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A Method for Computing the Damage Level Due to the Exposure to an Airborne Chemical with a Time-Varying Concentration

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The calculation of damage level due to the exposure to a toxic cloud is usually not included in most popular software, or it is included using techniques that do not take into account the variation in concentration over a period of time. In this work, a method is introduced for calculating the temporal evolution of the potential damage level and to obtain a more precise and descriptive estimation of this level. The proposed goal is:

- to estimate the maximum and minimum damage level experienced by a population due to the exposure to an airborne chemical with a time-varying concentration;
- to be able to assess the damage level experienced in a progressive way, as the exposure to the airborne chemical occurs.

The method relies on transformations of time-concentration pairs on a continuum of damage level curves based on the available guideline levels, obtaining maximum and minimum approximations of the expected damage level for any exposure duration. Consequently, applying this method to transport model output data and demographic information, damage evolution in relation to time and space can be predicted, as well as its effect on the local population, which enables the determination of threat zones. The comparison between the proposed method and the current (Spanish and ALOHA) ones showed that the former can offer a more precise estimation and a more descriptive approach of the potential damage level. This method can be used by atmospheric dispersion models to compute damage level and graphically display the regions exposed to each guideline level on area maps.

KEY WORDS: Acute exposure guideline levels; acute toxicity; damage differential coupling; time-varying concentration; toxic chemical release

1. INTRODUCTION

The methodologies often used for risk assessment and response to emergencies concerning acute exposures to hazardous substances (acute exposures are single, nonrepetitive exposures that do not exceed 8 hours(1)) consist basically of two parts: a model for the toxic chemical release and a representation of risk areas. These two parts are intertwined by means of some method that, for every location the toxic cloud passes by, analyzes the concentration profile and associates it with a level of concern (LOC), therefore identifying the different dangerous areas.

A toxic LOC is the value above which the toxic gas concentration might be high enough to harm people.(1) Currently, it is a common practice to employ a hierarchy of toxicological indices as LOCs for the exposure to different chemical substances in the air. For

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the estimation of the damage caused by this kind of exposure, the preferred indices are the Acute Exposure Guideline Levels (AEGL), if available for the substance involved. Otherwise, the Emergency Response Planning Guidelines (ERPG) are the second best option, and ultimately the Temporary Emergency Exposure Limits (TEEL) are used.(2–6)

The AEGLs represent threshold exposure limits for the general public and are applicable to emergency exposure periods ranging from 10 minutes to 8 hours. The NAC/AEGL's standing operating procedures define the concept of AEGLs as the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience several symptoms. Three different guideline levels were established, corresponding to increasingly severe symptoms (AEGL_1, AEGL_2, and AEGL_3).(3,7) The multiple periods available for each damage level enable a reliable interpolation for different times. AEGLs have been published for several chemicals. The current status of this project can be found by going to the EPA website.(8–19)

Among the application programs for accident scenarios, which simulate emissions and generate risk maps, areal locations of hazardous atmospheres (ALOHA) is one of the most popular and it is particularly convenient since it is available on the Internet for free.(20) ALOHA can model a pollutant cloud dispersion in the atmosphere and display a diagram that shows an overhead view of the regions, or threat zones, in which it predicts which key hazard levels will be exceeded.

In ALOHA, when modeling a toxic chemical release, you can choose AEGLs as your LOCs if they have been defined for that chemical. Even though AEGLs are available for five exposure durations, only the 60-minute AEGL is provided in ALOHA because it models the release for 60 minutes from your start time. This software defines the damage level from the maximum concentration observed during the total time of exposure for every analyzed geographical position. Whenever the maximum concentration observed for a determined location is greater than a particular LOC, even for just one particular instant, that location poses a risk characterized by that LOC. It has to be noted that the ALOHA program uses these LOCs as constant concentration levels.(1,21)

In Spain, on the other hand, the new "Directriz Básica de Protección Civil para el Control y Planificación ante el Riesgo de Accidentes Graves en los que intervienen Sustancias Peligrosas" (Civil Protection Basic Directive for Control and Planning in cases of Serious Risk of Accidents Related to Hazardous Substances) uses a popular method for determining different planning areas in case of an accident, from now on called the Spanish method. This method uses concentration profiles obtained from some transport model. Not only does this method use the reference periods given for every AEGL damage level, but it also uses a time-concentration representation of the AEGL, ERPG, or TEEL indices, where the values are extended for periods different to the reference ones by means of adequate interpolations and extrapolations. For determining different planning areas, the Spanish method is based on the cloud passage times and the maximum concentrations associated with the observed profiles at different distances from the toxic chemical release. To outline the toxic cloud, a minimum concentration threshold is determined. The total time of cloud passage is defined as the period during which the profile concentration is greater than that minimum concentration threshold. The pairs formed by each time and its corresponding maximum concentration are represented in the same diagram as the time-concentration pairs for the two damage levels (level 1 and level 2) of the available index (AEGL, ERPG, or TEEL), obtaining two intersection points (see Fig. 1), which will determine the values (concentration and total time of exposure) to define the distances for intervention and alert. The concentrations that characterize the intervention and alert areas are entered into the software, determining the maximum distances where those concentrations will be reached.(2)

The difference between the ALOHA and the Spanish method is that the former uses the whole simulation time (60 minutes) while the latter uses only the time above a threshold. Also, the Spanish method uses the five exposure durations available for AEGLs while the ALOHA only uses the 60-minute AEGL. Finally, both use the same concentration (the maximum).

It is not our intention to evaluate the models for toxic chemical release simulation or risk area representation, but in the following paragraphs we shall analyze some of the limitations observed in the methods using these tools as well as establish the objectives of our work:

- Approximation of the time-varying concentration profile to a constant one, with a concentration equal to the maximum over the

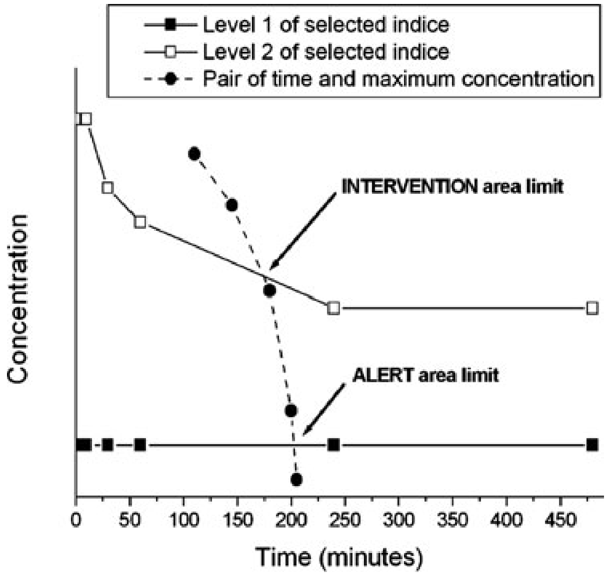

Fig. 1. Generic representation of levels 1 and 2 of the available index (AEGL in this case) and a typical graph obtained by linking time-concentration pairs (pairs of time of passage of the cloud and maximum concentration). The intersection points determine the characteristic values (concentration and exposure time) to define the distances for intervention and alert.

exposure time considered, generally leads to an overestimation of the damage level, which depends on the degree of variability of the analyzed profile. This conservative approach to calculation is based on the methodology carried out for the determination of the guideline levels where the concentration of exposure remains constant during the whole analysis period for each researched substance.(2,22)

- The current methods do not provide information about the damage evolution as a function of time. Only the expected final situation is provided. This fact does not enable a timely planning of actions during the cloud passage.
- The current methods do not provide information about the minimum damage level expected. Considering that the damage level assessed is far greater than the actual one, it would be useful to provide those responsible for the emergency management with an estimation interval that assures as well the minimum damage or response level the population will experience as the mildest consequence.
- The current methods do not quantify the severity between two isodamage data curves. Regardless of the proximity of the concentration-time pair to the isodamage data curves only an integer value of damage is provided.

All these factors can cause inadequate actions from those responsible for the emergency management, who could dismiss certain interventions considering them futile, while they could still bring about positive, even life-saving, results.

In this work, we develop and illustrate a method denominated damage differential coupling (DDC) to estimate a range of damage that a population may experience when exposed to a time-varying concentration, using the same toxicological indices employed by the currently used methods, but in a progressive and more precise way. We consider that having these advantages is critical for appropriate emergency management.

2. DDC METHOD

This method gets a progressive estimate of the damage experienced while people are exposed to chemicals. Also, it enables the estimation of the maximum and minimum damage level resulting from the exposure.

The DDC method implies the use of the toxicological indices and time-varying concentration profiles as tools for the damage estimation. Also, it assumes that there is a continuous field of the toxicological indices for time and concentration, and that the incremental calculation of the damage by means of exposure differentials (*coupling*) is not commutative.

2.1. Toxicological Indices

The equivalent duration of exposure to a plume will rarely be equal to one of the five time periods for which AEGLs are defined (10 minutes, 30 minutes, 1 hour, 4 hours, and 8 hours). EPA has not provided any explicit guidance on how to determine AEGL values for durations between the defined times. Although there are other interpolation methods such as that proposed by Stage,(7) we decided to apply the relationship between concentration and time followed in AEGL development:(3,7,23–32)

- For cases where a response is viewed as a concentration threshold and independent of time, the same value may be used at all periods. An example would be the AEGL_1 response to an irritant.

- Extrapolations involving data derived from one time-concentration pair to another can be estimated with Haber's rule, which states that the product of concentration × time is equal to a constant (toxic load equal to constant). This relationship appears to be applicable primarily over short intervals and mostly to direct acting chemicals, such as hydrogen chloride and dibutylhexamethylenediamine:$L = C * t$.
- ten Berge evaluated this relationship and concluded that the relationship is more general with the product of concentration to the *n*th power times time being equal to a constant (toxic load equal to constant): $L = C^n * t$. For a wide variety of industrial gases n takes values between 1.0 and 3.5, and the most common values of n are between 2 and 3. Ammonia is an example of this relationship where $n = 2$.

The representation for AEGL indices is a set of three continuous curves that connect the points related to the same damage level (from now on, we shall call these *isodamage data curves*).

Particularly, for times less than 10 minutes, it can be assumed that the damage does not depend on the exposure time but rather on the concentration, that is, we suppose that in those cases people are exposed to that concentration during all the time. This conservative approach guarantees that the damage caused to people due to any time-concentration pair obtained will never be greater than the one defined by the damage level considered.(2)

On the other hand, the ERPG and TEEL indices provide only one time-concentration pair. If no additional toxicological information is available, the extrapolation from both indices is carried out using the same criteria as for the AEGLs. A complete discussion of the interpolation for these indices is given by González Ferradás.(2)

Fig. 2 shows a graphic representation of the indices with the interpolations and extrapolations aforementioned.

2.2. Profiles

A profile describes the concentration values observed during the cloud passage through a certain geographical location.

To outline the toxic cloud and optimize the computational cost, it will be assumed that a minimum threshold concentration exists, above which the substance is perceived by any of the senses.

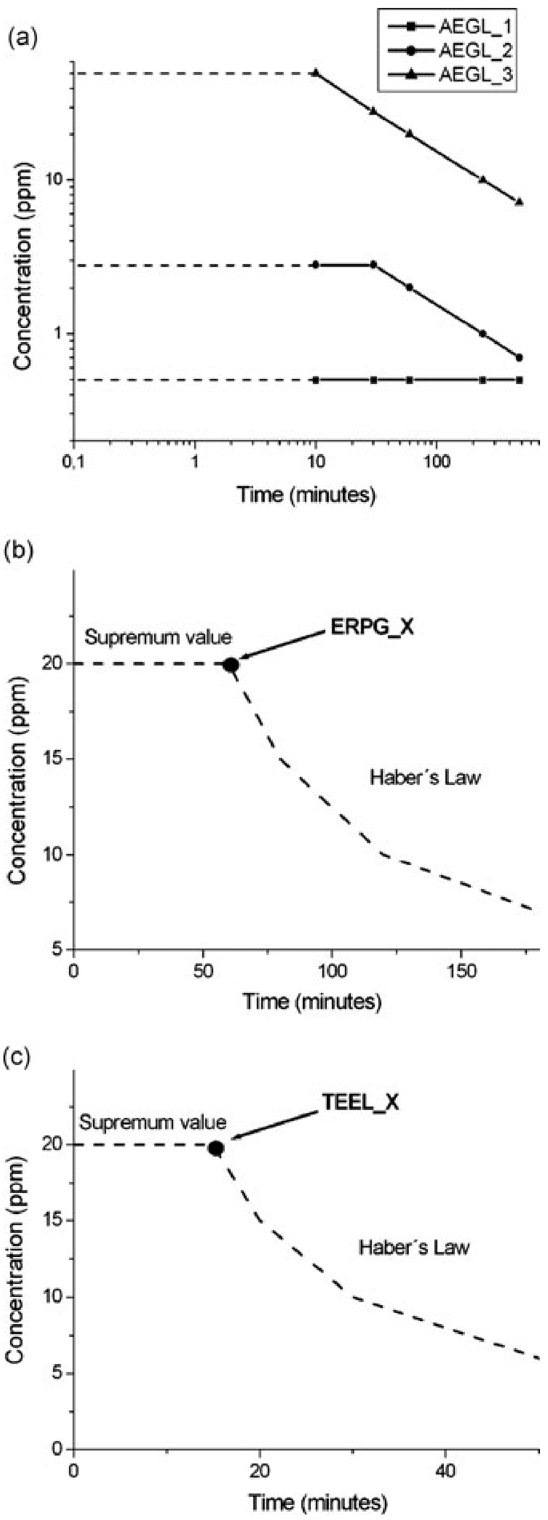

Fig. 2. (a) Representation of the isodamage data curves corresponding to the three levels of AEGLs for chlorine. In (b) and (c) the extrapolations applicable to the ERPGs and TEELs indices, respectively, are shown.

There have been attempts to deal with the spatiotemporal varying concentration profiles, for example, by simplifying the fluctuating time series, or by developing models of probability distribution and statistical simulation methods, which more realistically addresses concentration variability. The random variability in airborne chemical concentration over time and space can conduce to uncertainty in the estimate of the size of potentially affected areas by use of AEGLs, widely applied as "threshold."(33–37)

In our method, any profile will be approximated by decomposition in pairs $(\Delta t, \bar{C})$ such that their summation is an approximation to the integral of the profile. Therefore, exposure (E) can be calculated as:

$$E = \int_0^{t_{exp}} C.dt \approx \sum_{i=1}^{n} \bar{C}.\Delta t\,,$$

where $\bar{C} = \frac{C_i + C_{i-1}}{2}$, with C_{i-1} = observed concentration for the lowest endpoint of the interval Δt, and C_i = observed concentration for the greatest endpoint of the interval Δt.

2.3. Existence of a Continuous Field

A continuous field of isodamage curves is included between the isodamage data curve level 3 and the minimum threshold curve (associated with a damage level 0), traced according to the values established by U.S. Environmental Protection Agency.(38) Hence, there is always an isodamage curve associated with any pair (t, C) as long as the concentration is greater than or equal to the threshold concentration for that time. To estimate the damage value associated with a pair (t, C), a function for *damage level* is defined. Its domain is the Cartesian product of the interval (0, 8] (left-open and right-closed) times the set of positive real numbers. The interval (0, 8] includes all possible exposure times (measured in hours), and the set of positive real numbers the possible concentrations, measured in ppm or mg m^{-3}. And the image of the function for damage level is the set of all numbers between (and including) 0 and 3. Therefore, if we put $\Omega = (0, 8] \times \mathrm{R}^{+}$ we define a function $D(t, C)$ such that $D: \Omega \rightarrow [0, 3]$.

Toxic exposure can have periods where the level of damage is associated with the time of exposure, in a dependent or independent way. For this reason, it is necessary to distinguish two types of vertical interpolation, according to the type of the isodamage data curve immediately above the pair (*DCIA*) or immediately below the pair (*DCIB*). We shall call n_{DCIA} and n_{DCIB} the characteristic exponents of *DCIA* and *DCIB*, respectively, where n is the exponent of the equation of ten Berge.

- If both the *DCIA* and the *DCIB* are exposure time dependent, then the damage level is interpolated from the toxic load (L) value,

$$D(t, C) = D(t, C_{DCIB}) + \frac{(C^{n}.t - L_{DCIB})}{(L_{DCIA} - L_{DCIB})}\,,$$

  where C_{DCIB} is the concentration that causes a damage equivalent to that of the *DCIB* in a time t, L_{DCIB} is the toxic load for the isodamage *DCIB* the pair (t, C), L_{DCIA} is the toxic load for the isodamage *DCIA* the pair (t, C).
- If either or both of the *DCIA* or the *DCIB* are exposure time independent, then the damage level is interpolated from the concentration (C) value,

$$D(t, C) = D(t, C_{DCIB}) + \frac{(C - C_{DCIB})}{(C_{DCIA} - C_{DCIB})}, \tag{1}$$

  where C_{DCIA} is the concentration that causes a damage level equivalent to that of the *DCIA* in a time t.

Furthermore:

- If the pair (t, C) is above the isodamage data curve level 3, then $D(t, C) = 3$.
- If C is less than $C_{\text{minimum threshold}}$, $D(t, C) = 0$.
- If the pair (t, C) is below the isodamage data curve level 1, but above the minimum threshold curve, Equation (1) is used with $D(t, C_{DCIB}) = D\left(t, C_{\text{mimimum threshold}}\right) = 0$.

  Particularly, in those cases when the substance causes some damage with concentrations lower than this established threshold, the lowest threshold concentration and isodamage data curve level 1 will coincide.

Fig. 3 shows the AEGL reference values for chlorine, the isodamage data curves that connect them, and the continuous field of indices, in 0.1 damage intervals arbitrarily selected.

2.4. Noncommutativity

The coupling of the partial effects due to the exposure to different concentrations as time passes (different pairs $(t, C)_i$ where $i = 1, \ldots, n$, that are the

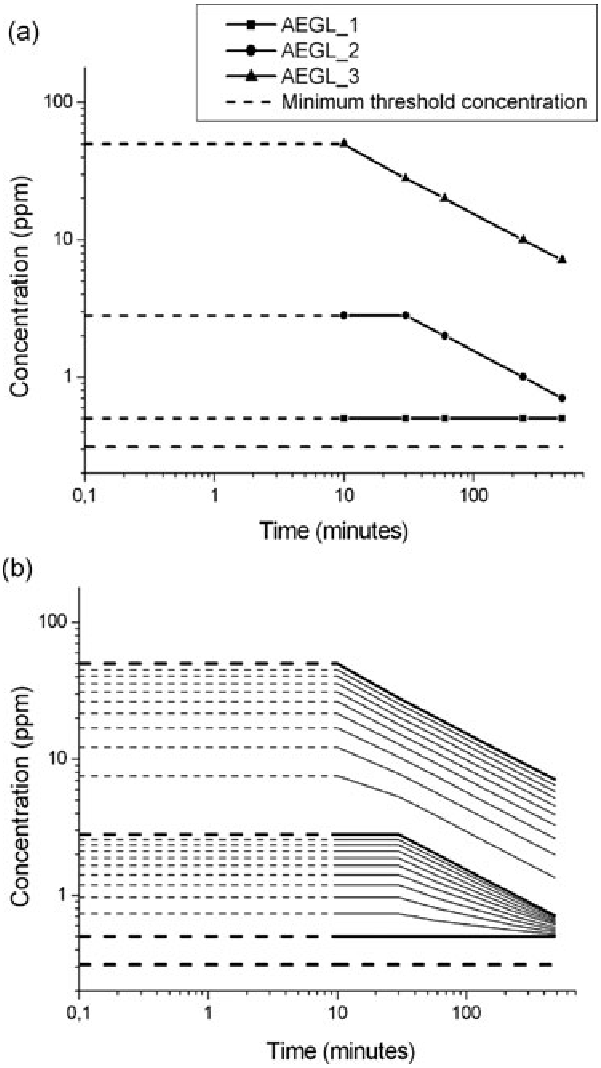

Fig. 3. (a) Graphic representation of the isodamage data curves for chlorine. (b) The continuous field of the isodamage data curves for chlorine, with a ΔAEGL of 0.1.

consecutive events or profile partitions) depends on the temporal order of pairs and therefore is *not commutative*. The damage level caused by an exposure characterized by a pair $A = (t, C)_1 = (t_1, C_1)$ after an exposure characterized by a pair $B = (t, C)_2 = (t_2, C_2)$ may be different from the damage level caused by an exposure characterized by a pair B after an exposure characterized by a pair A, that is to say:

$$D(A \oplus B) \neq D(B \oplus A) \ ,$$

where $\oplus$ is the symbol chosen to express the damage level coupling operation.

In Section 2.5.2 we shall present a concrete example in which the commutativity fails.

2.5. Estimation of the Maximum and Minimum Damage Level

Through the DDC, a maximal and a minimal approximation to the damage level during the toxic cloud passage can be obtained. This progressive estimate bases its methodology on a recursive algorithm: coupling of the successive partitions of the concentration-time profile, which will name A the first pair to couple and B the second pair to couple.

The DDC's users can run any profile of concentration, limited only by the memory available on their computer. This limitation is closely related to the time step, when $\Delta t \rightarrow 0$ implies a better fit to the profile. Therefore, the concentration fluctuations shall be better provided with Δt tending to zero.

The shape of the isodamage curves within the continuous field forces us to select different coupling operations to obtain the maximum and the minimum damage level as well as to guarantee their minimal and maximal status. For that purpose, two types of coupling are defined: direct coupling (*DC*) and reverse coupling (*RC*). *DC* is a process physiologically preferable to *RC* because the former respects the temporal order of pairs for the coupling of the partial effects, which is closely related to concept of tolerance.

2.5.1. Direct Coupling

This kind of coupling is applied to estimate both the maximum and the minimum damage level, which will coincide.

DC can be applied provided the concentration in pair B is less than or equal to the maximum concentration of the damage curve that contains the pair A.

To add exposures with different times, it is necessary to express the first pair A as a function of the concentration of the second pair B keeping the identity of each event (damage level).

As shown in Fig. 4, the pair A is transformed into $A' = (t'_1, C_2)$ through a translation along the isodamage curve, where $D(A) = D(A')$. Then, t'_1 and t_2 are added. The damage due to the consecutive exposures represented by A and B, $D(A \oplus B)$, is equivalent to that represented by $D(t'_1 + t_2, C_2)$. Then $DC = D(t_1, C_1) \oplus D(t_2, C_2) = D\left(t'_1 + t_2, C_2\right)$.

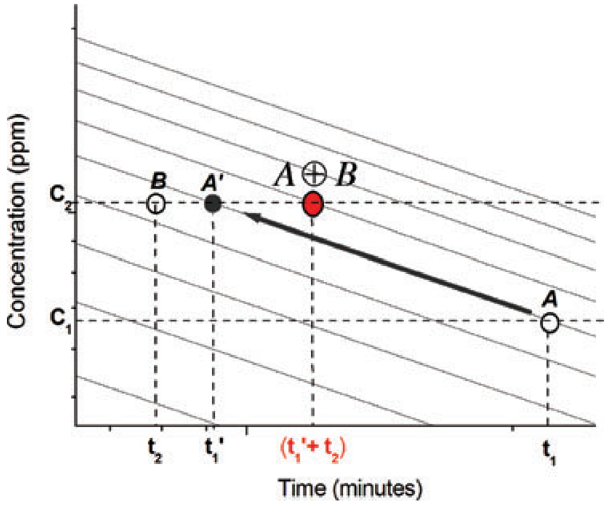

Fig. 4. DC of $A \oplus B$, according to the AEGL indices for chlorine. The damage due to the consecutive exposures represented by A and B, $D(A \oplus B)$, is equivalent to that represented by $D(t_1' + t_2, C_2)$. Then $DC = D(t_1, C_1) \oplus D(t_2, C_2) = D(t_1' + t_2, C_2)$.

For reasons inherent in the shape of the isodamage data curves, if the coupling operation falls between a time-dependent $DCIA$ and a time-independent $DCIB$, or between two time-dependent data curves with $n_{DCIA} > n_{DCIB}$, DC may need to be corrected accordingly to minimize the approximation error.

a) If $C_2 > C_1$, DC returns a underestimated value but it may be optimized. Fig. 5(a) shows that $D(\alpha) = D(t_1 + t_2, C_1)$ exists, and it can safely be considered as minimal because it represents the damage level caused by the exposure to the least concentration of those two during the total time $t_1 + t_2$. Let $D(\beta) = D\left(t_1' + t_2, C_2\right)$. If $D(\beta) < D(\alpha)$, then $DC = D(\alpha)$.

b) If $C_2 < C_1$, DC returns an overestimated value. Fig. 5(b) shows that $D(\alpha) = D(t_1 + t_2, C_1)$ exists, and it can safely be considered as maximal because it represents the damage level caused by the exposure to the greater concentration of those two during the total time $t_1 + t_2$. Let $D(\beta) = D\left(t_1' + t_2, C_2\right)$. If $D(\beta) > D(\alpha)$, then $DC = D(\alpha)$.

2.5.2. *Reverse Coupling*

When the concentration in pair B is greater than the maximum concentration of the damage curve that contains the pair A, DC operation cannot be applied and RC is an alternative to estimate the damage level. RC operation produces a divergence between the maximal and minimal values, which represents upper and lower bounds for the expected damage level.

(1) Maximal reverse coupling (MRC).

MRC used two overestimation methods ($Alt1$ and $Alt2$) to obtain the resulting damage, and the overestimation with a lesser damage level is selected. In this way, maximality is guaranteed and overestimation is minimized.

To apply $Alt1$, it is necessary to invert the order in which the exposure is experienced. $B \oplus A$ is obtained instead of $A \oplus B$. Under these conditions, the second pair B is expressed as a function of the concentration of the first pair A. As shown in Fig. 6(a), the pair B is transformed into $B' = (t_2', C_1)$ through a translation along the isodamage curve that contains the pair B, where $D(B) = D(B')$. Then t_1 and t_2' are added. Through this procedure, a pair $(t_2' + t_1, C_1)$ is determined, the damage level of which is $D(t_2' + t_1, C_1)$.

The damage due to the consecutive exposures represented by B and A, $D(B \oplus A)$, is equivalent to that represented by $D(t_2' + t_1, C_1)$. Then $MRC_{Alt1} = D(t_2' + t_1, C_1)$.

As shown in Fig. 6(b), $Alt2$ compares the damage levels associated with pairs A and B and chooses the greatest. This overestimation method represents the damage level caused by the exposure to the greater concentration (C_g) during the total time $t_1 + t_2$; therefore, it can safely be considered an overestimation. The damage is equivalent to that represented by $D(t_1 + t_2, C_g)$. Then $MRC_{Alt2} = D(t_1 + t_2, C_g)$.

From the case where both the DC as well as the MRC can be applied, it can be proved that $DC \leq MRC$, so the result from the MRC is always greater than or equal to that from the DC. Effectively, by the aforementioned, Fig. 7 shows an example in which $D(A \oplus B) < D(B \oplus A)$ and therefore the commutativity fails. From the toxicological perspective, this case illustrates the concept of tolerance. This concept of decreased responsiveness to a toxic effect establishes that the exposure before a toxic substance (always to sublethal levels) gives place to a protective effect to the

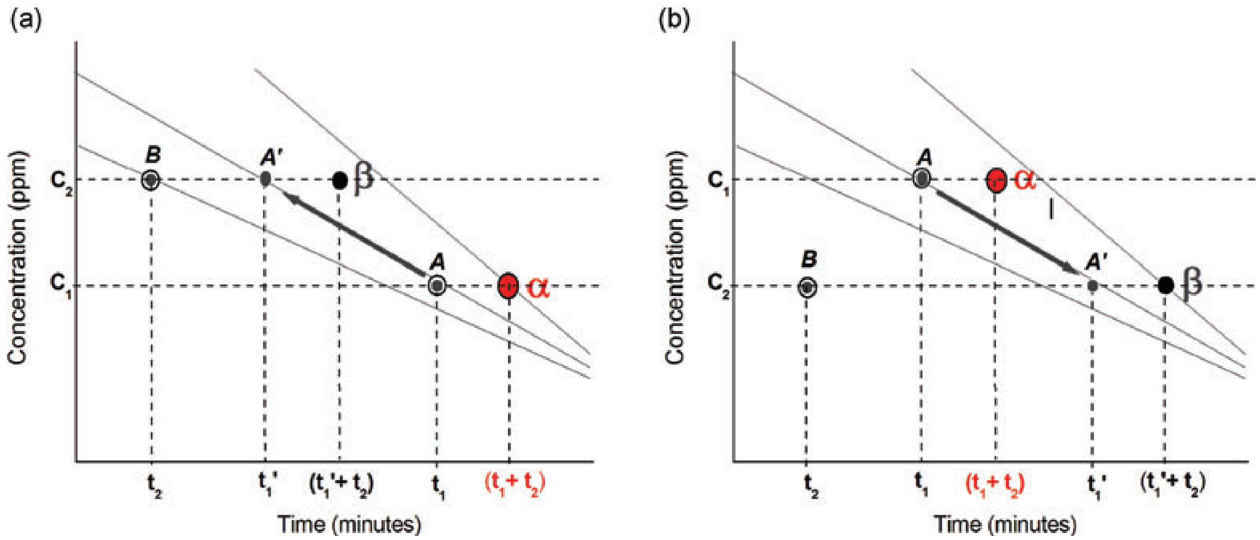

Fig. 5. Optimization for *DC*, when the coupling operation falls between a time-dependent *DCIA* and a time-independent *DCIB*, or between two time-dependent data curves with $n_{DCIA} > n_{DCIB}$. (a) Special case for $C_2 > C_1$ and (b) special case for $C_2 < C_1$.

second exposure to major concentration, with a minor level of associate damage.(39)

(2) Minimal reverse coupling (mRC).
mRC used two subestimation methods (*Alt*1 and *Alt*2) to obtain the resulting damage, and the subestimation with a greater damage level is selected. In this way, minimality is guaranteed and subestimation is minimized.
As shown in Fig. 8(a), *Alt*1 compares the damage levels associated with pairs *A* and *B* and chooses the least. This subestimation method represents the damage level caused

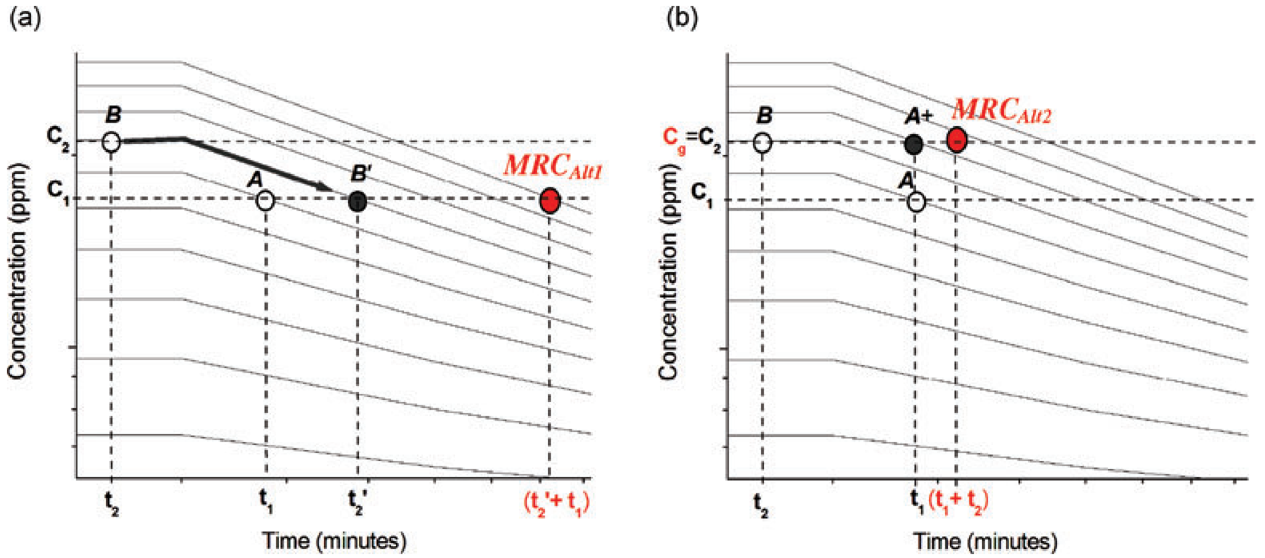

Fig. 6. *MRC* compared *Alt*1 (a) and *Alt*2 (b), and the overestimation when a lesser damage level is selected. (a) The pair *B* is expressed as a function of the concentration of the pair *A*. The damage due to the consecutive exposures represented by *B* and *A*, $D(B \oplus A)$, is equivalent to that represented by $D(t_2' + t_1, C_1)$. Then $MRC_{Alt1} = D(t_2' + t_1, C_1)$. (b) The *Alt*2 compares the damage levels associated with pairs A and B and chooses the greatest value. The damage is equivalent to that represented by $D(t_1 + t_2, C_g)$. Then $MRC_{Alt2} = D(t_1 + t_2, C_g)$.

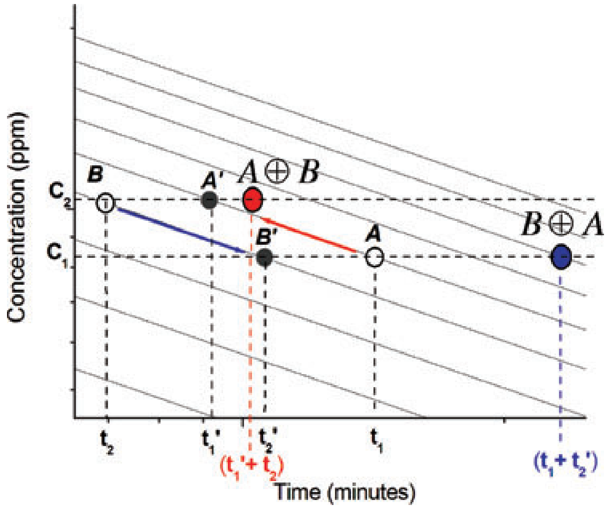

Fig. 7. This example shows that the coupling of the partial effects cannot be commutative and *MRC* is greater than that from *DC*: $D(A \oplus B)\ <\ D(B \oplus A)$.

by the exposure to the least concentration (C_l) during the total time $t_1 + t_2$; therefore, it can safely be considered a subestimation. The damage is equivalent to that represented by $D(t_1 + t_2, C_l)$. Then $mRC_{Alt1} = D(t_1 + t_2, C_l)$. On the other hand, as shown in Fig. 8(b), *Alt*2 compares the damage levels associated with pairs *A* and *B* and chooses the greatest. Then, t_1 and t_2 are added. Finally, an equivalent concentration (C_{eq}) exists that describes the greater damage level resulting from $t_1 + t_2$. The damage is equivalent to that represented by $D(t_1 + t_2, C_{eq})$. Then $mRC_{Alt2} = D(t_1 + t_2, C_{eq})$.

3. RESULTS AND DISCUSION

Below, the creativity, advantages, and applications of DDC are shown through examples and an application to a hypothetical chemical release in comparison to the most frequently used methodologies.

3.1. Quantitative Comparison of the Methods

The damage level caused by the exposure to a constant concentration during a time interval T is equal to the damage level resulting from the exposure to the same concentration during n consecutive time intervals t_i such that $T = \sum_{i=1}^{n} t_i$. This statement gives the possibility to monitor the damage level caused at different exposure periods and to correlate the results of DDC and those of the currently used methods.

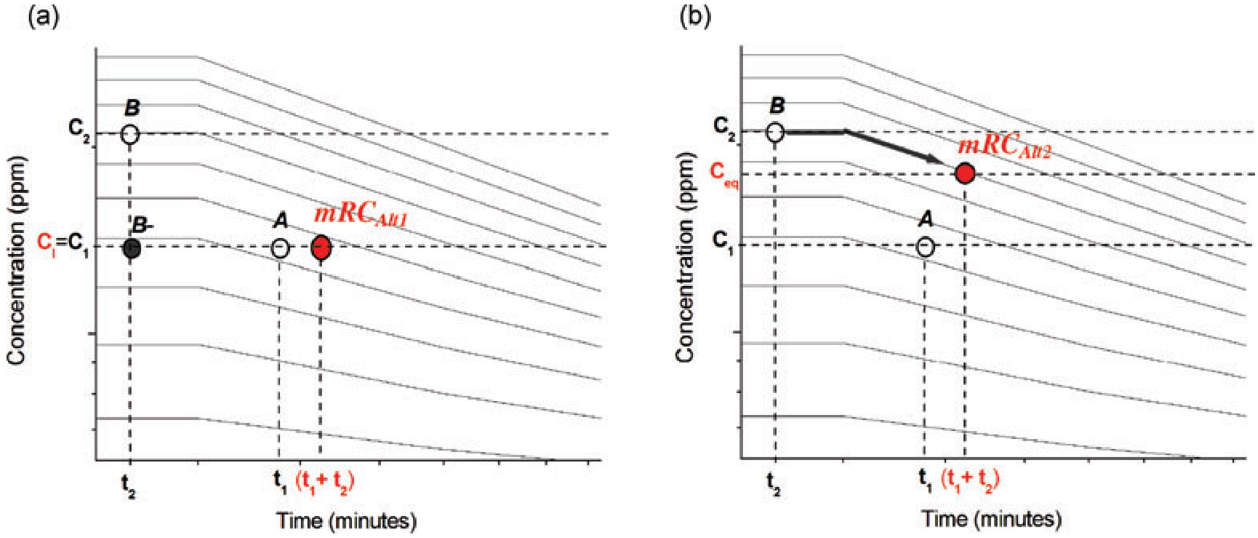

Fig. 8. *mRC* compared *Alt*1 (a) and *Alt*2 (b), and the subestimation with a greatest damage level is selected. (a) *Alt*1 compares the damage levels associated with pairs A and B and chooses the least value. The damage is equivalent to that represented by $D(t_1 + t_2,\ C_l)$. Then $mRC_{Alt1} = D(t_1 + t_2, C_l)$. (b) *Alt*2 compares the damage levels associated with pairs A and B and chooses the greatest value. The damage is equivalent to that represented by $D(t_1 + t_2, C_{eq})$. Then $mRC_{Alt2} = D(t_1 + t_2, C_{eq})$.

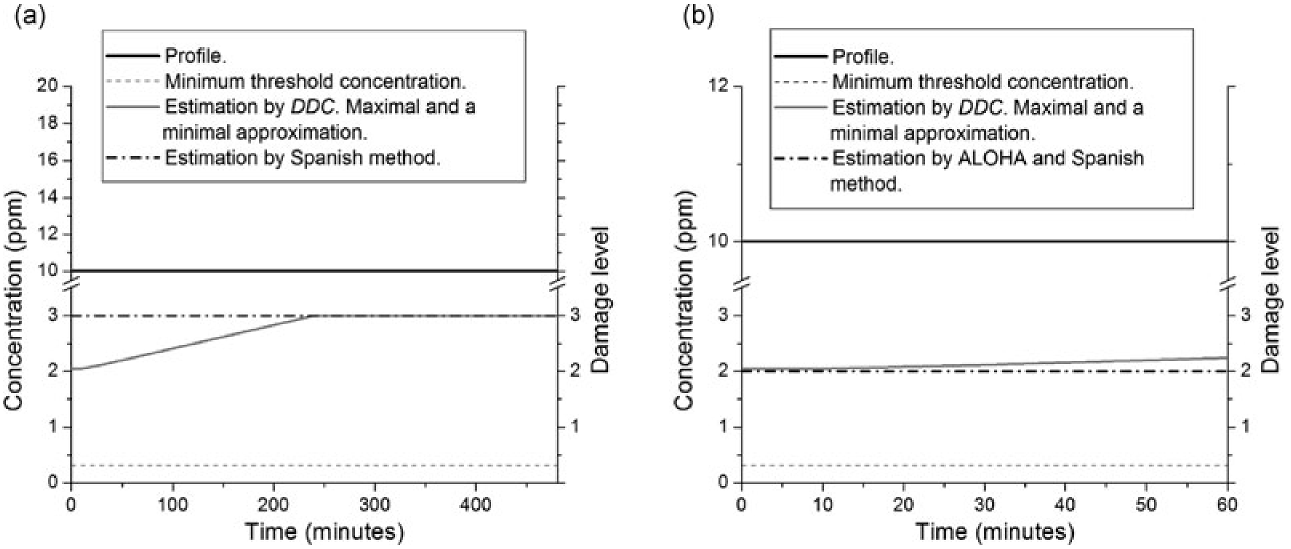

Fig. 9. (a) Representation of the profile for a constant airborne concentration of 10 ppm of chlorine during 480 minutes. The damage estimation through the Spanish method and DDC have the same final result and also the maximal and minimal approximation coincide, but only DDC can estimate both the damage level progressively and the severity between two isodamage data curves. DDC shows damage level 3 will be reached after 240 minutes of exposure. (b) Representation of the profile for a constant airborne concentration of 10 ppm of chlorine during 60 minutes. Both the Spanish method and ALOHA provide an integer value of damage level equal to 2 and DDC gives a value of 2.24; thus DDC provides information about the proximity to the isodamage data curves and therefore it provides a measure of severity within the damage level. The time step (Δt: 0.1 minute) was selected arbitrarily; we only took into account that $\Delta \rightarrow 0$ implies a better fit to the profile.

The first example is intended to represent the significant contribution of both the progressive estimation and the degree of approximation to the isodamage data curves, while in the second example from discrete appreciation an overestimation of the damage level using current methods is shown.

As a first example, Fig. 9(a) shows an exposure to 10 ppm of chlorine gas for 480 minutes. We used a time step $\Delta t = 0.1$ minutes. Due to the operating way of the Spanish method, when the real profile is a constant it is to be expected that the damage estimation through the Spanish method and DDC have the same final result and also the maximal and minimal approximation coincide. However, only DDC can estimate both the damage level progressively and the severity between two isodamage data curves.

In this example, the Spanish method predicts that the population could experience life-threatening adverse health effects or death, which is equivalent to damage level 3, if it is exposed to a toxic cloud with the characteristics of the concentration-time profile shown in Fig. 9(a). However, the estimation through DDC shows that this damage level will be reached after 240 minutes of exposure. Although the final result of the two methods seems to be consistent and the same damage level is observed after the cloud passage, the detailed information provided by DDC can help the persons responsible for emergency management make the right decisions, taking into account the time they have to take action before damage level 3 is actually reached.

As mentioned in Section 1, ALOHA is limited to 60 minutes and 10 km from the emission origin. This limitation does not allow us to apply ALOHA to the given example. However, if the exposure had been for only 60 minutes, as it is shown in Fig. 9(b), both the Spanish method and ALOHA would provide an integer value of damage level equal to 2 and DDC would give a value of 2.24; thus DDC would provide information about the proximity to the isodamage data curves and thus it would provide a measure of severity within the damage level.

On the other hand, as a second example, Fig. 10(a) shows a profile similar to that in Fig. 9(a), with the occurrence of a concentration peak of 20 ppm after 20 minutes of exposure, during 4 minutes. It is to be expected that this much higher concentration, added to the base constant concentration, will increase the damage level from the same instant when the concentration soared. Also, it is reasonable

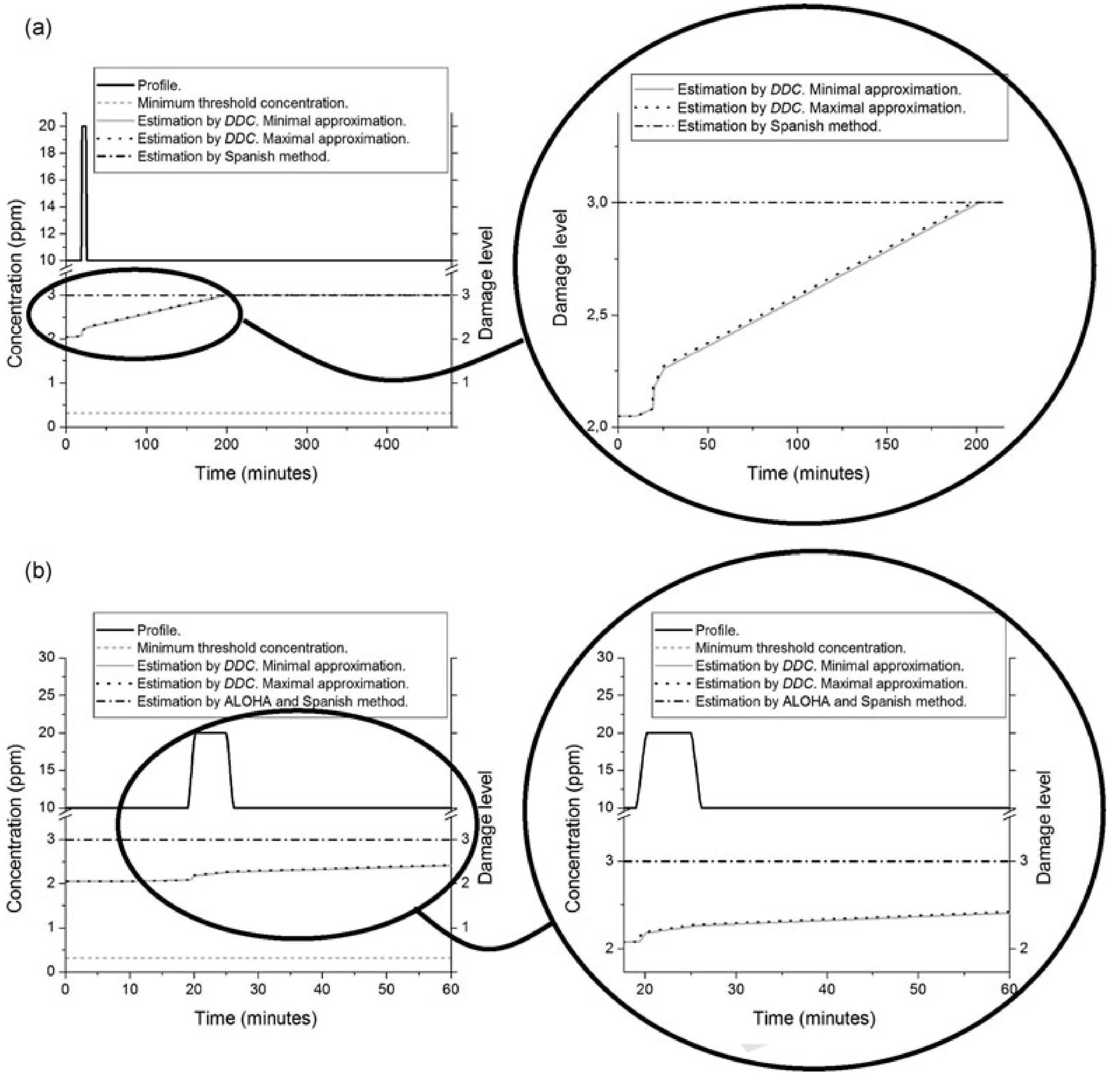

Fig. 10. (a) Representation of the profile for a constant airborne concentration of 10 ppm of chlorine during 480 minutes with the occurrence of a concentration peak of 20 ppm after 20 minutes of exposure, during 4 minutes. It is reasonable to consider that the increase rate will be higher during the peak period, but this rate will not keep rising when the concentration has returned to its base value. While the Spanish method predicts a damage level 3 without taking into account the profile characteristics, the maximum estimation of DDC predicts that this damage level will be reached after 198.2 minutes, or after 201.6 minutes, according to the maximal or minimal estimation, respectively. (b) Representation of the profile for a constant airborne concentration of 10 ppm of chlorine during 60 minutes with the occurrence of a concentration peak of 20 ppm after 20 minutes of exposure. Both the Spanish method and ALOHA provide a damage level 3, while DDC gives a final damage value of 2.40 and 2.42 for the minimal and maximal approximation, respectively.

to consider that the increase rate will be higher during the peak period, but this rate will not keep rising when the concentration has returned to its base value. In Fig. 10(a), the difference between the curve obtained through the Spanish method and that obtained through the DDC method can be clearly noticed. While the Spanish method predicts a damage level 3 without taking into account the profile characteristics, the maximum estimation of DDC predicts that this damage level will be reached after 198.2 minutes, or after 201.6 minutes, according to the maximal or minimal estimation, respectively. According to these numbers, the exposed population could experience life-threatening adverse health effects or death after 201.6 minutes at the latest, and after 198.2 minutes at the soonest.

If the exposure had been for only 60 minutes both the Spanish method and ALOHA would provide a damage level 3, as is shown in Fig. 10(b), while DDC would give a final damage value of 2.40 and 2.42 for the minimal and maximal approximation, respectively. Taking into account that the Spanish method and ALOHA calculate the damage level according to the maximum concentration experienced during the complete exposure period, as seen in this example, these methodologies will overestimate the damage level, since they do not take into account the peak length, which could lead those responsible for emergency management to make wrong decisions.

3.2. Application to Hypothetical Chemical Release Scenario

The proposed emergency scene is the Parque Industrial Pilar (PIP, Pilar Industrial Park), in the province of Buenos Aires, Argentina, where in March 1992, in a chemical plant producing chlorine, sodium hydroxide, and sodium hypochlorite, an accident that involved the release of 5,000 kg of chlorine occurred. A series of malfunctions at the brine entrance cell of the electrolysis plant caused an elevated level of chlorine in the tanks. Since the workers at the plant could not control the raise in pressure inside the tanks, they shut down the system, but they could not stop the chemical reaction, which kept elevating the pressure continually, and consequently an explosion and a chlorine leak occurred.(40)

The PIP is one of the most important industrial parks in South America, in terms of the amount of factories located in it, and it is located 5 km away from the nearest urban center, Pilar (see Fig. 11). Fortunately, on this occasion, the cloud was directed by the wind to an open area away from Pilar.(41,42) In order to compare the three methods, we assume the same scene but with a predominant wind blowing in a southeast direction and one release of 3,300 kg/min of chlorine during 8 minutes.

As a significant characteristic of this simulated emission, it is important to mention that chlorine vapor is denser than air and, therefore, it is very likely that a dense toxic cloud is formed, unless due to the atmospheric conditions or to the characteristics of the emission function a neutral cloud is formed. Dense clouds are more dangerous than neutral ones since they generally remain at low heights, affecting what is most vulnerable: living beings. On the other hand, the dilution of dense clouds is slower than that of neutral gases, and the former is capable of traveling longer distances and staying a longer time at higher concentrations. Moreover, the substance involved in this scene is highly irritant and corrosive. The response to its inhalation, depending on the concentration and the total time of exposure, can vary from sensory irritation and bronchoconstriction reflex to death by pulmonary edema or lack of oxygen during an asthma attack. According to Amoore and Hautala, the odor threshold is 0.31 ppm, and a range of 0.2–0.4 ppm was reported in other studies.(2,14,43,44)

Fig. 12 shows a diagram representing the risk areas as traced by ALOHA for this accident scene, whose characteristics are detailed in Table I. The red (colors visible in online version) AEGL_3 damage area, with the greatest exposure level, is predicted to extend 5.9 km downwind of the release. The orange AEGL_2 and the yellow AEGL_1 threat zone are predicted to extend for more than 10 km.

Fig. 13 shows the concentration profile observed in the City of Pilar. ALOHA predicts that, under the conditions of this scenario, the chlorine cloud would arrive at the City of Pilar in about 28 minutes. According to the maximum concentration observed (27.1 ppm), ALOHA locates the city within the area with the greatest exposure level (greater than 20 ppm, which is the AEGL_3 for 60 minutes). Also, through the observation of the diagram, it is clear that the total time of exposure in that location is about 32 minutes. With that information, those responsible for emergency management should be capable of taking the right decisions. But, due to either the lack of a time-related analysis or the discrete appreciation of the damage level, the information turns out to be impaired. Nevertheless, it is possible to get more complete and sensitive information through the DDC method.

Estimating the damage level through the three methods discussed in certain locations through which the cloud passes leads to an interesting contrast. For this purpose, the three methods are applied for locations at 4, 4.5, 5, and 5.5 km ($X = 4$, 4, 4.5, 5, and 5.5 km) downwind distance from the emission origin (following the emission axis $Y = 0$). Fig. 14

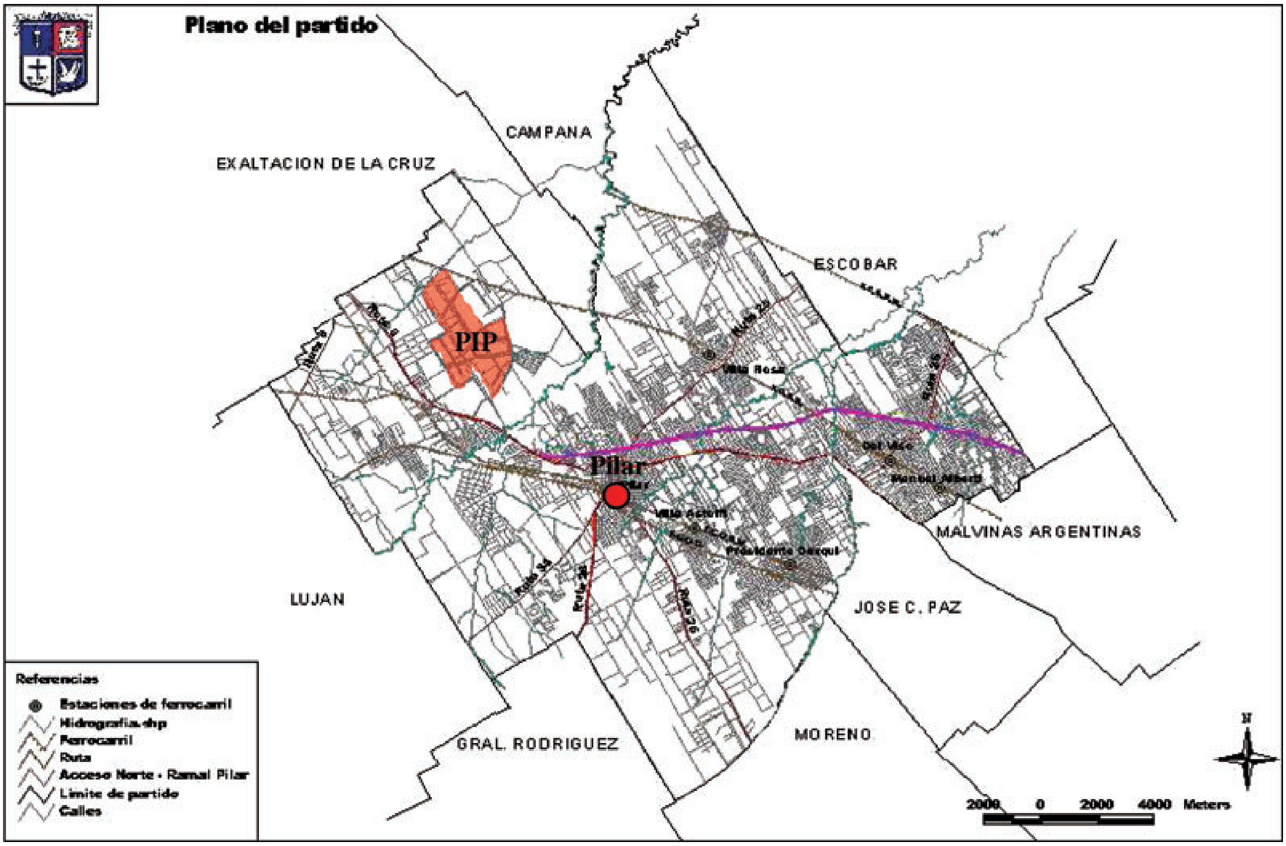

Fig. 11. Map of the administrative area of Pilar (source: Municipalidad de Pilar(42)), with the City of Pilar and the PIP located.

shows the profiles observed in the aforementioned locations, and Table II details their main characteristics. To have access to the concentration values instant by instant of these profiles, necessary to run DDC, an adjustment according to a log-normal distribution based on the information in Table II has to be made.

To show the assessment made using each of the profiles, in Fig. 15 the profile observed at a 5.5 km downwind distance and the estimation of the damage level through each one of the methods are represented.

During the first 10 minutes of exposure (between 29 and 39 minutes), the maximal and minimal estimations of DDC are markedly different and this is due both to the independence over time of the AEGLs in this period, and to the maximal and minimal guarantee offered by the approximations. After this period, they tend to be very similar, marking a narrow range that contains the "true" damage level. Due to that DDC relates the shape of the profile to the damage level growth rate; therefore, after reaching the maximum concentration in the profile, the growth rate decreases but the damage level never does.

Finally, after assessing the damage level and observing evolution in the different proposed locations, it is clear that the damage levels estimated by the three methods differ. This example shows features that have or may have marred the current methods: *overestimation*, *discrete appreciation by a lack of sensitivity,* and *no detail on the evolution of the damage level.* On the one hand, ALOHA gives an overestimated damage level to the given profile, while the Spanish method provides a damage level that, although the expected result after the passage of the cloud coincides with the value of damage given by the DDC, does not provide details of the proximity to the isodamage data curves, and none of the methods calculates the temporal evolution of the damage level.

The damage levels assessed after the passage of the toxic cloud are shown in Table III. Due to the aforementioned attributes of DDC, it does give a more accurate estimation and a more descriptive

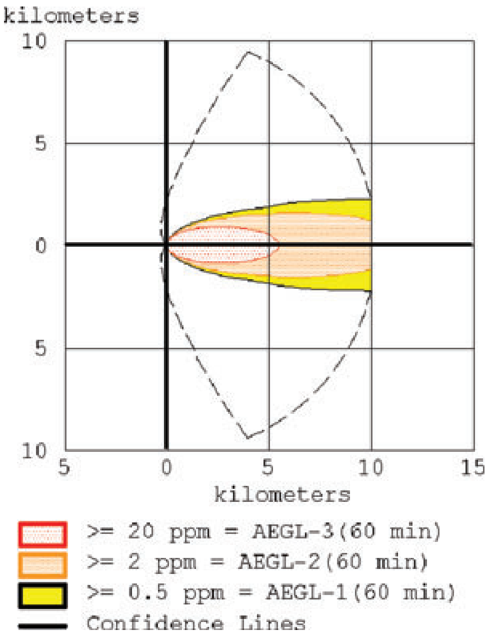

Fig. 12. Simulation of a chemical discharge in Pilar made with ALOHA. On the plot, the red, orange, and yellow (colors visible in online version) regions represent the areas where chlorine concentrations are predicted to exceed the corresponding AEGL values at some time after the release begins.

approach of the potential damage level, offering those responsible for emergency management an interval between the maximal and the minimal approximations.

A future software development of the División Modelado y Manejo de Crisis (Modeling and Crisis Management Division) of CITEDEF will allow us to trace risk areas corresponding to damage levels and time-varying concentration assessment, offering those responsible for emergency management a tool that provides more precise results, instant by instant, than those used currently.

3.3. DDC: Advantages and Limitations

Below is a detailed list of advantages of the method:

- *DDC provides a progressive estimate of the experienced damage.* Hence, chronological data of the potential effects experienced by the population exposed are available and in turn a log can be kept to register the most likely consequences for the population's health. What is interesting about the DDC is that the resulting pair in each coupling transforms into another pair with same damage level but expressed in actual time from exposure to the toxic cloud and an equivalent concentration. Hence, by using the continuous field of toxicological indices, it is always possible to find a pair $(t_{\text{current}}, C_{\text{equivalent}})$ with the same damage level that the pair $(t, C)_i$ resulting from the coupling i.
- *The strength of DDC lies in the coupling operations,* which require the existence of a continuous field of toxicological indices to carry out. Therefore, DDC can use whenever possible the implementation of an interpolation and extrapolation method in time for the indices. Finally, the improvement of the toxicological indices contributes to the improvement of DDC as it is feasible to have extrapolation and interpolation methods to implement.
- *DDC always takes into consideration the degree of proximity to the isodamage data curves*, so that, considering that it is based on the notion of a continuous field of curves, it results in a more descriptive approach. The current methods do not quantify the severity between two isodamage data curves; only an integer value of damage is provided.
- *DDC provides information about the minimum and maximal damage level expected*; it would be useful to provide those responsible for emergency management with an estimation interval that assures as well the minimum damage or response level the population will experience as the mildest consequence.
- *It is possible to enter results from experimental studies associating time-concentration pairs with damage* or response levels for diverse chemical substances into the algorithm, so that it can provide more detailed information.

The limitations of DDC, which are possible lines of research for the future, are the following:

- The method couples the damage increasingly whenever the exposure concentration is greater than or equal to the minimum threshold concentration. When the concentration is less than the minimum threshold concentration, it is assumed that the exposure to the toxic cloud has ended and any effect related to a previous cloud passage does not interfere in the damage caused by the future exposures. This boundary condition is stated since, on one hand, it is necessary to establish a

Table I. Input Information for ALOHA Run

SITE DATA	*Location*	Pilar, Argentina.
	Chemical Name	Chlorine
	Ambient Boiling Point	−34.2° C
	Vapor Pressure at Ambient Temperature	greater than 1 atm
CHEMICAL DATA	*Ambient Saturation Concentration*	1,000,000 ppm or 100.0%
	Molecular Weight	70.91 g/mol
	AEGL_1(60 min)	0.5 ppm
	AEGL_2(60 min)	2 ppm
	AEGL_3(60 min)	20 ppm
	Wind	2.3 meters/second from NW at 10 meters
	Cloud Cover	5 tenths
ATMOSPHERIC DATA	*Air Temperature*	20° C
	Stability Class	B
		No Inversion Height
	Relative Humidity	50%
	Source Height	0
SOURCE STRENGTH	*Release Duration*	8 minutes
Direct Source	*Release Rate*	3,300 kilograms/min
	Total Amount Released	26,400 kilograms
THREAT ZONE	*Model Run*	Heavy Gas

minimum threshold concentration to set the limits of the toxic cloud and, on the other hand, the contributions of low concentrations to general toxicity are unknown.

- If both the DCIA and the DCIB are exposure time independent, a different coupling operation should be carried out. Therefore, it compares the damage levels associated with pairs A and B and chooses the greatest value for the maximal estimation (which coincides with the maximum concentration), and the least one for the minimal estimation (which coincides with the minimum concentration). Then, t_1 and t_2 are added. While operating among this type of curves, the minimal estimation may decrease, which is a valid situation in order to guarantee its minimal status. Finally, the damage is equivalent to $D(t_1 + t_2, C_l)$ for the minimal estimation and $D(t_1 + t_2, C_g)$ for the maximal estimation.

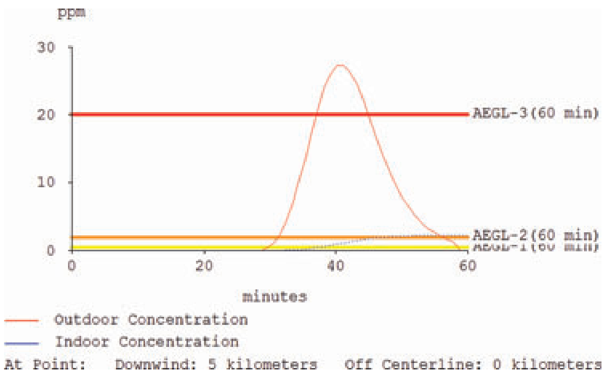

Fig. 13. Representation of the concentration profile observed in the City of Pilar. The horizontal axis of this graph represents time (from 0 to 60 minutes after the release starts), and the vertical axis represents concentration at the location expressed in ppm. Made with ALOHA.

- The simulation time of DDC is limited to 8 hours because it applies the definition of acute exposure presented in Ref. 1. Nevertheless, it is possible to assume a behavior of the toxicological indices for longer times of exposure, as seen in the Spanish method, and therefore expand the range of DDC.

4. CONCLUSIONS

The method presented in this work adds important features for the estimation of the damage level and the consequent tracing of the risk areas. The DDC method (1) enables a continuous monitoring with the progressive estimate of the damage level caused by the exposure to a time-varying concentration, (2) provides information about the minimum and maximal damage level expected, (3) takes into consideration the degree of proximity to the isodamage data curves, so that, considering that it is

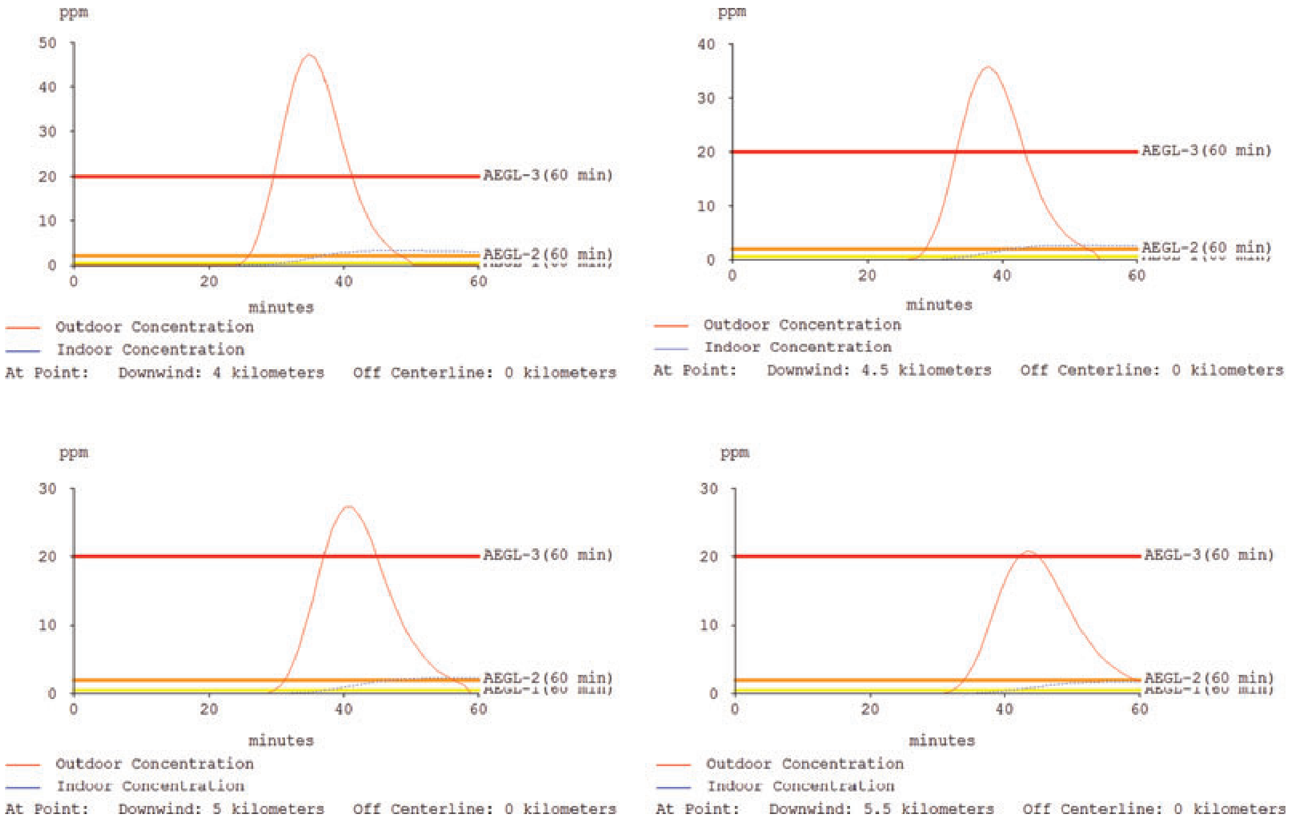

Fig. 14. Profiles observed 4, 4.5, 5, and 5.5 km away from the release ($Y = 0$). Made with ALOHA.

based on the notion of a continuous field of curves, it provides a more descriptive approach, (4) can use whenever possible the implementation of an interpolation and extrapolation method in time for the indices as the strength of DDC lies in the coupling operations, (5) can include results from experimental studies associating time-concentration pairs with damage into the algorithm, so that it can provide more detailed information, (6) facilitates environmental health protection decisions using criteria consistent with the application of toxicological indices to identify threat zones, and (7) a more precise and dynamic estimate of damage level allows a better understanding of the situation and the available time for timely intervention.

Table II. Main Characteristics of the Profiles Observed 4, 4.5, 5, and 5.5 km Away from the Emission

Location Relative to the Release Point (Kilometers). Y = 0	Maximum Concentration (ppm)	Duration of Exposure (Minutes)
4	47	29
4.5	35.3	29
5	28.3	33
5.5	20	34.5

The comparison between the DDC method and the current (Spanish and ALOHA) ones showed that the former can offer a more precise estimation and a more descriptive approach of the potential damage level, offering those responsible for emergency management an interval between the maximal and the minimal approximations. Due to the operating way of the current methods, these could overestimate the damage level, since they do not take into account the shape of the profile, which could lead those responsible for emergency management to make wrong decisions.

The relevant limitations of the DDC, which are common to all three methods, are given by (a) the lack of toxicological information for exposures less than 10 minutes and (b) the lack of knowledge about the response to very low concentrations. Future studies should be encouraged to address these limitations of this first effort to compute the evolution of the

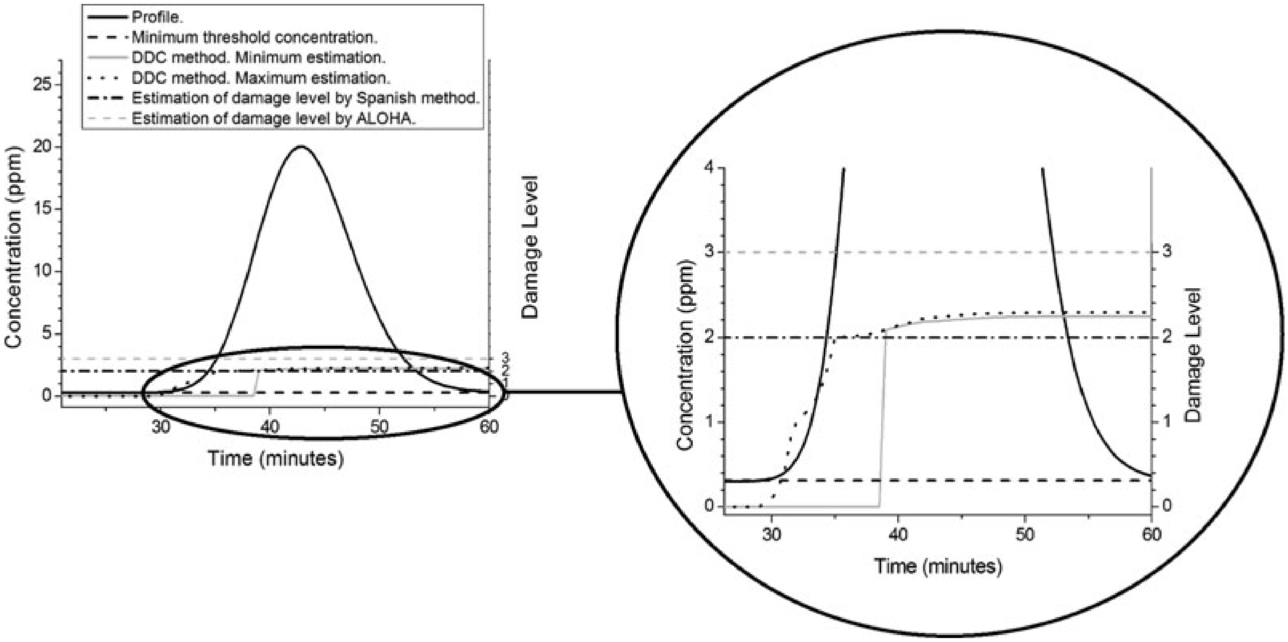

Fig. 15. Profile observed 5.5 km away from the discharge ($Y = 0$), together with the assessment of the damage level through the different methods. On the right, an enhanced detail of the evolution of the damage level is shown.

damage level and to quantify the severity between two isodamage data curves.

Finally, nowadays, it is implicitly assumed that the uptake of any exposure concentration is instantaneous, recovery does not occur so toxic load increases indefinitely with time and repeated exposures, and saturation of biological uptake pathways does not occur. Although none of these assumptions are justifiable for real exposures and responses, they were used for the development of the AEGLs. In this sense, the implementation of alternative methods to consider the aforementioned properties (i.e., that given by Hilderman *et al.*)(25) to extrapolate AEGL values from one period to another is one possible line of research for the future, but it is necessary that these improvements are implemented by the AEGL developers.

Table III. Damage Levels Estimated After the Passage of the Toxic Cloud

	Location Relative to the Release Point (Kilometers). $Y = 0$			
Estimation Method	5.5	5	4.5	4
ALOHA	3	3	3	3
Spanish	2	3	3	3
DDC	2.28	2.5	2.76	3

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