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Development and Implementation of an Algorithm for Predicting the Intensity of Sorption of Hazardous Gaseous Materials

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Abstract. An algorithm for predicting the intensity of sorption of gaseous materials released into the atmosphere as a result of an accident is proposed. The algorithm consists of three hierarchical levels: monitoring the parameters of gaseous material emission, predicting the consequences of gaseous material emission before and after sorption, and making a management decision. The first hierarchical level includes 4 blocks: obtaining information from the chemical reconnaissance group and the facility representative on the type, amount of hazardous gaseous materials, release intensity and scale of the accident; obtaining information from the hydrometeorological service on temperature, atmospheric pressure, wind direction and speed in the accident area; processing the information received; information on the availability of forces and means for sorption of hazardous gaseous materials. The second hierarchical level also includes 4 blocks: readiness of forces and means for sorption of hazardous gaseous materials; calculation with sorption; calculation without sorption; determination of the boundaries of the chemical damage zone according to the established criteria. At the third hierarchical level, there is 1 block: making a management decision. The software implementation of the proposed algorithm was carried out. The use of the developed algorithm and its software implementation will increase the speed and accuracy of predicting the consequences of the release of hazardous gaseous materials in an accident.

1 Introduction

Today's industry requires the use of a large number of different, including hazardous, chemicals. Even under conditions of normal operation of industrial enterprises, a significant amount of them is released into the environment, which negatively affects air, water and soil [1, 2]. Despite considerable efforts to comply with the rules of safe operation, emergencies occur at facilities where hazardous chemicals are handled [3].

2 Problem Formulation

In the event of large-scale releases of hazardous chemical materials (HCM), early prediction of the possible consequences of chemical contamination is necessary to ensure the safe evacuation of the population and material assets, as well as the safety of rescuers [4, 5].

Various algorithms and programs [6, 7] are used to promptly predict the consequences of chemical pollution of the atmosphere by HCM.

The forecasting process is particularly important in the event of an emergency involving the release of gaseous hazardous chemicals. To ensure sufficient accuracy in calculating the size of chemical pollution zones, it is necessary to take into account a significant number of factors that can be divided into two blocks: meteorological conditions and release parameters. Meteorological conditions include wind direction and speed, temperature and humidity, and atmospheric pressure. The release parameters include the type of chemical, its temperature, density and storage pressure, and release intensity.

Existing approaches to eliminating the consequences of emergencies characterized by the release of harmful and radioactive substances into the atmosphere are based on the use of liquid curtains with the help of ground-based rescue equipment [8, 9]. This involves the deposition of harmful and radioactive substances from the atmospheric air by a finely dispersed stream of water formed by means of emergency rescue equipment [10]. In the presence of a release zone deposition process, these factors are supplemented by another block, which includes the intensity of the liquid flow to the deposition, the deposition area, the presence of a chemical reaction of the liquid with a hazardous chemical, etc. All of this significantly complicates the work of environmental safety control services and emergency rescue units to eliminate atmospheric pollution.

3 Analysis of Publications

One of the methods for predicting the consequences of atmospheric pollution by HCM is to forecast the future situation based on the analysis of the dynamics of its development [11]. This approach allows taking into account all factors of possible accident development. This is achieved by processing an array of monitoring information using recurrent analysis [12]. However, the accuracy of forecasting directly depends on the size of the monitoring data base. In the event of an accident, it is usually impossible to collect a large amount of data with the required accuracy.

The most common are express methods that take into account only the most important factors with a certain step of parameter change [13]. Such methods allow to simplify the calculation procedure and increase the efficiency of work, but have low forecasting accuracy.

To ensure sufficient accuracy in calculating the size of the contamination zones with HCM, it is necessary to take into account a significant number of factors that can be divided into three blocks: meteorological conditions, emission parameters and parameters of deposition (sorption) of HCM. Meteorological conditions include wind direction and speed, air temperature and humidity, and atmospheric pressure [14]. The release parameters include the type of HCM, their temperature, density, storage pressure, and release intensity. When localizing the area of HCM release, another block is added, which includes the intensity of liquid supply for deposition (sorption), deposition area, ability of the supplied liquid to absorb or react chemically with HCM, etc. This complicates the work on predicting the extent of the damage, which can lead to delayed and erroneous management decisions [15].

Ukraine has approved a national methodology for predicting the consequences of accidents involving the release of Hazardous Chemicals (Order of the Ministry of Internal Affairs of Ukraine No. 1000 of 29.11.2019). The methodology makes it possible to simplify the calculation of the size of the HCM cloud spreading zone by tabulating the main indicators. However, the methodology does not allow you to automatically see the results of the forecast. The methodology can be used for long-term (operational) and emergency forecasting in case of accidents at chemically hazardous facilities (CHF) and transport, as well as for determining the degree of chemical hazard of CHF and administrative-territorial units [16]. The methodology is applicable only to HCM stored in gaseous or liquid form and which, at the time of release, turn into gaseous form and create a primary or secondary cloud of HCM, and provides for calculations for planning measures to protect the population only at heights up to 10 m above the ground. The results are presented in the form of tables, which makes it impossible to perform lengthy calculations and allows for prompt forecasting of the scale of pollution. On the basis of this methodology, the «DSNS GIS» software was developed and implemented; the interface of the results of predicting the chemical contamination zone with the help of this software is shown in Fig. 1.

The Ministry of Ecology of Ukraine recommends the use of software developed on the basis of Gaussian mathematical models and equations of turbulent diffusion of HCM: «EOL», «EOL+FON», «PLENER», «EOL+», «EOL-2000[h]», «EOL (GAS)-2000[h]», and «Ecologist-Gas». The programs are designed to calculate pollution from stationary sources of industrial enterprises in the surface and upper atmosphere.

A program «Air» developed by the Institute of Mathematical Machines and Systems of the National Academy of Sciences of Ukraine can significantly simplify the process of predicting the consequences of a hazardous substance release. The program is designed to implement one of the most urgent tasks of operational modelling of the consequences of a spill/release of HCM at stationary CWS [17]. A program «Air» generates a release forecasting log and provides the ability to perform both emergency modelling performed immediately after an accident and long-term forecasting to determine possible consequences of a HCM release.

Fig. 1. Interface of the results of predicting the chemical damage zone of the program «DSNS GIS»

Also, a number of works by domestic authors, in particular [18–28], are devoted to the assessment of the hazardous effects of HCM on the environment and humans.

Paper [18] developed a method for the rapid detection of hazardous urban air pollution. Paper [19] analyses the correlation dimension of the state of the gas environment during early ignition of materials. Paper [20] proposes an improved installation for extinguishing fires with fine water. Paper [21] is devoted to the experimental study of fluctuations in the parameters of the gas environment as early signs of fire. In [22, 23], a mathematical model was built to determine the risk to human health of a dangerous state of urban air pollution based on the measurement of current concentrations of pollutants. Paper [24] is devoted to improving the environmental safety of power plants by streamlining the pollutant neutralization system. Paper [25] developed a method of frequency-time representation of changes in gaseous medium parameters during a fire. Paper [26] is devoted to the construction of a method for calculating a structural function in a moving window of a fixed size, based on measuring the vector of current concentrations of arbitrary air pollutants. Paper [27] uses the uncertainty function to identify hazardous states of the air pollution vector. Paper [28] investigates the impact of carbon monoxide on people in the event of a fire in a building.

Well-known global implementations of HCM distribution models are the program «HGSYSTEM» and a number of programs by TNO (Holland), Det Norske Veritas (Norway), U.S. Environmental Protection Agency (EPA), NIST (National Institute of Standards and Technology), and DEGADIS [29]. The most common programs recommended by the EPA and used in the USA, Canada, and the EU are: «AERMOD», «CALPUFF», «BLR», «CALINE3», «ALOHA» [30].

The program «AERMOD» has four modules: AERMOD (module for mathematical modelling of impurity dispersion in the atmosphere); AERMET (module for determining the required meteorological data); AERSURFACE (for reproducing the terrain); AERMAP (software tools designed to link the model to three-dimensional data of local terrain and objects). The software contains tools that allow taking into account the peculiarities of EWM spread over roads, water obstacles, forests, etc. The use of program «AERMOD» involves significant costs and effort in preparing input data and makes sense when assessing environmental risks from industrial pollution sources [31].

The program «CALPUFF» uses a state-of-the-art, non-stationary, multi-layer, multi-functional model that simulates the spread of pollutants from emissions of various pollution sources under changing meteorological conditions, taking into account the interaction of substances with the environment. The main components of the modelling system are: CALMET (diagnostic three-dimensional meteorological model), CALPUFF (air quality dispersion model), CALPOST (processing package).

The program «BLR» uses Gaussian dispersion models and can be used for cases where HCM enter the upper atmosphere.

The program «CALINE3» was developed by the California Department of Transportation to determine the level of HCM pollution emitted by internal combustion engines. The programme is based on a multifaceted stationary Gaussian dispersion model of the spread of HCM downwind of highways and city streets in relatively simple terrain.

The peculiarities of the considered programs are the need to use multi-core hardware due to complex algorithms for obtaining an analytical solution. This greatly complicates the forecasting process, which is a significant drawback in the context of a time limit in the process of eliminating accidents.

In the USA, program «ALOHA» (Area Locations of Hazardous Atmospheres) is also used to help emergency responders make calculations during a HCM spill. Program «ALOHA» uses a graphical interface to enter data and display results. The effects of toxic HCM vapours, overpressure, thermal radiation or areas where flammable gases are present are presented graphically and in text.

The core of the methodology of the program «ALOHA» is an air dispersion model to assess the inhalation risk associated with toxic chemicals in the air and the extent of the flammable cloud. This model is used to predict the change in concentration of a pollutant released into the atmosphere depending on the time and location of the release. Program «ALOHA» includes two semi-empirical air dispersion models: A Gaussian model (for predicting the direction of cloud propagation, which is lighter than air) and a Heavy Gas model (for pollutant clouds that are heavier than air) (Fig. 2).

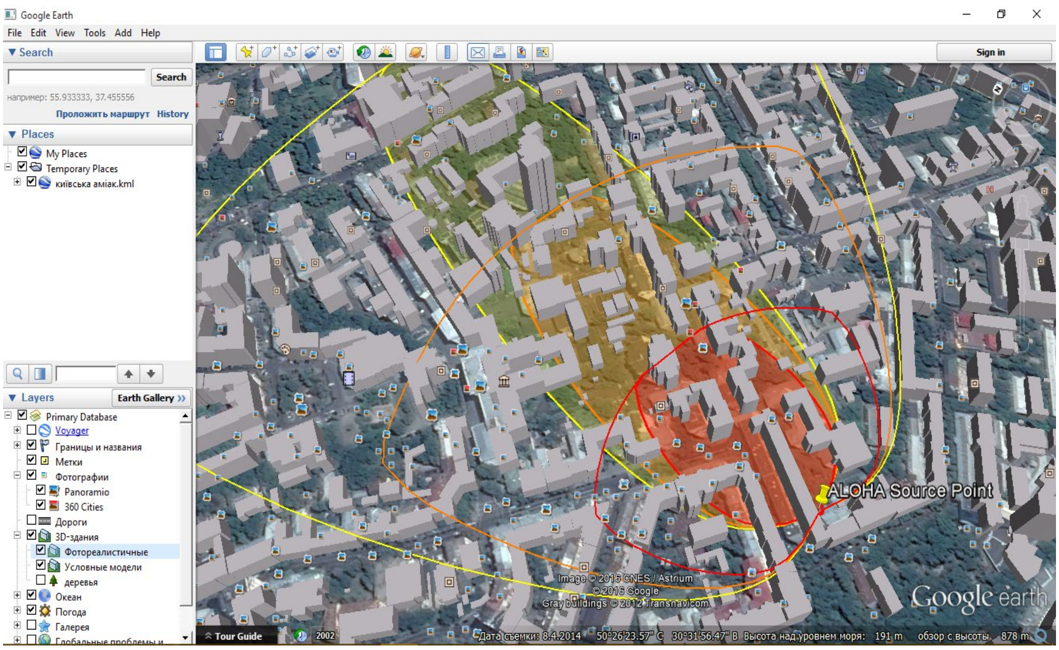

Fig. 2. Forecasting results using the application program «ALOHA»

All the above-analysed programs and works do not take into account the possibility of deposition of the HCM cloud by the forces of operational and rescue units. The deposition of HCM from the atmosphere occurs due to sorption processes [32]. At the same time, the intensity of sorption depends not only on the surrounding conditions, but also on the surface properties of the liquid and the physical and chemical properties of HCM [33]. For example, the intensity of ammonia sorption by pure water is 7-8 times higher than that of chlorine under the same conditions. For the theoretical description of the sorption process, both continuous molecular dynamics models [34] and layer-by-layer mass transfer models [35] are used. However, such models do not take into account the spatial distribution of the gas and its dynamics under the influence of external conditions. In [36], assumptions were made that can be used to describe the overall process of HCM propagation in space during its sorption (deposition) by dispersed water jets. In [37–40], a model for predicting the scale of chemical damage under conditions of deposition of HCM and an algorithm for its use were proposed.

4 Aim of Paper

The above analysis of domestic and foreign algorithms and programs for predicting hazardous chemical materials contamination zones has shown that each of them has its advantages and disadvantages. It has been established that today there is no universal algorithm and program for predicting the consequences of accidents involving the release of hazardous chemical materials that would take into account all the features of the accident development.

The aim of this work is to develop an algorithm and a program for predicting the consequences of accidents involving the release of hazardous chemical materials, which take into account the process of sorption of hazardous chemical materials from the atmosphere by dispersed streams.

5 Materials and Methods of Research

In this paper, we consider "light" gases, i.e. those with a density less than atmospheric air. These gases primarily include ammonia, methane, carbon monoxide, and others. The modelling of the dynamics of such gases in the air was based on Gaussian models, taking into account the restrictions that the release of hazardous chemical materials is a point release with a constant intensity. As the main component of the model that took into account deposition, the process of sorption of hazardous chemical materials by a fine flow was considered. The software implementation of the obtained theoretical results was carried out on the basis of the DELPHI platform with the integration of an interactive terrain map.

6 Research Results

In [25–28], a mathematical model for predicting the size of the release zone of gaseous hazardous materials under different conditions of sorption of HCM from the cloud by water was proposed.

In the absence of HCM sorption, its concentration q1(x,y,z,t) in the air at time τ is calculated by the equation:

$$q_1(x,y,z,\tau)=\frac{E}{8\cdot(\pi\cdot D)^{3/2}}\int_0^{\tau}\frac{1}{(\tau-t)^{3/2}}\cdot p[-\frac{(x-v_x\cdot(\tau-t))^2+(y-v_y\cdot(\tau-t))^2}{4\cdot D\cdot(\tau-t)}]\cdot$$
$$\cdot\{\exp[-\frac{(z-v_z\cdot(\tau-t)-z_0)^2}{4\cdot D\cdot(\tau-t)}]+ +\exp[-\frac{(z-v_z\cdot(\tau-t)+z_0)^2}{4\cdot D\cdot(\tau-t)}]\}dt, \text{кг/м}^3, \quad (1)$$

where x, y, z – coordinates of the Cartesian system,

E – the intensity of the HCM emission carried out at the point (0, 0, z_0),

D – diffusion coefficient in the horizontal and vertical directions,

v_x, v_y – horizontal components of wind speed along the x and y axes, respectively, m/s,

v_z – is the vertical component of the wind speed due to the stability of the atmosphere and the density of HCM, m/s.

During the sorption of HCM with water, its concentration q(x,y,z,t) in the air at time τ in the sorption band is calculated by the equation:

$$q(x,y,z,\tau)=\exp(A_1\cdot x+A_2\cdot y+A_3\cdot z+B\cdot\tau)\cdot u(x,y,z,\tau), \quad (2)$$

where $A_1 = \frac{v_x}{2 \cdot D}$,

$A_2 = \frac{v_y}{2 \cdot D}$,

$A_3 = \frac{v_z}{2 \cdot D}$,

$B = -\beta - \frac{v_x^2 + v_y^2 + v_z^2}{4 \cdot D}$,

$\beta = \frac{\alpha \cdot D \cdot C \cdot r}{H \cdot R_0 \cdot T}$,

α – the gas adaptation coefficient on the surface of the HCM,
C – the volume concentration of water droplets, $1/m^3$,
r – the average radius of water droplets in the flow, m,
H – Henry's constant, mol/(Pa-m)3,
R_0 – the universal gas constant, J/(mol·K),
T – the temperature, K,

$$u = D \cdot \int_0^{\tau} dt \int_{-\infty}^{\infty} d\eta \int_0^{\infty} d\zeta q_1(x_1, \eta, \zeta, t) \exp(-A_2\eta - A_3\zeta - Bt) \cdot \left. \frac{\partial G(x, y, z, \xi, \eta, \zeta, \tau - t)}{\partial \xi} \right|_{\xi=0}$$

$G(x, y, z, \xi, \eta, \zeta, \tau)$ – Green's function, calculated by the equation:

$$G(x, y, z, \xi, \eta, \zeta, \tau) = \frac{1}{8(\pi D\tau)^{3/2}} \{\exp[-\frac{(x - \xi)^2}{4D\tau}] - \exp[-\frac{(x + \xi)^2}{4D\tau}]\} \cdot \exp[-\frac{(y - \eta)^2}{4D\tau}] \cdot \{\exp[-\frac{(z - \varsigma)^2}{4D\tau}] +$$

$$+ \exp[-\frac{(z + \varsigma)^2}{4D\tau}] + 2A_3\sqrt{\pi D\tau} \exp[k^2 D\tau - A_3(z + \zeta)] \cdot \operatorname{erfc}(\frac{z + \zeta}{2\sqrt{D\tau}} - A_3\sqrt{D\tau})\}$$

During the sorption of HCM with water, its concentration q(x,y,z,t) in the air at a time τ along the sorption band is calculated by the formula :

$$q(x, y, z, \tau) = \exp(A_1 \cdot x + A_2 \cdot y + A_3 \cdot z + N \cdot \tau) \cdot w(x, y, z, \tau), \quad (3)$$

де $N = -\frac{v_x^2 + v_y^2 + v_z^2}{4 \cdot D}$,

$$w = D \cdot \int_0^{\tau} dt \int_{-\infty}^{\infty} d\eta \int_0^{\infty} d\zeta q_2(x_1, \eta, \zeta, t) \exp(-A_2\eta - A_3\zeta - Bt) \cdot \left. \frac{\partial G(x, y, z, \xi, \eta, \zeta, \tau - t)}{\partial \xi} \right|_{\xi=0},$$

$q_2 = q(0, y, z, \tau)$.

For the numerical solution of equations (1)-(3), we used the mathematical package MAPLE (Canada), version 18.

Fig. 3.a shows the results of modelling the process of HCM (ammonia) propagation during deposition (sorption) by fine water jets (dependence of the concentration q of HCM in the x and y axes at an air velocity of 5 m/s). In the modelling, it was taken into account that the sorption of HCM takes place in the atmosphere by the surface of a fine water stream with a dispersion of 1 mm and a flow rate of 2 l/s. The sorption zone with a width of 5 m is located at a distance of 10 m from the HCM release.

Fig. 3. b shows the spatial distribution of the concentration difference Δq of HCM in the absence (q_1) and in the presence (q) of deposition (dependence $\Delta q = q_1 - q$ in the x and y axes at an air velocity of 5 m/s).

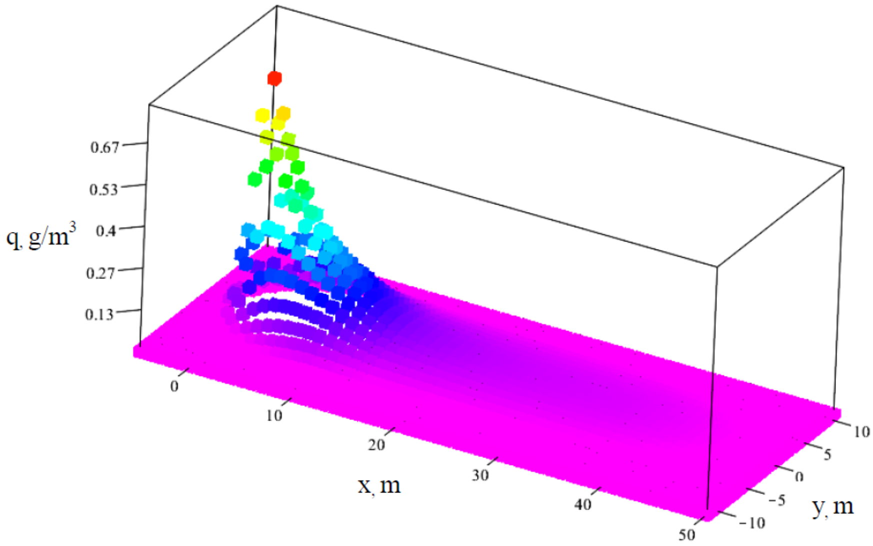

Fig. 3. a. The results of modelling the process of HCM (ammonia) propagation during deposition (sorption) by fine water jets (dependence of HCM concentration q in the x and y axes at an air velocity of 5 m/s)

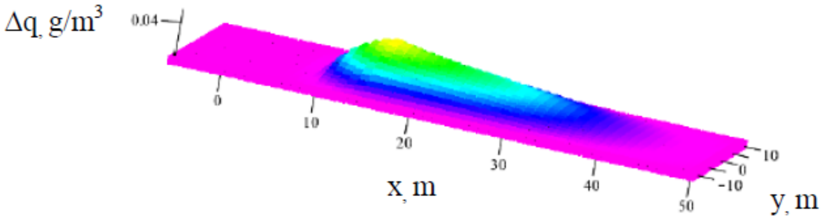

Fig. 3. b. Spatial distribution of the concentration difference $\Delta q = q_1 - q$ of NGM (ammonia) in the absence and presence of deposition

As can be seen from Fig. 3, the condition of continuous gas emission from a point source with a constant intensity is modelled. Calculations have shown that at a flow rate of more than 2 l/s and a gas emission rate of 0.1 kg/s, the concentration of hazardous gas practically drops to 0.

In order to integrate the developed mathematical models of the dynamics of HCM into practical activities, we propose an algorithm for predicting the intensity of sorption of HCM released into the atmosphere as a result of an accident, based on equations (1)–(3) (Fig. 4).

When localizing the accident, the following deposition parameters are determined: the intensity of the sorbent liquid supply, the dispersion of the sorbent liquid and the possible size of the deposition zone. At the same time, the size of the affected area is predicted in the absence and presence of sorption of HCM. In the absence of sorption, the prediction is made using formula (1).

After calculating the size of the chemical contamination zone and mapping the boundaries of the hazardous area, the emergency response manager makes a management decision on the methods of emergency response and the need to evacuate people and property.

The proposed algorithm consists of 9 parts placed on three hierarchical levels, connected by direct links.

The first hierarchical level consists of 4 blocks. Firstly, information about the accident is obtained and systematized from the available automatic alarm systems, from the facility representative or from the chemical reconnaissance group. To perform a qualitative forecast of chemical contamination zones, it is necessary to obtain accurate information on the main meteorological parameters from the hydrometeorological service. Also, the emergency response manager should have data on the available forces and means for HCM sorption.

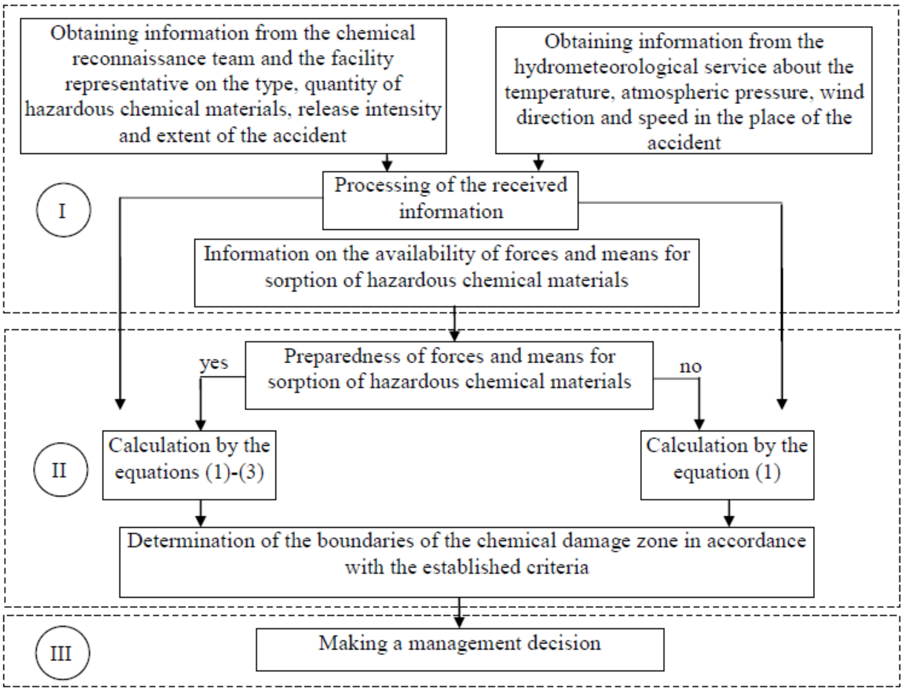

Fig. 4. Algorithm for predicting the intensity of sorption of HCM released into the atmosphere as a result of an accident

The second step is to calculate the size of the chemical contamination zones. To do this, the emergency manager must determine the hazard criterion. As a hazard criterion, the maximum permissible concentration of HCM is usually chosen. After that, the emergency manager determines the possibility of sorption of the HCM cloud.

One of the disadvantages of the proposed model is the assumption that the sorption of the HCM cloud occurs throughout the entire depth and height of the HCM cloud. That is, the boundary conditions for using the model are the technical capabilities of operational rescue units to supply sprayed water (sorbent). The technical capabilities of the fine spray range for carriage guns are up to 40 m, depending on the modification. That is, when using two carriage tubes on opposite sides of the HCM cloud, the depth of the sorption zone can be up to 80 m. If we consider the technical possibilities in terms of the height of the sorbent spray feed, then two options for feeding the jet should be taken into account - ground and using lifts. The ground-based method of supplying a sprayed sorbent jet can provide a height of up to 20 m. The use of mechanical lifts can increase the height of the sorbent jet supply up to 50 m. In other words, the dimensions of the chemical contamination zone to be able to use the proposed model to predict its size should be within the range of width up to 80 m and height up to 50 m, depending on the technical feasibility of sorption. Thus, the use of the model is advisable when sorption is carried out at the initial stage of an accident or near the HCM release zone. This is true since it is near the release source that operational and rescue units carry out work to rescue victims and localize the HCM release.

Thus, the proposed algorithm for predicting the intensity of sorption by water jets of HCM released into the atmosphere as a result of an accident is based on the sequence of three parts – monitoring the accident area, predicting the consequences of the accident, and making a management decision.

The monitoring part of the HCM release area includes collection and processing of data on meteorological conditions in the accident area, the nature of damage to process equipment, the type and amount of HCM available to all civil protection services for HCM sorption.

The predicting part includes input of the obtained input parameters and calculation of the size of the chemical damage zone depending on the number and sequence of stages of HCM spreading and sorption.

The making a management decision part includes determining the hazard criterion, the geographical location of the affected area boundaries, and the definition of measures to eliminate the accident and evacuate the population.

In order to ensure the practical use of the developed algorithm for predicting the intensity of sorption by water jets of HCM released into the atmosphere as a result of an accident, the software package «Forecast of HCM» was developed, the interface of which is shown in Fig. 5.

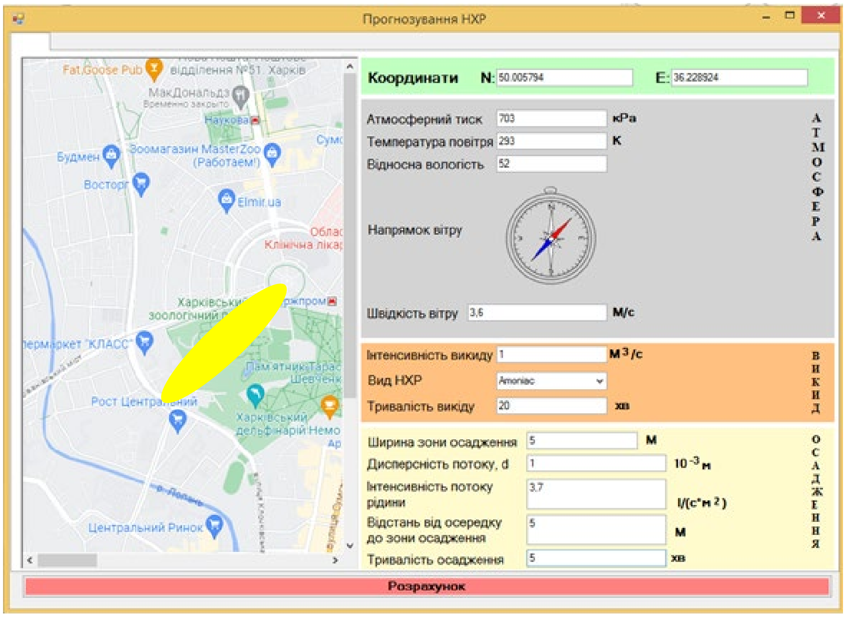

Fig. 5. Interface of the software complex «Forecast of HCM»

The interface of the software complex «Forecast of HCM» is divided into several workspaces. The largest part is occupied by an interactive map of the area integrated with the Google Maps service. This allows you to quickly search for the coordinates of the epicenter of an HCM release or, conversely, display the epicenter on the map using known coordinates. The coordinates of the epicenter of the HCM release are entered in a separate area in the upper right part of the interface.

A separate part of the interface is the block «Atmosphere», which contains the most important meteorological parameters of the atmosphere: temperature, pressure, wind speed and direction. These parameters can be easily obtained from a portable weather station or from the Hydrometeorological Centre.

A separate part contains the parameters of HCM emission. From the library of the most common HCM, the operator selects the required one and enters the intensity of its emission from the process apparatus.

The last block of the interface is intended for entering the parameters of sorption of HCM, namely: the width of the sorption zone, the intensity and dispersion of the sorbent (water flow), the distance from the emission point to the beginning of the sorption zone.

7 Conclusion

An algorithm for predicting the intensity of sorption of HCM released into the atmosphere as a result of an accident is proposed. The algorithm is a sequence of three parts: monitoring the accident area, predicting the consequences of the accident, and making a management decision.

The monitoring part of the HCM release area includes collection and processing of data on meteorological conditions in the accident area, the nature of damage to process equipment, the type and amount of HCM available to all civil protection services for HCM sorption.

The predicting part includes input of the obtained input parameters and calculation of the size of the chemical damage zone depending on the number and sequence of stages of HCM spreading and sorption.

The making a management decision part includes determining the hazard criterion, the geographical location of the affected area boundaries, and the definition of measures to eliminate the accident and evacuate the population.

On the basis of the proposed algorithm, a computer program «Forecast of HCM» was created, which allows predicting the consequences of accidents with the release of HCM in the presence and absence of HCM sorption. The program «Forecast of HCM» consists of parts «Atmosphere», «Release», «Deposition» for entering input parameters and an interactive map of the area for displaying the results of forecasting.

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