Accidental release of toxic chemicals: Influence of the main input parameters on consequence calculation

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Abstract

In the present paper the accidental release of toxic chemicals has been taken into consideration, and a sensitivity analysis study of the corresponding consequences calculation has been carried out. Four different toxic chemicals have been chosen for the simulations, and the effect of the variability of the main input parameters on the extension of the impact areas has been assessed. The results show that the influence of these parameters depends on the physical properties of the released substance and that not always the widely known rules of thumb, such as the positive influence of the wind velocity on gas dispersion, apply. In particular, the boiling temperature of the chemical has revealed to be the main parameter affecting the type of dependence of the impact distances on the input variables.
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1. Introduction

The magnitude of the impact area generated by an accidental release of a toxic chemical depends on a number of parameters related to the modalities of the release under consideration, to the external conditions under which the dispersion will occur (meteorological, environmental, associated to the type of terrain, etc.), and to the chemical itself (physical properties and toxicity). Therefore, the calculation of these areas by means of the available mathematical models requires the quantification of a number of input parameters, which are specific to the models adopted, and whose values will affect the results of the calculation [1]. Since risk analysis is based on a probabilistic approach, these calculations have to be repeated for all the identified accident scenarios, derived by techniques such as HAZOP, FMEA and others [2]. The results are then combined to give an overall value of the risk corresponding to a given activity/installation. In principle, the higher the number of scenarios analyzed, the higher the accuracy of the risk estimate.

On the other hand, consequence calculation is a very time consuming step, and so it is thoroughly carried out only in few cases, while in most of the applications some shortcuts are introduced, such as limiting the analysis at the worst credible scenarios, the most probable and so on [3,4]. By the way, in order to adopt these criteria, some estimate of the probabilities of the scenarios is also required.

A more effective approach would consist in analyzing only those scenarios which significantly differ in the values of the generated impact areas, and grouping all those which are characterized by very similar areas under one single reference scenario, to which a global value of the probability will be assigned. This would allow to obtain a final quantification of the risk, very close to the "actual" one, but with a much smaller computational effort.

However, in order to apply this approach, the proper reference scenarios have to be known in advance and this, in turn, requires an "a priori" knowledge of the effect of the variability of the input parameters on the results of the consequence calculation. At present, no consistent and thorough investigation is available in the literature, and few studies address more aspects at the same time [5].

In the present paper, the main input parameters involved in the calculation of the impact distances following the accidental release of a toxic chemical have been selected, and the effect of

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Nomenclature

d	release hole diameter
D	maximum downwind impact distance
F	flash fraction
P	pressure
P_s	equilibrium vapor pressure
T_{amb}	ambient temperature
T_b	boiling temperature
v	wind velocity
W	maximum crosswind impact distance

Table 1
Selected substances and their toxicity

Substance	T_b (°C)	ERPG-2 (ppm)	IDLH (ppm)
Hydrogen chloride	−85	20	50
Ammonia	−33	150	300
Trimethylamine	3	100	200
Bromine	59	0.5	3

their variability within some specific intervals on the results of the calculation has been evaluated.

In order to assess the dependence of the above effect on the substance under investigation, all the calculations have been repeated for four chemicals, characterized by different physical and toxicity properties.

2. Selected substances and scenarios

In Table 1 the chemicals selected for the study are reported along with the corresponding levels of toxicity. This latter characteristic is not univocally defined among the analysts, and different parameters can be arbitrarily adopted, such as IDLH, ERPG (1, 2 or 3), TLV, EEGL, and others. However, based on a recent trend followed by the analysts and on the availability of the data in the literature, ERPG-2 [6] and IDLH [7] have been adopted in the present study, and the maximum distances covered by the dispersing toxic cloud corresponding to those concentrations have been calculated.

As far as the release scenario is taken into account, conditions as close to a real accidental event as possible have been selected. Thus, it is assumed that the release will occur through a hole on a storage tank where the substance is contained in the liquid state at ambient temperature (T_{amb}). For chemicals with boiling temperature (T_b) lower than T_{amb}, the pressure inside the tank is assumed equal to the equilibrium vapor pressure of the substance

at T_{amb}; differently, when $T_b > T_{amb}$, the tank pressure will be fixed at a value slightly higher than 1 bar, as will be detailed in Section 3.3. The storage vessel is cylindrical horizontal, 10 m long with 3 m diameter with a total volume of about 70 m³, and the hole is located on the bottom side of the shell. This implies that the release will always be in the liquid phase and at the maximum flow rate. Furthermore, a mitigation time of 15 min after the initial release is adopted, assuming that at that time the operators are able to stop the release from the tank and/or the evaporation from the possibly generated liquid pool.

All the above geometrical parameters have been kept constant for all the simulation runs, except for the hole diameter which has been varied during the study, assessing its effect on the impact areas.

The parametric analysis has been carried out by varying one parameter at a time, within its variability range, and keeping all the others at a constant "average" value. The investigated parameters are reported in Table 2, and their average values are marked in bold. As can be seen from the table:

- four different atmospheric conditions have been adopted, two in daytime (classes A and D) and two in night-time (classes D and F);
- the values for the wind velocity are consistent with each Pasquill stability class and have been derived from a statistical analysis of the records issued by the Italian meteorological stations network [8];
- different temperature ranges have been used for daytime and night-time conditions, the corresponding values being derived from the mentioned meteorological records;
- the intensity of solar radiation is set consistently with the period of the day and the stability class;
- the hole size is the same for all the assumed weather conditions.

A further parameter which can influence the dispersion of a toxic cloud is represented by the surface roughness, which is a raw measure of the obstacles surrounding the release point. It is usually calculated as approximately one-tenth the average obstruction (trees, buildings, equipment) height and, in the case of an industrial site, as it is assumed in the present analysis, a value of 0.3 m is usually adopted. This value has been kept constant for all the calculations.

3. Results and discussion

The calculation of the impact areas has been carried out for each substance with reference to the toxicity levels reported in

Table 2
Variability ranges of the investigated parameters

Period of the day	Pasquill stability class	Wind velocity (m/s)	Temperature (°C)	d-Hole (mm)	Solar radiation (W/m²)
Day	A	0.5; **1.5**; 2.5	−5; 10; **25**; 40	10; **30**; 50	700
	D	5; **6**; 7			300
Night	D	3; **5**; 7	−10; 0; **10**; 20		0
	F	0.5; **1.5**; 2.5			0

Table 1, and for a release time of 15 min. Typically, risk analysts adopt widely available software tools for their analyses (either free or proprietary), so, similarly, a commercial software has been adopted in the present study (Trace 9.0, by Safer Systems, USA). This software allows to make both release and dispersion calculations automatically, without the need for handling externally the results of the first step in order to setup the second one. This avoids introducing possible errors due to improper data handling. It also has the capability of automatically identifying whether or not the initial dispersion phase requires a heavy gas modeling and, correspondingly, it identifies the occurrence of the transition phase from high- to low-density cloud behavior. Differently from other similar codes, it is possible to set the values of the storage parameters (in particular pressure and temperature) independently, so that a wider range of conditions can be investigated, as was done in the present work for bromine. Despite some limitations when treating fires from releases of flammables, in the case of dispersion analysis it is rather flexible, allowing to choose among different models. Further details about the models can be found in [9].

It is worth noting that it was not the aim of this work to assess the accuracy of the mathematical code adopted, so the results of the calculations will be assumed as "correct" and only the effect of the variation of the input parameters will be analyzed here. Nonetheless, for the sake of completeness, some of the runs have been repeated by using ALOHA [10], a widely known and used simulation code. Despite it does not allow to model all the

conditions adopted in the present study, for the selected scenarios and chemicals, the results obtained with ALOHA agree quite well with those calculated with Trace. A brief account of these comparisons is reported in the sections corresponding to the different chemicals.

The results of the simulations are presented here at increasing values of the normal boiling temperature of the substances.

3.1. Hydrogen chloride

Hydrogen chloride has a boiling temperature $T_b = -85\,°C$. Due to the high temperature difference with T_{amb}, the whole released flow rate quickly evaporates and disperses as a vapor cloud, without formation of a liquid pool. The actual release mass flow rate depends on the pressure inside the tank, and, at $25\,°C$, it is initially around $40\,kg/s$.

The distances calculated with Trace for the standard "average" conditions, i.e. 6.5 and 4 km for a concentration of 20 and 50 ppm, respectively, are in excellent agreement with those obtained by ALOHA (6.67 and 4.1 km).

3.1.1. Effect of wind velocity
With reference to the ERPG-2 concentration, in Fig. 1(a), the maximum downwind (D) and crosswind (W) distances covered by the cloud during dispersion as a function of the wind velocity (v) are reported. The results for all the analyzed meteorological conditions are shown.
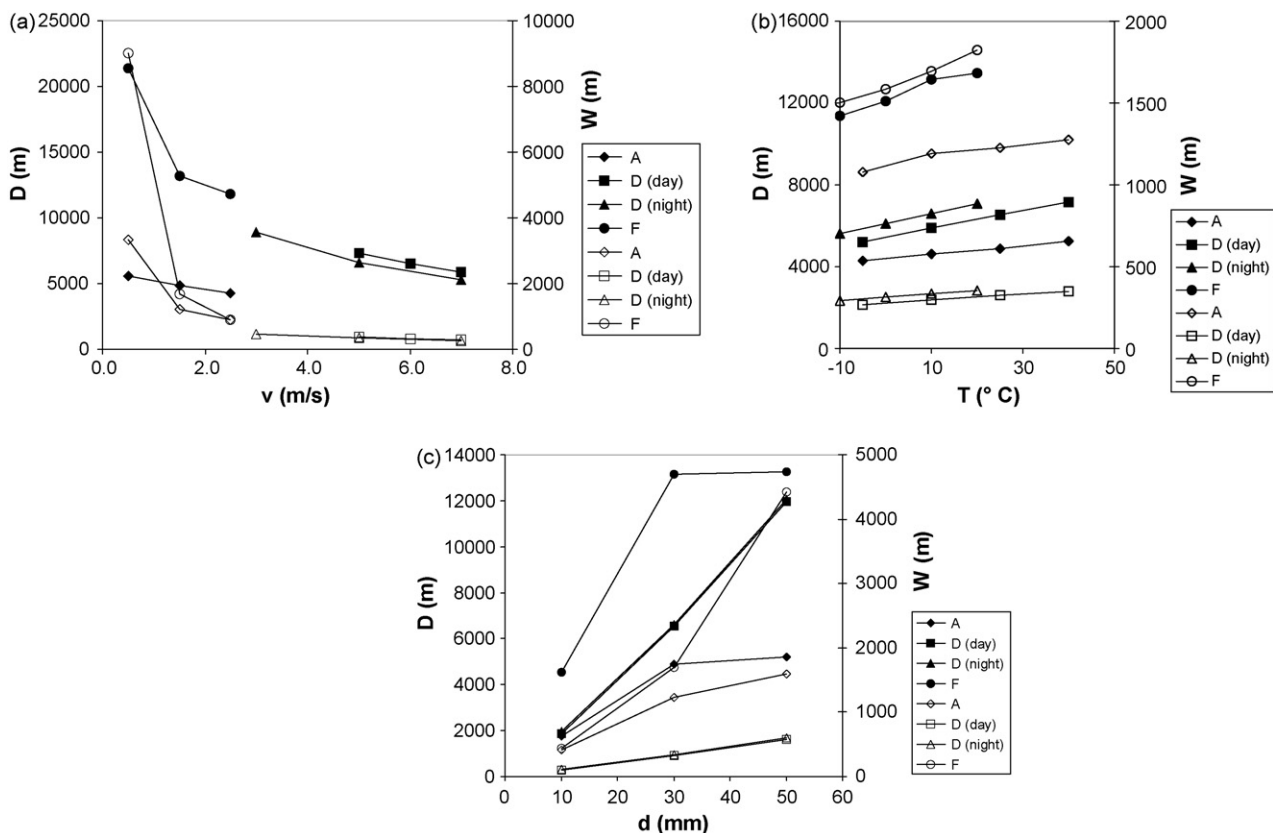

Fig. 1. Hydrogen chloride. Maximum downwind (D) and crosswind (W) distances corresponding to the ERPG-2, as a function of: (a) wind velocity; (b) ambient temperature; (c) hole diameter.

Table 3
Slopes (m) and correlation coefficients (r^2) of the regression lines for HCl

Stability class		v (m/s)				T (°C)				d (mm)			
		ERPG-2 (20 ppm)		IDLH (50 ppm)		ERPG-2 (20 ppm)		IDLH (50 ppm)		ERPG-2 (20 ppm)		IDLH (50 ppm)	
		D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)
A	m	−647	−1206	−752	−1111.5	21.066	4.193	8.713	3.08	861.5	294.25	639.75	245.25
	r^2	0.999	0.846	0.973	0.840	0.995	0.932	0.956	0.903	0.818	0.954	0.885	0.981
D- day	m	−728	−36	−447	−24.5	43.34	1.826	25.786	1.153	2519	119.5	1630.2	80
	r^2	0.998	0.997	0.997	0.996	0.999	0.997	0.997	0.995	0.998	0.998	0.995	0.998
D- night	m	−900.25	−51.75	−549.25	−38	48.41	2.03	30.04	1.3	2517.5	123.25	1639	84
	r^2	0.974	0.960	0.974	0.956	0.999	0.998	0.999	0.995	0.997	0.997	0.994	0.997
F	m	−4756.5	−4061.5	−1993.5	−2647	73.32	10.75	45.35	6.77	2179.5	997	1599.2	668
	r^2	0.851	0.823	0.920	0.828	0.962	0.990	0.959	0.992	0.759	0.956	0.909	0.966

It can be observed that, under any meteorological condition, higher values of the wind velocity give rise to shorter impact distances, i.e. the wind velocity has a positive effect on the dispersion of the toxic cloud. With reference to the stability classes, class F is characterized by the largest distances as compared with the other classes, in accordance with rather common results reported in the literature. This behavior is due to the high stability of this class that hampers a fast dispersion of the cloud and to the low absolute values of the wind velocity. However, the very unstable class A presents maximum downwind distances lower than class D, irrespectively of the lower wind speed, but higher crosswind distances. Finally, no significant differences can be found for class D during daytime and night-time, even though, at equal wind speed, slightly higher distances are found in daytime, the reason being the higher average ambient temperature during daytime, which implies a higher vapor pressure inside the tank and, as a consequence, a higher released mass flow rate (around 40 against 35 kg/s, respectively).

In order to easily compare the dependence of the obtained results among the different stability classes and with those relevant to the other substances investigated, the calculated distances have been correlated by means of a simple linear interpolation line, and the corresponding coefficients are reported in Table 3.

As can be seen from both Fig. 1(a) and Table 3, class F, besides having the highest absolute values of D and W, is also characterized by the strongest dependence on the wind velocity. The other stability classes present similar slopes for the downwind impact distances with v, but class A is more sensible in terms of W.

3.1.2. Effect of ambient temperature

The influence of the ambient temperature on the maximum impact distances covered by the cloud is reported in Fig. 1(b), where it can be seen that, with the exception of a few cases (see Table 3), quite linear trends are observed (r^2 close to 0.99). Class F again represents the "worst case" weather condition, showing the largest impact areas, while class A has a different behavior in terms of downwind (they are the smallest distances of all classes) and crosswind (they are among the largest) distances. Again no significant difference can be observed for class D in daytime and night-time; however, differently from the previous case, at equal ambient temperature, slightly larger distances are found during night-time, due the lower average wind speed for this latter condition. As for the case of wind velocity, class F is again characterized by the highest slope m, but differently from all other parameters, in this case, the differences in the slopes for the stability classes are rather small.

It is worth noting that, due to the normal boiling temperature of HCl, the only effect of T_{amb} will be that of modifying the release rate via the tank pressure, since $P = P_s(T)$. The differences in the impact distances are directly linked to the different release rates, and in fact, the same behavior will be found when comparing these results to those obtained by varying the hole diameter. If we plot together all the results (either D or W) obtained by varying T_{amb} and d, all together as a function of the total mass release rate, a single profile is observed [11]. However, since this consideration is not applicable to the other

substances of the study, the effects of the two parameters (T_{amb} and d) have been kept distinct and analyzed separately.

3.1.3. Effect of hole diameter

A variation in the hole size only affects the released flow rate, while all other parameters remain the same, and a more direct comparison between the dispersion conditions can be performed. In fact, since, for a given period of the day, both the temperature and the release size are the same, the differences in the impact areas are associated to the atmospheric conditions (wind velocity and stability class) only.

In accordance with the results in Section 3.1.1, from Fig. 1(c) it can be seen that class F always presents the largest distances, while, in daytime, class A has the lowest downwind but the largest crosswind distances. The impact distances for the two class D conditions are practically identical.

3.1.4. Comparison within a class

In order to compare the effects of the different parameters on the resulting impact distances, for a given atmospheric stability class, the so-called index of importance has been introduced. This parameter represents the maximum variation of the dependent variable (here the impact distance) over the whole range of variability of a given input parameter (independent variable).

With reference to class A, in Fig. 2(a) the indices of importance for the different parameters are shown, in terms of the difference in the distances corresponding to the lower and upper limits of the range of variability of each parameter (v, T_{amb}, d), as reported in Table 2. The largest variations in the maximum

distances are associated to the release hole size, as might be expected, but a remarkable influence is also linked to the wind velocity (especially with reference to the crosswind distances); on the contrary, ambient temperature has the lowest influence on the variability of the impact distances.

The decisive influence of the release size is even more apparent in Fig. 2(b) and (c), corresponding to class D, while from Fig. 2(d), it can be seen that under F atmospheric conditions the wind velocity has a much greater importance, comparable to that of the size of the release hole.

In practice, when calculating the consequences of a HCl release, the variability of T_{amb} might be neglected (a single average value might suffice), while more scenarios characterized by different values of the wind velocity and, above all, of the release size, should be taken into account.

3.2. Ammonia

Ammonia has a boiling temperature $T_b = -33\,°C$, so that, when released to atmosphere, part of the flow rate will rapidly evaporate (*flash*) forming a vapor cloud, its amount being a function, among others, of the storage temperature. Another fraction of the release flow rate will stay suspended in the cloud as entrained liquid droplets (*aerosol*), generated by both mechanical and thermal effects. This amount depends on the initial thermodynamic conditions, e.g. the storage temperature, and on mechanical parameters, such as the discharge velocity through the release hole. No single equation or method is commonly accepted for this calculation but different models are available in the literature [4,12–14]. In the case of the adopted simulation
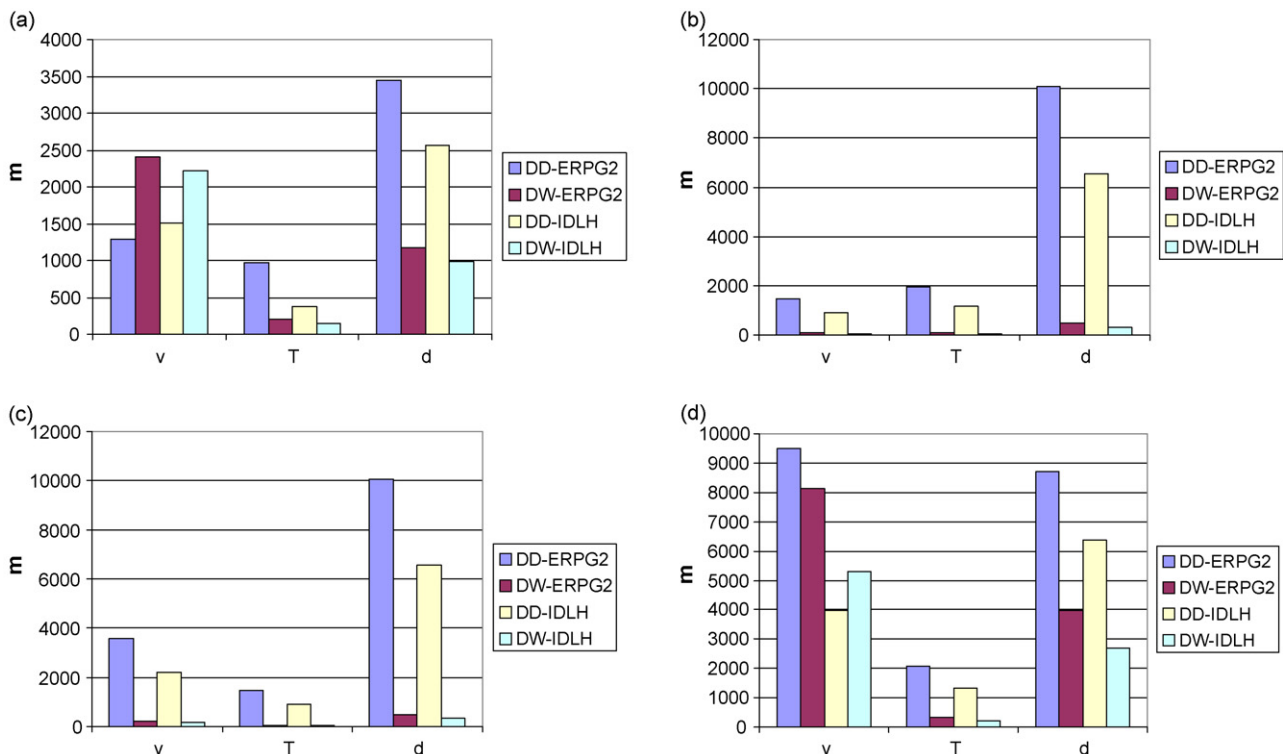

Fig. 2. Hydrogen chloride. Index of importance for the investigated parameters: (a) class A; (b) class D-day; (c) class D-night; (d) class F.
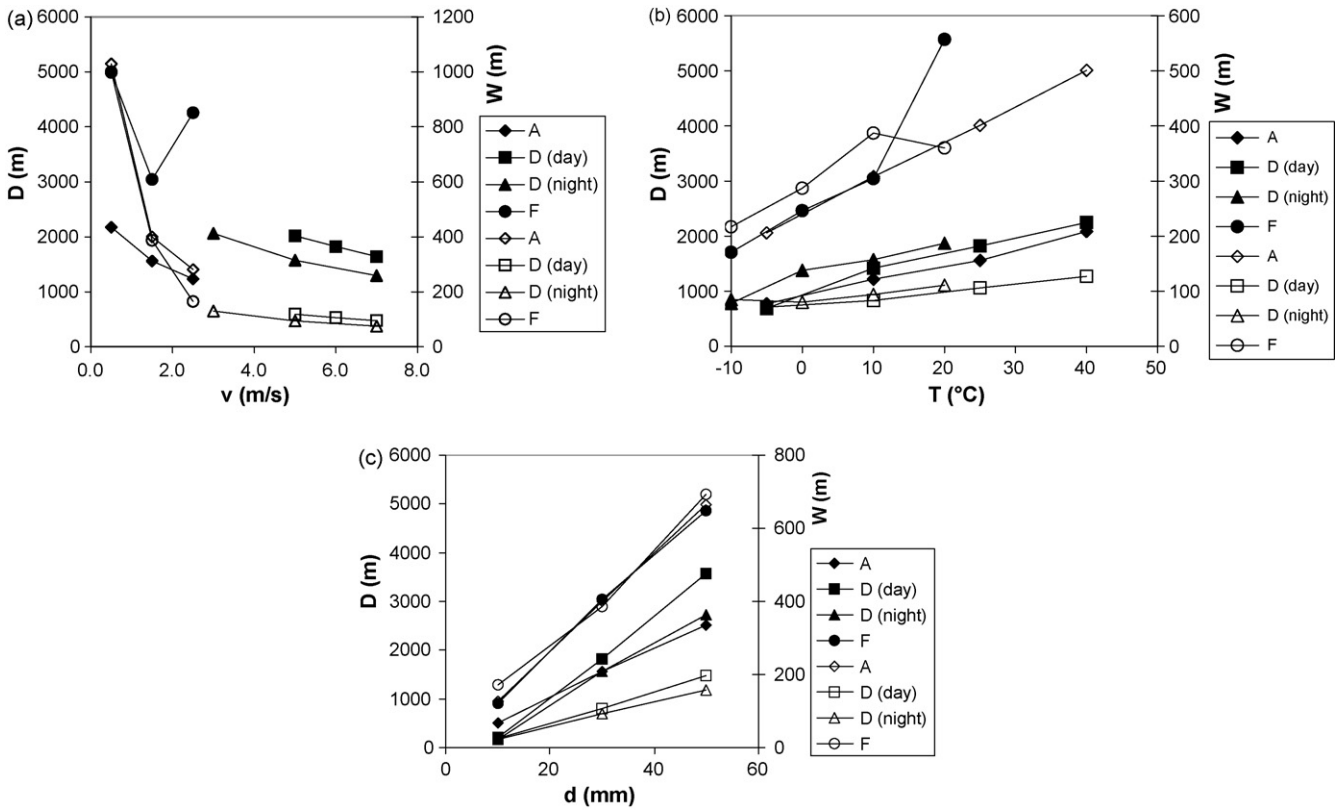
Fig. 3. Ammonia. Maximum downwind (D) and crosswind (W) distances corresponding to the ERPG-2, as a function of: (a) wind velocity; (b) ambient temperature; (c) hole diameter.

code, it is possible to set the aerosol fraction at a constant value (ranging from 0 to 100%, based on user's knowledge), or let it vary based on the flash fraction value F. The latter option has been adopted in the calculations. Specifically, the code assumes that for flash fractions less than 5%, no aerosol is formed (low flashing release, and pool fraction $= 1 - F$), while for F greater than 25% (high flashing release) no pool is formed and aerosol fraction $= 1 - F$. Actually, this is in agreement with experimental results reported in the literature [1,15,16]. Between these two limits, pool and aerosol are both present and the aerosol fraction is an increasing linear function of F.

The remaining part of the released flow rate will drop on the ground forming a liquid pool, from which further vapor will be generated by gradual evaporation. The evaporation rate will depend on a number of parameters (boiling temperature of the liquid, equilibrium vapor pressure, wind velocity, and so on), and the produced vapor will increase the mass of the toxic chemical in the dispersing cloud and affect the impact distances.

In the case of ammonia, the comparison Trace/ALOHA for the standard conditions provides the following results: 1.8/2.1 and 1.3/1.4 km for ERPG-2 and IDLH concentrations, respectively.

Table 4
Slopes (m) and correlation coefficients (r^2) of the regression lines for NH$_3$

Stability class		Parameter											
		v (m/s)				T (°C)				d (mm)			
		ERPG-2 (150 ppm)		IDLH (300 ppm)		ERPG-2 (150 ppm)		IDLH (300 ppm)		ERPG-2 (150 ppm)		IDLH (300 ppm)	
		D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)
A	m	−470	−374	−395	−338.5	28.56	6.52	18.31	5.06	50.125	13.425	37.15	10.5
	r^2	0.969	0.865	0.957	0.851	0.993	0.999	0.995	0.998	0.999	0.999	0.999	0.999
D-day	m	−188	−12	−134	−9.5	33.86	1.27	24.96	1.12	84.22	4.27	56.52	3.2
	r^2	0.999	0.997	0.999	0.999	0.977	0.984	0.959	0.998	0.999	0.999	0.999	0.999
D-night	m	−192.5	−13.75	−135.75	−11	34.75	0.92	26.09	1.02	63.8	3.425	44.7	2.6
	r^2	0.974	0.969	0.987	0.967	0.944	0.759	0.932	0.966	0.997	0.999	0.995	0.998
F	m		−417.5		−221	121.71	5.29	72.18	3.23	98.7	13.025	56.425	11.45
	r^2		0.931		0.993	0.879	0.796	0.817	0.369	0.997	0.989	0.999	0.992

3.2.1. Effect of wind velocity

With reference to the ERPG-2 concentration, in Fig. 3(a), the maximum impact distances for all the meteorological conditions as a function of the wind velocity (v) are shown. With the exception of one case (downwind D under class F), at increasing values of v, lower distances are calculated, again confirming that higher wind velocities promote a fast dilution of the cloud. Disregarding class F, which will be analyzed separately, it is found that class A is the most sensitive to changes in v (see coefficients in Table 4), while class D during daytime and night-time present quite similar behaviors in terms of m slopes. Again, at the same wind speed, higher distances are found for D-day as compared with D-night, the corresponding release mass flow rates being about 15 and 12 kg/s, respectively. Altogether, the impact distances for all these classes range in the same interval of variability.

With reference to the downwind distance under the stable atmospheric condition F, after an initial decrease, it can be seen that when the wind velocity increases from 1.5 to 2.5 m/s, an increase in the maximum impact distance is obtained. This unexpected result can be explained by observing that, under these stable conditions, the wind velocity has two opposing effects: on one hand a higher velocity will improve the dilution of the toxic cloud with "fresh" air; on the other hand, a higher wind velocity will increase the mass transfer coefficient of the liquid in the pool, increasing the evaporation rate and, as a consequence, the total mass in the cloud. Based on these considerations, the same effect is expected to be found for other substances as well. Finally, even for this substance, referring to dispersion, class F represents the worst atmospheric condition among those investigated.

3.2.2. Effect of ambient temperature

In the case of ammonia, ambient temperature plays a more complex role as compared to the case of HCl. In fact, besides the influence on the release flow rate via the tank pressure, T_{amb} also influences the flash vapor fraction after release and the evaporation rate from the pool. For example, at the average temperature corresponding at daytime conditions (25 °C) the vapor mass fraction in the release is 69%, while during night-time (10 °C) it reduces at 47%.

At the same T_{amb}, class A is characterized by the lowest absolute downwind distances (Fig. 3(b)), but the crosswind ones are only slightly lower than those corresponding to class F. Finally, this latter class shows a trend of the distance as a function of T different from linear, with a much larger increase in the impact distances at high T_{amb}'s.

3.2.3. Effect of hole diameter

As can be seen from Fig. 3(c) and Table 4, the trend of the impact distance as a function of the hole size is always quite linear (regression coefficients higher than 0.99) and class F is still the worst weather condition. However, differently from HCl, rather larger distances are obtained for class D-day, as compared to D-night, this latter providing distances very close to those corresponding to class A. This highlights the increasing importance of ambient temperature with respect to the wind velocity. As already found with HCl, class A presents a different behavior in terms of crosswind and downwind distances. In fact, while the downwind distances are the lowest compared to all other classes, the crosswind distances are higher than those for neutral conditions and very close to those corresponding to the stable class F.
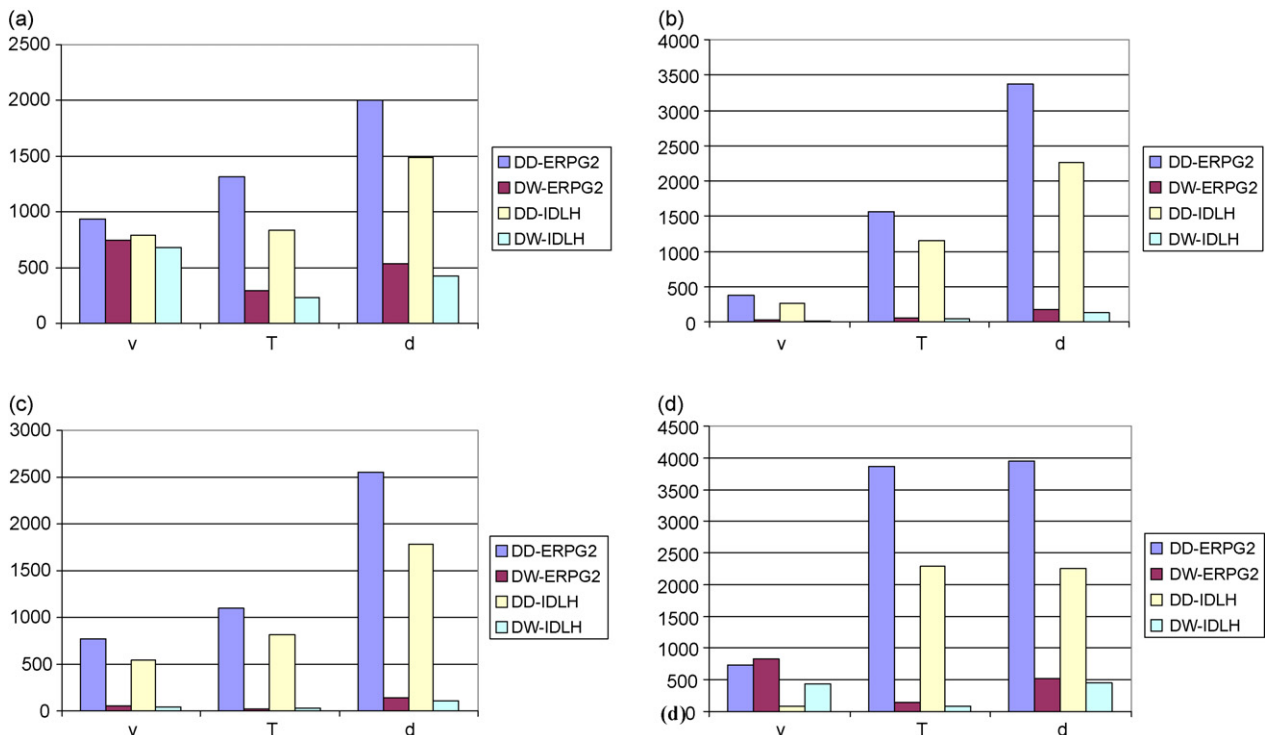

Fig. 4. Ammonia. Index of importance for the investigated parameters: (a) class A; (b) class D-day; (c) class D-night; (d) class F.

3.2.4. Comparison within a class

The indices of importance of the parameters under the 4 stability classes are reported in Fig. 4(a)–(d). The release hole size is still the main parameter affecting the impact areas under all atmospheric conditions, but a different ranking is observed with reference to v and T_{amb}. In fact, differently from the case of HCl, where the ambient temperature has little influence on D and W and the wind velocity (especially for the very stable and very unstable classes, F and A) was much more important, in the case of NH_3 the opposite is true. A relatively high influence of the wind speed is only found in the correspondence of class A (in particular for crosswind distances, W).

As a consequence, in the case of limited resources availability, particular attention should be devoted to the influence of the release hole size (release rate) and, secondly, to that of the ambient temperature, while relatively less attention can be devoted to the wind velocity.

3.3. Trimethylamine

The boiling temperature of trimethylamine is +3 °C. In order to avoid vacuum conditions in the tank when T_{amb} is below +3 °C (e.g. possibly during night-time), a positive pressure is maintained in the storage tank. Thus, a padding pressure slightly higher than one atmosphere has been assumed inside the tank for all these conditions.

Also, due to this relatively high value of the boiling temperature, the flash fraction after release is rather low, being 39% (both vapor and aerosol) during daytime, and only 4% during night-time. Based on this consideration, it is expected that the characteristic parameters of liquid pool evaporation will have a remarkable influence on the dynamics of the cloud formation and dispersion.

Even in this case the comparison with the results calculated with ALOHA provides excellent agreement: 760 and 525 m for Trace, 800 and 520 m for ALOHA, at concentrations of 100 and 200 ppm, respectively.

3.3.1. Effect of wind velocity

In Fig. 5(a) the trends of the impact distance as a function of the wind velocity are reported, for all the stability classes. As a first consideration, it can be seen that, as already partly found with ammonia, under the F stability class an increase in the maximum downwind impact distance is observed over the whole range of variability of v. In this regard, it must be considered that, at relatively low temperature, almost all the release remains in the liquid state and the evaporation from the pool will be very much influenced by mass trans-
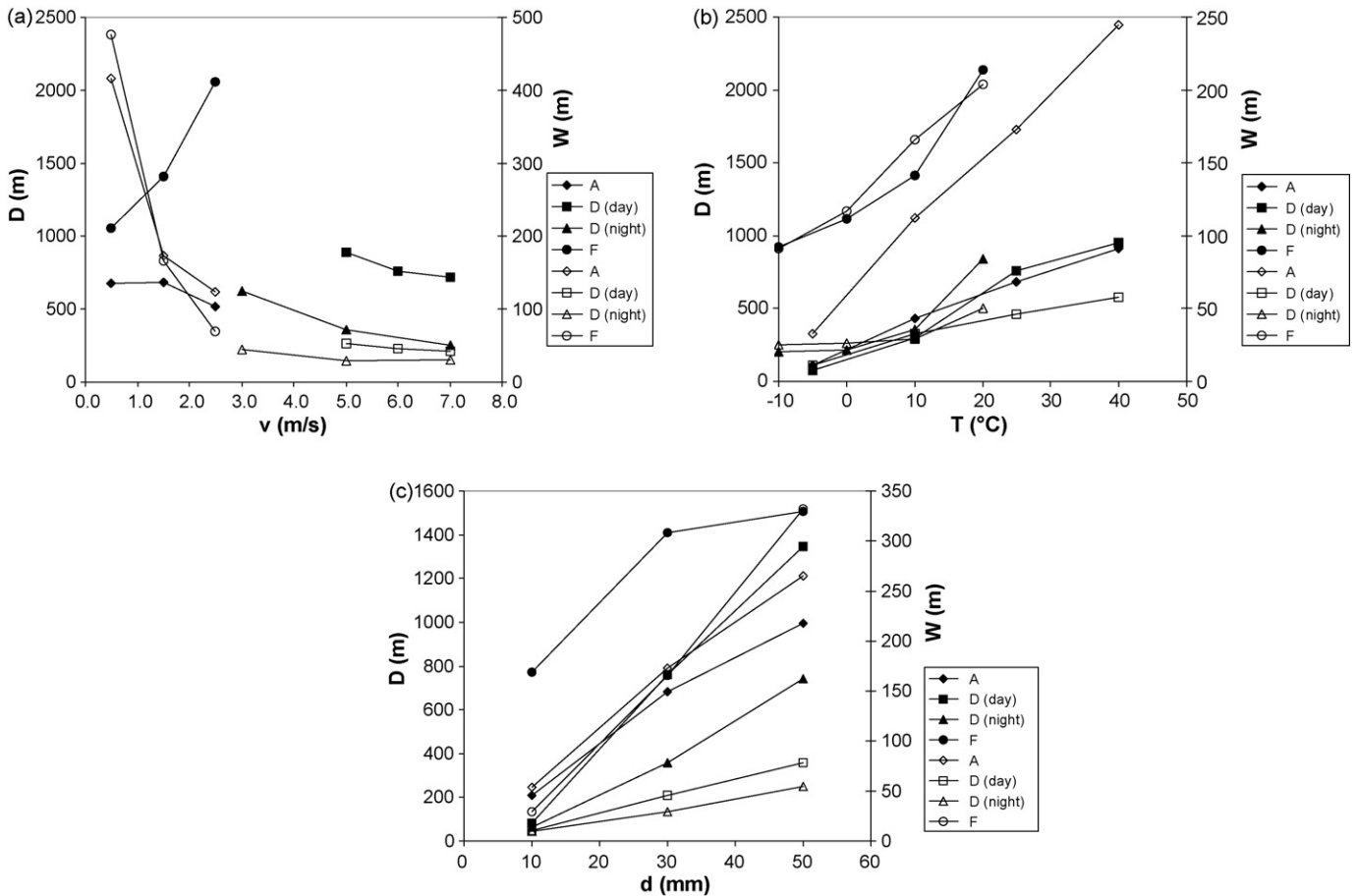

Fig. 5. Trimethylamine. Maximum downwind (D) and crosswind (W) distances corresponding to the ERPG-2, as a function of: (a) wind velocity; (b) ambient temperature; (c) hole diameter.
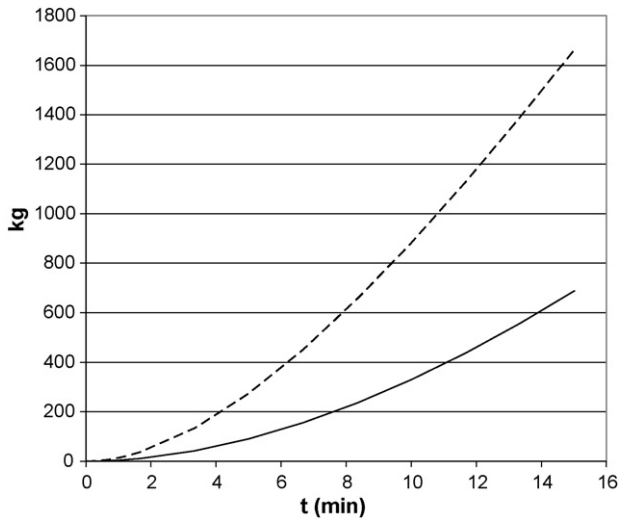
Fig. 6. Total evaporated mass from a liquid pool of trimethylamine, as a function of time. Solid line: wind velocity 0.5 m/s; dashed line: wind velocity 2.5 m/s.

fer with air. This effect, together with the high atmospheric stability, eventually will give rise to the observed increase in the impact areas. As a consequence, for this substance, the worst condition is not high stability-low wind, but high stability-high wind (consistently with the proper range of variability).

In order to better illustrate this effect, in Fig. 6 the total mass evaporated from the pool over the 15 min release time is reported for the extreme values of wind velocity, i.e. 0.5 (solid line) and 2.5 (dashed line) m/s: in the latter case a much faster evaporation occurs.

Under all other conditions, the usual decrease of the impact distances is observed, and, by looking at Tables 3–5, it can be seen that a continuous and marked reduction in the dependence on v is found, the largest dependence being for HCl.

3.3.2. Effect of ambient temperature

An increasing trend of the impact distances with T_{amb} (Fig. 5(b)) is observed for trimethylamine as well as for the previously analyzed chemicals. Class F still represents the worst condition, and the crosswind distances for class A are much larger than those for neutral conditions. Differently from the case of wind velocity, the regression parameters found for T_{amb} (Table 5), for the different stability classes, are very close to each other.

3.3.3. Effect of hole diameter

The trend of the impact distances as a function of the release hole size (Fig. 5(c)) is as usual, and the correlation parameters (slopes m in Table 5) are much smaller than those for HCl, but larger than those relative to NH_3 and no clear trend can be observed.

3.3.4. Comparison within a class

In Fig. 7(a)–(d) the indices of importance for the investigated parameters are reported, under the four atmospheric conditions.

Table 5
Slopes (m) and correlation coefficients (r^2) of the regression lines for C_3H_9N

| Stability class	Parameter	v (m/s)				T (°C)				d (mm)			
		ERPG-2 (100 ppm)		IDLH (200 ppm)		ERPG-2 (100 ppm)		IDLH (200 ppm)		ERPG-2 (100 ppm)		IDLH (200 ppm)	
		D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)
A	m	−78.5	−146	−45.5	−119	17.59	4.647	13.02	3.61	197	52.75	142.75	40.5
	r^2	0.721	0.87	0.50	0.86	0.993	0.997	0.990	0.996	0.986	0.994	0.988	0.996
D-day	m	−86	−5	−59	−4	20.65	1.03	14.05	0.79	316.5	16.75	220.25	12.5
	r^2	0.909	0.949	0.915	0.923	0.973	0.976	0.947	0.984	0.998	0.999	0.998	0.999
D-night	m	−91.75	−3.5	−70.5	−3	20.54	0.78	14.89	0.45	169	11.25	91	7
	r^2	0.936	0.644	0.961	0.923	0.785	0.729	0.810	0.6	0.993	0.992	0.999	0.998
F	m	502	−203.5	327	−92	39.34	3.88	20.02	3.73	183.25	75.75	130.25	59.5
	r^2	0.972	0.914	0.913	0.986	0.909	0.987	0.945	0.950	0.845	0.996	0.936	0.996
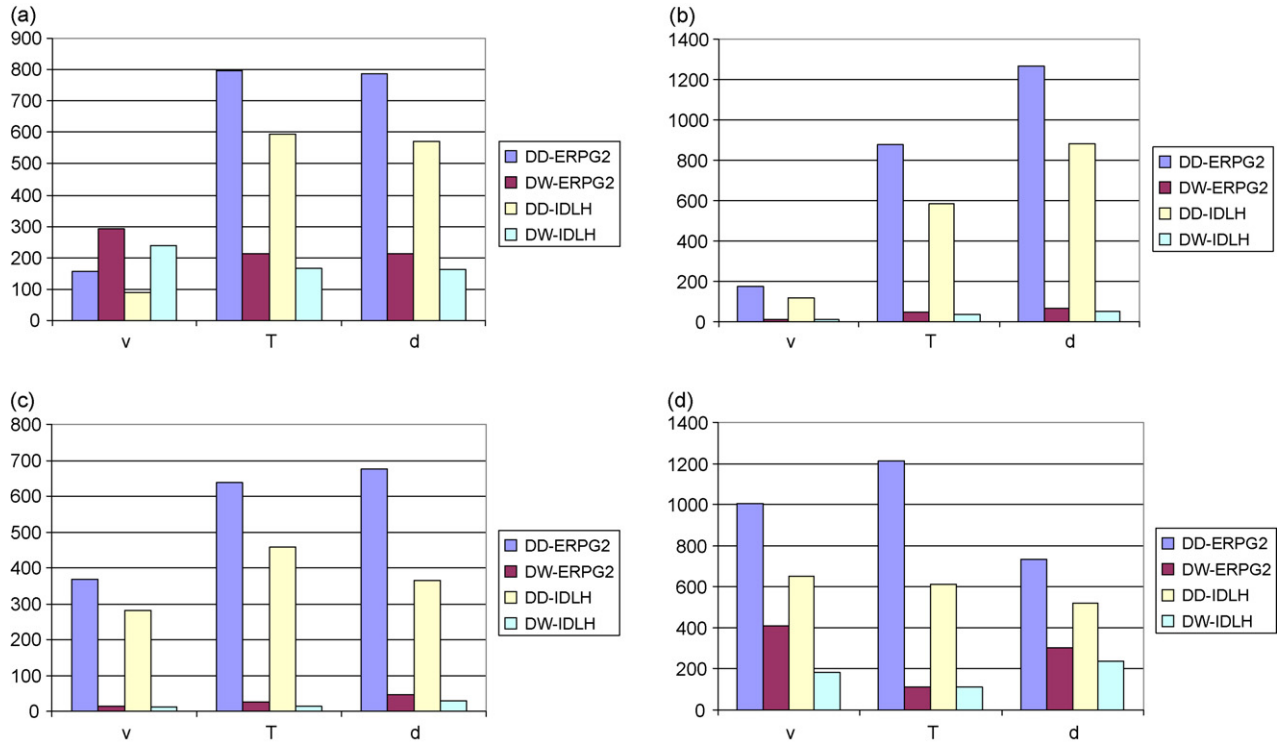
Fig. 7. Trimethylamine. Index of importance for the investigated parameters: (a) class A; (b) class D-day; (c) class D-night; (d) class F.

It can be generally observed that, for this substance, the ambient temperature has a large influence on the maximum distances' variability, comparable with that of the release size. In the case of class F, this influence is even larger than that of the release size, indicating that, for this condition, characterized by low temperature and vapor formation, the largest contribution to the cloud formation comes from pool evaporation. Conversely, and in accordance with a trend already observed moving from HCl to NH$_3$, the wind velocity is the least influencing parameter, with particular reference to the neutral conditions D (both during daytime and night-time). Finally, it is worth reminding that under class F, v has now assumed an opposite effect, providing larger downwind distances at higher wind velocities.

3.4. Bromine

Among the chemicals studied in the present work, bromine is characterized by the highest boiling temperature ($T_b = 59\,^\circ$C). As a consequence, after release, and under any conditions, the whole released flow rate will stay in the liquid state forming a pool on the ground, and the toxic cloud will be fed by the evaporation from the pool, only. So, consistently with the results and the comments already seen for trimethylamine, the parameters of the dispersion are expected to be dependent mainly on the pool dynamics.

Furthermore, it must be noticed that, due to the high toxicity of this chemical (ERPG-2 = 0.5 ppm, see Table 1), in some of the conditions adopted, very large impact distances are calculated
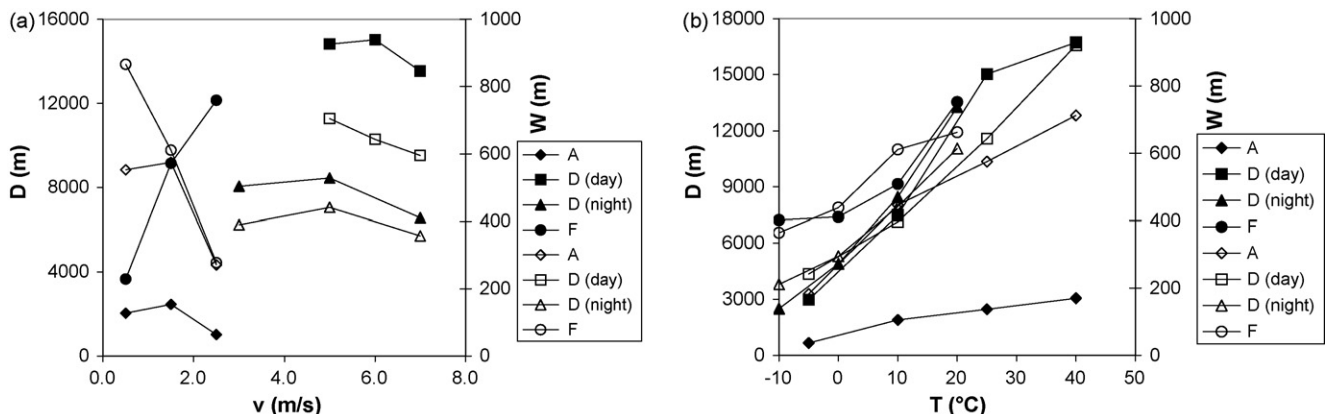

Fig. 8. Bromine. Maximum downwind (*D*) and crosswind (*W*) distances corresponding to the ERPG-2, as a function of: (a) wind velocity; (b) ambient temperature.

(more than 10 km). Since most of the dispersion models available in the literature have a range of validity of about 10,000 m, the mentioned results must be taken with care.

Finally, as already explained at the beginning of this section, for this substance, the comparison with ALOHA cannot be done.

3.4.1. Effect of wind velocity

As already found for trimethylamine, from Fig. 8(a) it can be seen that, under stability class F, a continuous increase of the downwind impact distance is calculated, indicating that the wind velocity has a fundamental importance in promoting the evaporation from the liquid pool. This is also shown in Fig. 9, where the evaporation rates from the pool for two wind velocities under class F are reported. The increase in the evaporation rate with time is due to the increasing diameter of the pool. Dimensions and temperature of the pool are the same in the two cases, and the difference in the evaporation rate is due to the different wind velocities, only.

Furthermore, even under the other weather conditions, increasing the wind velocity will give rise to an initial slight increase in the impact distances, followed by a subsequent decrease; under two stability conditions (D-night and A), this is true for the crosswind distance also. However, the variation in the absolute values of the distances in these latter cases is relatively small as compared to that obtained for class F (approximately from 4000 to 12,000 m).

A further important observation which can be drawn from Fig. 8(a) is that, for this substance, class F does not represent the worst condition, the distances calculated for class D-day being much larger. In this latter case, the higher average temperature (via the vapor pressure of Br_2) certainly plays some influence, as will be shown in Section 3.4.2. However, at the same conditions (class F and D-night) the calculated distances are comparable (though, for class F, they are much more dependent on v, than for class D-night), which was not the case for all previous substances. Similarly, in daytime conditions, the distances calculated for class D are far more markedly larger with respect to class A than already seen in advance.
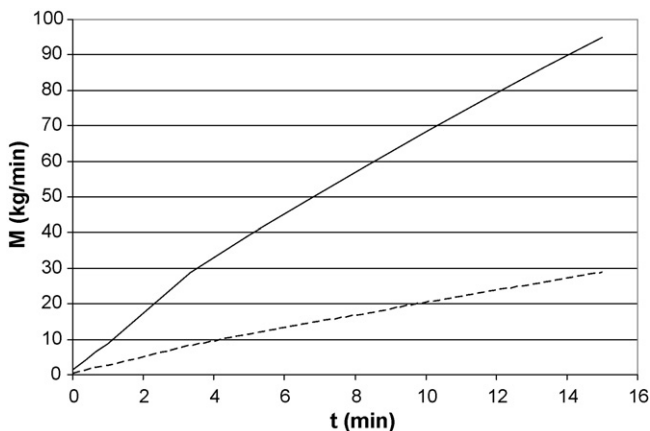
Fig. 9. Evaporation rate from a liquid pool of bromine as a function of time. Solid line: wind velocity 2.5 m/s; dashed line: wind velocity 0.5 m/s.

Table 6
Slopes (m) and correlation coefficients (r^2) of the regression lines for Br_2

Stability class	Parameter	v (m/s)						T (°C)						d (mm)					
		ERPG-2 (0.5 ppm)		IDLH (3 ppm)		ERPG-2 (0.5 ppm)		IDLH (3 ppm)		ERPG-2 (0.5 ppm)		IDLH (3 ppm)		ERPG-2 (0.5 ppm)		IDLH (3 ppm)			
		D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)	D (m)	W (m)		
A	m	−509.30	−140.60	−309.00	−105.50	51.77	11.46	26.55	6.08	520.25	81.25	288.50	38.25		
	r^2	0.477	0.690	0.614	0.904	0.961	0.967	0.973	0.973	0.998	0.895	0.998	0.784		
D-day	m	−643.50	−55.00	−160.00	5.50	325.48	15.23	43.07	2.94	5431.00	123.00	2477.50	46.00		
	r^2	0.629	0.995	0.998	0.976	0.953	0.985	0.990	0.979	0.933	1.000	0.966	0.850		
D-night	m	−374.00	−8.25	−50.25	14.50	358.68	13.53	42.08	3.14	3331.75	113.25	1208.25	24.00		
	r^2	0.564	0.152	0.922	0.776	0.978	0.978	0.925	0.990	1.000	0.715	0.966	0.898		
F	m	4241.50	−294.00	1561.00	−143.50	206.71	10.67	105.18	2.30	384.50	149.75	174.25	68.00		
	r^2	0.972	0.994	0.979	0.985	0.826	0.957	0.805	0.294	0.861	0.818	0.964	0.860		

Finally, for this relatively high-boiling substance, with the exception of class F, for which a clear and continuous trend is observed, for all other classes, the diluting effect of the wind is counteracted by its effect on the evaporation and, altogether, a very limited influence on the impact distances is derived. This is reflected in the interpolation parameters of Table 6.

3.4.2. Effect of ambient temperature

The impact distances calculated at varying T_{amb} are reported in Fig. 8(b): the largest distances are obtained for class D-day at high temperature. At the same temperature, the distances calculated under class F, still higher than those under the other conditions, nonetheless are much closer to these latter than for the previous materials, characterized by higher volatilities. This confirms the strong influence exerted by the wind velocity for this relatively "high-boiling" substance.

As seen from Table 6, with the exception of class F, rather good linear trend of the data are generally found. In particular, for classes D-day and D-night, almost coincident lines are obtained with very similar values of the parameters, so that they might be correlated by a single equation.

3.4.3. Effect of hole diameter

Due to the low volatility of bromine, in the case of 10 mm diameter hole, no appreciable impact areas were calculated. So, in order to have the same number of hole size cases as for the other substances, the following hole sizes were here adopted: 30, 50, 70 mm. By comparing the results obtained under the various classes, it is found again that class F is not the worst condition, but both class D-day (by far the worst stability class) and

D-night are characterized by larger distances. However, these values greatly exceed the limits of applicability of the models, and they were not reported here. Finally, besides the usual considerations, it is worth noting that, in the case of bromine, for daytime conditions the slopes of the correlating lines are much higher (almost double) than those for night-time. For example under the D-day class a coefficient of about 5400 is found, while for D-night it is only 3330. The origin of this difference lies in the different average ambient temperature and wind velocity, which control the evaporation from the pool, and which are both higher during daytime. These results are very different from those obtained for HCl (Table 3), where almost identical coefficients were found, and again highlights the influence of the parameters affecting the liquid pool dynamics. Furthermore, the coefficient for class A is higher than that for class F, showing that the influence of these parameters is even larger than that of the stability class. This behavior was already, partly, found for the previous substances and represents a constant trend linked to the boiling temperature of the substance.

3.4.4. Comparison within a class

After stressing the result that for this substance the worst weather condition is represented by a neutral (D) daytime stability class, the relative importance of the input parameters can be seen in Fig. 10(a)–(d). It can be noticed that a different distribution is obtained depending on the stability class. In particular the only common characteristic is the importance of the ambient temperature, which is rather high for all classes. As might be expected from the above discussion, due to the oppositely competing actions exerted by the wind, the importance of the wind
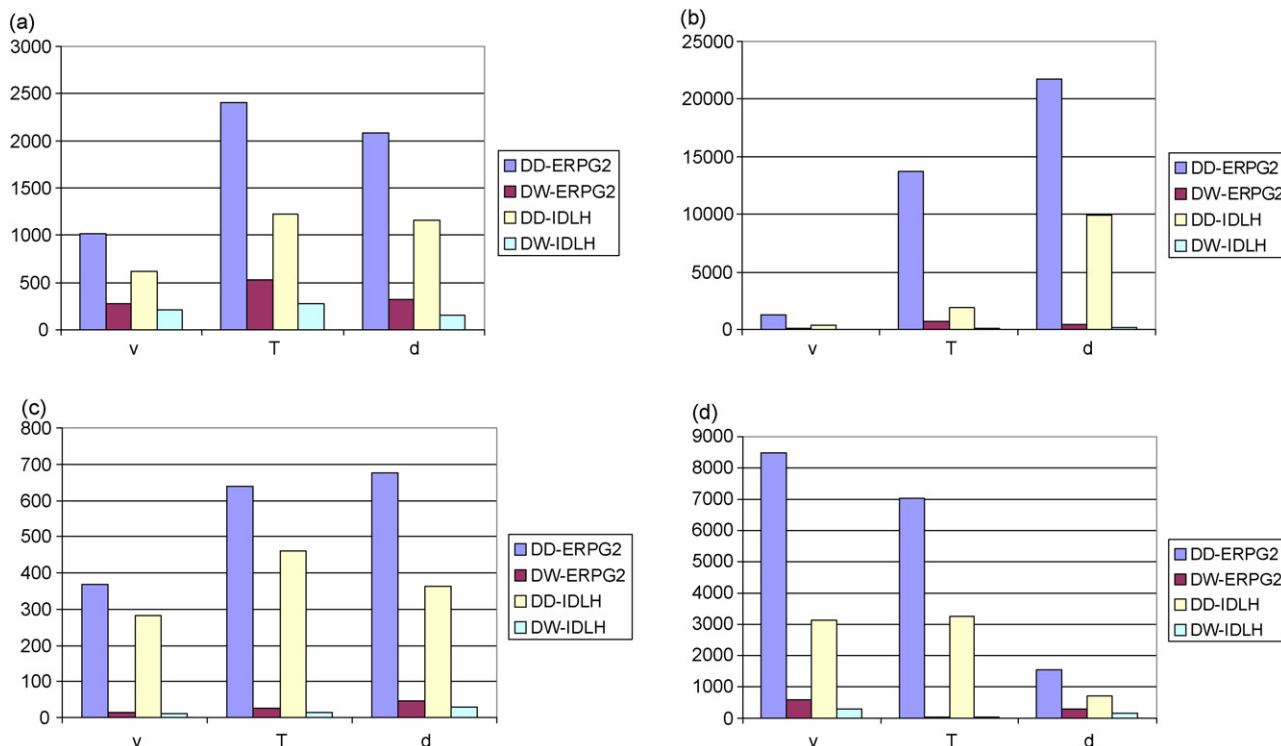

Fig. 10. Bromine. Index of importance for the investigated parameters: (a) class A; (b) class D-day; (c) class D-night; (d) class F.

velocity is small for all classes, except for F, where a constant effect (increasing distances) of v was found. In fact, for this latter class, the wind velocity is the main influencing parameter, while the release size is the least. Finally, it must be observed that the scale of the y-axis of the figures varies widely from class to class, much more markedly than for the other substances analyzed, the larger variability being associated with the D-day class.

4. Conclusions

In the present paper the effect of the main parameters influencing the maximum impact distances covered by a vapor cloud originated by the accidental release of a toxic substance has been analyzed. The results show that these areas depend both on the substance involved and on the ambient conditions and, even if no general rule can be drawn, yet some guidelines can be given.

The widely known rules of thumb, such as those related to the diluting effect of the wind, the negative influence of stable atmospheric conditions, etc., actually reliably apply only to substances which, on release, instantaneously generate a substantial amount of vapor, such as HCl and, partly, NH_3. For these substances the worst condition is represented by a combination of high stability and low wind velocity (e.g. F1 rather than F2); wind velocity shows a remarkable influence only in atmospheric conditions different than neutral (i.e. A and F) and ambient temperature has a very limited influence.

As soon as the boiling temperature of the chemical increases, the fraction of the released material remaining in the liquid state increases, too, and the influence of the input parameters markedly change, those linked to the pool dynamics gaining importance. In particular, the main results can be summarized as follows:

- the influence of the storage temperature on the impact distances increases, becoming gradually comparable, or even larger, than that relevant to the release size (especially for classes F and A). On the contrary, for high boiling chemicals, the wind velocity has a minor influence with respect to the other parameters, except for very stable conditions (class F);
- under stable conditions, the influence of the wind speed markedly changes with T_b, the impact distances dramatically increasing with the wind velocity, for high boiling substances;
- from the above results, depending on the substance, it may happen that the worst dispersion condition is no longer the usual reference case F2, but a neutral class at higher temperature and wind velocity, such as D5 or D6. This is particularly important if we consider that neutral class D has a much higher frequency of occurrence than, for example, class F, and that it is quite common in daytime, when the average temperature is higher.

The results here reported can be of some help for risk analysts in optimizing the resources allocation when carrying out risk analysis studies, where, in order to reduce the computational effort, a limited number of reference ambient conditions are taken into consideration for risk quantification.

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