VISUALIZATIONAND RISK ESTIMATION OF HARMFUL SUBSTANCES LEAKAGE BASED ON ALOHA CODE

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Abstract: Air pollution caused by leakage of dangerous chemicals is a serious threat to the living world and the environment. Predicting the consequences of pollution by mathematical simulation of leakage has become an important method in the field of environmental protection. In this study, two registered accidents of leakage of chemicals on the territory of the Republic of Serbia were analysed, the leakage of hydrochloric acid and the leakage of ammonia. The areal location of hazardous atmospheres (ALOHA) model was selected together with accurate data on geographic location and meteorological conditions for simulation and evaluation of the effects of harmful evaporation on the environment, Additional analyzes of the same accidents were performed for different meteorological conditions and a comparison of the results was done.The simulation confirmed that the extent of the pollution largely depended on the type of chemical pollutantsand then on their release in given meteorological and geographical conditions.

Keywords: Chemical accidents, ALOHA, Risk analysis, Health risk, Serbia

INTRODUCTION

Industrial development of a country implies the construction of factories and facilities, modernization and introduction of new technological processes, transportation and storage of chemicals for the needs of various industrial branches. During all these processes, various chemical accidents often occur, and then the living world becomes the victim of the release of dangerous substances into the environment. Some of the most important goals of the sustainable development

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concept are to prevent or reduce the release of toxic chemicals into the atmosphere, to quickly anticipate and remedy the consequences of an accident.

The air quality assessment by determining the concentration of harmful substances plays an important role in environmental protection. Various methods are used for this purpose such as direct measuring using fixed or mobile measuring stationsor air pollution mathematical modeling based on dispersion models or usage of biomonitoring for pollution determination in particular part of an area.

The significance of mathematical modeling is to help predict and reduce threats and consequences from possible hazards and provide time for preparatory activities before rescue. Assessing the consequences of risks such as the release of hazardous chemicals into the environment is one of the most important activities for increasing the level of safety at the design stage or activity of industries (Beheshti et al., 2018).

The Areal Locations of Hazardous Atmospheres model (ALOHA software, 2016) was selected to simulate two real cases of leakage of toxic chemical, ammonia and hydrochloric acid. Simulation results by ALOHA code are widely used for modeling dispersion of air pollution (Jacimovski et al., 2018). They can also be the basic for relevant effects analysis and pollution risk assessments (Tseng et al., 2012, Salam, 2013).

Ammonia and hydrochloric acid are chemical compounds that are often used in technological processes of various industries. A large amount of ammonia produced is spent on the production of artificial fertilizers, ammonium nitrate and nitric acid. Other quantities are used in the chemical and textile industry, as well as in food industry for food freezing. A lot of hydrochloric acid is used for cleaning, polishing and etching of metals, in the chemical industry for obtaining different inorganic and organic chloride compounds, in the paint and food industry or for the production of aluminum oxide by acidic process (Harvey, 2003).

At ordinary temperatures, ammonia is a colorless gas of a sharp, characteristic odor that is the first warning sign of possible exposure to this gas. Liquid ammonia is a 10-33% solution of ammonia gas. The risks and consequences of exposure to ammonia depending on concentrations are as follows:

400 ppm (278 mg / m^3) = instant throat irritation; 700 ppm (487 mg / m^3) = eye irritation; 1700 ppm (1182 mg / m^3) = coughing,2500-6500 ppm (1738-4519 mg / m^3) = life-threatening after 30 minutes and 5000-10000 ppm (3476-6953 mg / m^3) = death ("HIP-AZOTARA"d.o.o. Pančevo, Safety Data Sheet – Ammonia, 2016).

Diluted hydrochloric acid (mass fraction up to about 25%) is classified as an irritant. Concentrated acids to a theoretical maximum of ~ 40 % are classified as a corrosive substance. The severity of the damage depends on the acid concentration in the solution and duration of exposure. Vapor or dispersed concentrated acid liquid can cause irritation of the nasal cavity, throat pain, choking, coughing and difficulty in breathing (50-100 ppm). Exposure to high concentrations (e.g., 1000-2000 ppm), in duration of even just a few minutes, can cause lung water accumulation (edema of the lungs). Symptoms of edema of the lungs, such as breathlessness, may last for several hours after exposure (RollingCo, Safety Data Sheet – Hydrochloric acid 31-33%, 2015).

PREDICTION OF THE DISPERSION

An air dispersion model (ALOHA software, 2016) was developed by the Environmental Protection Agency (EPA). The ALOHA model was built upon the Gaussian dispersion model of continuous air pollution flumes to predict how gases that are about as buoyant as air will disperse in the atmosphere (Thoman et al., 2006; Tseng et al., 2012). This program code is suitable for dispersion simulation for over 900 chemicals and especially suitable for the simulation of accidental release of hazardous substances.

The basic form of the Gaussian plume model (Hanna et al., 1982) is given as Eq.1:

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u} e^{-\frac{y^2}{2\sigma y^2}} \left[e^{\frac{-(z-h)^2}{2\sigma_z{}^2}} + e^{\frac{-(z+h)^2}{2\sigma_z{}^2}} \right] \tag{1}$$

where *C* is atmospheric concentration (mg/m^3) for chemical releases, *Q* is the source release rate (usually expressed in mg/s for chemicals), *h* is the effective release height (relative to the ground, in m), *y* is crosswind distance relative to plume centerline, in m), *z* is vertical axis distance relative to the ground, in m), *u* is the average wind speed and $ó_y$, $ó_z$ are horizontal and vertical dispersion coefficients representing the standard deviations of the pollutants concentration distribution in the crosswind axis direction and in the vertical axis direction (in m), respectively. According to the classification scheme developed by Pasquill and Gifford, each $ó_y$ or $ó_z$ curve represents a different atmospheric stability condition. Different classes of atmospheric stability range from very unstable conditions (A) to very stable conditions (F) and they are shown, along with the parameters for the $ó_y$ and $ó_z$ calculation, in Table 1 (Zannetti, 1990, Thoman et al., 2006, Lazaridis, 2011, Lazareviж, 2012, Salam, 2013).

Table1 *Parameters for óy and óz determination*

		A	a	B	b
Highly unstable	A	0.527	0.865	0.28	0.90
Unstable	B	0.371	0.866	0.23	0.85
Mildly unstable	C	0.209	0.897	0.22	0.80
		A	a	B	b
Neutral	D	0.128	0.905	0.20	0.76
Stable	E	0.098	0.902	0.15	0.73
Highly stable	F	0.065	0.902	0.15	0.67

In order for the ALOHA model to be applied, it was necessary to determine the following parameters: the location of the emission source (latitude, longitude and elevation), the atmospheric conditions (ambient air temperature, relative humidity, wind speed and direction and cloudiness of the sky) and the source parameters description (the source height, emmisions flow rate and temperature).

RESULTS AND DISCUSSION

Two cases of hazardous chemical leakage documented in the records of the Ministry of Internal Affairs of the Republic of Serbia, have been chosen for analysis. Simulation was performed using the ALOHA model to obtain the threat zones of toxic materials dispersion.

The first case analyzed pertains to hydrochloric acid leak in January 2009 in Belgrade. The second case occurred in August 2010 in PadinskaSkela, when a large amount of ammonia was released.

In addition to the analysis of cases in the real environment conditions in which they occurred, the effects of pollution in completely opposite weather conditions were simulated and analyzed.The aim was to determine the conditions under which the worst-case scenario would occur.

The threat zones will be shown in diagrams as a result of the simulation in the ALOHA software and will vary in color depending on the degree of threat to the environment.

All zones marked in red represent areas where the population may have serious health consequences due to pollution. The zones marked in orange are potentially highly hazardous to the lives of those people belonging to sensitive categories, such as children, elderly people, patients with chronic pulmonary disease, pregnant women, etc. The population inside the yellow zone would likely not have had serious consequences on health.

Analysis of leakage of hydrochloric acid (Case 1) Case 1, Scenario 1

On January 28, 2009 around 3 p.m., on the premises of BIP (*Belgrade Industry of Beer*), there was a leakage of an overhead tank in which there was about 25 tons of hydrochloric acid (HCl). The exact location where this happened is 44°47’46” of northern latitude and 20°27’07” of eastern longitude. Belgrade is at 132 m of altitude.

The weather data required for the simulation were obtained from the annual report of the Republic Hydrometeorological Service of Serbia for the year 2009 and given in Table 2 (RHMZ, 2009).

Table 2 *Configurations of the release scenario*

Parameters	Winter conditions
Temperature	3.6°C (2 p.m.)
Wind direction	west-northwest
Wind speed	4.4 m/s
Humidity	50%
Cloudiness	10/10
Atmospheric stability level	D

According to the possibilities offered by the software, the source of pollution was chosen to be represented by the puddle of liquid.The mass and diameter of the puddle were 25t and 40 m respectively. The total amount of released pollutants in the atmosphere (hydrogen chloride, in this case) was 217 kg.The maximum average evaporation rate of the hazardous gas in these meteorological conditions was 4.07 kg / min. The release time of the pollutant is limited to 60 minutes.

The source strength slowly declines with time as can be seen in Fig.1.

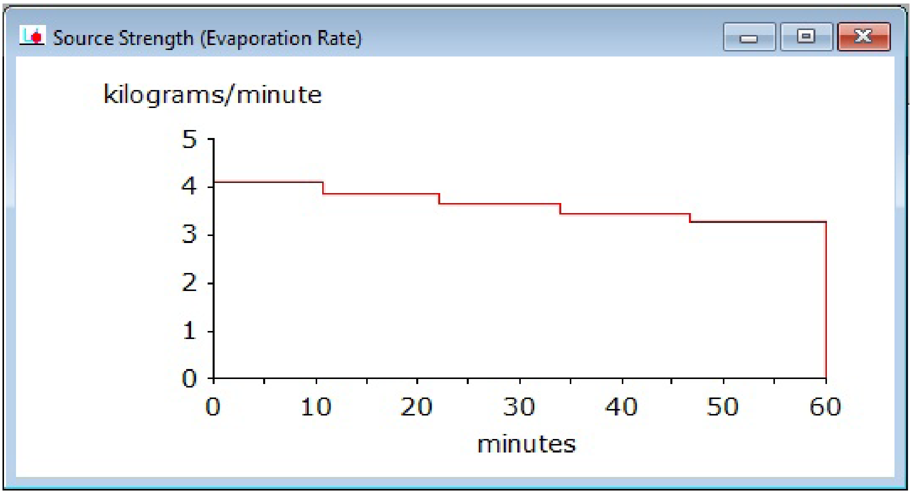

Figure 1. *Source strength in time function (case 1, scenario 1)*

According to the results of the simulation, it can be said that the concentration of the pollutant was relatively low. Maximal value of pollutants concentration in given conditions was 4.412 ppm or 0.44%. Based on the specified pollution threshold values of 100 ppm (0.01%) for the red zone, 22 ppm (0.0022%) for the orange and 1.8 ppm (0.00018%) for the yellow zone, it was calculated that the red zone (zone of the highest risk) covers 23 m from the source, the orange zone covers 53 m, while the furthest point of the yellow zone is 384 m from the source (Fig. 2).

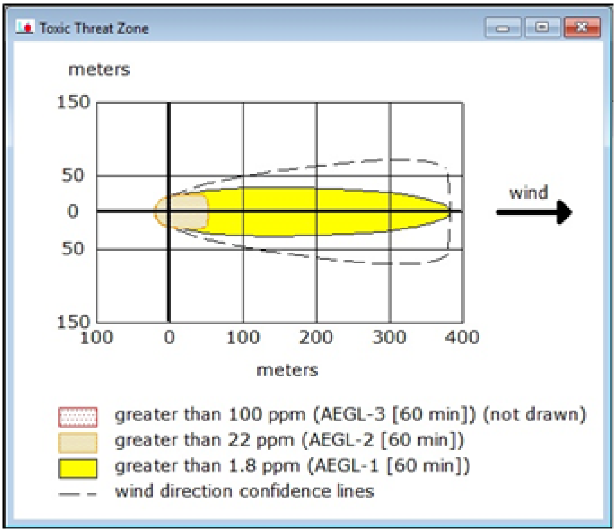

Figure 2. *Diagram of threat population (case 1, scenario 1)*

The red zone is not shown in this diagram, since the Gauss model does not provide reliable results of dispersion for such a short distance. Significant concentrations of pollutants are recorded at distances up to 400 m in the direction of the wind and the width of the accident zone is slightly greater than 50 m. Therefore, the danger zone is about 0.02 km^2 (2000 m^2), which is an area that is barely larger than the area covered by the puddle. In Fig.3 the geographical location of the threat zone with the limits of the orange and yellow zones is shown.

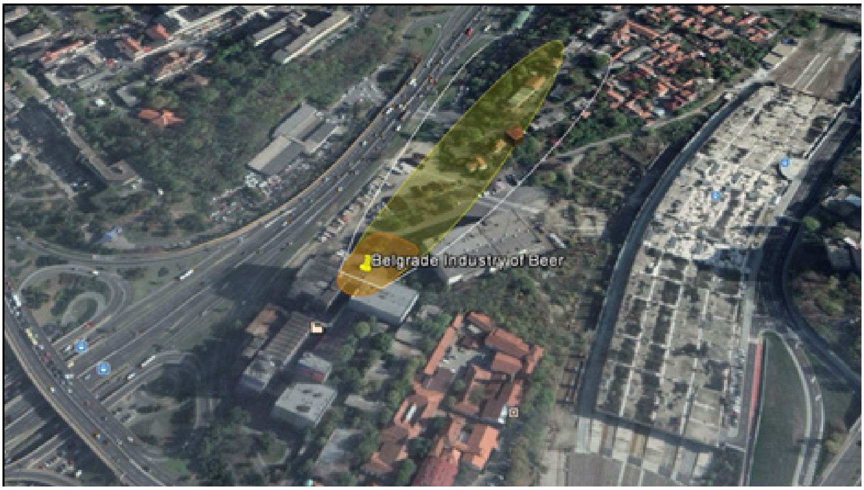

Figure 3. *Image of geographical location of the threat zone (case 1, scenario 1)*

Case 1, Scenario 2

An imagined scenario of the same chemical accident (leakage of 25 t of hydrochloric acid) in summer weather conditions on July 23, 2009 at 2 p.m. would have the parameters given in Table 3. The meteorological data required for the simulation was provided by the Republic Hydrometeorological Service of Serbia (RHMZ).

Table 3 *Configurations of the release scenario*

Parameters	Summer conditions
temperature	36°C (2 p.m.)
wind direction	south-southwest
wind speed	2.4 m/s
humidity	30%
cloudiness	0/10
atmospheric stability level	B

For the same input characteristics of the pollution source (a puddle whose mass was 25 t with a diameter of 40 m), the following output values were obtained: total amount of released hydrogen chloride was 923 kg and the highest average speed was 21.2 kg/min.

According to the simulation results for this scenario, the rate of evaporation is significantly higher, i.e. the strength of the source declines significantly over a time interval of 60 min (Fig.4).

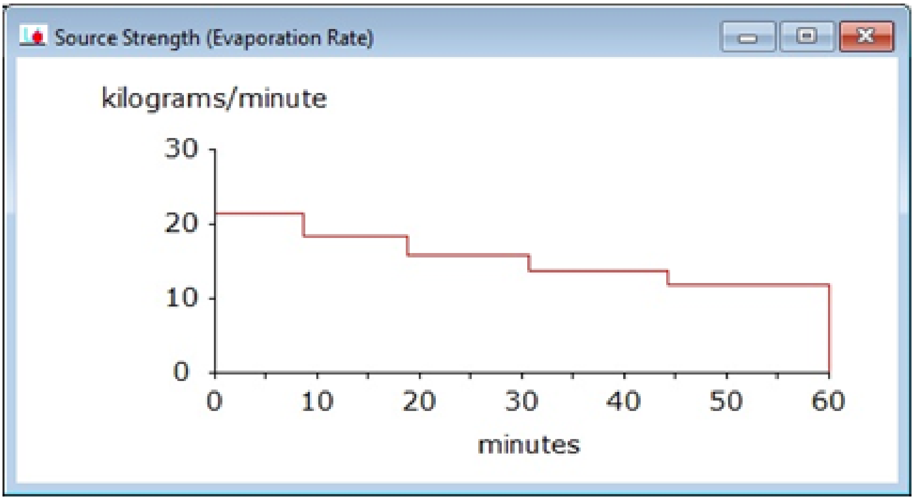

Figure 4. *Reducing the strength of the source with time(case 1, scenario 2)*

The maximum concentration of pollutants in summer weather conditions was significantly higher compared to winter conditions and amounted to 40.789 ppm (4.08 %). The threshold values in zones remained identical (100 ppmfor the red zone, 22 ppm for orange and 1.8 ppm for the yellow zone) and are shown in Fig.5.

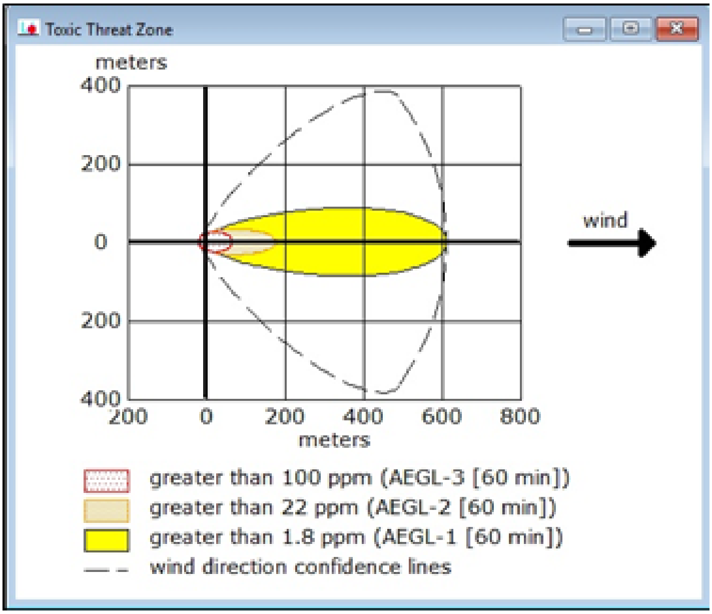

Figure 5. *Diagram of threat population (case 1, scenario 2)*

The results of the simulation show that in this scenario the red zone extends at a distance of 65 m from the source, the orange zone is at a distance of 179 m from the source, while the range of the yellow zone is estimated at 616 m from the source, all in the wind direction.The width of the zone under the influence of pollution was 400 m (Fig.5). Potential threat zone was around 0.24 km^2 or 240,000 m^2, which is a far greater area than in the first scenario, i.e. conversan area that is 190 times larger than the surface of the pollution source.

Based on the geographical location of the accident (Fig.6), it can be concluded that much wider area has been affected by the pollution. This is especially important when observing the red and orange zone concentration of pollutants.

Figure 6. *Geographical location of population threat zones (case 1, scenario 2)*

The simulation results defined the zones of threat under different weather conditions.The pollutant emissions expressed through the distance downstream the source are given in Table 4.

Table 4. *Summary of the simulation results of the pollutant emission downstream the source*

Range of zones with defined concentrations	winter weather conditions (case 1)	summer weather conditions (case 2)
red zone (100 ppm)	23 m	65 m
orange zone (22 ppm)	53 m	179 m
yellow zone (1.8 ppm)	384 m	616 m
potential threat zone	0.02 km^2	0.24 km^2

It can be seen from Table 4 that in case 2 (the hydrochloric acid was released in unstable summer weather conditions), the area that includes the wind direction confidence lines and the area of potential threat will be much larger (0.24 km^2). This means that this would be a worse scenario that would have a greater impact on people and the environment.

Analysis of leakage of ammonia (Case 2) Case 2, Scenario 1

On August 13, 2010 (3.25 p.m.) at a site called PadinskaSkela in the municipality of Palilula (44°56’28” of northern longitude, 20°25’45” of eastern latitude, the altitude is 132 m), an overhead tank burst and around 20 t of ammonia (NH_3) were released.

The meteorological data required for the simulation were provided by the Republic Hydrometeorological Service of Serbia (RHMZ) and were given in Table 5.

Table 5. *Configurations of the release scenario*

Parameters	Summer conditions
temperature	34°C (3.25 p.m.)
wind direction	south-southeast
wind speed	2.4 m/s
humidity	50%
cloudiness	0/10
atmospheric stability level	B

For simulation purposes, the characteristics of the source of pollution are as follows: it was an overhead tank of horizontal cylindrical shape, 5 m long and with 3 m base diameter, filled with ammonia to the top. The chemicals leakage occurred through an opening of a rectangular shape of 30 cm long and 5 cm at a height of 25 cm from the bottom of the tank.

For given parameters, the following results were obtained: total amount of released ammonia is 20.506 kg, maximal average speed of exposure is 19.800 kg/min and the estimated leakage time is about 2 minutes (Fig.7).

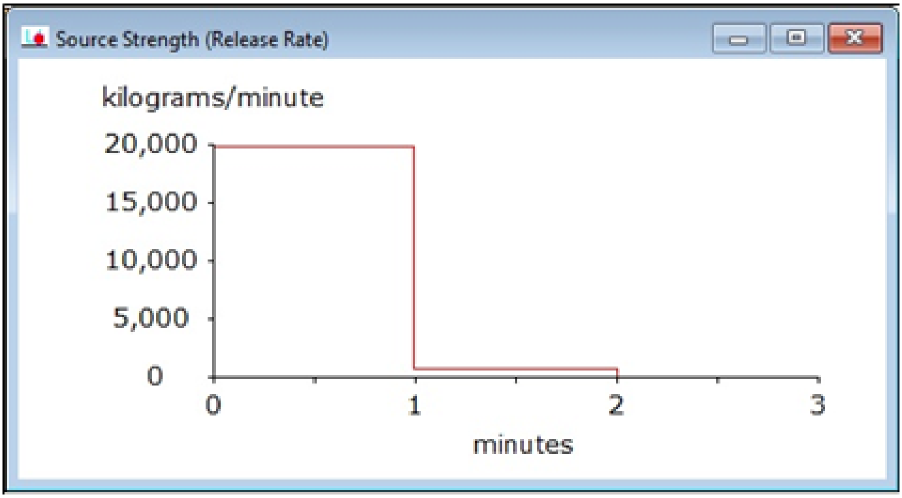

Figure 7. *Source strength depending on time (case 2, scenario 1)*

The source strength in this scenario rapidly declines with time and the tank is almost empty in a minute. Pollutants concentration is high.The definition of the threat-to-concentration zone is as follows: red zone – concentration is greater than 1.100 ppm, orange zone – 160 ppm, and yellow zone – 30 ppm. In this scenario, the red zone spreads in the area up to 900 m from the source, the orange zone is in the area up to 1.6 km, and the end border of the yellow zone spreads at the distance of more than 2.5 km from the source (Fig. 8).

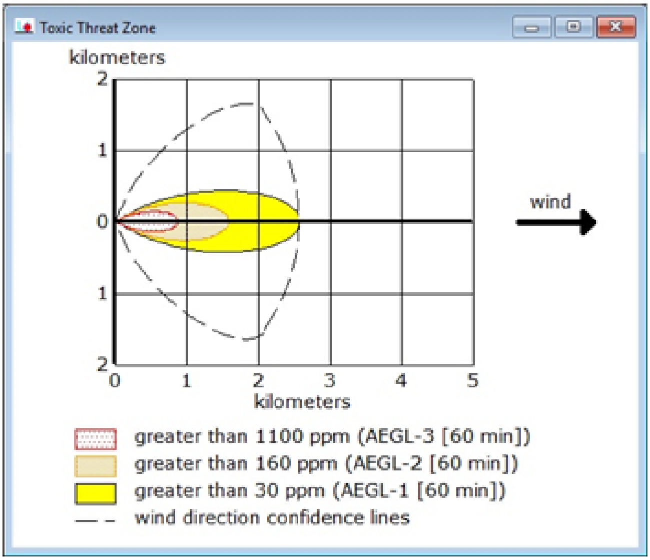

Figure 8. *Threat zone for the case 2, scenario 1*

The zone under the influence of the pollutants extended at a distance of 3 km from the source.

The width of accidental range was 2 km. According to the data, the threat zone about 6 km^2 is shown on Fig. 9.

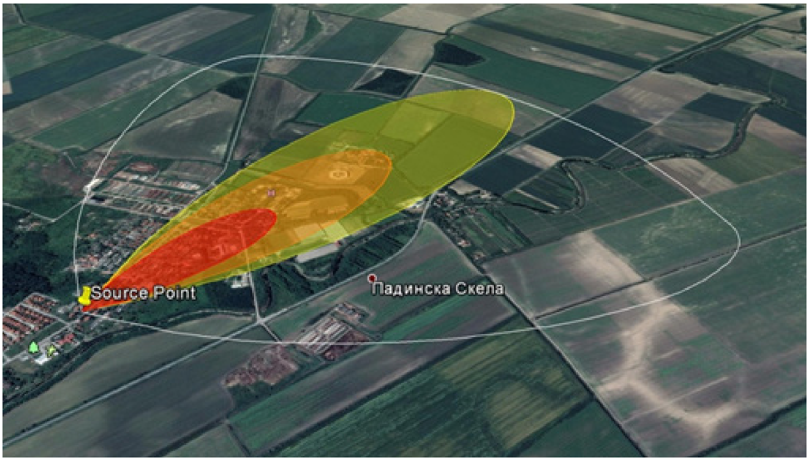

Figure 9. *Geographic image of population threat zones (case 2, scenario 1)*

Case 2, Scenario 2

An imagined scenario of the same chemical accident (leakage of ammonia) in Padinska Skela in winter weather conditions at 2 p.m. on January 28, 2010 would have the parameters given in Table 6.

Table 6. *Configurations of parameters*

Parameters	Winter conditions
temperature	-5°C (2 p.m.)
wind direction	west-southwest
wind speed	2.4 m/s
humidity	75%
cloudiness	10/10
atmospheric stability level	D

In order to compare the results of the simulation of the same chemical incident under different weather conditions, the input parameters for defining the source remained the same.The intention was to keep the concentration of pollutants constant in order to analyze the effects of pollution.

Obtained output data of the source is: substance amount that leaked is 20.587 kg, maximal average exposure speed is 10.100 kg/min, and total leakage time is 3 minutes.

According to this scenario, the strength of the source decreases rapidly over time, so it took about 2 minutes to release most of the liquid from the reservoir (Fig.10). Pollutants concentration is high.

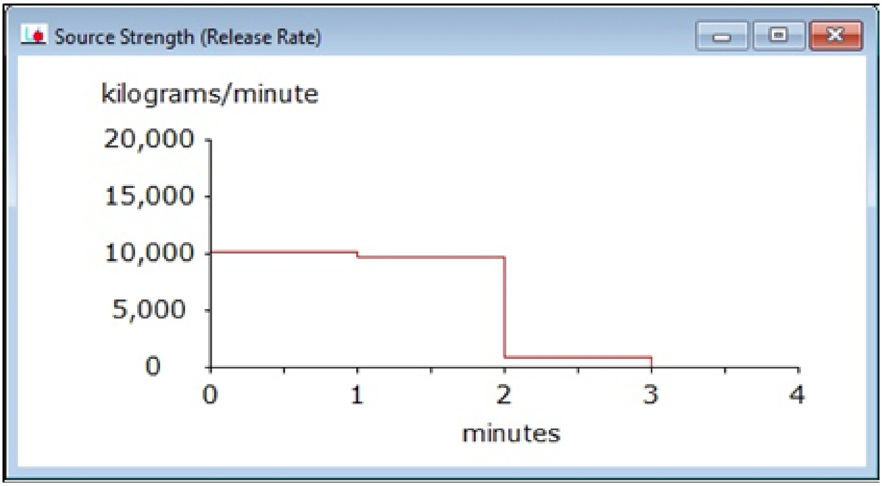

Figure10. *Release rate of the pollutants with the time (case 2, scenario 2)*

The results of the simulation show that, according to this scenario, the red zone extends to 1.4 km from the source, the orange zone covers up to 2.8 km and the final border of the yellow zone spreads at the distance more than 5 km from the source (Fig.11).

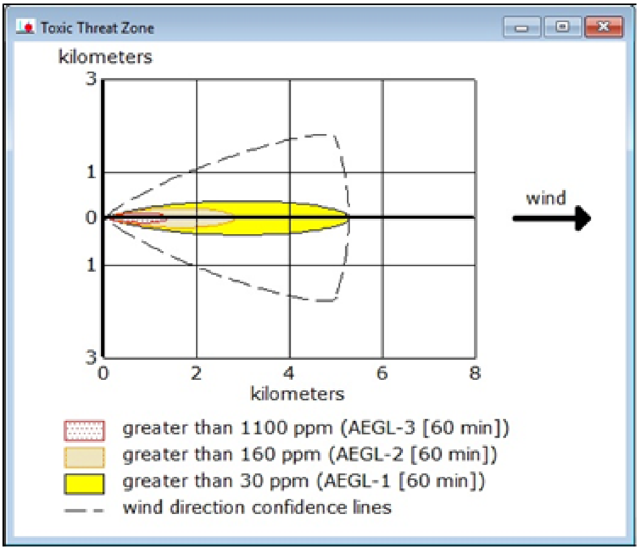

Figure 11. *Threat zones (case 2, scenario 2)*

Concentrations of pollutants are present at a normal distance of more than 5 km and at a width of 3 km. According to these data, the zone of threat is about 15 km^2 (Fig.12).

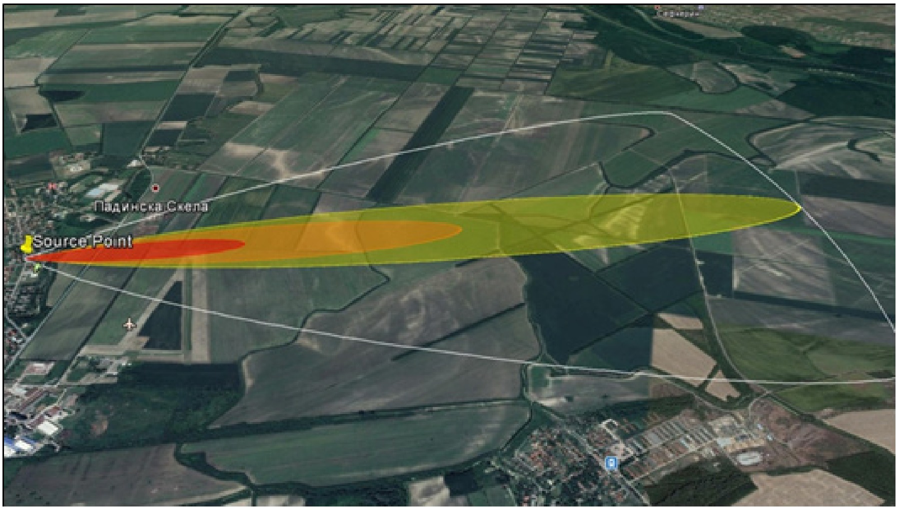

Figure 12. *Geographic image of threat zones (case 2, scenario 2)*

The range of zones with defined concentrations of pollutants expressed through the distance downstream the source are given in Table 7.

Table 7 *Summary of the simulation results of the pollutant emmision downstream the source*

Range of zones with defined concentrations	summer weather conditions (case 1)	winter weather conditions (case 2)
red zone (1100 ppm)	900 m	1400 m
orange zone (160 ppm)	1600 m	2800 m
yellow zone (30 ppm)	2500 m	5000 m
potential threat zone	6 km^2	15 km^2

Based on the results of the simulation from the Table 5, it can be concluded that the worse scenario is the case 2, where the zone of pollution with the ammonia covers an area of 15 km^2.

CONCLUSION

All accidents, regardless of their features and how they occured, are dangerous for the environment and humans. However, chemical accidents are exceptional. Given the fact that there is a need to use chemical substances in great quantities, as well as to store and transport them, it is obvious why chemical accidents are the most frequent ones.

For all of this, monitoring of tanks containing dangerous chemicals must be at a high level, and timely reactions involving the eventual evacuation of people and rehabilitation of the endangered areas due to hazard are mandatory.

The significance of applying mathematical software for the simulation of the pollution processes (ALOHA software) has been shown on the examples of two accidents that really happened. The first accident was the leakage of 25 t of the hydrochloric acid, and the second was the leakage of 20 t of ammonia. In order to analyse the worst possible cases, the imaginary scenarios with completely opposite meteorogical conditions were included in simulation.

From the results obtained by simulation of the leakage case of the hydrochloric acid on the premises of BIP (*Belgrade Industry of Beer*), it can be concluded that the evacuation was unnecessary in the first scenario. There was also no need to block the traffic. The danger zone covered an area of 0.02 km^2 and this indicates that only workers in the mentioned factory and rescue and firefighting service present in the source vicinity were at risk. On the other hand, the results of the simulation of the imagined leakage of acid scenario in summer meteorological conditions are significantly different from the first scenario results. The threat zone would cover an area of 0.24 km^2. The orange zone (concentrations greater than 22 ppm) would have covered a nearby traffic interchange, and even the red zone would have been of significant size. Obviously, for the second scenario of the first analyzed case, traffic would have to be stopped and that the rescue and fire fighting units would have to act extremely carefully, with warnings to the workers and the population in the affected area.

In the second analyzed case, i.e. the case of ammonia leakage from the tank, the situation was much more serious. Both scenarios of the second case point to a large red and orange zone (concentrations greater than 160 ppm).The first scenario required an evacuation because 50% of the settlements were covered by the zone of threat. Only due to the circumstances in the second scenario (geographical position, the width of accidental region, wind direction and intensity), it would be not necessary to evacuate the population of a nearby settlement. In the second scenario, it would likely be necessary to stop all the flights from a nearby military airport.

The analysis of two real and two imaginary scenarios of chemical accidents has shown that each accident is specific. The consequences of chemical accidents depend mostly on the type of pollutant (chemical substance), the location of the accident and meteorological conditions (mostly on temperature and wind speed and direction).

The application of mathematical models of dispersions, included in software packages for simulation of accidents, in the cases described above proved to be extremely important, either to predict possible consequences or to mitigate them.

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