MODELING PROTECTIVE ACTION DISTANCES

FOR CHEMICAL WARFARE AGENTS

Hypothetical Situation

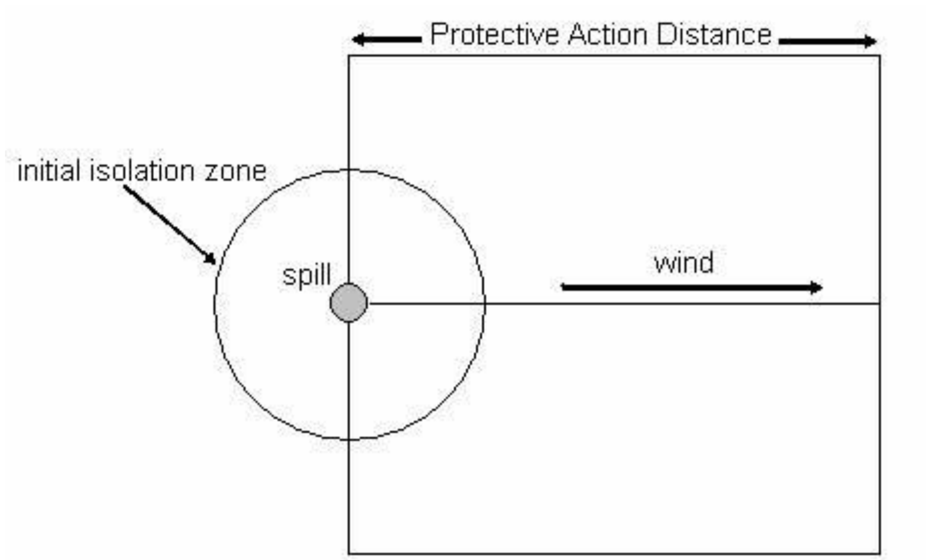
As part of your training, during a written exam question, you are asked to estimate a public evacuation zone for a chemical warfare agent (let us say Sarin) believed contained in a large package attached to what appears to be an explosive device. You don't know the amount of the warfare agent in the package, but you do know roughly the package size and there appears to be a small amount of leakage which evaporates. The package is outdoors at an urban location. A few people nearby have complained of nausea and difficulty seeing in dim light. The belief that the package may contain Sarin is based on an examination of the eyes of the people exposed, and pinpoint pupils were noted. The area has been blocked off preventing access, but a much wider public evacuation zone needs to be done. The public evacuation is based on an assumption that all of the package contents may become airborne as the result of an explosion before it can be disarmed.

When your estimate for public evacuation is compared with other estimates of your team you find that the estimates differ considerably. Why is this? The reason for the differences goes beyond differences in estimates of amount of Sarin released or weather conditions. The methodologies for estimating a Protective Action Distance (PAD) are different, and there is an uncertainty of what value to use as a level of concern.

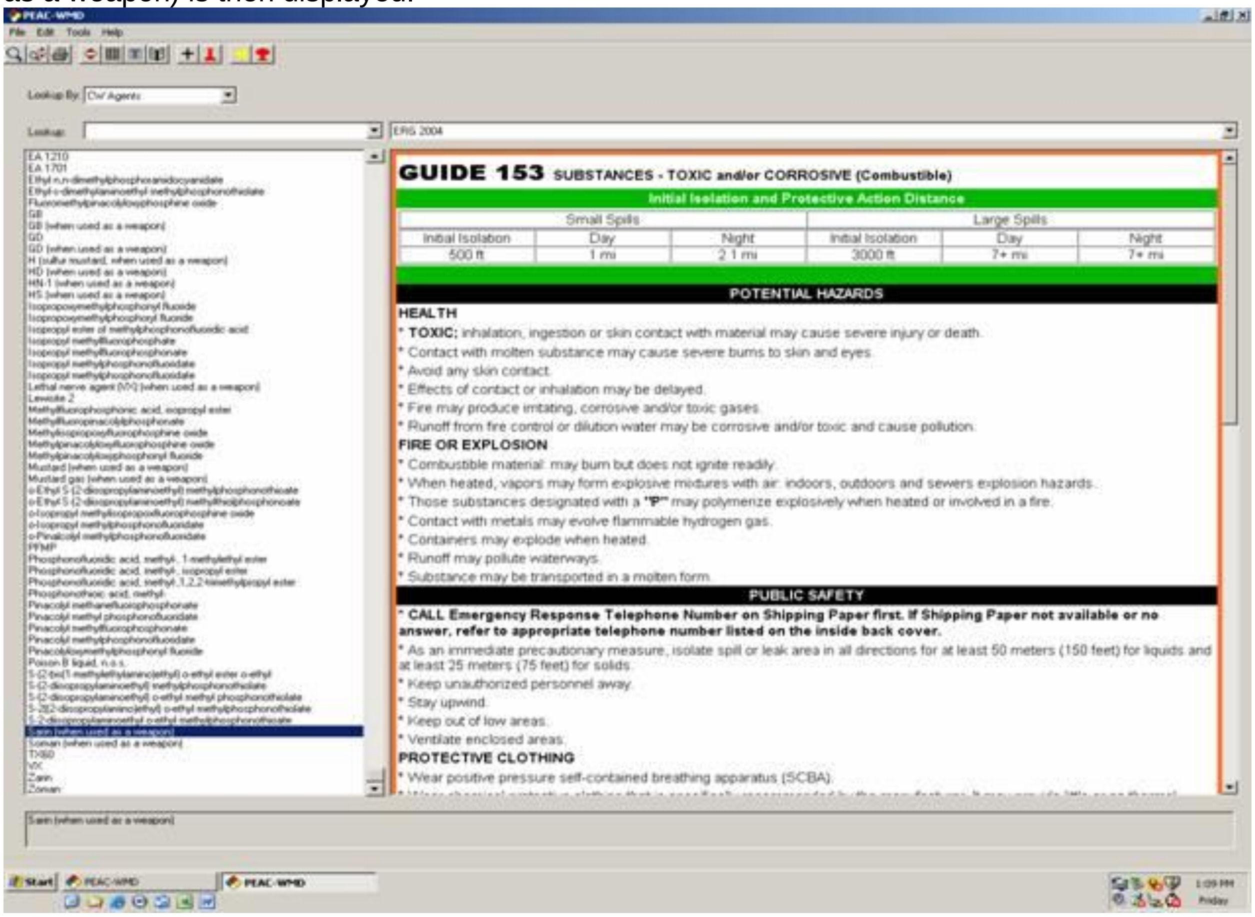
Let us look at different methods of estimating a Protection Action Distance as applied to chemical warfare agents.

2004 Emergency Response Guidebook (2004 ERG)

The Emergency Response Guidebook is published jointly by Transport Canada, U.S. Department of Transportation, and SCT (Mexico) at four-year intervals. It is designed to give information to emergency responders in case of a transportation accident involving hazardous chemicals.



The 2004 ERG gives a sketch showing an initial isolation zone, a protective action zone, and a protection action distance in the case of a spill of a hazardous chemical. The initial isolation zone represents the distance in all directions all persons must be removed from the spill. The Protective Action Distance (PAD) is the distance downwind for which protective action should be considered, whether this is an evacuation or shelter in place or a combination thereof. The Protective Action Zone is defined by a square whose length and width are the same as the downwind distance represented by the PAD. Anyone within this Zone is at risk for harmful exposure. A copy of the 2004 ERG can be obtained off the Internet at http://hazmat.dot.gov/pubs/erg/erg2004.pdf. The PEAC tool marketed by AristaTek also contains a copy of the 2004 ERG. To access the 2004 ERG information for Sarin via the PEAC tool, select “Sarin (when used as a weapon)” as a chemical choice on the left side of the PEAC tool, then select 2004 ERG at the upper right. The information pertaining to Sarin (when used as a weapon) is then displayed.



The Initial Isolation and PADs can then be read for Sarin (when used as a weapon)

Initial Isolation and Protective Action Distance					
Small Spills			Large Spills		
Initial Isolation	Day	Night	Initial Isolation	Day	Night
500 ft	1 mi	2.1 mi	3000 ft	7+ mi	7+ mi

“When used as a weapon” means that the chemical is aerosolized or gasified as in an explosion or using an aerosol device as opposed to “when spilled on land” which means a simple spill of the sarin liquid which puddles and evaporates. The initial isolation distance for small spills is 500 feet, and 3000 ft for large spills. The PAD is further subdivided into daytime and nighttime spills. The user can display the PADs in either English units (as shown) or metric units. Nighttime releases display a greater PAD than daytime releases because, on the average, the air is more stable and the chemical is less likely to be dispersed.

What is a “small spill” and what is a “large spill”? According to the instructions provided with the 2004 ERG, a small spill is from a 55-gallon drum or smaller, and a large spill is greater than 55 gallons. But chemical warfare agents are not normally shipped on the highways or by rail. There was a large public outcry when the military proposed to destroy old and possibly

leaking stockpiles of chemical warfare agents by incineration; one of the options considered was shipping to a centralized location (such as Tooele, Utah) for destruction (don't ship the stuff past my neighborhood, and don't incinerate the CWA here). So what size container was the 2004 ERG modeling based? The answer is in Table 2.4 of the following document,
D.F. Brown, W.A. Freeman, R.A. Carhart, and M. Krumpolc. "Development of the Table of Initial Isolation and Protective Action Distances for the 2004 Emergency Response Guidebook", Argonne National Laboratory, May 2005. A copy of this report can be downloaded from the Internet at http://hazmat.dot.gov/pubs/erg/Argonne_Report08042005.pdf .
Small release: 2 kg (Sarin, VX, Soman, Tabun, Lewisite, or Mustard HD).
Large Release: 100 kg (Sarin, VX, Soman, Tabun, Lewisite, or Mustard HD).
The 2004 ERG offers the user only two choices, ether a small spill of 2 kg (4.4 lbs) or a large spill of 100 kg (220 lbs) . If the user assumed that a small "spill" was 55 gallons or less, which is implied by a quick read of the 2004 ERG, a wrong answer would be obtained. A 55 gallon container of Sarin if full would contain 227 kg of Sarin. The 2004 ERG considers a release of 100 kg as a large spill.
Incidently, Brown's developmental document cited above uses 60 gallons or less for a small spill of industrial chemicals whereas the 2004 ERG lists the cutoff as 55 gallons or less for a small spill.

Levels of Concern

The distances listed in the 2004 ERG for the initial isolation zone and protective action distance is based on a level of concern. The 2004 ERG has adopted the American Industrial Hygiene Association's Emergency Response Planning Guideline Level 2 (ERPG-2) as the Level of Concern (LOC) for the PAD. If an ERPG-2 value has not been published, then the 1-hour LC_{50} /100 value is used as an approximation to ERPG-2. The Initial Isolation Zone distance is based on 0.05 times the 1-hour LC_{50} value. Earlier editions of the ERG used the Emergency Response Planning Guideline Level 3 (ERPG-3), the NIOSH IDLH, or other LOC criteria for the calculation of the Initial Isolation Zone distance.

Table 1. 1-hr LC_{50} Values for Chemical Warfare Agents used in the 2004 ERG

Chemical Warfare Agent	**1-hour LC_{50} , ppm**
HD, Bis-(2-chloroethyl) sulfide	2.3
GA, Tabun	0.18
GB, Sarin	0.1
GD, Soman	0.08
VX, O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	0.023

Definitions of these Levels of Concern are as follows:

ERPG-2: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects, or symptoms that could impair an individual's ability to take protective action.

ERPG-3: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

1-hour LC_{50} : The lethal concentration in air that 50% of the test animals (rats preferred) will die after exposure to the chemical for 1 hour.

These ERPG-2, ERPG-3, and LC_{50} concentrations only consider acute toxic effects and do not consider carcinogens nor explosive environments.

NIOSH IDLH: The National Institute for Occupational Safety and Health has established "Immediately Dangerous to Life and Health" concentrations for workers exposed to airborne chemicals. The IDLH value is the maximum concentration that a worker can be exposed to for up to 30 minutes without loss of life or irreversible health effects or severe eye or respiratory irritation that would prevent his/her escape. The IDLH value does consider explosive effects (either 10% of the Lower Explosive Limit concentration or toxic effects, or impairment of senses that might prevent escape).

This may seem straightforward, but every four years when a new ERG is published the criteria historically has changed. Also the numbers for ERPG and LC_{50} can change as more information becomes available. If a user has a 2000 ERG and compares initial isolation distances and PADs listed with the 2004 ERG, the distances are different for the same chemical. More changes can be expected for the 2008 ERG if the Acute Exposure Guideline Levels (AEGLs) developed by the Federal Advisory Committee (a collaborate effort of public and private sectors) are adopted for PAD and initial isolation distance criteria. The AEGLs are used by the U.S. Environmental Protection Agency.

As of 2005, no ERPGs have been established for chemical warfare agents. The 1 hour LC_{50} values used in the 2004 ERG for seleced chemical warfare agents are listed in **Table 1**. For example, the 1-hour LC_{50} is listed as 0.1 ppm for Sarin. The 2004 ERG PAD distance is based on 0.001 ppm Sarin as the Level of Concern.

The U.S. Department of Energy (DOE) has published [see http://www.eh.doe.gov/chem_safety/teel.html] what they call Temporary Emergency Exposure Limits (TEELs) to serve as surrogates until the American Industrial Hygiene Association publishes their ERPGs. ERPGs have been published for about 115 chemicals to date, but DOE has published TEELs for over 2000 chemicals. The 2004 ERG did not consider TEELs as Levels of Concern. ERPGs are also available at this website.

Table 2. DOE Published TEELs as Levels of Concern

Chemical Warfare Agent	**TEEL-2**	**TEEL-3**
HD, Bis-(2-chloroethyl) sulfide	0.002 ppm	0.6 ppm
GA, Tabun	0.02 ppm	0.5 ppm
GB, Sarin	0.009 ppm	0.1 ppm
GD, Soman	0.0002 ppm	0.005 ppm
VX, O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	0.0002 ppm	0.001 ppm

TEEL-2 may be considered as a surrogate for ERPG-2

TEEL-3 may be considered as a surrogate for ERPG-3

Acute Exposure Guideline Levels (AEGLs) are published at the EPA website, http://www.epa.gov/oppt/aegl/ . They are intended to describe the risk to humans resulting from rare or once-in-a-lifetime exposure to airborne chemicals. AEGLs are not now considered in the 2004 ERG, but the developmental document cited above hints that they may be considered in the future 2008 ERG. Three levels or considered:

AEGL-1: Airborne concentration of a substance at or above which it is predicted that the general population including “susceptible” but excluding “hypersusceptible” individuals could experience noticeable discomfort.

AEGL-2: Airborne concentration of a substance at or above which it is predicted that the general population including “susceptible” but excluding “hypersusceptible” individuals could experience irreversible or other serious, long-lasting effects or impared ability to escape.

AEGL-3: Airborne concentration of a substance at or above which it is predicted that the general population including “susceptible” but excluding “hypersusceptible” individuals could experience life-threatening effects or death

The AEGLs are exposure time dependent. Therefore AEGL values are given for various exposure times (5 minute, 10 minute, 30 minute, 60 minute, 4 hours, and 8 hours).

The U.S. Military with some exceptions has adopted the AEGLs for their Military Exposure Limits for Chemical Warfare Agents. The listings are in “TG 230 Chemical Exposure Guidelines for Deployed Military Personnel”, published by the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM), and can be obtained at http://chppm-www.apgea.army.mil/desp/pages/samp_doc.htm (2003 edition) or at http://chppm-www.apgea.army.mil/imo/ddb/dmd/DMD/TG/TECHGUID/Tg230.pdf (1999 edition).

Table 3 One-hour AEGLs for Chemical Warfare Agents (in ppm or mg/m^3)

Chemical Warfare Agent	AEGL-1	AEGL-2	AEGL-3
HD, Bis-(2-chloroethyl) sulfide	0.01 ppm 0.067 mg/m^3	0.02 ppm 0.1 mg/m^3	0.32 ppm 2.1 mg/m^3
GA, Tabun	0.00042 ppm 0.0028 mg/m^3	0.0053 ppm 0.035 mg/m^3	0.039 ppm 0.26 mg/m^3
GB, Sarin	0.00048 ppm 0.0028 mg/m^3	0.0060 ppm 0.035 mg/m^3	0.022 ppm 0.13 mg/m^3
GD, Soman	0.00018 ppm 0.0014 mg/m^3	0.0022 ppm 0.018 mg/m^3	0.017 ppm 0.13 mg/m^3
VX, O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	0.000016 ppm 0.00017 mg/m^3	0.00027 ppm 0.0029 mg/m^3	0.00091 ppm 0.01 mg/m^3

The values listed in **Tables 3** and **4** are the same but under categories of “Minimal”, “Significant”, and “Severe” or under AEGL levels. The PEAC tool lists the Military Exposure

Guidelines, not just for one-hour exposure but for 5 minute, 10 minute, 30 minute, 60 minute, 4 hours, and 8 hours, which are also the same as the AEGLs.

Table 4. One-hour Military Exposure Guidelines for Chemical Warfare Agents

Chemical Warfare Agent	Minimal	Significant	Severe
HD, Bis-(2-chloroethyl) sulfide	0.01 ppm 0.067 mg/m^3	0.02 ppm 0.1 mg/m^3	0.32 ppm 2.1 mg/m^3
GA, Tabun	0.00042 ppm 0.0028 mg/m^3	0.0053 ppm 0.035 mg/m^3	0.039 ppm 0.26 mg/m^3
GB, Sarin	0.00048 ppm 0.0028 mg/m^3	0.0060 ppm 0.035 mg/m^3	0.022 ppm 0.13 mg/m^3
GD, Soman	0.00018 ppm 0.0014 mg/m^3	0.0022 ppm 0.018 mg/m^3	0.017 ppm 0.13 mg/m^3
VX, O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	0.000016 ppm 0.00017 mg/m^3	0.00027 ppm 0.0029 mg/m^3	0.00091 ppm 0.01 mg/m^3

For comparison, a ten minute exposure limit for the same conditions are listed in **Table 5**. These are the same numbers as the corresponding AEGL-1, AEGL-2, and AEGL-3 listings for the same exposure time.

Table 5. Ten-minute Military Exposure Guidelines for Chemical Warfare Agents

Chemical Warfare Agent	Minimal	Significant	Severe
HD, Bis-(2-chloroethyl) sulfide	0.06 ppm 0.4 mg/m^3	0.09 ppm 0.6 mg/m^3	0.59 ppm 3.9 mg/m^3
GA, Tabun	0.001 ppm 0.0069 mg/m^3	0.013 ppm 0.086 mg/m^3	0.11 ppm 0.76 mg/m^3
GB, Sarin	0.0012 ppm 0.0069 mg/m^3	0.015 ppm 0.087 mg/m^3	0.064 ppm 0.38 mg/m^3
GD, Soman	0.00046 ppm 0.0035 mg/m^3	0.0057 ppm 0.044 mg/m^3	0.049 ppm 0.38 mg/m^3
VX, O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	0.000052 ppm 0.00057 mg/m^3	0.00065 ppm 0.0072 mg/m^3	0.0027 ppm 0.029 mg/m^3

The PEAC tool (as of 2004 and 2005) lists IDLH and TWA values for chemical warfare agents, even though none were established by OSHA or NIOSH at that time. These are values that came from DoD to serve as Military Exposure Guidelines (see the TG230 report cited above). In April 2005, OSHA and NIOSH proposed interim values of IDLH, STEL, and 8-hour TWA for chemical warfare agents. [STEL = short term exposure limit; 8-hour TWA = 8-hour worker time weighted average exposure limit]. Except for HD, the OSHA/NIOSH interim April

2005 values are more conservative than the values that the military uses; for example, compare the IDLH values in **Table 6**:

Table 6. Comparison of DoD "IDLH with OSHA/NIOSH April 2005 Proposed IDLH

Chemical Warfare Agent	**DoD "IDLH"**	**OSHA/NIOSH proposed interim IDLH**
HD, Bis-(2-chloroethyl) sulfide	0.0005 ppm 0.003 mg/m^3	0.7 mg/m^3
GA, Tabun	0.03 ppm 0.2 mg/m^3	0.015 ppm 0.1 mg/m^3
GB, Sarin	0.03 ppm 0.2 mg/m^3	0.0015 ppm 0.01 mg/m^3
GD, Soman	0.008 ppm 0.06 mg/m^3	0.006 ppm 0.05 mg/m^3
VX, O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	0.002 ppm 0.02 mg/m^3	0.0003 ppm 0.003 mg/m^3

The April 2005 OSHA/NIOSH Interim values also came from a DoD memorandum dated 18 June 2004 titled "Implementation Guidance Policy for New Airborne Limits for GB, GA, GD, GF, VX, H, HD, and HD" OASA (I&E). The reason for the low "IDLH" for HD in the earlier DOS "IDLH" is not clear, but IDLH and the 8-hour TWA were originally listed as the same for HD.

The point here is that different concentrations can be used as a Level of Concern depending upon the reference source. Because the Level of Concern is different, the Protective Action Distances or Evacuation Distances based on a Level of Concern will be different depending upon what information is used.

Models used to Predict Evacuation Distances

More than one gas dispersion model is available to predict downwind concentrations as a function of distance from the source. The models can give different answers because real data must be used to calibrate the model during model development, and the people who developed the models used different data sets. Let us examine some models:

- CASRAM Emission Model. This is the model used in the 2004 ERG when developing PADs. It has both Gaussian (passive) and dense gas components, the dense gas component being essentially the DEGADIS model. Details are in the development document (D.F. Brown, et al, cited previously). The development document hints that future editions of the CASRAM emission model may incorporate features from the HEGADAS dense gas model.
- CAMEO (ALOHA) Model. This is a popular model available from EPA and is widely used by governmental and civilian agencies. It has both dense gas and Gaussian (passive) components, and can be used to

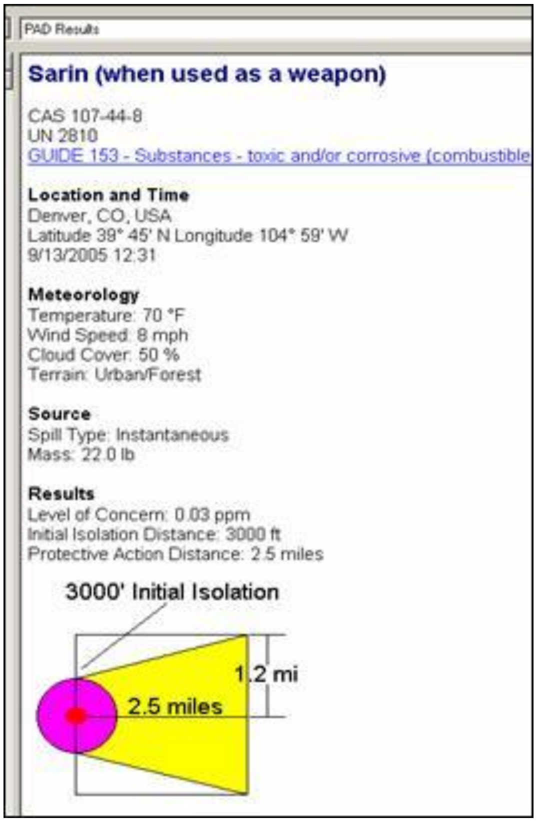
describe both continuous and instantaneous (“puff”) releases. The dense gas component is mostly based on the DEGADIS model but contains some features which provides a more conservative result. Details are in NOAA Technical Memorandum NOS ORCA-65, ALOHA^{tm} Theoretical Description.

- PEAC Tool. The PEAC tool incorporates both Gaussian (passive) and dense gas components. It can also be used in a continuous or instantaneous mode. As with ALOHA, meteorological conditions are assigned to one of six stability classes (A,B,C,D,E, or F) depending upon wind speed, cloud cover, and time of day. The dense gas component has features similar to SLAB and gives results (generally within 20%) close to SLAB.
- D2PC Model. This is a passive, Gaussian model used by the U.S. Military primarily to model chemical warfare agent releases. Details are in the following document: C.G. Whitacre, J.Griner, M.M. Myirski, and D.W. Sloop. “Personal Computer Program for Chemical Hazard Prediction (D2PC). CRDEC-TR-87021. U.S. Army Armament Munitions Chemical Command, Aberdeen Proving Ground. January 1987.
- SLAB Model. Details are in D.L. Ermak, “User’s Manual for SLAB: An Atmospheric Dispersion Model for Denser-than-air Releases”. Lawrence Livermore National Laboratory, Livermore CA, June 1990.

The 2004 ERG when applying the CASRAM Emission Model applies a statistical approach is specifying a PAD. Four categories are considered, (1) small daytime releases, (2) large daytime releases, (3) small nighttime releases, and (4) large nighttime releases. “Small” when applied to chemical warfare agents is 2 kg, and “large” is 100 kg, but this piece of information is not in the 2004 ERG. This information on amount released is in the developmental document. The statistical approach enters into the analysis when considering meteorological patterns for dispersal of airborne chemicals under different terrains or locations. A 90th percentile probability level is chosen, meaning, of possible combinations of meteorology and locations for many computer runs using the CASRAM Model, the PAD developed will be that distance or less for 90% of the situations. The other models allow the user to input the container size or amount released, the meteorology, and basic information about the terrain for the situation at hand.

<u>Hypothetical Situation Again</u>

Let’s get back to the hypothetical situation of a package suspected of containing Sarin attached to what appears to be an explosive device. From a distance, the package appears to measure 12” by 8” by 6”. The package is outdoors in an urban area. The time is late morning. The sky is partly cloudy, and winds are estimated at 8 mph. What public evacuation distance is recommended as a precaution, should the package explode before it can be disarmed?



The first step is to roughly estimate the amount of Sarin that the package might possibly contain. The PEAC tool contains a calculator where the user can input the package size. If the calculation is done by hand, the amount (in kilograms and pounds) is

$12x8x6x(2.54)^3x(1.09)/1000$ = 10.3 kilograms (kg) or 22 lbs.

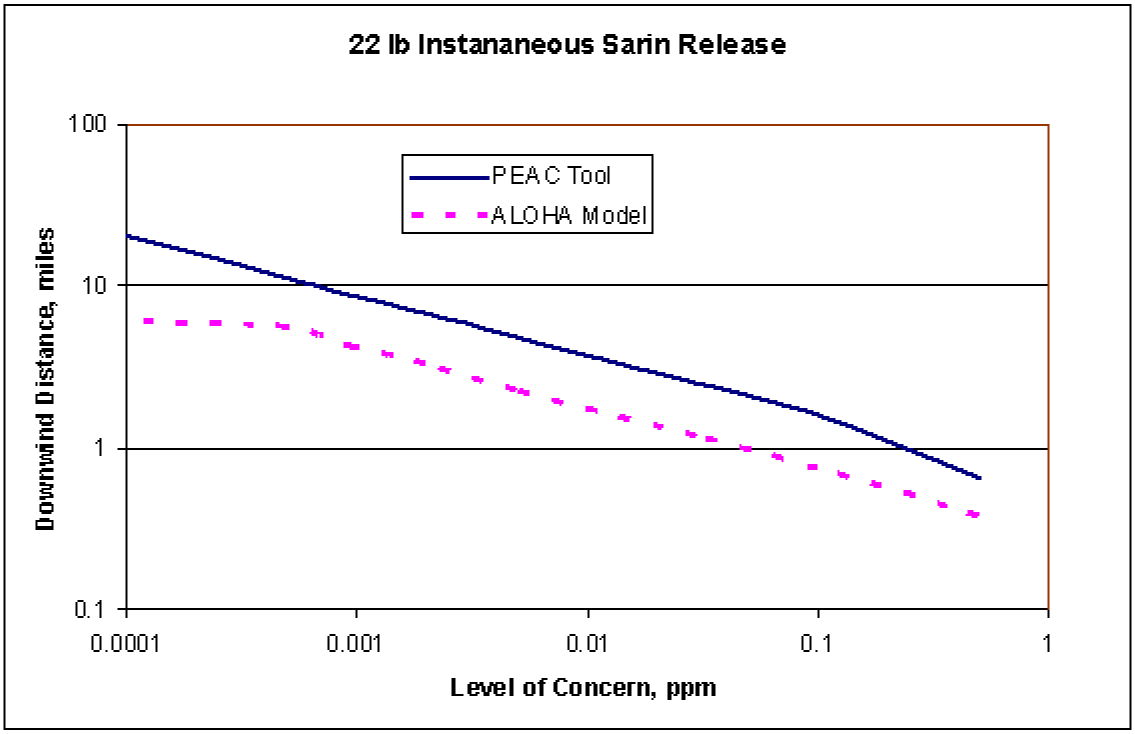
The 1.09 is the specific gravity of Sarin compared with water. The $(2.54)^3$ is a conversion factor between cubic inches and cubic centimeters. One cubic centimeter of water weighs one gram, and 1000 grams equals 1 kilogram. Multiplying 1 kiliogram by 2.2 gives pounds. Some responders might allow for packaging and estimate a smaller amount of Sarin could be present, but we will go with a 10 kg (22 lb) estimate.

If the 2004 ERG is used, 10 kg is intermediate between a small spill of 2 kg which has a PAD of 1 mile and a large spill of 100 kg with a PAD of 7+ miles.

Using the PEAC tool, we will estimate the protective action distance for a 22 pound release of Sarin. We will select Sarin as the CWA, and ask to calculate the PAD. We will arbitrary select Denver CO as the location, 70^oF, wind speed 8 mph, 50% cloud cover, and since all of the Sarin is released at once as in an explosion, we will use a 22 pound instantaneous release. The default condition for Level of Concern is 0.03 ppm, and the PEAC tool calculates a PAD of 2.5 miles. The PEAC printout for this condition is shown at the left.

The PEAC tool allows the user to input different concentrations as a Level of Concern. This can be done rapidly using the PEAC tool. Let us calculate PADs for different Levels of Concern and see what happens.

We will repeat this exercise again using the ALOHA model in CAMEO. The ALOHA model approximates the instantaneous 22 lb release as a 0.37 lb/s release over one minute. [0.37 x 60 = 22]. We will repeat the calculation for several levels of concern.



Note that the scale on the above figure is logarithmic. The two modeling methods give different results because different algorithms are used in the computation. The PEAC tool when operated in the Gaussian “instantaneous” or “puff” mode uses the same algorithms as in the DEGADIS manual which is available as an EPA document, EPA-450/4-89-019. If the D2PC Model, SLAB Model, or CASRAM Emission Model is used, different results would also be obtained because different algorithms are used. The algorithms in the PEAC tool give a “peak” instantaneous concentration, whereas the ALOHA model gives a more time-averaged concentration.

We have a situation where different answers are obtained depending upon the modeling method and the Level of Concern.

How can we resolve this situation? What should the Protective Action Distance be? The key is that the disarming of the device is taking place during the daytime, outdoors, the sun is shining, and wind will disperse the chemical if an explosion takes place. Sunlight and air humidity will react with Sarin to produce relatively less harmless chemicals. None of the models account for hydrolysis and decomposition of Sarin because of air moisture and sunlight. The models may predict airborne concentrations closer to the source, but after few miles downwind, airborne concentrations should be less than what models predict because of destruction of the chemical. This is good, because there probably would be no need to evacuate 5 or 10 miles downwind. At night or under very dry conditions, chemical destruction is much slower, and this reasoning would not apply.

The worst case is the situation where all of the chemical is released at once. A chemical cloud forms which travels downwind. The wind speed is 8 mph. The duration of the chemical cloud would be relatively short as it passes over a downwind spot. Therefore “shelter in place”, e.g. ordering people to stay indoors with windows closed is a viable option. The 10-minute AEGLs or Military Exposure Guidelines listed in **Table 5** should be applicable here as “Levels of Concern”, not the 1-hour exposure listed in tables 2, 3, or 4, or the values listed in **Table 6**. We are probably looking at a PAD of about 3 miles, which is also roughly in the ballpark of what the 2004 ERG would predict for a 10 kg release interpolating PADs for small (2 kg) and large (100 kg) spills.   If there is time and the risk is acceptable, evacuations may be ordered closer to "ground zero" , and shelter-in-place further away.

The conclusion is that while models and Levels of Concern are useful in predicting PADs or evacuation distances, the information must be tempered by an understanding of the particular situation at hand.

When complex information is conveyed in short concise statements in any situation, there are caveats or conditions that need to be understood as to the circumstances in which they apply, and many factors must be considered in making decisions.