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Comparative Analysis of the Actual Leakage Accident of Silicon tetrachloride and the Damage Effect of the Risk Assessment Program

By

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Abstract

The purpose of this study is to analyze which programs are suitable for field activities of firefighters in the event of chemical leakage by comparing the actual leakage range of silicon tetrachloride and the predicted damage impact range using a risk assessment program. Three risk assessment programs are used in the experiment: KORA and ALOHA, including CARIS, which firefighters currently use in case of chemical leakage. The researchers compared the damage impact range to see the difference between the predicted results from each program based on the program's process and weather condition data input and the actual scope of accident damage.

The results showed that the extent of damage impact yielded from ALOHA is most similar to the actual extent of the damage. On the other hand, the predictions of KORA and CARIS showed a wide range, incomparable to the extent of the damage. Therefore, when evaluating the risk of chemical leakage accidents, the fire department should first use ALOHA to evacuate the initial residents. Then, CARIS should be utilized to calculate the maximum extent of damage impact to respond to chemical leakage accidents.

Keywords: Silicon tetrachloride, Risk assessment, KORA, ALOHA, CARIS

1. Introduction

In Gunsan-si, Jeollabuk-do, a total of eight industrial complexes reside, including two national industrial complexes, two general industrial complexes, and four agricultural and industrial complexes. Chemical accidents (17 cases) frequently occurred in the Gunsan industrial complexes from 2014 to 2021, accounting for 51.5% of the number of chemical accidents (33 cases) occurring in 14 cities and regions in Jeollabuk-do. In particular, the silicon tetrachloride leak at a chemical plant in Gunsan General Industrial Complex in 2015 was the largest chemical accident in Jeollabuk-do in the 2010s. It resulted in the hospitalization of 310 residents, including one worker, and left damages to the 83,594 m2 farmland nearby. Due to the nature of chemical accidents, when a leakage accident occurs, the leaked material spreads to nearby areas through atmospheric flow, causing casualties and property damage to an extensive area. There will be numerous casualties if residential areas such as apartment complexes are located near industrial complexes. In order to secure the safety of residents near the accident, an early evacuation warning should be made by predicting a more accurate extent of damage impact. When predicting the extent of damage impact, underestimating the scope or an over-prediction may not guarantee the safety of residents but rather create unnecessary fear, increasing social anxiety.

Under the Chemical Substances Management Act, all workplaces dealing with chemical substances must submit a chemical accident prevention management plan, including an external impact assessment that may occur in the event of a chemical leak. In order to evaluate the external impact, the workplaces use KORA, a general-purpose program provided by the Korea Institute of Chemical Safety. On the other hand, fire and other chemical accident response agencies use the National Institute of Environmental Research's CARIS to check and take responsive actions. Therefore, it is necessary to compare the scope of damage impact conducted for the external impact assessment by the company and the results of risk assessments conducted by the responsible agencies during hazardous substance leaks. C.-M. Seo (2020) compared the scope of damage impact by designing a case similar to the Hube Globe hydro fluoride leakage in 2021 in Gumi using three programs: KORA, ALOHA, and PHAST. He also compared the characteristics of each program by adding the accident-causing materials and designing a scenario.

Y.-H. Seo (2018) designed and compared the impact ranges of three substances: nitric acid, ammonia, and toluene. She showed the characteristics of the two programs to help the workplaces use a program suitable for their respective environment. Previous studies are to predict and compare the extent of damage caused by leakage accidents using programs mainly used in workplaces dealing with hazardous chemicals. This study aims to confirm the program's validity by comparing the extent of the damage from leakage and the risk assessment program. A scenario similar to the case of silicon tetrachloride leakage in Gunsan-si was designed using three programs: KORA, ALOHA, and CARIS. We aim to present the methods and results of predicting the damage impact range in the event of silicon tetrachloride leakage using the programs and compare and analyze the impact range in contrast to the 2015 accident to examine whether the damage impact ranges are valid.

2. Risk Assessment Program

2.1 KORA(Korea Off-site Risk Assessment Supporting Tool)

Anyone intending to install and operate a hazardous chemical handling facility must submit a chemical accident prevention and management plan (referred to as the "plan"). The Institute of Chemical Safety, a related organization, created and distributed KORA, a preparation support program to facilitate the drafting of plans. The characteristics of KORA include a risk evaluation of processing devices, affected cities in case of an accident, and risk analysis. KORA can get all results at once and print plans too. Leakage diffusion models used in the program were the Gaussian diffusion model, the SLAB model, the fire facing (Pool Fire) model of the Center for Chemical Process Safety (CCPS), and the high-pressure eruption fire model of the American Petroleum Institute (API) (Y.-J. Kim, 2017). The diffusion model applied to KORA is summarized in Table 1 by molecular weight and types of fire.

<Table 1> Diffusion model according to the molecular weight and fire types of leakage material.

By molecular weight	Diffusion Model	Fire types	Diffusion Model
Diffused material > Diffused air	Gaussian Diffusion Model	Facing Fire	CCPS Facing Fire
Diffused material < Diffused air	SLAB Model	Eruption Fire	API high-pressure eruption fire model

2.2 ALOHA(Areal Location of Hazardous Atmospheres)

ALOHA is a program developed by the National Oceanic and Atmospheric Administration (NOAA) and used jointly with the Environmental Protection Agency (EPA) in the United States (H.-S. Kim, 2016). In this program, the extent of damage impact is calculated using the Gaussian diffusion model and the DEGADIS leakage model. <Table 2> summarizes the diffusion models by a molecular weight of leakage substances applied in ALOHA. The most noticeable feature is that the extent of damage impact can be directly plotted on the map by linking with the Google Earth program.

<Table 2> Diffusion model according to the molecular weight.

Types	Diffusion Model
In General	Gaussian Diffusion Model
Diffused Material > Diffused air or Cryogenic gas.	DEGADIS Diffusion Model

2.3 CARIS(Chemical Accident Response Information System

CARIS is an information system that provides information on the chemical and the company handling the chemical. Such information and the results of calculated damage prediction are used by the response action agencies such as the Ministry of Environment and firefighting in the event of a chemical accident or terrorism. The diffusion model is the most significant difference between the above two programs and CARIS. KORA or ALOHA applied the Gaussian diffusion model, whereas CARIS applied the 3D vapor and atmospheric diffusion model to indicate the diffusion range of hazardous chemicals (C. Kim et al., 2003). Its significant feature is that it uses the geographic information system of the National Geographic Information Service to show the extent of damage and provides a series of information on the company handling the chemical, chemical risks, response, and control methods at once. Therefore, one of the program's pros is that the accident response agencies can quickly collect information. <Table 3> below summarizes the diffusion model used in this study based on the information stated above.

<Table 3> A diffusion model applied according to the risk assessment program in case of silicon tetrachloride leakage.

Risk Assessment Program	KORA	ALOHA	CARIS
Applied Models	Gaussian Diffusion Model	DEGADIS Leakage Model	3D vapor & atmospheric diffusion model

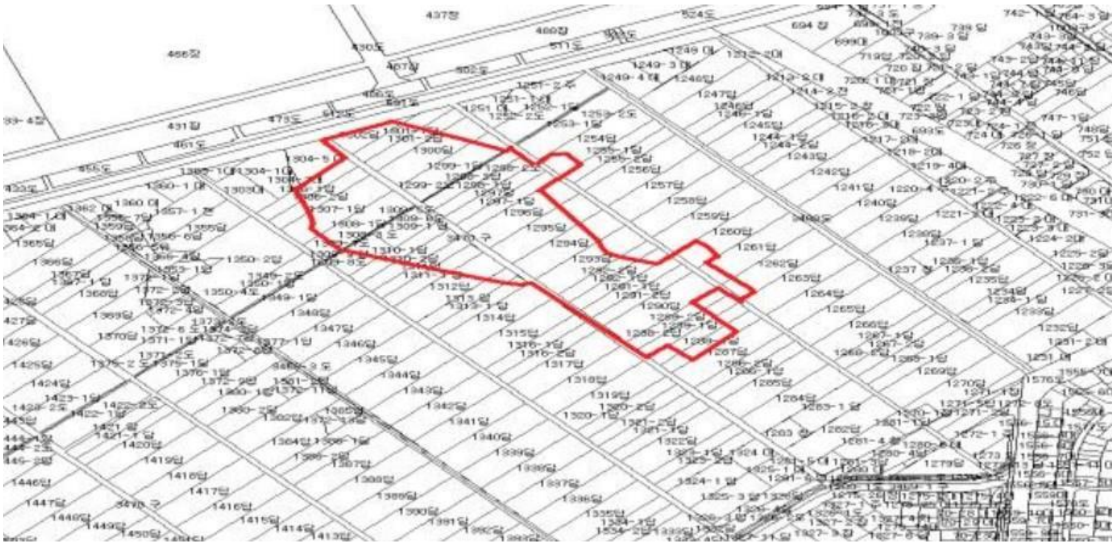
3. Silicon Tetrachloride Leakage Status

A total of four silicon tetrachloride leaks that occurred in Jeollabuk-do from 2015 to 2021 were reported to the Korea Institute of Chemical Safety, as summarized in Table 4. Three leak accidents from 2017 to 2021 did not significantly affect the off-site local communities because only a small amount of the substance was leaked. But the 2015 accident was a large-scale leakage with an estimated silicon tetrachloride mixture leak amounting to 150 kg.

<Table 4> Silicon Tetrachloride Leakage Status in Jeollabuk-do

Date	Reasons	Leakage (estimate)
2021-06-07	Did not qualify the safety requirement	30 [L]
2018-11-21	Facility Defect	5~10 [L]
2017-06-24	Facility Defect	1~2 [kg]
2015-06-22	Facility Defect	153 [kg] (Korea Occupational Safety & Health Agency, 2017)

In particular, the leaked silicon tetrachloride reached an area of 500m outside the factory due to the influence of the wind direction, causing damage to the surrounding villages and vegetation. The extent of damage to the rice plantation near the factory is shown in Figure 1.



[Fig. 1] Damage range caused by silicon tetrachloride leakage to the nearby rice plantation

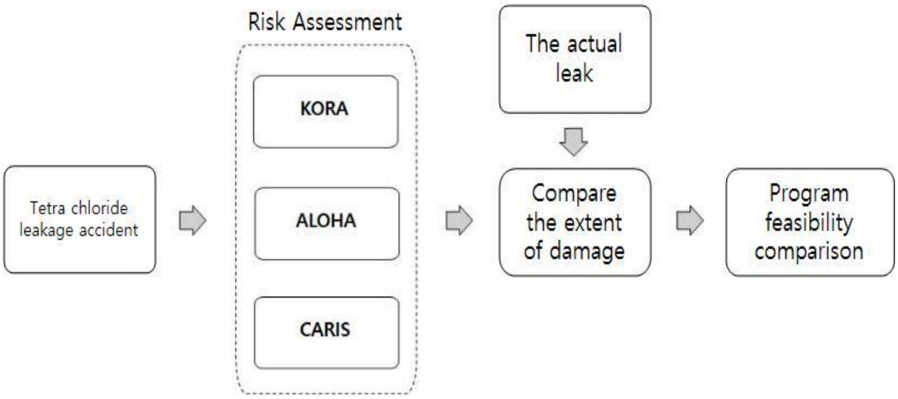
The overall status of the damage is summarized in Table 5. Three hundred ten people were treated at the hospital for casualties, of which 105 were mentioned to carry side effects.

<Table 5> Damage status of the 2015 leakage accident

Casualties	**In hospital**	**Estimated number of people with possible health issues**
	310	105
Loss in Property	Range	Amount (In Korean Won)
	83,594 m2	100,436,406

4. Experiment

There are a total of three types of software used in this study: KORA of the Institute of Chemical Safety, CARIS of the National Institute of Environmental Research, and ALOHA of the EPA, U.S.A. Using the three types of software, we designed a silicon tetrachloride leakage scenario, similar to that from the 2015 Gunsan General Industrial Complex to check the extent of the damage impact of each software and to review which software is appropriate for firefighting response activities. The research system is in Figure 2 as follows.



[Fig. 2] Experiment models.

4.1. Definition of Input Data

In order to design an actual accident as a program, it is not necessary to separately define the different measurements and the recorded values. For example, the leaked substance in the accident is a silicon tetrachloride mixture, but the program restricts the mixture input. And the restrictions are defined on several items such as leakage method, size, time, and weather conditions on the day of leakage.

First, the silicon tetrachloride leakage accident in Gunsan (or referred to as the "Gunsan accident") occurred in the process of increasing the purity of silicon tetrachloride, and the leakage material is a mixture of silicon tetrachloride, 20.7%, 2.5% hydrogen, 1.8% nitrogen, and 0.3% trichloride. However, the scenario was designed by defining a single substance, silicon tetrachloride or hydrogen chloride, as an accident material since it is difficult to input a mixture into each software.

Second, the leakage point of the Gunsan accident was the neck of the bellows valve installed on the pipe in between tanks. However, due to the limitations of the software, inputting a crack on the neck as the cause of the accident was difficult. Thus, it was only supposed as a container leak. If so, assuming a container leak, the volume of the container should be determined. Therefore, the researchers used the sum of the state of the gas, which is the part of the tank, and the volume of a pipe connected to the following procedure.

Third, the leakage point located at 7.62cm in the neck of the bellows valve had an irregular shape with cracks and operating pressure of 2.559 MPa. Thus, the researcher used the diameter of the leakage point as the size of the leakage point.

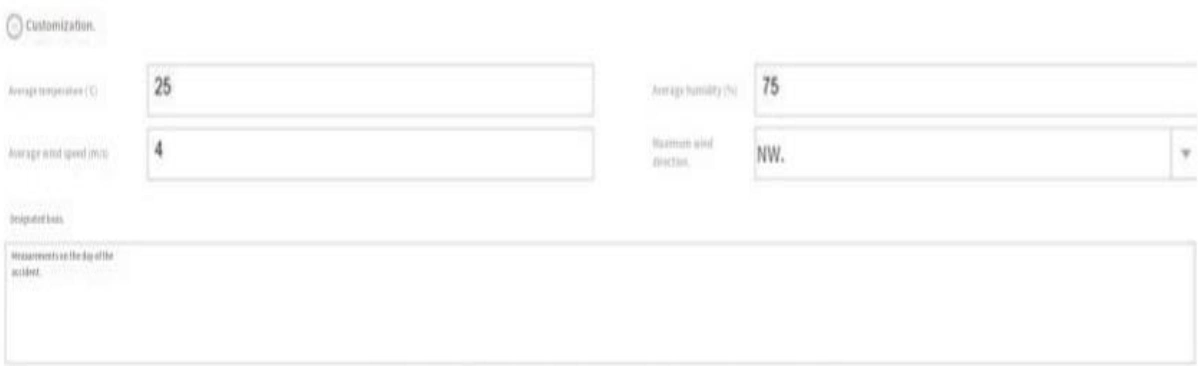
Fourth, the leakage time was set from when the accident occurred to when nitrogen gas began to flow into the accident tank T-149. This is because as nitrogen gas begins to flow into the tank, the material from the accident would dilute with nitrogen gas, decreasing concentration.

Fifth, on the day of leakage, the weather was set to 4 $^{m}/_{s}$ wind speeds, west/ northwest directions, temperature 25°C, relative humidity 75%, and atmospheric stability set as C.

4.2. Data Input

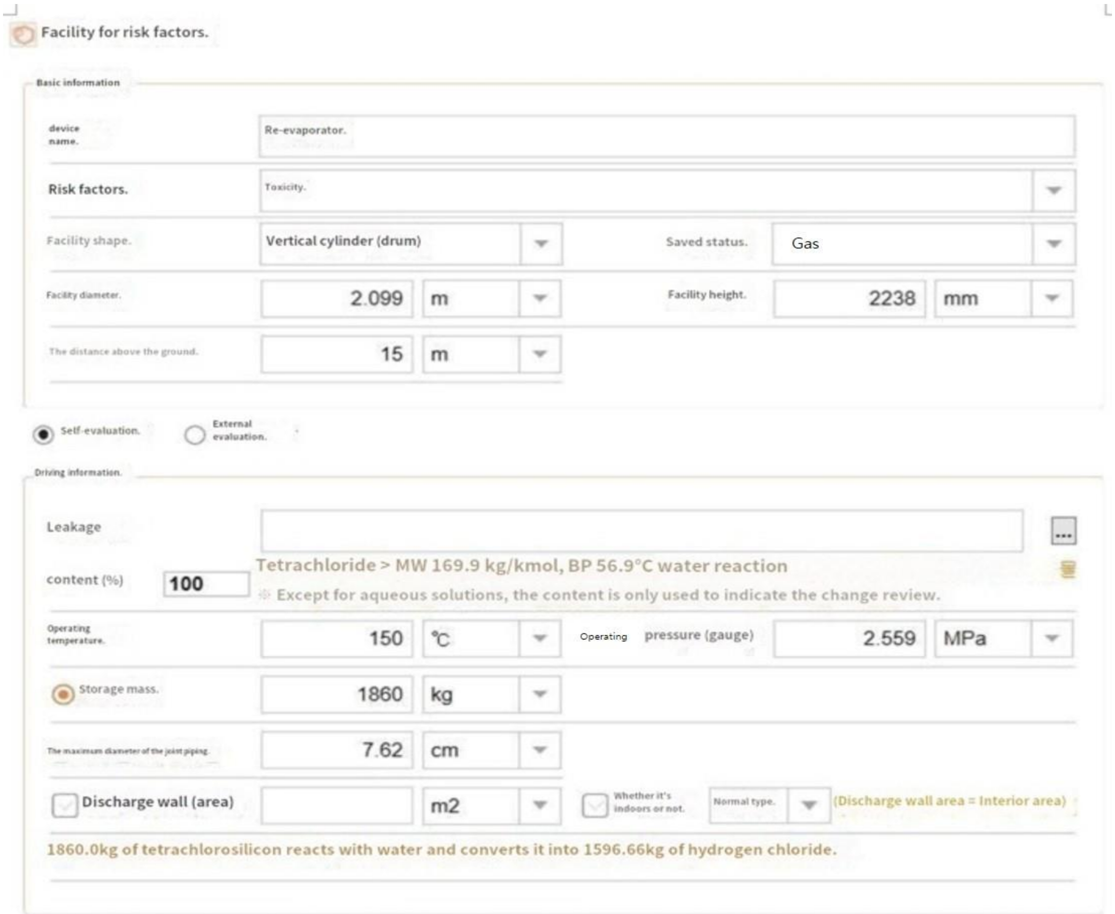
4.2.1. KORA

The KORA used in this study is version 5.0. Unlike ALOHA and CARIS, KORA automatically converts and applies hydrogen chloride production when silicon tetrachloride leaks into the atmosphere, so the accident material was set as silicon tetrachloride, and data were entered as shown in [Fig. 3].



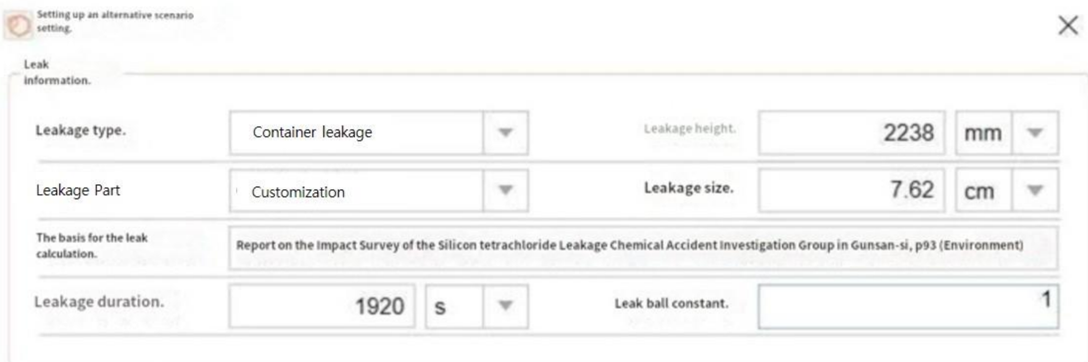
[Fig. 3] KORA weather input value

As shown in [Figure 4], a vertical cylinder was selected since the shape of the facility was assumed to be a container leak. And the facility diameter and height values were calculated based on the sum of 7.75 m2 of the gas volume present in a gaseous state on the container and pipe and the height of the valve. The separation in the distance above the ground is assumed to be 15m high because the process exists at the height equivalent to a 3-story building above the ground. As for the operating temperature and pressure under the operation information, the actual operation status was entered. The maximum diameter of the binding pipe was 7.62 cm (3 inches), the size of the bellows valve connection pipe.



[Fig. 4] KORA Silicon tetrachloride basic information and operating information input value

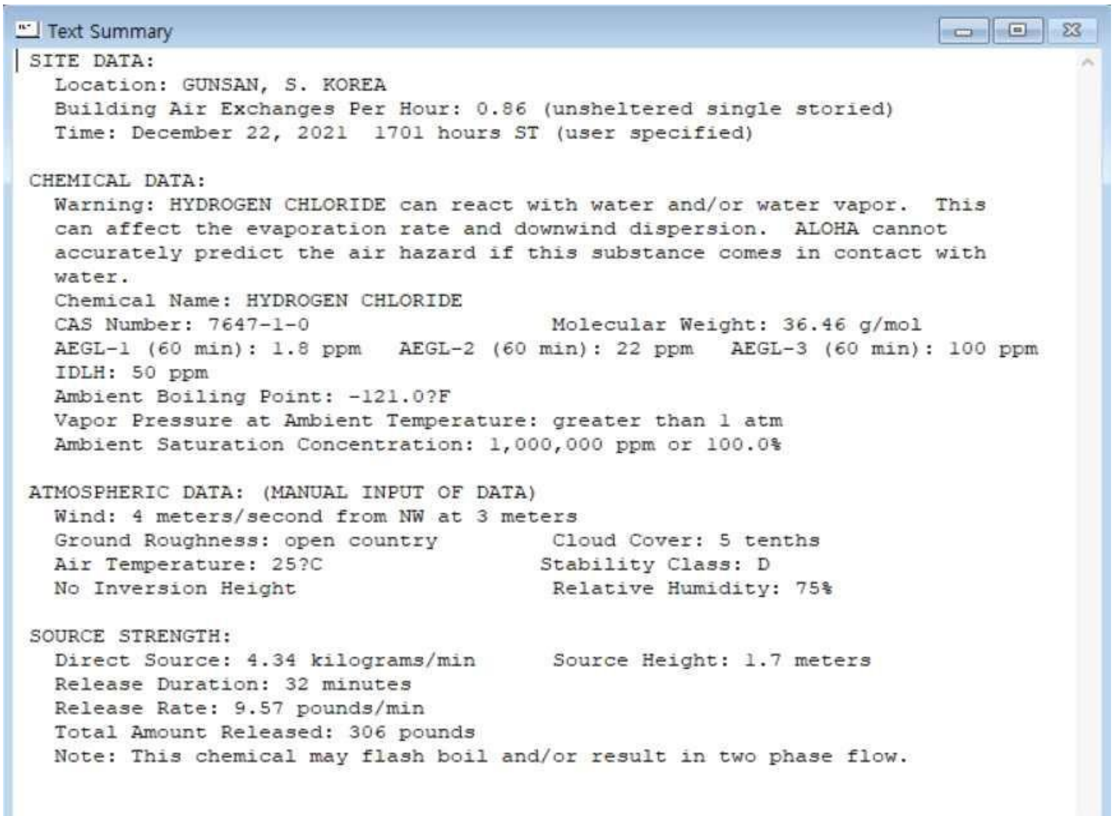
As shown in [Fig. 5], since the alternative scenario is very likely to occur in reality, it was designed to be similar to the actual case by entering the values defined above. The leak was 7.62 cm (3 inches) in diameter of the pipe connected to the bellows valve.



[Fig. 5] KORA silicon tetrachloride alternative scenario input value

4.2.2. ALOHA

The ALOHA used in this study is version 5.4.7. Unlike KORA, hydrogen chloride production is not automatically calculated and applied when silicon tetrachloride leaks into the atmosphere. Thus, the scenario was designed using hydrogen chloride as the accident material (shown in [Fig. 6]). The leakage form is supposed to be a container leak. It was a continuous leak with an assumed leakage amount of 4.34 kg/min for 32 minutes. The reason for the assumption of 4.34 kg/min was that it took 32 minutes for nitrogen gas to flow into the tank (T-149), and the leak amount decreased from 6.79 kg/min to 1.89 kg/min after 33 minutes at the beginning of the accident, resulting in a linear decrease in 32 minutes.



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Text Summary
SITE DATA:
   Location: GUNSAN, S. KOREA
   Building Air Exchanges Per Hour: 0.86 (unsheltered single storied)
   Time: December 22, 2021  1701 hours ST (user specified)

CHEMICAL DATA:
   Warning: HYDROGEN CHLORIDE can react with water and/or water vapor.  This
   can affect the evaporation rate and downwind dispersion.  ALOHA cannot
   accurately predict the air hazard if this substance comes in contact with
   water.
   Chemical Name: HYDROGEN CHLORIDE
   CAS Number: 7647-1-0                    Molecular Weight: 36.46 g/mol
   AEGL-1 (60 min): 1.8 ppm   AEGL-2 (60 min): 22 ppm   AEGL-3 (60 min): 100 ppm
   IDLH: 50 ppm
   Ambient Boiling Point: -121.0?F
   Vapor Pressure at Ambient Temperature: greater than 1 atm
   Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
   Wind: 4 meters/second from NW at 3 meters
   Ground Roughness: open country          Cloud Cover: 5 tenths
   Air Temperature: 25?C                  Stability Class: D
   No Inversion Height                     Relative Humidity: 75%

SOURCE STRENGTH:
   Direct Source: 4.34 kilograms/min       Source Height: 1.7 meters
   Release Duration: 32 minutes
   Release Rate: 9.57 pounds/min
   Total Amount Released: 306 pounds
   Note: This chemical may flash boil and/or result in two phase flow.
```

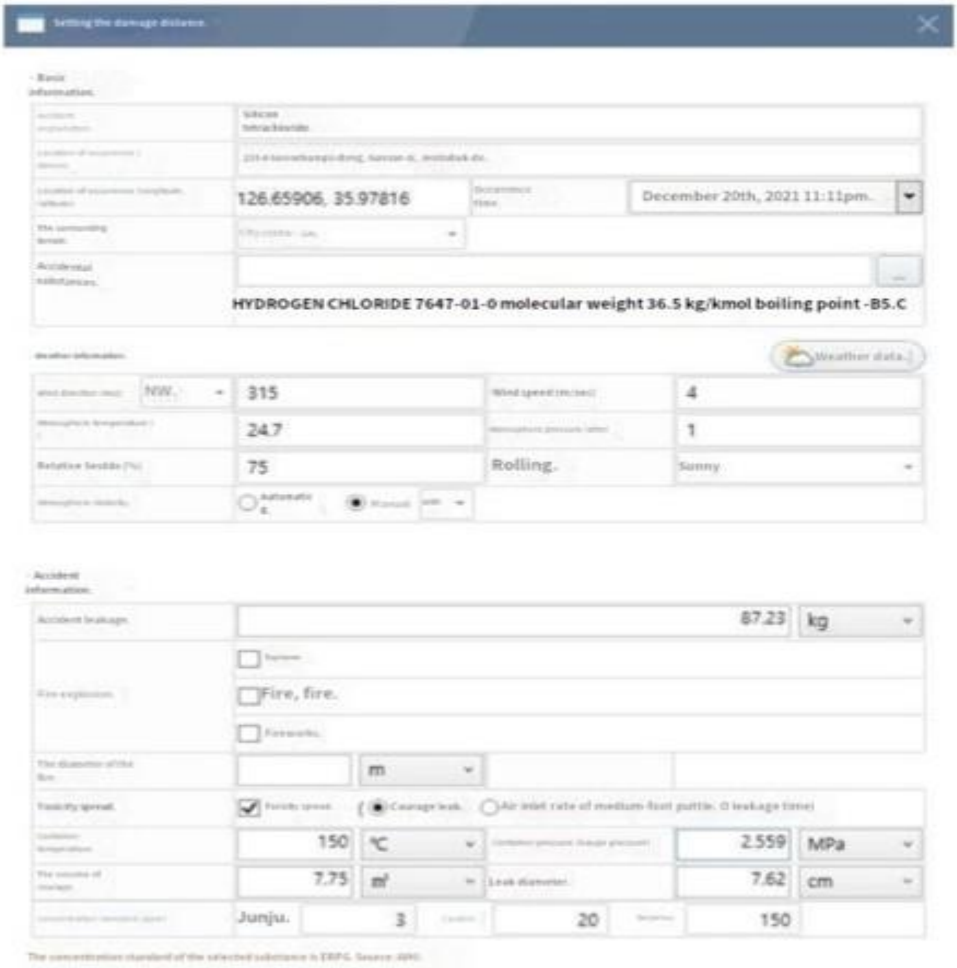
[Fig. 6] ALOHA Hydrogen chloride data input value

4.2.3. CARIS

The CARIS used in this study is version 3.1.3.9. As shown in [Fig. 7], when the program is executed, the address, material handling companies, related agencies, response agencies, and disaster prevention companies are displayed on the left, and the map is displayed on the right. Right-click on the map enables users to select "calculating the distance in damage at a designated location," which allows you to enter basic information, weather information, and accident information necessary to calculate the damage impact range.

CARIS does not automatically reflect the production of hydrogen chloride when silicon tetrachloride leaks into the atmosphere, just like ALOHA. Therefore, it was regarded as a hydrogen chloride leakage accident, and the material of the accident was searched for and entered as hydrogen chloride in the basic information.

The accident information input was assumed to be a container leak in the same manner in the two programs. The leakage amount of 87.23kg (Ministry of Environment, 2015), the temperature and pressure of the container were input to the actual values of 150°C and 26 kg/㎠. The volume and leakage diameter of the container were input to the data values of 7.75 m3 and 7.62cm.



[Fig. 7] CARIS Hydrogen chloride data input value

5. Experiment Result

5.1 KORA

The alternative scenario to be compared with the actual Gunsan accident when silicon tetrachloride leak was found to have a radius of about 1,860m and an outside distance of 1,560m, as shown in <Table 6>.

<Table 6> KORA silicon tetrachloride leaks damage range

The Worst Scenario		The Alternative	
Radius	**Outside**	**Radius**	**Outside**
2,242,2m	1,942.0m	1,860.8m	1,560.6m

In the KORA program, the toxic diffusion, among the damage impact models, is marked in circles and is not affected by wind direction. In [Fig. 8], the place marked "re-evaporator" on the map is the approximate processing location where the accident occurred, and the part under the red shade is the approximate location where the damage to the plantation actually occurred. The point where the damage occurred is located southeast of the accident location. With the wind direction headed to the west/ northwest at the time, the area is highly likely to have been affected by the actual accident. The alternative scenario calculated by KORA was displayed up to a distance of about twice the actual damage range.

[Fig. 8] KORA damage range of silicon tetrachloride and the impact

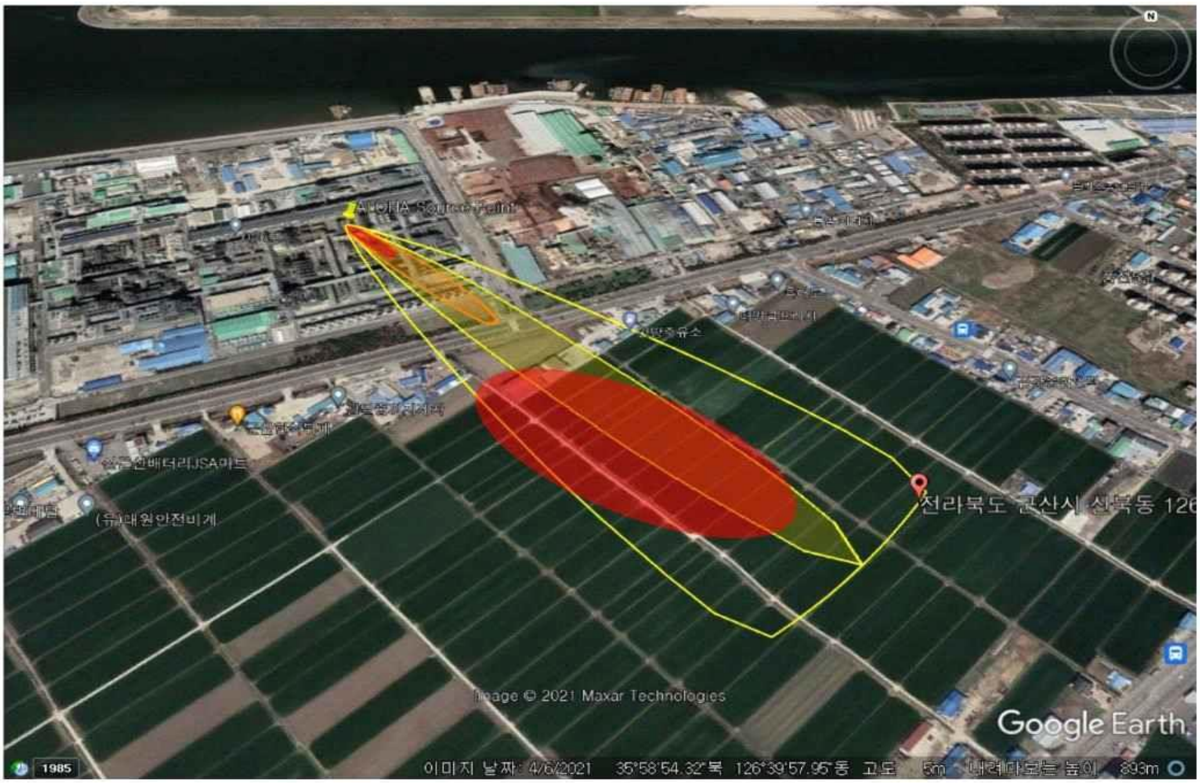
5.2. ALOHA

In ALOHA, an area is marked as a risking area when 150 ppm of hydrogen chloride is detected, a semi-risk area when 20 ppm is detected, and a boundary area when 3 ppm is detected. When hydrogen chloride was leaked, the risking area was 127 yards (116 m), a semi-risk area was 366 yards (335 m), and the boundary area was 993 yards (908 m).

<Table 7> ALOHA hydrogen chloride damage range

Types	Risking Area	Semi-risk	Boundary
Range	116	335	908

[Fig. 9] The yellow pin on the map locates the place where there is leakage processing, and the red-shaded area is the damage range. ALOHA showed a remarkably similar damage range to the actual damage range. Hydrogen chloride leaked in the program spread to the southeast under the influence of the northwest wind, which almost coincided with the actual damage range.



[Fig. 9] The damage range and impact of hydrogen chloride urbanized on Google Earth

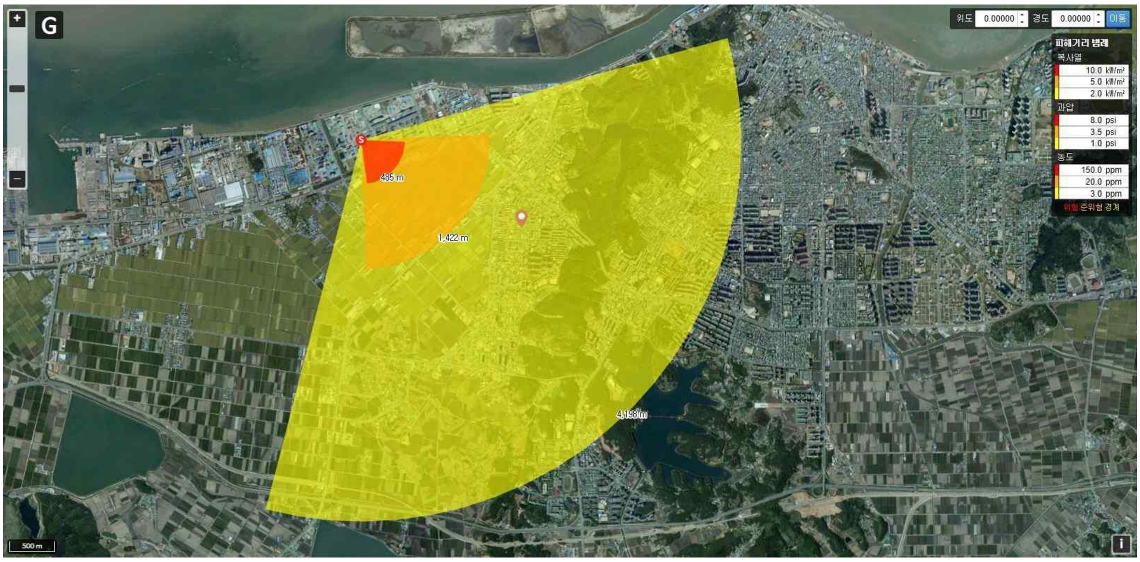
5.3. CARIS

CARIS uses the same detection amount and classification as ALOHA for hydrogen chloride. It also has a risking area, semi-risk area, and boundary area. When hydrogen chloride leaks, CARIS predicted that the extent of the damage would be off-site, far from the factory range and the surrounding areas. This result differs significantly from the actual extent of the damage.

<**Table 8**> CARIS hydrogen chloride damage range (in m)

Types	**Risking Area**	**Semi-risk**	**Boundary**
Range	485	1,422	4,198

As shown in [Fig. 10], the toxic diffusion of CARIS was affected by the wind direction, which spread with the downward wind in a fan shape. Compared to the above two programs, the damage range was calculated extensively. This result hints that CARIS is using a different diffusion model from other programs. The 3D weather and atmospheric diffusion model applied to CARIS are largely affected by the day's weather, especially the wind's speed and direction. The wind speed at the time of the accident was 4m/s, which seems to have been affected by the wind speed of about a maximum of 4.6m/s.



[Fig. 10] CARIS hydrogen chloride damage range

5.4. Result Comparison

The results of risk assessment in the event of silicon tetrachloride leakage using three risk assessment programs are summarized in [Table 9]. The actual damage distance (range) was about 500m, but the risk assessment programs yielded 1,860m, 908m, and 4,198m. Among the three programs, ALOHA's yield was close to this study's actual accident.

<**Table 9**> Damage range per risk assessment program

	Actual Accident	**KORA**	**ALOHA**			**CARIS**		
Leaked materials	Silicon tetrachloride mixture.	Silicon tetrachloride	Hydrogen chloride			Hydrogen chloride		
Range	Damage range in Vegetation	Range	Risk Area	Semi-risk	boundary	Risk Area	Semi-risk	boundary
	500m	1,860.8m	116m	335m	908m	485m	1,422m	4,198m

6. Conclusion

Currently, firefighters use the CARIS program to calculate the extent of damage impact, in addition to collecting other data. Based on the study results, the purpose of this study is to test which are more useful for firefighters to calculate the extent of the impact when hazardous chemicals leak.

We compared the predicted extent of damage calculated by three software, KORA, ALOHA, and CARIS, under an assumed case of silicon tetrachloride or hydrogen chloride leak to the actual extent of the damage. The predictions were close to the actual value in the following order: ALOHA>KORA> CARIS. Although KORA showed a circular range, it took precedence over CARIS in that the damage radius was smaller than CARIS. However, compared to ALOHA, the ranges yielded by KORA and CARIS were extensively different. Thus, the researchers recommend giving less meaning to accuracy.

(1) KORA is a program used to draft a chemical accident prevention management plan at workplaces that deal with hazardous chemicals. It calculates the extent of damage based on the worst-case scenario and feasible alternative scenarios in reality. Yet, calculating the scope of toxic damage impact without considering wind direction provides an overly extensive area for firefighters to respond in case of accidents. This makes it challenging to respond to accidents quickly and determine the range of the residential areas necessary for evacuation.

(2) ALOHA can illustrate the extent of damage impact with intuitive use and simple input. It is also similar to the actual range in predicting the spread of toxic substances with molecular weights greater than air.

(3) CARIS can be said to be a total solution for chemical accidents that provides information on the company responsible for the accident, disaster control agencies, and various accident responses within the program. However, CARIS provides a wide range like KORA, which may make it difficult for fire departments to respond quickly. Therefore, if the fire department uses CARIS to respond to accidents, it should prioritize taking responsive action in highly dangerous areas.

Since each of the three programs has advantages and disadvantages, the researchers propose using two programs that would help firefighting at the site of a hazardous chemical leak.

First, the program with a close damage impact range to the actual accident is ALOHA in this study. Therefore, it is necessary to use the program to induce rapid evacuation of residents in the initial stages of the accident,

Second, use CARIS as auxiliary data for calculating wind direction and maximum range.

This study compared and analyzed only one case of leakage of silicon tetrachloride or hydrogen chloride. Therefore, it has limitations in application to other thousands of chemicals. In the future, more research needs to take place to characterize the substances with small proportions in steam, flammable substances, and others that often cause accidents to determine the extent of damage using the programs.

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