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Artigo

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## Limites de Exposição e suas Aplicações em Guerra Química

**Resumo**: A literatura técnica proporciona aos profissionais de saúde e de segurança vários limites de exposição a substâncias químicas, enquanto manuais mais específicos fornecem outro conjunto de limites de exposição de referência à agentes de guerra química. Além disso, manuais fornecem dados diferentes para doses seguras e doses letais. O pesquisador ou o profissional que atua em defesa química, precisa tratar com o devido cuidado estes dados, sabendo quais as limitações e significados dos valores em uma determinada tabela. Portanto, este artigo revisa os conceitos chave de limites de tolerância, discute a sua representação na legislação brasileira e sua importância nas atividades de defesa química.

***Palavras-chave:*** Limites de exposição; dose letal; guerra química.

## Abstract

The technical literature provides to health and safety personnel several exposure limits, while more specific handbooks provide another set of reference exposure limits for chemical warfare agents. Furthermore, biology handbooks provide different data for safe and lethal doses. A researcher or a chemical response team member, who deals with chemical defense, needs to face these data carefully and knows correctly which are the limitations and the proper meaning of the values in a given table. Therefore this paper review the threshold values available, discusses their representation in the Brazilian legislation and analyses how they can be of use in chemical defense.

***Keywords:*** Threshold exposure limits; lethal dose; chemical warfare.

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# Exposure Limits and its Applications in Chemical Warfare

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## 1. Introdution

Today, despite the fact that some countries still hold some storage of chemical agents, it has been prohibited by the Organization for the Prohibition of Chemical Weapons (OPCW)[1], an United Nations organism that works to develop means of response to any given chemical treat.

The response methods rely upon deployment of experts and military personnel to the target area. The target areas likely to be contaminated with a given chemical agent are classified as hot zones and any incursion demands all kinds of preparations, protection and detection means. Furthermore, detection is not enough; since some response team leader must take a decision whether or not quarantine the area, as well as an entire set of further actions. To allow this person to make accurate decisions, along with detections, the response team must determine which chemical agent was deployed in the area, as well as evaluate its concentration. Once determined the agent's concentration, this value must be compared with information available in handbooks and other documents. Hence, the information a team leader need to make accurate decision are limits towards which the exposure is deadly, hazardous or harmless. These limits are under study in this work.

## 2. Exposure Limits Overview

Exposure limits have different meaning, depending upon its purpose or context. To illustrate, the US Department of Labor, Occupational Safety and Health Administration[3] on occasion has proposed exposure limits based on their own research. Other groups such as the American Conference of Governmental Industrial Hygienists (ACGIH)[4] propose guidelines based on their research. Guidelines are not always legally enforceable unless adopted by a regulatory authority. WorkSafeBC[5], the regulatory agency in British Columbia, for example, adopted most but not all exposure limits proposed by ACGIH as regulatory limits.

Almost every health and safety manual and handbook define exposure limit as the concentration of a chemical agent or the intensity of a physical agent to which the majority of the population can be occupationally exposed and it is not expected to become ill from this very same exposure[6–8]. This definition implies that there is a certain amount of a given chemical agent that is safe to be exposed at, as long as it remains within "occupational conditions". Occupational conditions relates closely to exposure over time, in which a test subject is continuously exposed to a certain amount of a given compound. The time frame considered to evaluate occupational exposure is a working week (around 40 hours per week), and the concentration of a chemical agent or intensity of a physical agent are expressed in terms of average values.

However, the exposure times may not be constant during the week nor it is realistic to pretend that the levels of a given chemical agent in a workshop will be constant. From that, the threshold exposure limit is better represented as an integral. Figure 1 presents a plot representing a more realistic exposure and the standard threshold.

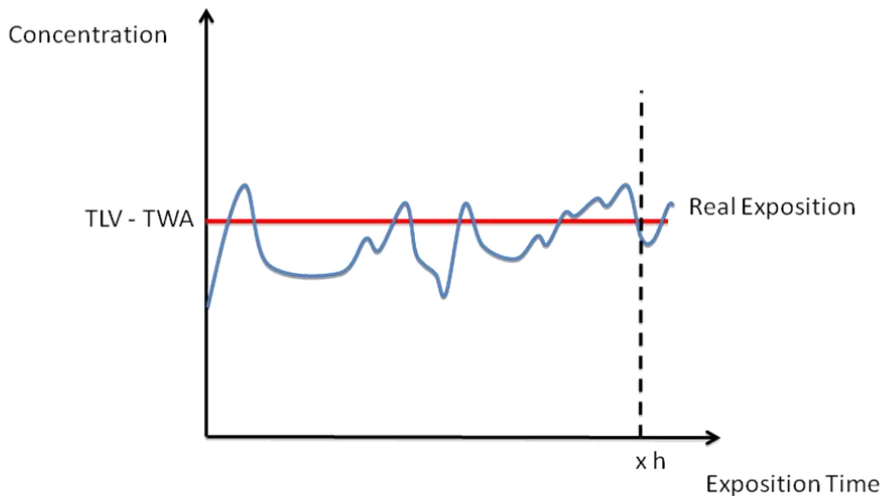



**Figure 1**. Real Exposure and the Standard Threshold

Hence, for determining if the exposition in a given workshop is above or below the threshold limits one should compare the areas under both curves. The standard area is a simple rectangle, while the real exposition may demand more robust mathematical calculations (integral). The plots presented in Figure 2 indicate the reference area and the area under the real exposure curve. If the real exposure area is bigger than the reference value, the straightforward conclusion is that working in that given environment represents a risk.

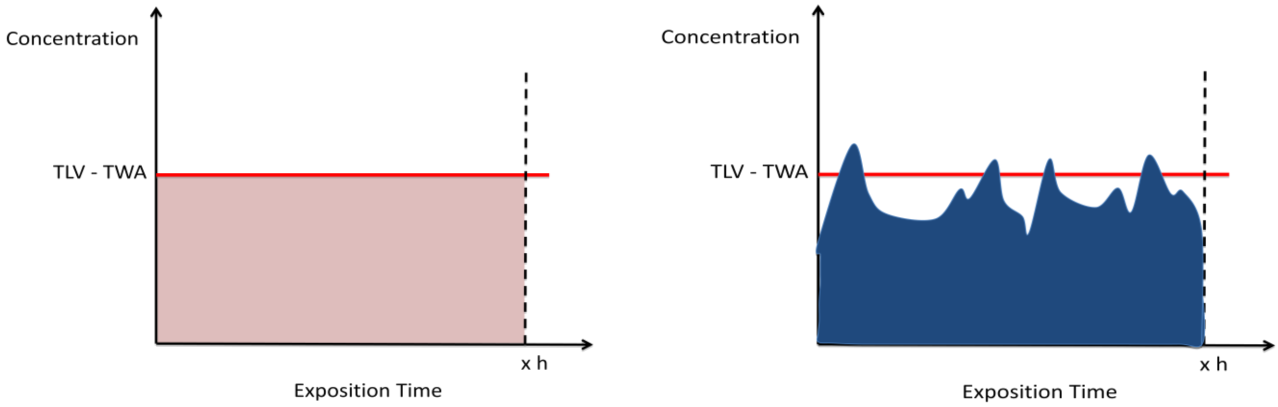



**Figure 2**. Exposure: Integral method of comparison

### 2.1. Threshold Limit Values

There are many exposure limits, defined and determined by several approaches. However, the threshold limit values mostly accepted for occupational hazard are those proposed by the ACGIH.[4] For the concentration in air exposure limits, ACGIH folds them into three separate groups. Each group presents a concentration higher than the previous one, since the exposure is more hazardous and the effects will be more severe. The definitions are as follows:

1. TLV-TWA - Threshold Limit Value - Time-Weighted Average

2. TLV-STEL - Threshold Limit Value - Short-Term Exposure Limit

3. TLV-C - Threshold Limit Value - Ceiling

The TLV-TWA stands for the average weight concentration of a given chemical agent through time. The time frame taken is a standard working day, which consists of 8 hours per day of exposure. The TLV-TWA is a reference number that represents the maximum concentration (or intensity) of a given agent towards which it is expected that a long term exposure will not cause any health issue to the majority of the exposed population. Its value is determined as a weighted average concentration (calculated for a standard workday of eight hours and/or 40-hour working week) to which it is believed that nearly all workers may be repeatedly exposed day after day without showing adverse effects. Therefore, TLV-TWA is a concentration limit for long term exposures.

For short term exposures, one should consider the use of TLV-STEL and TLV-C. The first (TLV-STEL) is the concentration believed to be safe for workers to be exposed continuously for a short period of time without arising irritations, chronic or irreversible damage to the tissues and reducing the state of attention; while the second (TLV-C) is the concentration that should be avoided at all costs, due to immediate risks to health, as well as possibility of death.

Since it is expected a variation in the concentrations of a chemical agent or intensity of a physical agent through time, the exposure limits should be determined taking this into account. The technique to do so is to consider the threshold of exposure limit as the average concentration in a given time frame. For occupational purposes, this time frame is a daily journey of 8 hours. Regarding chemical agents, it is necessary to determine which method fits better to calculate the average concentration. Since the biological effects are related to the quantity (mass) available in the environment of a given chemical agent, the average is calculated in weight.[6]

Hence, for chemical agents the exposure limits are calculated as a threshold weight average. The ACGIH calls these limits TLV-TWA, which stands for threshold value limits - threshold weight average. These should be used in the event of a long-term exposure, considering a continuously eight hour per day contact with the agent.

Furthermore, the nature of a TVL-TWA is that it is the limit considered safe for someone be exposed to during a working day. However, as discussed in section 2.1, the concentrations of a chemical agent vary through time, being below and above the TVL-TWA. Since the TVL-TWA is considered the safe limit for exposure over time, being below that amount is ideal. However, being above might be a problem to be addressed.

In terms of occupational exposure, it is considered safe to work in an environment in which the average concentration (in terms of integral over time) is kept below the TVL-TWA, as long as it is always below a maximum allowed concentration, called ceiling limit, or TVL-C. The TVL-C stands for the concentration considered immediate dangerous to life of those exposed.

The plots in Figure 3 represent a real exposure (in blue) that should be avoided if the measured concentration surpasses the TVL-C (on the left). Additionally, one can realize that, even before the exposures moves to values above TVL-C, it is already considered dangerous, since it has already moved to levels above the TLV-STEL and remained in that layer of exposure.[6]

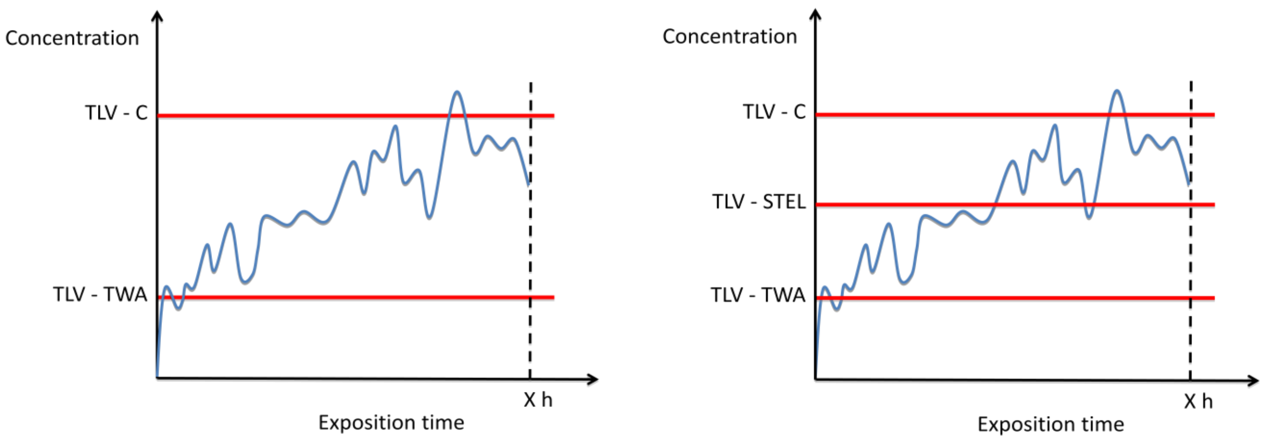



**Figure 3**. Representations of TLV-TWA, TLV-STEL and TLV-C

### 2.2. Lethal Dose and Lethal Concentration

The TLV-C, as defined by ACGIH[4] is closely related to the lethal dose of a substance. Both stand for amounts of chemical agents considered dangerous to life in a short time exposure. However, TVL-C is a value of the maximum allowed concentration of a chemical agent in air, while the lethal dose is the considered lethal amount of a chemical to a given individual per unit of body mass.

Adding to the TLV-C, the Immediate Dangerous to Life and Health (IDLH) (short term exposures) values published by the National Institute for Occupational Safety and Health (NIOSH)[9] should be considered. Complementary, in case of chemical emergency response, one can also rely upon the exposure limits published by the American Industrial Hygiene Association in the yearly reviewed "Emergency Response Planning Guidelines".[10] However, regardless the reference used, the actual values for the exposure is alike.

### 2.3. Exposure Limits in Brazil

The exposure limits in Brazil are

determined by the government, under the responsibility of the Minister of Working and Employment,[11] which is done using a three parts commission: Government representatives, Unions representatives and enterprises representatives. These commissions work in creating and developing many standards for several issues related to the working environment, such as occupational hazard and occupational hygiene.[11]

From the work of one of those commissions, there is in brazil the standard known as "NR 15".[12] This bill was originally issued in 1978, when it was presented a list of exposure limits for roughly 180 chemical agents. This list was developed after the list published by ACGIH in 1976. Since that time the list of agents covered by Brazilian legislation has remained unchanged. The most recent list is covered by NR 15[12] in its annex 11.[13]

Furthermore, the Brazilian exposure limits are concerned in addressing a working environment for long term exposure. Due to that, the limits in the bill[12,13] are for the average exposure, being related to the TLV-TWA in the ACGIH. There is no mention to a TLV-STEL equivalent as defined by ACGIH. As for the TLV-C, the Brazilian legislation informs that, for some agents, a "ceiling" exists, but marks its value as the same as the long-term exposure.

## 3. Health and safety

The main issue to be discussed in this article is when it is reliable to use health and safety reference values for a safety exposure in a chemical warfare environment. Health and safety environment are mainly concerned with long-term exposures, since the working personnel should be in a given environment for many years. Therefore, exposures in a working environment should be understood as chronic exposures in opposition to acute exposures.

A chronic exposure is when the concentrations are considered low, but the exposure times are long, in opposition to an acute exposure, in which the concentrations tends to be high, but the considered time frame is short. The time frame for an acute exposure is usually within 24 hours. The plot in Figure 4 illustrates chronic and acute exposures over time.

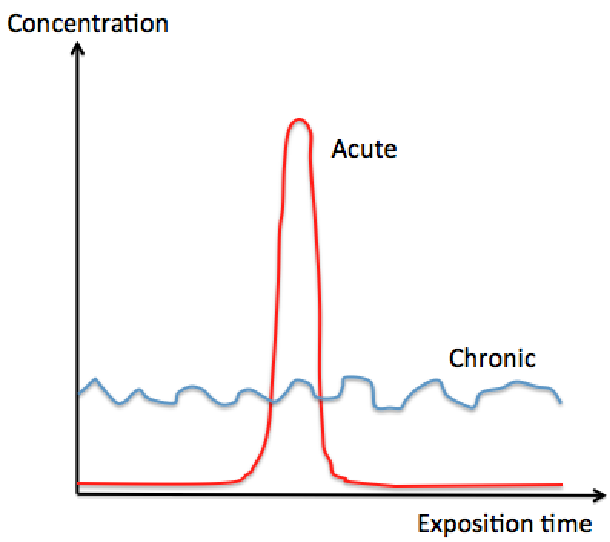



**Figure 4**. Chronic and Acute exposures

In both cases, the overall concentration towards which the subject was exposed can be determined by integrating the curves in Figure 4. Over time, a chronic exposure can produce worse results to the subject than the acute, taking into account that the area under the curve may be larger since the time-frames tend to be a life-time of work. However, an acute exposure may extrapolate the metabolic limits of an organism to deal with the chemical agent. That is the most dangerous part in an acute-type exposure, which is exactly the type of exposure expected to occur in a chemical warfare situation.

### 3.1. Chemical Warfare

The use of any given chemical compound in chemical warfare aims towards acute effects, due to the short exposure time characteristic of a chemical attack. A chemical agent, when used in war, is classified according to its tactical application, physiological effects or resilience. Table 1 presents a summary of those classes:

**Table 1**. Chemical agent classifications[14]

| Classification | Type | Description |
|---|---|---|
| Classification by tactical application | Killing agents<br>Disturbing agents<br>Incapacitating agents | cause death or permanent damage<br>cause sensorial irritation<br>cause mental confusion |
| Classification by physiological effect | Neurotoxic<br>Blistering agents<br>Blood toxics<br>Asphyxiating<br>Vomiting<br>Tear agents | act upon the nerve system<br>cause chemical burns upon contact<br>interfere in the cellular respiratory process<br>Interfere with the respiratory system<br>cause irritation in the air ways<br>cause irritation upon the eyes |
| Classification by resilience | Resilient<br>Non-resilient | remain in the area for long times<br>quickly disperse after deployed |

Furthermore, opposing to an agent used in the industry, where it is intended to negate harm effects by controlling the exposures, in chemical warfare a suitable agent should present the following requirements: 1) high toxicity; 2) enough stability to be stored; 3) resistance to heat dispersion; 4) resistance to environmental degradation and 5) low cost and ease of production.

In order to indicate the level of toxicity a chemical agent is expected to present, there is a comparison between TLV-TWA of the chemical agents presented in Table 2 with some of the chemical compounds used in the industry (Table 3), and grasp the toxicity levels of a chemical warfare agent. The information regarding the time duration for the $LC_{50}$ determination (1 hour, 4 hours, 8 hours), as well as the survival time following the exposure are left within the source used to compile these tables.

**Table 2**. Toxicity of chemical agents[6]

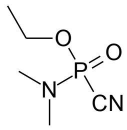
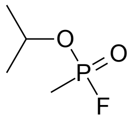
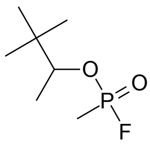
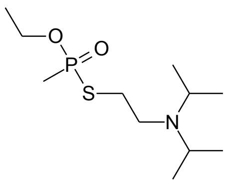
| Agent | $LCt_{50}$ (inhalation) (mg.min/m$^3$) | $LD_{50}$(skin) (mg) | TLV-TWA (mg/m$^3$) |
|---|---|---|---|
|  Tabun (GA) | 400 | 1000 | 0,0001 |
|  Sarin (GB) | 100 | 1700 | 0,0001 |
|  Soman (GD) | 50 | 350 | 0,00003 |
|  VX | 10 | 6 - 10 | 0,00001 |
| HCN | 2500-5000 | -- | 11,0 |

**Table 3**. Industrial compound toxicity[6]

| Agent | $LCt_{50}$ (inhalation) (mg.min/m$^3$) | $LD_{50}$(skin) (mg) | TLV-TWA (mg/m$^3$) |
|---|---|---|---|
| $HNO_3$ | --- | --- | 7,352 |
| $NH_3$ | --- | --- | 17,380 |
| $Cl_2$ | --- | --- | 1,431 |
| $CH_3OH$ | --- | --- | 261,759 |

Furthermore, for a chemical compound be used in war it also requires some key additional conditions, such as: the weather and conditions on the ground; the type of dispersion system; the amount and physical state of the agent used and its physical-chemical properties.

The differences in effectiveness of chemicals used in day-to-day activities and in chemical warfare are significant when comparing toxicity. Table 4 presents examples of toxicity of some agents, measured using lethal doses.

It is important to state that lethal doses are evaluated for ingestion, while lethal concentration can be used for dispersion of an agent. Table 5 presents some examples regarding such values.

**Table 4**. Toxicity – Lethal doses[15]

| Toxicity | $LD_{50}$ (mg $_{agent}$ /Kg $_{target}$) | Description |
|---|---|---|
| Extreme | <1 | Fluoracetates |
| High | 1 to 50 | Potassium cyanide |
| Moderate | 50 to 500 | DDT |
| Low | 500 to 5.000 | Acetanilide |
| Very low | 5.000 to 15.000 | Ketone |
| Non-toxic | >15.000 | Glycerin |

**Table 5**. Toxicity – Lethal Concentration[15]

| Toxicity | $LC_{50}$ ($mg/m^3$) | Description |
|---|---|---|
| Extreme | < 50 | Ozone |
| High | 50 to 100 | Phosgene |
| Moderate | 100 to 1.000 | HCN, $SO_2$ |
| Low | 1.000 to 10.000 | $NH_3$ |
| Very low | 10.000 to 100.000 | Toluene |
| Non-toxic | >100.000 | Fluorcarbons |

One should note that, for a chemical agent to be used in war, it needs duration as well as effectiveness. Gases and volatile liquids evaporate quickly and produce a vapor cloud which quickly disperse due to the wind; while solids and liquids disperse upon the soil and, therefore, may remain in the target area for long periods (after precipitation), generating a risk of contact or inhalation and negating the area to enemy troops.

## 4. Conclusions

The inherent differences in scenarios between chemical warfare and occupational hazards, such as exposure times and type of agent used, require serious considerations before making decisions based upon threshold limits alone.

It is by design that a chemical agent used in war has a very low lethal dose and lethal concentration, as well as a low TLV (regardless of which TLV). However, the actual number is determined by experiments, which are hardly able to mimic the harsh reality of an area after a chemical attack. Hence, the NBC officer need to understand that there are gaps in knowledge for applying occupational parameters in war. For that reason, the NBC officer should favor the use of lethal limits, since they reflect more closely the reality of an effect on populations of people without the large protective safety factors. Authorities will be forced to use these values in an effort to protect exposed people from real effects at unavoidable levels of exposure.

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