Journal of Hazardous Materials, 3 (1980) 201—220

CALCULATION OF THE AMOUNT OF GAS IN THE EXPLOSIVE REGION OF A VAPOUR CLOUD RELEASED IN THE ATMOSPHERE

C.J.P. VAN BUIJTENEN

Prins Maurits Laboratorium, Department of Chemical Research, 2280 AA Rijswijk (The Netherlands)

(Received April 5, 1979; accepted May 1, 1979)

Summary

Formulae were derived and calculations made for the amount of gas in the explosive region of a vapour cloud or plume. It appears that, for an instantaneous source, a large fraction of the total amount released (e.g. 50% for methane) can be in the explosive region, irrespective of source strength and meteorological conditions. On the other hand, for a continuous source, the amount in the explosive region is strongly dependent on source strength and meteorological conditions.

To assist in the hazard analysis, a computer program was written to calculate the concentration as a function of time for a quasi-instantaneous spill of LNG on water.

1. Introduction

From the point of view of the explosion hazard of a vapour cloud, there are two quantities of special interest. The first is the total amount of gas between the flammability limits at a given moment. From this quantity can be calculated the total energy that could be released after ignition of the cloud, and this, in turn, could be used in a procedure to estimate the blast and possible damage caused by the explosion. The second quantity of interest is the maximum distance from the source where delayed ignition is possible. Because variations in the concentration are usually large, ignition of the cloud or part of it is still possible at a distance where the average concentration is lower than the lower flammability limit (LFL). Therefore, the distance is usually calculated for a certain fraction of the LFL (e.g. between 0.5 and 0.1) depending on the circumstances. In establishing a safe distance, different criteria may apply for instantaneous and continuous sources. For a continuous source, the flame could travel back to the source, whereas, for an instantaneous source with an expected maximum average concentration equal to LFL, probably only "pockets" in the cloud are still flammable. It has been shown in [1], that for the tests described in [2], at a distance where the average concentration was ½LFL, ignition of parts of the cloud would have been possible during approximately 10% of the passage time of the cloud. Similar data are given in [3].

2. Amount of gas in the explosive region

To calculate the amount of gas in the explosive region of an instantaneous cloud or continuous plume a three-dimensional integration must be carried out. The starting point should preferably be a simple formula for the concentration as a function of the three space coordinates and, for an instantaneous cloud, also of time. The Gaussian plume model seems most appropriate for the present problem, as it is relatively simple, especially for a point source, and still a sufficiently accurate representation. It also facilitates the derivation of analytical approximations, which give a general insight concerning the amount of gas in the explosive region under different conditions.

2.1 Instantaneous source

For a point source the Gaussian plume model leads to the following formula (see [4]):

$$C(x,y,z,t) = \frac{m}{(2\pi)^{3/2}\,\sigma_{xI}\sigma_{yI}\sigma_{zI}} \exp\left(-\frac{(x-Ut)^2}{2\sigma_{xI}^2}\right) \exp\left(-\frac{y^2}{2\sigma_{yI}^2}\right) \times \left[\exp\left(-\frac{(z-H)^2}{2\sigma_{zI}^2}\right) + \exp\left(-\frac{(z+H)^2}{2\sigma_{zI}^2}\right)\right] \qquad (1)$$

For σ_{xI}, σ_{yI} and σ_{zI}, generally accepted data from the literature are used (see Appendix). For a source with initial dimensions L_x, L_y and L_z (defined in such a way that the total dimensions are $2L_x$, $2L_y$ and $2L_z$), the equation obtained by integrating eqn. (1) is (see [5]):

$$C(x,y,z,t) = \frac{m}{64\,L_xL_yL_z}\left[\operatorname{erf}\left(\frac{L_x - x + x_0}{\sigma_x\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_x + x - x_0}{\sigma_x\sqrt{2}}\right)\right] \times \left[\operatorname{erf}\left(\frac{L_y - y}{\sigma_y\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_y + y}{\sigma_y\sqrt{2}}\right)\right] \times \left[\operatorname{erf}\left(\frac{L_z - z + H}{\sigma_z\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_z + z - H}{\sigma_z\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_z - z - H}{\sigma_z\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_z + z + H}{\sigma_z\sqrt{2}}\right)\right] \qquad (2)$$

(It should be noted that for a source with $L_z > 0$, but touching the ground, $H = L_z$ must be used). See list of symbols for the meaning of all the variables.

2.1.1 Analytical solution for a point source

For a point source it is possible to obtain, by integration of eq. (1) between the flammability limits, the following equation:

$$\frac{m_E}{m} = \mathrm{erf}\left[\sqrt{\ln\left(\frac{P}{P_2}\right)}\right] - \mathrm{erf}\left[\sqrt{\ln\left(\frac{P}{P_1}\right)}\right] - \frac{2P_2}{P\sqrt{\pi}}\sqrt{\ln\left(\frac{P}{P_2}\right)} + \frac{2P_1}{P\sqrt{\pi}}\sqrt{\ln\left(\frac{P}{P_1}\right)} \quad (3)$$

where:

m_E = amount of gas in the explosive region (not including air),
m = total amount of gas released,
P = concentration in the centre of the cloud at the time for which m_E is calculated,
P_1 = upper flammability limit (UFL),
P_2 = lower flammability limit (LFL),
erf (x) = error function (see [6]).

If $P < P_1$, then the equation reduces to:

$$\frac{m_E}{m} = \mathrm{erf}\left[\sqrt{\ln\left(\frac{P}{P_2}\right)}\right] - \frac{2P_2}{P\sqrt{\pi}}\sqrt{\ln\left(\frac{P}{P_2}\right)} \quad (4)$$

Equations (3) and (4) are valid only for a cloud at ground level or for a cloud completely free from the ground. Although eqns. (3) and (4) are derived for a point source, their use can be extended by applying the concept of a virtual source. However, this is subject to the condition that one distance can be used for all three dimensions.

For this idealised case, it is found that the maximum amount of gas that can be in the explosive region at one time (expressed as a fraction of the amount released) is determined only by the ratio of UFL to LFL. Differentiating eqn. (3) with respect to P shows that the maximum m_E/m is reached for:

$$\ln(P) = \frac{P_1^2 \ln(P_1) - P_2^2 \ln(P_2)}{P_1^2 - P_2^2} \quad (5)$$

This can be substituted in eqn. (3). For convenience, however, it is of advantage to put first:

$$v = \frac{P_1}{P_2} \quad (6a)$$

$$v_1 = \frac{\ln(v)}{v^2 - 1} \quad (6b)$$

$$v_2 = \frac{v^2 \ln(v)}{v^2 - 1} \quad (6c)$$

which finally leads to:

$$\left(\frac{m_E}{m}\right)_{max} = \text{erf}(\sqrt{v_2}) - \text{erf}(\sqrt{v_1}) - \frac{2}{\sqrt{\pi}}\exp(-v_2)\sqrt{v_2} + \frac{2}{\sqrt{\pi}}\exp(-v_1)\sqrt{v_1} \quad (7)$$

2.1.2 Partial analytical solution for a cloud with initial dimensions

In order to study the influence of the initial size of the cloud, analytical integration was also attempted for a spherical cloud with initial radius R_0. The results can also be used for an ellipsoidal cloud, because such a shape can be transformed into a sphere by a simple co-ordinate transformation. The condition remains, therefore, that the cloud should be completely free from the ground or at ground level so that the cloud can be treated as one half of an ellipsoid. The initial ellipsoid should have the same ratio of the main axes as σ_x, σ_y and σ_z. For the concentration, the following equation can be derived (analogous to eqn. (2), see [5]):

$$C(R_1) = \frac{m\sigma}{\frac{4}{3}\pi R_0^3 R_1\sqrt{2\pi}}\left[\exp\left(-\frac{(R_0+R_1)^2}{2\sigma^2}\right) - \exp\left(-\frac{(R_0-R_1)^2}{2\sigma^2}\right)\right] + \frac{m}{\frac{8}{3}\pi R_0^3}\left[\text{erf}\left(\frac{R_0-R_1}{\sigma\sqrt{2}}\right) + \text{erf}\left(\frac{R_0+R_1}{\sigma\sqrt{2}}\right)\right] \quad (8)$$

A solution analogous to eqn. (3), thus giving the amount in the explosive region directly, as a function of UFL and LFL, has not been found. However, it is possible to integrate eqn. (8) between two values of R_1. The values of R_1 corresponding with UFL and LFL must be determined separately. This procedure still saves a considerable amount of computer time compared with a completely numerical solution. For the sake of convenience we first define two functions

$$F_1(R_i,R_j) = \left[1 + \left(\frac{R_i}{R_j}\right)^3\right]\frac{1}{2}\text{erf}\left(\frac{R_i+R_j}{\sigma\sqrt{2}}\right) \quad (9a)$$

$$F_2(R_i,R_j) = \frac{\sigma}{R_j^3\sqrt{2\pi}}\left[R_i^2 + R_j^2 - R_iR_j - \sigma^2\right]\exp\left(-\frac{(R_i+R_j)^2}{2\sigma^2}\right) \quad (9b)$$

For the mass of the gas between radius R_1 and R_2 ($R_1 < R_2$), it is then found that:

$$\frac{m(R_1, R_2)}{m} = F_1(R_2,R_0) + F_1(R_2,-R_0) - F_1(R_1,R_0) - F_1(R_1,-R_0) + F_2(R_2,R_0) + F_2(R_2,-R_0) - F_2(R_1,R_0) - F_2(R_1,-R_0) \quad (10)$$

2.1.3 *Numerical solution*

In the course of the investigation a numerical integration of eqn. (2) was also worked out. The program was first written to give the amount in the explosive region, as a function of the distance travelled for a cloud initially box-shaped. Later it was used to produce more general tables for quick reference (eqn. (10) was derived later). The program was also used for mutual checks against the results described in Sections 2.1.1 and 2.1.2.

2.1.4 *Results*

Generally, the behaviour of the amount of gas in the explosive region of an instantaneous cloud can be described as follows. If the gas is released without considerable initial mixing, then the concentration in many cases will be higher than UFL and the amount in the explosive region will be relatively small. As the cloud travels downwind, turbulent mixing dilutes the cloud, the concentration decreases and the amount in the explosive region increases. When the cloud has travelled such a distance that the concentration in the centre is slightly higher than UFL, the amount of gas in the explosive region will reach a maximum. As the concentration decreases further, the amount in the explosive region also begins to decrease. When finally the maximum concentration in the cloud drops below LFL, then the amount in the explosive region becomes zero.

This is illustrated in Fig. 1 for the case of methane using the numerical solution.

Using an approximation according to [6] or [8] for the error function, eqn. (7) was calculated for increasing ratios of UFL and LFL to give the graph

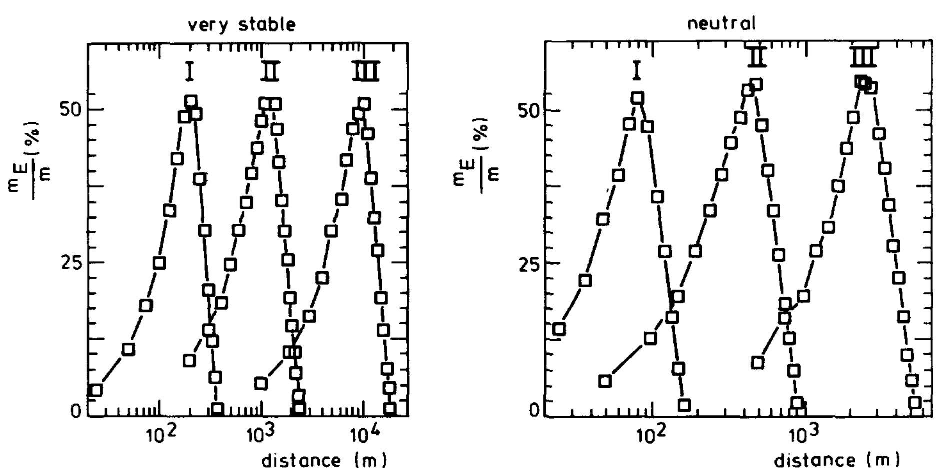


Fig. 1. m_E/m in percent as a function of the distance travelled by the cloud.
I 10^3 kg, L_x = 10 m, L_y = 10 m, L_z = 1 m and H = 1 m;
II 10^5 kg, L_x = 50 m, L_y = 50 m, L_z = 10 m and H = 10 m;
III 10^7 kg, L_x = 250 m, L_y = 250 m, L_z = 20 m and H = 20 m.
No correction is made for a density difference, diffusion parameters adapted to [7].

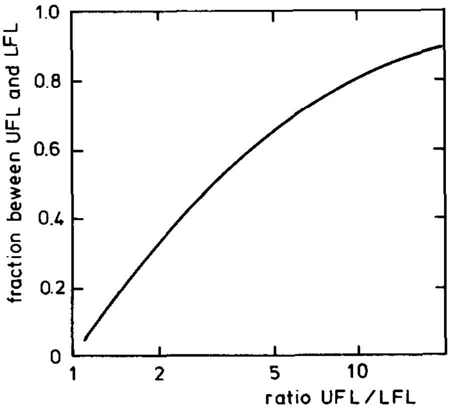


Fig. 2. Maximum fraction of gas in the explosive region of an instantaneous cloud as a function of the ratio UFL/LFL.

shown in Fig. 2.The maxima of approx. 50% in Fig. 1 differ only slightly from the theoretical maximum for methane of 48.4% (Fig. 2).

To give an example of the results of eqns. (8), (9) and (10), a table was computed giving the amount of gas in various concentration intervals for an instantaneous cloud of 10^5 m^3 gas. A numerical searching routine was used to find for eqn. (8) the distance from the centre corresponding to a given concentration. Table 1 gives the results for very stable meteorological conditions and without special corrections for density differences. Table 2 gives the results for the same case, but computed with the numerical solution. The differences are mainly due to the different initial shape (ellipsoid or box) and some inaccuracy due to the limited number of steps in the numerical integration.

2.2 Continuous source

The starting point for the calculations for this case is the equation for the continuous point source treated as Gaussian plume (see [4]):

$$C(x,y,z) = \frac{m_s}{2\pi U \sigma_y(x)\sigma_z(x)} \exp\left(-\frac{y^2}{2\sigma_y^2(x)}\right)\left[\exp\left(-\frac{(z-H)^2}{2\sigma_z^2(x)}\right) + \exp\left(-\frac{(z+H)^2}{2\sigma_z^2(x)}\right)\right] \tag{11}$$

For σ_y and σ_z, generally accepted data from the literature are used (see Appendix). For a source with initial dimensions L_y and L_z (for a continuous source, L_x is usually not taken into account), corrections can be made by the

TABLE 1

Amount of gas in various concentration regions expressed as percentage of the total amount released (in m^3 gas), calculated using eqns. (8), (9) and (10), for several distances, source strength 100,000 m^3, meteorological conditions very stable

Example: after travelling 500 m the amount between 10 and 15% is 8.6 × 100,000/100 = 8,600 m^3 gas (not including air).

(Dispersion parameters according to [7].)

Distance	Percentage																				
	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10	15	20	30	40	50	60	70	80	90	100
100	0.10	0.22	0.22	0.24	0.24	0.21	0.24	0.25	0.26	0.26	1.4	1.5	3.2	3.6	4.1	4.7	5.6	7.0	9.9	57	
120	0.14	0.28	0.29	0.29	0.30	0.31	0.31	0.31	0.32	0.33	1.7	1.8	3.9	4.3	4.8	5.5	6.4	7.9	11	50	
150	0.18	0.37	0.38	0.39	0.39	0.40	0.41	0.41	0.41	0.42	2.1	2.3	4.8	5.3	5.8	6.5	7.5	9.0	12	41	
200	0.27	0.55	0.54	0.56	0.56	0.56	0.56	0.58	0.57	0.59	3.0	3.1	6.4	6.8	7.3	8.0	8.9	10	13	28	
250	0.36	0.74	0.74	0.75	0.76	0.74	0.75	0.74	0.76	0.76	3.8	3.9	8.0	8.3	8.7	9.2	9.8	11	13	17	
300	0.49	0.96	0.96	0.94	0.96	0.95	0.94	0.93	0.96	0.94	4.7	4.7	9.5	9.6	9.8	10	10	11	11	9.3	
350	0.61	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.1	5.7	5.6	11	11	11	11	11	10	9.4	3.4	
400	0.75	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.3	1.4	6.6	6.5	13	12	12	11	10	9.1	6.2	0.095	
450	0.93	1.8	1.7	1.7	1.7	1.6	1.6	1.6	1.6	1.6	7.6	7.3	14	13	12	11	9.5	7.2	1.6		
500	1.1	2.1	2.0	2.0	2.0	1.9	1.8	1.9	1.8	1.8	8.6	8.2	15	14	12	11	8.2	3.4			
600	1.5	2.8	2.6	2.6	2.5	2.5	2.4	2.3	2.3	2.3	11	9.9	18	15	12	8.1	1.4				
700	1.9	3.6	3.4	3.3	3.2	3.0	3.0	2.9	2.8	2.8	13	11	19	15	9.0	0.58					
800	2.4	4.5	4.2	4.1	3.8	3.7	3.5	3.5	3.3	3.3	15	13	20	12	0.89						
900	3.0	5.5	5.1	4.8	4.6	4.4	4.2	4.0	3.9	3.7	17	14	19	3.6							
1000	3.7	6.7	6.1	5.7	5.3	5.0	4.9	4.6	4.3	4.3	18	14	13								
1100	4.4	7.8	7.2	6.6	6.1	5.8	5.5	5.1	4.9	4.6	19	13	4.5								
1200	5.2	8.9	8.3	7.5	6.9	6.4	6.1	5.7	5.3	4.9	20	9.4									
1500	7.7	13	11	10	9.2	8.1	7.4	6.5	5.7	4.7	6.9										
2000	12	21	17	14	11	7.5	2.8														
2500	17	28	20	11	0.52																
3000	23	32	12																		
3500	28	28																			
4000	31	14																			
4500	33	3.0																			
5000	24																				
6000	6.1																				

TABLE 2

Amount of gas in various concentration regions, expressed as percentage of the total amount released (in m^3 gas), computed by numerical integration of eqn. (2), source strength 100,000 m^3, meteorological conditions very stable

(Dispersion parameters to [7].)

Distance	Percentage																			
	0.5	1	2	3	4	5	6	7	8	9	10	15	20	30	40	50	60	70	80	90	100
100	0.042	0.11	0.13	0.16	0.22	0.47	0.21	0.33	0.46	0.25	1.7	1.9	4.6	4.3	5.8	6.6	6.7	10	12	43	
120	0.042	0.11	0.16	0.18	0.20	0.28	0.25	0.33	0.35	0.63	2.1	2.4	4.6	6.2	6.3	6.6	9.4	8.9	13	36	
150	0.091	0.23	0.33	0.47	0.62	0.40	0.46	0.75	0.41	0.41	3.2	3.1	5.7	6.7	8.3	7.8	9.1	12	14	25	
200	0.26	0.54	0.60	0.73	0.64	0.82	0.58	1.1	0.50	0.61	3.9	4.0	8.1	8.7	10	9.5	10	13	15	9.9	
250	0.34	0.69	0.73	0.83	0.69	0.99	0.71	0.84	1.1	1.1	4.7	4.9	11	9.7	11	12	12	13	12		
300	0.47	1.0	1.1	1.3	1.1	1.4	1.1	1.2	1.3	1.0	5.9	6.2	12	12	14	12	14	13	0.36		
350	0.70	1.5	1.5	1.6	1.4	1.7	1.2	1.6	1.5	1.3	7.2	7.0	14	13	15	12	13	3.4			
400	0.96	1.8	1.8	1.7	1.8	1.7	1.8	1.7	1.8	1.9	8.2	8.1	16	15	15	14	6.1				
450	1.1	2.2	2.2	2.1	2.1	1.9	2.1	2.1	2.2	1.9	9.8	9.4	18	16	15	11					
500	1.4	2.6	2.5	2.4	2.4	2.5	2.1	2.5	2.6	2.0	11	10	19	17	14	3.4					
600	1.8	3.4	3.4	3.1	3.3	2.9	3.2	2.8	2.8	2.9	13	13	22	17	3.4						
700	2.3	4.4	4.3	3.9	4.0	3.6	4.0	3.4	3.6	3.6	16	14	23	7.4							
800	3.0	5.4	5.3	4.9	4.7	4.8	4.1	4.5	4.0	4.1	18	16	18								
900	3.6	6.6	6.3	5.6	5.8	5.2	5.0	4.7	5.0	4.2	20	16	7.5								
1000	4.3	7.8	7.5	7.0	6.4	6.2	6.1	4.8	5.7	4.4	22	13	0.40								
1100	5.1	9.3	8.2	8.3	7.2	6.7	6.5	6.2	5.9	5.4	20	4.8									
1200	5.9	11	9.6	9.0	8.4	7.4	7.0	6.6	6.3	5.4	17										
1500	8.6	16	13	12	10	9.5	7.6	7.0	4.5	2.0											
2000	14	24	18	14	9.5	2.8															
2500	19	31	18	5.4																	
3000	25	33	5.6																		
3500	30	23																			
4000	32	9.7																			
4500	31	0.35																			
5000	20																				
6000	2.4																				
7000																					

use of a virtual point source or by using the following equation:

$$C(x,y,z) = \frac{m_s}{16\,UL_yL_z}\left[\operatorname{erf}\left(\frac{L_y - y}{\sigma_y\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_y + y}{\sigma_y\sqrt{2}}\right)\right]$$
$$\times\left[\operatorname{erf}\left(\frac{L_z - z + H}{\sigma_z\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_z + z - H}{\sigma_z\sqrt{2}}\right) + \operatorname{erf}\left(\frac{L_z - z - H}{\sigma_z\sqrt{2}}\right)\right.$$
$$\left. + \operatorname{erf}\left(\frac{L_z + z + H}{\sigma_z\sqrt{2}}\right)\right] \tag{12}$$

2.2.1 Analytical solution

The amount of gas in the explosive region of the plume resulting from a continuous point source can be calculated by integrating eqn. (11) analytically, provided that σ_y and σ_z are described by simple power laws:

$$\sigma_y = ax^b \tag{13a}$$

$$\sigma_z = cx^d \tag{13b}$$

The result can be written as:

$$\frac{m_E}{m_s} = \frac{b + d}{b + d + 1}\,\frac{x_2 - x_1}{U} \tag{14}$$

where:
x_2 = maximum distance to LFL
x_1 = maximum distance to UFL

Eqn. (14) again is subject to the restriction that either the source must be at ground level or the plume must be free from the ground. Since in these cases x_1 and x_2 can be calculated from m_s (using the inverse of eqn. (11)), this leads to:

$$\frac{m_E}{m_s} = \frac{b + d}{(b + d + 1)U}\left(\frac{m_s}{\pi Uac}\right)^{1/(b+d)}\left[\left(\frac{1}{C_{LFL}}\right)^{1/(b+d)} - \left(\frac{1}{C_{UFL}}\right)^{1/(b+d)}\right] \tag{15}$$

for $H = 0$ (see also [9]).

Several remarks should be made with respect to eqn. (15):

For a plume free from the ground in eqn. (15) the group πUac becomes $2\pi Uac$.

If the concentration at the source is already lower than UFL, x_1 in eqn. (14) and the term containing C_{UFL} in eqn. (15) must be put equal to zero.

Note that for the continuous source the ratio m_E/m_s is dependent on m_s, i.e. m_E increases significantly faster than linear with increasing m_s.

A formula analogous to eqn. (10) has not been found for a continuous source with initial dimensions >0. If the initial dimensions are such that they can be described with sufficient accuracy with one virtual distance x_V, then m_E can be calculated for the virtual point source and the contribution over x_V can be subtracted. A distinction must be made between two cases:

(a) The maximum concentration at the source is greater than UFL. This leads to:

$$\frac{m_E}{m_s} = \frac{1}{U}\left[\frac{(b+d)(x_2 - x_1)}{b+d+1} - \frac{x_V^{b+d+1}}{b+d+1}\left(\frac{1}{x_1^{b+d}} - \frac{1}{x_2^{b+d}}\right)\right] \tag{16}$$

(b) The maximum concentration at the source is smaller than UFL. This leads to:

$$\frac{m_E}{m_s} = \frac{1}{U}\left[\frac{(b+d)x_2}{b+d+1} - x_V + \frac{x_V^{b+d+1}}{(b+d+1)x_2^{b+d}}\right] \tag{17}$$

with x_1 and x_2 now measured from the virtual point.

Because, for the calculation of m_E the concentrations in the plume at one moment are the relevant concentrations, x_V, x_1 and x_2 must be calculated with the σ_y-values for an instantaneous source!

2.2.2 Numerical solution

A computer program was written to integrate eqn. (12) numerically over the explosive region. This solution can be used as a mutual check against the results described in Section 2.2.1, but also makes it possible to use other functions than power laws for σ_z and to study the influence of the dimensions of the source.

2.2.3 Results

For methane, eqn. (15) gives for various meteorological conditions, using dispersion data according to [4]:

very stable	$m_E = 33.95\ (m_s/U)^{1.636}$	(18)
stable	$m_E = 19.2\ (m_s/U)^{1.613}$	
neutral	$m_E = 12.6\ (m_s/U)^{1.601}$	
light unstable	$m_E = 8.23\ (m_s/U)^{1.589}$	
unstable	$m_E = 5.53\ (m_s/U)^{1.583}$	
very unstable	$m_E = 3.71\ (m_s/U)^{1.567}$	

with m_E in m^3, m_s in $m^3\ s^{-1}$, U in m s^{-1}.

To give a further impression of the results of the present equations, Table 3 has been calculated using the dispersion parameters in a form adapted to [4].

TABLE 3

Values of $m_E U/m_s$ (in m) for various concentration regions calculated with eqn. (16) for some values of m_s/U (in m^2) for very stable meteorological conditions

Concentration	m_s/U						
	1.000	3.000	10.00	30.00	100.0	300.0	1000
0.50—1.0	104.8	210.8	453.4	911.8	1961	3943	8480
1.0—2.0	67.42	135.6	291.6	586.4	1261	2536	5453
2.0—3.0	27.63	55.56	119.5	240.3	516.7	1039	2234
3.0—4.0	15.67	31.52	67.79	136.3	293.1	589.5	1268
4.0—5.0	10.31	20.73	44.58	89.65	192.8	387.7	833.7
5.0—6.0	7.383	14.85	31.93	64.21	138.1	277.7	597.1
6.0—7.0	5.592	11.25	24.19	48.64	104.6	210.3	452.3
7.0—8.0	4.407	8.863	19.06	38.33	82.42	165.8	356.4
8.0—10	6.546	13.16	28.31	56.93	122.4	246.2	529.4
10—15	9.628	19.36	41.64	83.74	180.1	362.1	778.7
15—20	5.333	10.73	23.07	46.39	99.75	200.6	431.4
20—30	5.759	11.58	24.91	50.09	107.7	216.6	465.8
30—40	2.996	6.024	12.95	26.05	56.02	112.7	242.3
40—50	1.755	3.529	7.588	15.26	32.82	65.99	141.9
50—60	1.078	2.169	4.663	9.378	20.17	40.56	87.22
60—70	0.6643	1.336	2.873	5.778	12.42	24.99	53.73
70—80	0.3902	0.7847	1.687	3.394	7.298	14.68	31.56
80—100	0.2559	0.5146	1.107	2.226	4.786	9.625	20.70

3. Concentration as a function of time and distance

To assess the possibility of ignition of a cloud it is necessary to know the maximum concentration as a function of the downwind distance. For instantaneous or short-duration releases, it is therefore necessary to determine the maximum concentration during passage of the cloud. It was therefore decided to write a computer program to give the concentration as a function of time and distance for a quasi-instantaneous release of a gas or a fast evaporating liquid. In Section 4 the model for the initial behaviour of the cloud (gravitational spreading and gas entrainment) will be explained. As one of the cases of interest is a spill of LNG on the sea, a literature search for data on dispersion above the sea was made. Direct measurements of such dispersion seem scarcely available. Some indication, however, could be obtained from [10], [11] and [12]. It seems that for a sea surface not too far removed from land, unstable, neutral and stable conditions can occur for which the dispersion can be assumed to be equal to that for Pasquill classes B, D and F, respectively, corrected for the normally small roughness length of the sea surface.

3.1 Time-dependent model

The numerical model is built up as follows. The initial cloud is assumed to be stationary at the source with the shape of a flat cylinder, of which the diameter and height are known as a function of time. It is assumed that "slices" of the cloud (see Section 4) drift downwind. After a certain time a great number of slices are under way, as indicated in Fig. (3). To calculate the concentration at a given point at a given time, the contribution of all the slices must be

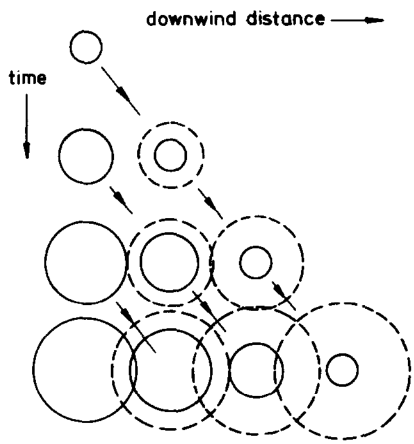


Fig. 3. Schematic diagram of "slices" of a cloud moving downwind with time. The dashed circles indicate that each slice grows by turbulent diffusion while travelling downwind.

added. As the slices can be of the same order of magnitude as the distance from the source where the concentration is calculated, the slices are divided into bands (with length in the crosswind direction) to maintain a reasonable accuracy. The contribution of each band is calculated with the aid of eqn. (2). The program can fairly easily be adapted to other initial shapes than circular.

3.2 Comparison with literature data

The model contains three parameters which must be adapted to experimental data for gases heavier than air because the cold methane vapour is also heavier than air. The first is the entrainment* rate (kg m^{-2} s^{-1}) which is assumed to be constant over the top surface of the cloud. This was done by comparing the source model with the data of [2] concerning the vapour flow rate (see Section 4). The result:

$$E_r = 0.0025\ U \text{ kg m}^{-2} \text{ s}^{-1}$$

was used in the present model. The second and third parameter to adapt are the vertical dispersion and the effective windspeed for the cloud. References [2] and [13] give examples of the concentration as a function of time. Comparison with the model leads, in both cases, to the conclusion that the vertical dispersion is comparable to that for Pasquill's F-class, and that the effective windspeed for the cloud is low, i.e. approximately 1 m s^{-1} (see Figs. 4 and 5). As the tests were performed under neutral conditions, this means a considerable reduction in vertical dispersion, but less than proposed in [14]. The difference lies in the large value for σ_y observed in [14] at 1,000 m from the source. Since at that distance the passage-time is already in the order of 300 s, a random shift can easily occur during that time, upsetting the calculation of

*See section 4.

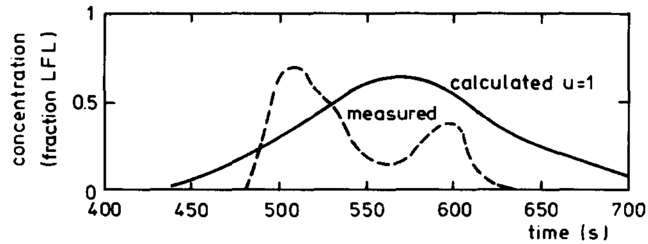


Fig. 4. Comparison of the present computer model with data from [2] concerning trial 10A: Spill size 2,200 kg, windspeed 2.2 m s^{-1}, sensor distance 520 m, and meteorological conditions neutral. Windspeed adjusted to give the same arrival time as measured.

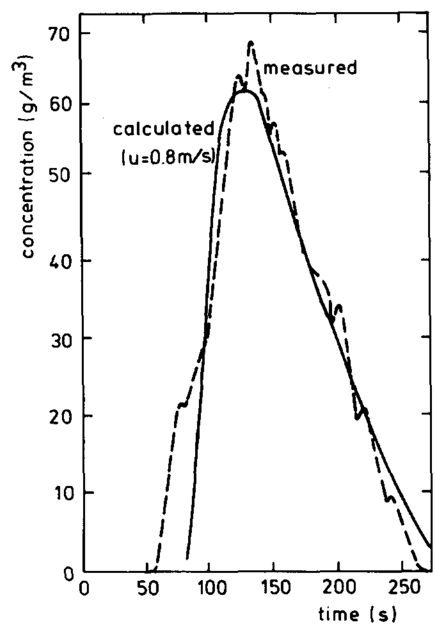
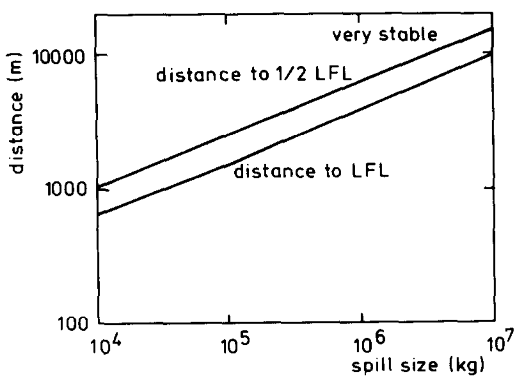


Fig. 5. Comparison of the present computer model with data from [13]: Quasi-instantaneous release of 1,000 kg Freon. Initial dilution 11 times (v/v) according to [14], windspeed 3 m s^{-1}, meteorological conditions neutral, windspeed adjusted to give the same arrival time of the cloud as measured.

the material balance. The dosage (at 1,000 m) of approximately 270 g s m^{-3} is correctly reproduced by the present model using the F-class σ_z values. As explanation for the fact that the vertical dispersion is not further reduced than to values equivalent to the F-class, it can be argued that the combination of entrainment and dispersion reduction is a self-limiting process. Because, if vertical dispersion is nearly completely suppressed, then the entrainment by turbulent mixing will tend to zero, but without entrainment there would be no dispersion reduction. It is therefore reasonable that a fairly constant and relatively small entrainment rate would establish itself quickly above a heavy gas layer. However, many experiments under different meteorological conditions are still necessary to study these effects quantitatively.

3.3 Some results for LNG

Essentially the present model is used to extrapolate from spill sizes as used in experiments to very large spills. Figure 6 gives the maximum distance to LFL and ½LFL for various spill sizes. Figure 7 gives the concentration as a function of time at a distance of 10 km from a spill of 10^7 kg LNG (25,000 m^3).



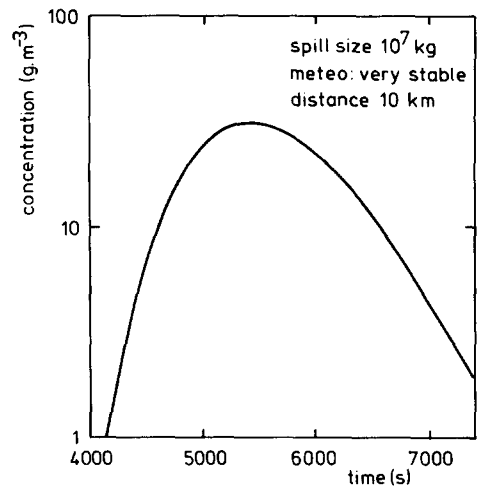


Fig. 6. Maximum distance to ½LFL and LFL for a spill of LNG on the sea as a function of the amount released, under stable meteorological conditions.

Fig. 7. Concentration as a function of time for a spill of 10^7 kg LNG on the sea under stable meteorological conditions.

4. Source model for a quasi-instantaneous LNG spill on water

The model used to describe the spreading of liquid and vapour at the source can be set out as follows. When the liquid is spilled, a cylindrical pool is formed which spreads gradually over the water. For a cryogenic liquid the evaporation rate is so high that not all the gas produced can be immediately carried away by the wind (see [2]). Therefore, a flat cylindrical cloud forms above the liquid pool. As the vapour is heavier than the surrounding air, the behaviour of the "vapour-pool" is not unlike that of the liquid pool, i.e. it also starts spreading over the water surface. From this vapour-pool a certain amount per second is carried away by the wind, here called entrainment (see [15], [16]) and expressed in kg m^{-1} s^{-1} *. The entrainment is analogous to

*In the literature, entrainment often indicates the mixing of air into a cloud.

the evaporation of a liquid with a boiling point well above the ambient temperature (see Fig. 8).

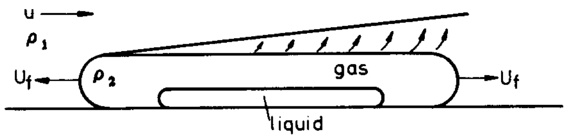


Fig. 8. Schematic diagram of a source consisting of a spreading liquid pool, accompanied by a spreading vapour cloud and entrainment of the vapour by the wind.

4.1 Some formulae used in the source description

As part of the present project, a literature study was made of the behaviour of cryogenic liquids spilled on water. From those results (see [17]) the following equations were used:

$$m_r = 0.05 \text{ kg m}^{-2} \text{ s}^{-1} \tag{19}$$

for the rate of evaporation, which means that a fixed evaporation rate is used. The diameter of the liquid pool is calculated from:

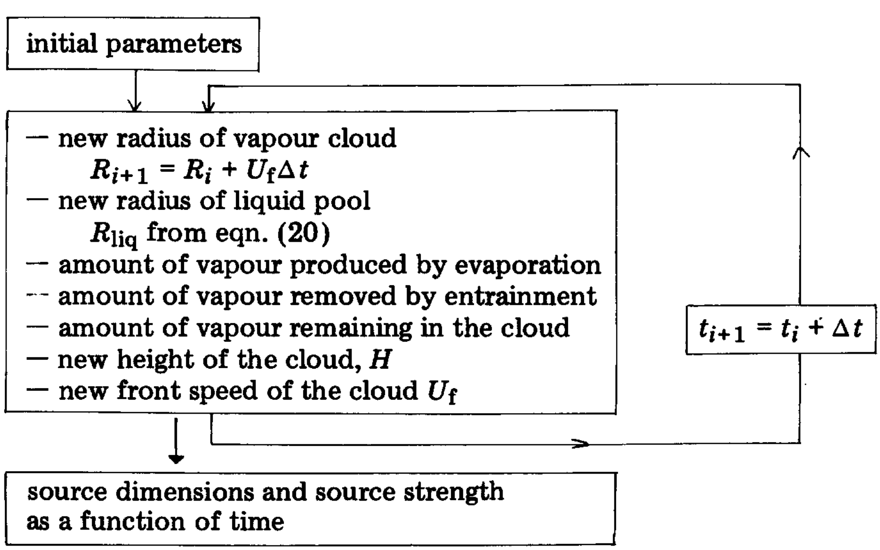
$$D_{\text{liq}} = 0.76\, W^{1/4}\sqrt{t} \tag{20}$$

where W is the total amount of LNG in kg. For the spreading velocity of the gas pool an equation derived from ref. [14] is used:

$$U_f = \frac{dR}{dt}\sqrt{g\left(\frac{\rho_2 - \rho_1}{\rho_2}\right)H} \tag{21}$$

4.2 Computational loop for source parameters

Assuming for the moment that a value is known for the entrainment, the following computational loop will give a numerical simulation of the source dimension as a function of time:



In [2] the total amount of vapour carried away by the wind per second was determined for a number of experiments (there indicated as vapour flow rate). By fitting the present source model to those data it was possible to determine the entrainment (see [18]):

$$E_r = 0.0025\,U \text{ kg m}^{-2} \text{ s}^{-1} \qquad (22)$$

The determination of E_r has a limited accuracy, because as E_r increases the vapour-pool diameter decreases, resulting in only a small change in the total vapour flow rate. On the other hand, this argument implies that for the calculation of the maximum concentration, the value of E_r is not very critical.

5. Conclusions

From the results presented, it can be concluded that for neutral gases, a reasonable estimate of the amount of gas in the explosive region can be made using the formulae derived from the conventional dispersion models.

More difficulties are encountered in establishing a model for large amounts of a gas heavier than air. Here the effort was concentrated on predicting downwind concentrations. As it happens, the results of tests with 1,000—4,000 kg can be numerically simulated, provided that three quantities are adjusted in a suitable manner, i.e. the rate of entrainment of the gas by the air stream, the vertical dispersion and the effective speed of the cloud. However, the available experiments do not allow one to test separately the assumptions implied in the values used for the three quantities. To achieve this, many more experiments under a variety of conditions will be necessary.

List of symbols

a, b, c, d, e	coefficients in approximating σ_y and σ_z
$C(x,y,z,t)$	concentration (kg m^{-3})
erf (x)	error function
E_r	rate of entrainment (kg m^{-2} s^{-1})
H	source height (m)
L_x	source dimension in x-direction (m)
L_y	source dimension in y-direction (m)
L_z	source dimension in z-direction (m)
ln (x)	natural logarithm of x
m	source strength for instantaneous source (kg)
m_E	total amount in explosive region (kg)
m_r	rate of evaporation (kg m^{-2} s^{-1})
m_s	source strength for continuous source (kg s^{-1} or m^3 s^{-1})
P	concentration in centre of instantaneous cloud at the time for which m_E is calculated (kg m^{-3}, or %v/v, or fraction)
P_1	upper explosion limit (UFL) (dimension, see P)
P_2	lower explosion limit (LFL) (dimension, see P)

R_0	initial radius of instantaneous cloud (m)
R_1	radius for given concentration
t	time (s)
U	windspeed (m s^{-1})
v	ratio of UFL to LFL
v_1	auxiliary variable
v_2	auxiliary variable
x	co-ordinate in wind-direction (m)
y	crosswind co-ordinate (m)
z	vertical co-ordinate (m)
x_0	position of centre of the cloud (m)
x_1	distance to UFL
x_2	distance to LFL
ρ_1	density of the surrounding air
ρ_2	density of the gas
σ	standard deviation for spherical cloud (m)
σ_y	standard deviation crosswind for continuous source (m)
σ_z	vertical standard deviation for continuous source (m)
σ_{xI}, σ_{yI}, σ_{zI}	standard deviation for an instantaneous cloud (m)

References

1 J.A. Fay and D.H. Lewis Jr., The inflammability and dispersion of LNG vapors, Proc. 4th Int. Symp. on Transport of Hazardous Cargoes by Sea and Inland Waters, Jacksonville, U.S.A., 26—30 Oct. 1975, pp. 489—498.
2 Esso Research and Engineering Co., Spills of LNG on water: vaporization and downwind drift of combustible mixtures, Report No. EE61-72, sponsored by API, May 1972.
3 S. Harris, W.G. May and W. McQueen, The persistence of visible fog from an LNG spill, Fall Meeting Combustion Inst. (East States section), Upton, N.Y., 1975.
4 F. Pasquill, Atmospheric Diffusion, Ellis Horwood Ltd., Chichester, revised edn., 1974 (distributed by Wiley).
5 J. Crank, The Mathematics of Diffusion, Oxford University Press, London, 1956.
6 M. Abramowitz and I.A. Stegun, Handbook of Mathematical Functions, Dover Publications Inc., N.Y., 1965.
7 F. Pasquill, Atmospheric Diffusion, Van Nostrand, London, first edn., 1962.
8 J.F. Hart, Computer Approximations, (part of the Series in Applied Mathematics), Wiley, New York, 1968.
9 D. Burgess, J.N. Murphy, M.G. Zabetakis and H.E. Perlee, Volume of flammable mixture resulting from the atmospheric dispersion of a leak or spill, 15th Int. Symp. on Combustion, Tokyo, 1974.
10 R.P. Hosker, A comparison of estimation procedures for over water plume dispersion, Proc. Symp. on Atmospheric Diffusion and Air Pollution, Santa Barbara, 1974, pp. 281—288.
11 F.T.M. Nieuwstadt, The dispersion of pollutants over a water surface, 8th Int. Tech. Meeting on Air pollution modelling and its application, Louvain-la-Neuve, Belgium, Sept., 1977.
12 A.C. van de Berg, personal communication.
13 J.F. van de Wal, Report BL72 of IGM-TNO Delft, 1974 (in Dutch).
14 A.P. van Ulden, On the spreading of a heavy gas released near the ground, in C.H. Buschmann (Ed.), Proc. First Int. Loss Prevention Symp., Delft, Netherlands, May 1974, Elsevier, Amsterdam, 1974, p. 221.

15 R.A. Cox and D.R. Roe, A model of the dispersion of dense vapour clouds, 2nd Int. Symp. on Loss Prevention and Safety Promotion in the Process Industries, Heidelberg, FRG, Sept. 1977.
16 P.H.M. te Riele, Atmospheric dispersion of heavy gases emitted at or near ground level, 2nd Int. Symp. on Loss Prevention and Safety Promotion in the Process Industries, Heidelberg, FRG, Sept., 1977.
17 G. Opschoor, Investigations into the spreading and evaporation of LNG spilled on water, CTI-TNO report 74-04694, Jan. 1975.
18 C.J.P. van Buijtenen, Calculation of the amount of gas in the explosive region of a vapour cloud released in the atmosphere at ground level, Chem. Lab.-TNO report 1976-3
19 KNMI, Luchtverontreiniging en weer, Staatsuitgeverij, 's-Gravenhage, Netherlands, 1974 (in Dutch).
20 Methods for the calculation of the physical effects of the incidental release of hazardous materials (liquids and gases), Report by TNO, Delft, Netherlands (Revised edition in prep.)
21 KNMI, Frequentietabel van de stabiliteit in de atmosfeer, from series: Klimatologische gegevens van Nederlandse stations, No. 8, KNMI, 1972, 150-8 (in Dutch).

Appendix

Pasquill's system for dispersion calculations

Pasquill's system for dispersion calculations can be divided into three parts:
(i) Definition of stability classes.
(ii) Graphs for σ_y and σ_z as a function of the distance from the source for each class.
(iii) Data giving the frequency of occurrence of the stability classes.

Definition of stability classes

In view of the limited accuracy of dispersion calculations, it appears to be more practicable to divide all possible meteorological conditions into, for example, 6 classes, labelled A, B, . . ., F, from very unstable to very stable conditions. For planning purposes the classes can also be interpreted as representative cases for which calculations are carried out. Pasquill determines the class from the insolation and the windspeed. A modified definition of the classes was constructed for the Dutch climate by the Royal Netherlands Meteorological Institute, using cloud cover, windspeed, season and time of the day to determine the stability class [19]. When used as representative cases a windspeed was assigned to each class: B, 2: C, 5; D, 5; E, 3; F, 2 m s^{-1}.

Size of the cloud

The growth of the cloud or plume is quantified by the horizontal and vertical standard deviations σ_y and σ_z. In the original reports of this study the values for σ_y and σ_z were chosen in accordance with Pasquill's recommendations of 1962 [7], with the exception that class A was not used. In the computer programs

$\sigma_y = ax^b$ and $\sigma_z = cx^d + e$

were used, with constants as given in Table 4. The σ_y and σ_z thus calculated can be considered to be 10-minute average values. When values for σ_x were necessary, $\sigma_x = 2\sigma_y$ was used, which later turned out to be a reasonable approximation for neutral conditions only (see below). In the present paper these data were used only in Fig. 1, and Tables 1 and 2. For the other figures and tables, the calculations have been repeated following the more

TABLE 4

Constants for the calculation of σ_y and σ_z according to Pasquill's recommendations of 1962 [7]

For the approximation of σ_z it was necessary to divide the downwind distance into several segments, each with its own values for the constants. An extrapolation was made for $x < 100$ m.

Stability	*a*	*b*
B	0.371	0.866
C	0.209	0.897
D	0.128	0.905
E	0.098	0.902
F	0.065	0.902

Stability	Distance				
	1—10	10—100	100—1 000	1 000—20 000	20 000—10^5
Values for c					
B	0.15	0.1202	0.0371	0.054	0.0644
C	0.15	0.0963	0.0992	0.0991	0.1221
D	0.15	0.0939	0.2066	0.9248	1.0935
E	0.15	0.0864	0.1975	2.3441	2.5144
F	0.15	0.0880	0.09842	6.5286	2.8745
Values for d					
B	0.8846	0.9807	1.153	1.0997	1.0843
C	0.7533	0.9456	0.9289	0.9255	0.9031
D	0.6368	0.8403	0.7338	0.5474	0.5229
E	0.5643	0.8037	0.6865	0.4026	0.3756
F	0.4771	0.7085	0.7210	0.2593	0.30103
Values for e					
B	0	0	3.1914	2.5397	0
C	0	0	0.2444	1.7383	0
D	0	0	−1.3659	−9.0641	0
E	0	0	−1.1644	−16.3186	0
F	0	0	−0.3231	−25.1583	0

TABLE 5

Constants for the calculation of σ_y (as ax^b) and σ_z (as cx^d) adapted to [4]

σ_y is to be considered as a 10-minute average value, σ_z for z_0 = 0.1 m and source height <20 m. x, σ_y and σ_z in m.

		a	*b*	*c*	*d*
very unstable	(A)	0.527	0.865	0.28	0.90
unstable	(B)	0.371	0.866	0.23	0.85
slightly unstable	(C)	0.209	0.897	0.22	0.80
neutral	(D)	0.128	0.905	0.20	0.76
stable	(E)	0.098	0.902	0.15	0.73
very stable	(F)	0.065	0.902	0.12	0.67

recent recommendation by Pasquill in 1974 [4], shown in Table 5, and using some other literature data given in [20].

σ_y is multiplied with a correction factor for other averaging times:

$$C_T = \left(\frac{T}{600}\right)^{0.2}$$

with T in seconds and a minimum value for C_T of 0.5, also used for instantaneous sources. σ_z is multiplied with a correction factor for other roughness lengths:

$$C_{z_0} = (10z_0)^{0.53x^{-0.22}}$$

No special values for σ_z are used for an instantaneous source. For σ_x

$$\sigma_x = 0.13x$$

is used (for all stability classes).

Frequency of occurrence of stability classes

The Royal Netherlands Meteorological Institute has compiled data for The Netherlands concerning the frequency of occurrence of the various stability classes [21].