inch diameter pipeline attached to the tank at the ground level.*
8	*40*	*1549.65 & 1448.30*	*B: 2 inch diameter rupture on the wall of the tank at the ground level.*

Table 3. Properties of anhydrous NH_3 and ambient conditions used in the methods.

Molecular weight (MW)	*17,03*
Normal boiling point	*-33,3°C*
ERPG-1, ERPG-2, ERPG-3 values [22].	*25 ppm, 150 ppm, 1500 ppm*
Density of ammonia in the tank [21].	ρ_{liquid} = *630.95 kg/m³ @ 5°C, 616.7 kg/m³ @ 15°C, 594.3 kg/m³ @ 30°C, 578.53 kg/m³ @40°C*
C_p/H_v *[10].*	*0,00401*
Weather condition	*Neutral*
Wind speed	*5 m/sec*

20]. Threat zones or hazard distances indicate the areas where the toxic concentration is predicted to exceed the corresponding ERPG values at some time in the hour after the release begins [20].

Explanation of The Scenarios

In this study, the effect of the storage temperature of anhydrous ammonia on the hazard distances was examined for two different scenarios and via two methods. The initiating event in the scenarios, that was, the event that caused the transition from the normal to the abnormal mode of the process, was considered as stress corrosion. The following events were stress corrosion cracking and full rupture of pipeline or on the wall which could be called loss of containment. The loss event, that was, the event that caused the transition from the abnormal mode to the emergency mode of the process was the release of ammonia. One of these accident scenarios resulted in the release of anhydrous ammonia because of a full rupture of the 2-inch diameter pipeline attached to the tank at ground level, and the other with a 2-inch diameter rupture on the wall of the tank at ground level.

The results obtained from both two methods were compared. The accident scenarios that were thought to be occurred in a 3 m diameter and 20 m long horizontal cylindrical tank in which anhydrous ammonia was stored at ambient temperature and its vapor pressure were given in Table 2.

Properties of anhydrous NH_3 and ambient conditions used in the methods were shown in Table 3.

Table 4. Hazard distances from DOW CEI and ALOHA.

Scenarios number and description of the scenario	Storage temperature (°C)	HD1(m)			HD2 (m)			HD3 (m)		
		DOW CEI	ALOHA (Open country)	ALOHA (Urban or forest)	DOW CEI	ALOHA (Open country)	ALOHA (Urban or forest)	DOW CEI	ALOHA (Open country)	ALOHA (Urban or forest)
1, A	5	9595	4900	4000	3879	1900	1500	1224	513	412
2, B	5	9595	9000	7500	3879	3500	2900	1224	918	742
3, A	15	10000	5600	4600	4450	2100	1700	1404	587	472
4, B	15	10000	10000	8200	4450	3900	3100	1404	1000	822
5, A	30	10000	6700	5500	5045	2600	2100	1592	702	569
6, B	30	10000	10000	9300	5045	4400	3600	1592	1200	943
7, A	40	10000	7400	6100	5410	2800	2300	1707	783	636
8, B	40	10000	10000	10000	5410	4700	3800	1707	1300	1000

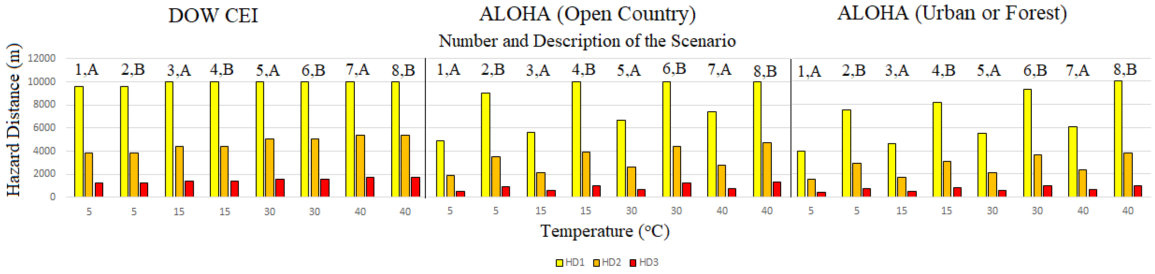

Figure 1. Change of hazard distances with temperature; A: Full rupture of the 2-inch diameter pipeline attached to the tank at the ground level, B: 2-inch diameter rupture on the wall of the tank at the ground level.

RESULTS AND DISCUSSION

Hazard distance (HD1, HD2, HD3) obtained from both methods were given in Table 4. In addition, in the ALOHA method, the effect due to the structure of the terrain (open country and urban or forest) was also shown. While different values can be chosen for the speed of the wind and weather conditions in ALOHA, all CEI calculations assume a wind speed of 5 m/sec and neutral weather conditions. To keep the results consistent, these values were also chosen in ALOHA.

Fig. 1 depicts the effect of temperature rise on hazard distances that constitute the threat zone. As seen from Fig. 1 the higher the temperature was, the longer the all hazard distances were in both two methods. Increasing the ambient (storage) temperature from 5°C to 40°C increased HD2 and HD3 by 40% for scenario A according to the DOW CEI method. In the ALOHA method for open country, these increases for HD2 and HD3 were on average % 50. Although the results stated as 10,000 m in Table 4 were actually more, they were limited to 10,000 m by two methods. Because it was not known what the wind speed and direction were 10 kilometers away [20]. This limitation made some real difference smaller than its accurate value when the temperature raised from 5°C to 40°C for HD1. For the same scenarios at the same temperatures, the values of hazard distances obtained from the Dow CEI method were always greater than the values obtained from the ALOHA method. In another study, the only study in the literature where both methods were compared, hazard distances based on ERPG-2 were higher using CEI than ALOHA [16]. These differences were considerably big for scenario A, twice as much on average, while very small for scenario B. In the Dow CEI, while there was no difference between the results obtained from scenario A and scenario B, there was a big difference in the ALOHA. Dow CEI does not take into account whether the release is from the pipe or the wall of the tank. On the contrary, whether the release comes from the pipe or the wall of the tank changes the result in the ALOHA. Since this method took into account the effect of liquid friction inside the pipe, the hazard distances caused by the liquid release from the pipe were lower, so it gave distant results to the Dow CEI method for scenario A.

ALOHA also allows the results to be seen visually. Threat zone, on the open country terrain, outputs at 5°C and 40°C of two different scenarios (A and B) were shown in Fig. 2. From the figure, it was observed that hazard distances increased with the increase of temperature, and for the same temperature, NH_3 releasing from the pipe (A) created a lower hazard distance than releasing from the wall (B).

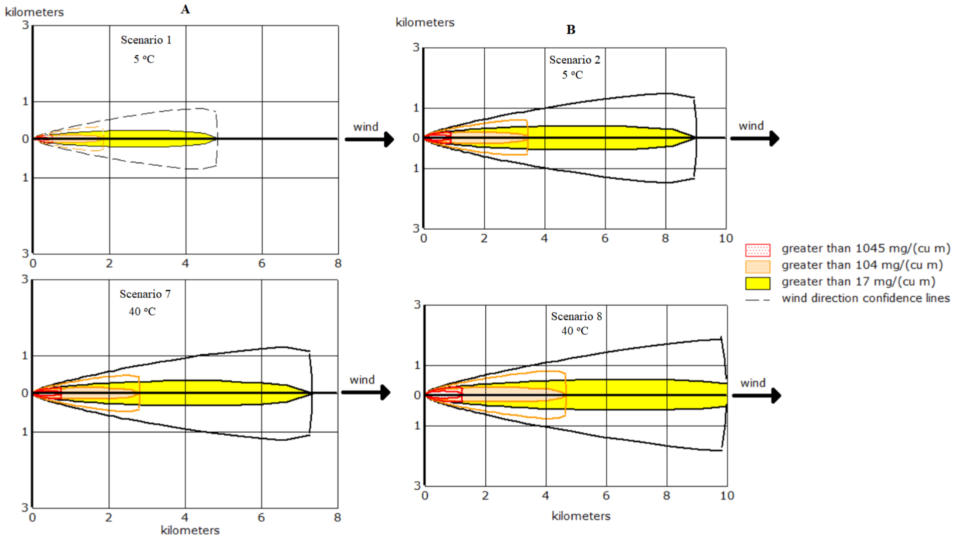

Figure 2. Threat zone outputs at 5°C and 40°C of two different scenarios (A and B) on the open country terrain.

Since the Dow CEI method did not use different formulas according to whether the terrain had low roughness or high, the same results were obtained for both cases. On the other hand, the results of the ALOHA method varied according to the roughness of the terrain. The changes according to the roughness of the terrain were compared using open country and urban or forest options. Fig. 3 shows the results of open country and urban or forest options for scenario 8 that gave the highest hazard distances. When using the open country option the hazard distances were larger than the urban or forest option. This result was compatible with a study that used chlorine gas that examined the effect of ground roughness (rural or urban) on hazard distances [23]. As mentioned above, due to the limitation of the method, the threat zone picture was truncated at the 10 km limit. Open country type of terrain has low roughness and low turbulence because the chemical cloud is traveling over an area with only small or isolated roughness elements. Urban or forest type of terrain has high roughness and high turbulence because the chemical cloud is traveling over an area with many friction-generating roughness elements, such as trees or small buildings. Increased atmospheric turbulence causes the chemical cloud to dilute more quickly [20]. Therefore, when using the open country option, there was less dilution because of the less turbulence and the hazard distances were larger than in the urban or forest option. If an operator who wants to determine the hazardous distances of the toxic cloud that will occur as a result of an accident scenario and does not have information about the roughness of the land or is uncertain, he should choose the open country in the ALOHA method. Because such a preference will ensure that the hazard distances are found larger and therefore, to remain on the safe side.

Using ALOHA, the threat can be assessed at any location. According to Fig. 4, ALOHA predicts that a cloud of ammonia would arrive at the location point 1, 630 m downwind direction and 100 m crosswind direction, in about 2 minutes (that is when the concentration line begins to rise steeply) and immediately the concentration would exceed Red LOC (concentration for HD 3) and then leaves this value after about 27 minutes from the release begins. The location point 2, a point between the outermost black line and colored areas, even if it is not in a dangerous area, concentration may exceed LOCs here, if the wind shifts direction. At any point outside of the outermost black line, concentration is lower than LOCs.

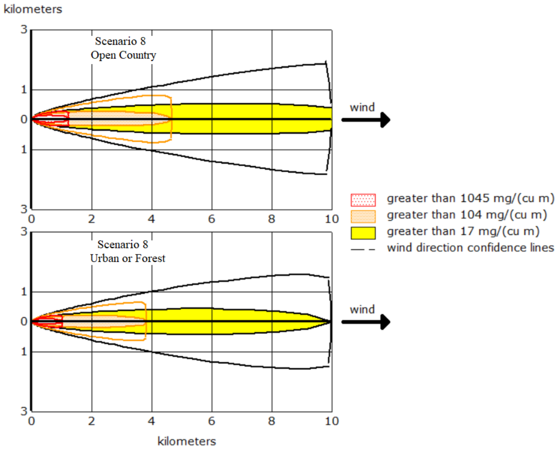

Figure 3. Threat zone outputs of scenario 8 (40°C, B: 2-inch diameter rupture on the wall of the tank at the ground level) for open country and urban or forest kinds of terrain.

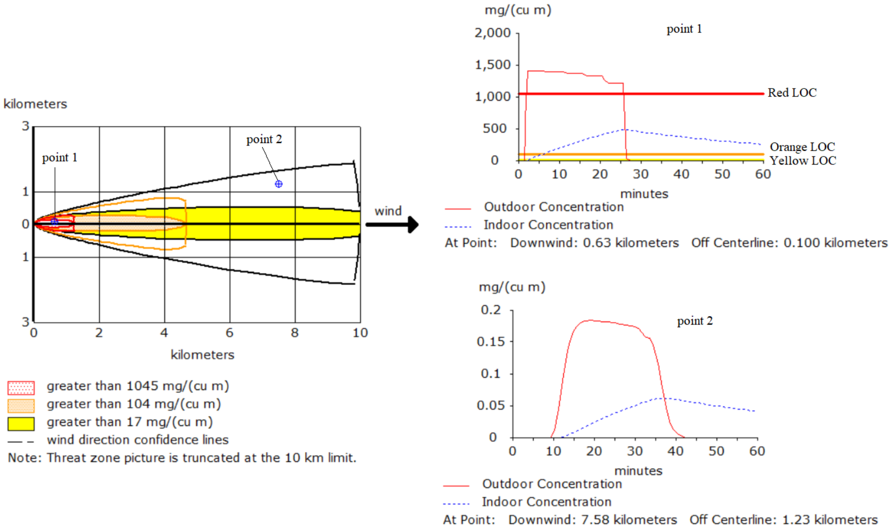

Figure 4. Concentration at two sample points.

It should not be forgotten that it would not be correct to think of a line that definitely separates the dangerous zone from the non-dangerous zone. Someone, more sensitive to the chemicals, who is at a position below the yellow LOC (concentration for HD1) may experience more serious health effects than other who is at a position that exceed the yellow line [20].

CONCLUSION

Ammonia, widely used in the industry, causes adverse effects on human health from injury to death as a result of accidental release. If the occurrence of this release cannot be prevented despite the precautions taken, the harmful consequences should be minimized. To minimize the harmful consequences, preparing an effective and realistic emergency plan is essential. Estimating the threat zone caused by the accidental release will serve this purpose. The size of the threat zone depends on meteorological conditions and operating parameters. In this study, the effect of storage temperature on the threat zone, which has never been studied in the literature, was investigated. It has been revealed that the threat zone increased with the increasing storage temperature of ammonia.

As a result of this study, when preparing an emergency plan, it is recommended that operators and public authorities should take into account that ammonia is stored at different temperatures depending on the seasonal conditions, resulting in different threat zone. In addition, it should not be ignored that the methods used give different results. According to the results of this study, the threat zone obtained from DOW CEI was always larger than obtained from ALOHA. The results obtained from ALOHA as a result of a rupture occurring in the open country terrain and on the tank wall were very close to the results obtained from DOW CEI. In such a case, it will be more practical to use ALOHA as it is easy to use. Since ALOHA took into account the friction in the pipe in case of a rupture in the pipe, it revealed a smaller threat zone. In such a situation, using DOW CEI will provide a safer side, but ALOHA will give a more realistic result.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

AUTHOR CONTRIBUTION

Idea, concept, design, design, sources, data collection, analysis, literature review, author and critical review are obtained by both authors whose names are mentioned in the article.

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