MODELING A CHEMICAL RELEASE

A chemical release incident has occurred or can potentially occur. The chemical is toxic if inhaled. Decisions must be made quickly on a safe evacuation distance for the general public, or whether to shelter-in-place if there is insufficient time to do an evacuation. There are many issues involved: what is happening, what chemicals are involved, is there fire, is the chemical escaping to the air, what are the hazards, how should the information be communicated to the public. The first responder may have a gas dispersion model available which predicts a protective action distance based on a downwind concentration based on some level of concern, and then order a public evacuation distance based on that level of concern. When a decision is made on a safe evacuation distance, there will always be critics who have the benefit of hindsight saying (1) the model was too conservative and over predicted evacuation distances, or (2) this situation was more dangerous and more people should have been evacuated, or (3) authorities failed to communicate instructions to the general public in time.

We will model two hypothetical examples of a toxic chemical release incident, and try to understand what is going on.

Chlorine Rail Car Accident
A 90-ton capacity rail car is involved in an accident, and a strong odor of chlorine is present. As far as we can tell, there are no large volumes of liquid chlorine coming from the tank, but the accident scene is obscured by yellowish-greenish gas. Responders can't get near to see what exactly is happening. There is no fire. There are no other rail cars containing flammables or other hazardous substances which might react with chlorine causing an explosion. There are causalities. How should this situation be modeled to estimate a public protective action zone?

Potential Terrorist Incident
A suspicious item is discovered under the bleachers of a stadium prior to a soccer game. The item appears to be a quart or liter container of clear liquid attached to an explosive device. It could be a hoax, or the liquid could be some smelly material designed to disrupt the game. The liquid could be nitroglycerine or even a chemical warfare agent. The stadium is evacuated. What protective action distance should be established under a worst-case situation that the container might contain the toxic chemical warfare agent Sarin?

Modeling the Chlorine Rail Car Incident
In a real incident, responders rarely have all the necessary information required to do gas dispersion modeling. Reasonable guesses must be made.

On 6 January 2005, at about 2:30AM, three 90-ton chlorine rail cars were involved in an accident at a crossing siding in Graniteville, SC. The resulting chlorine gas leak killed nine people and sent over 350 people to a nearby hospital for chlorine inhalation. About 5,400 people were evacuated within a one-mile radius. Initially, responders did not know how many rail car tanks were leaking chlorine. It was established the next day that chlorine was leaking from only one rail car tank, and that perhaps possibly 40% of the chlorine still remained in the tank. The chlorine gas continued to escape from a fist-sized hole in the tank. On January 9, when a temporary patch was used to plug the hole

in the tank, it was estimated that 30 tons of chlorine remained in the tank and 60 tons had escaped. More details on the accident are in an EPA report available at http://www.epa.gov/region4/graniteville/#environmental .

There were reports that the ALOHA gas dispersion model was used to estimate a protection action distance for the Graniteville incident, and that this model grossly over predicted concentrations as a function of distance downwind. If the modelers assumed that all of the chlorine were released at once or during a relatively short time period, e.g. 60 minutes, the default time in ALOHA, very large concentrations would be predicted downwind. The chlorine release rate was much slower in the Graniteville incident but still deadly.

The chlorine inside a 90-ton rail car would be shipped as a liquid under its own vapor pressure. Probably about 85% of the volume inside the tank would be liquid and the remaining amount vapor and some nitrogen. Assuming an ambient temperature of 50°F, the pressure (gage) inside the tank would be about 60 psi before the breach. If the hole is at the top of the tank, chlorine gas will be released. The drop in pressure inside the tank would cause the chlorine liquid to boil resulting in more chlorine escaping. As the chlorine boils, the tank will become chilled reducing the evaporation rate. It will take many days to empty the tank.

On the other hand, if there is a large hole at the bottom of the tank, the pressure will force chlorine liquid out the hole. The tank will empty much sooner. The chlorine liquid on the ground will also quickly evaporate. Maximum chlorine concentrations in the air will be much greater.

The 2004 Emergency Response Guidebook lists Initial Isolation Zone and Protective Action Distances for hazardous chemicals involved in transportation accidents. This guidebook is published jointly by Transport Canada, U.S. Dept. of Transportation, and Secretariat of Transport (Mexico), and is available at http://hazmat.dot.gov/pubs/erg/erg2004.pdf .

The user need only consider four categories for each chemical when looking up the Initial Isolation Zone and Protective Action Distances in the Emergency Response Guidebook. The categories are (1) small spills, daytime conditions, (2) large spills, daytime conditions, (3) small spills, nighttime conditions, and (4) large spills, nighttime conditions. A breach in a 90-ton railcar is a large spill. The Emergency Response Guidebook lists the Initial Isolation distance for large spills as 0.24 km, and the Protective Action Distance as 2.4 km (daytime conditions), or 7.4 km (nighttime conditions)
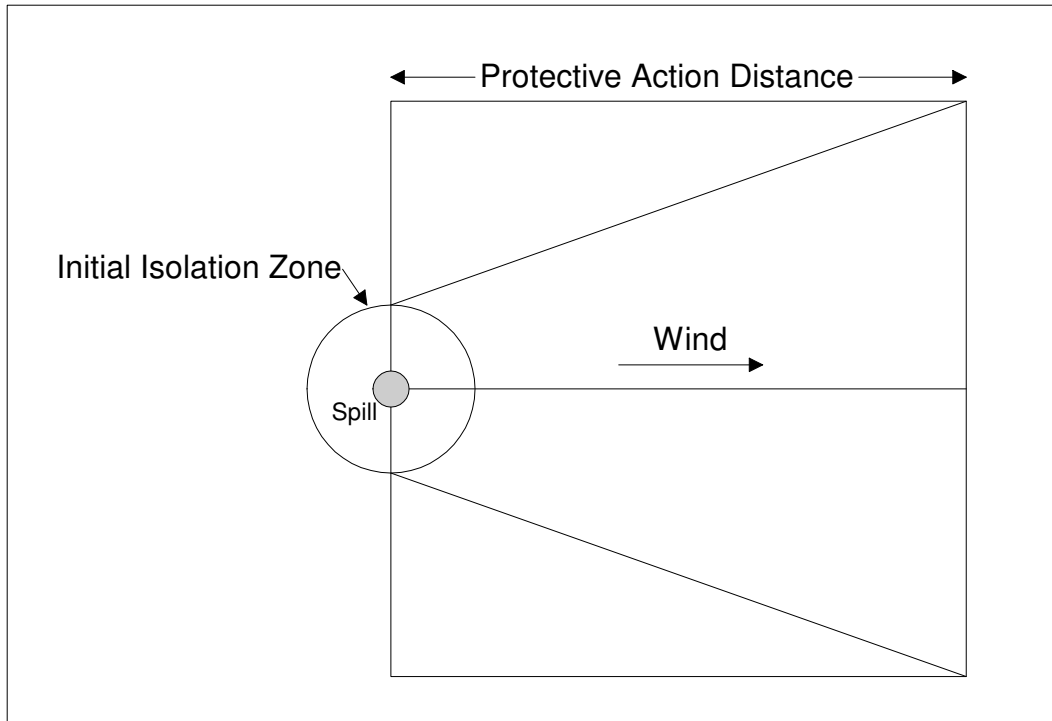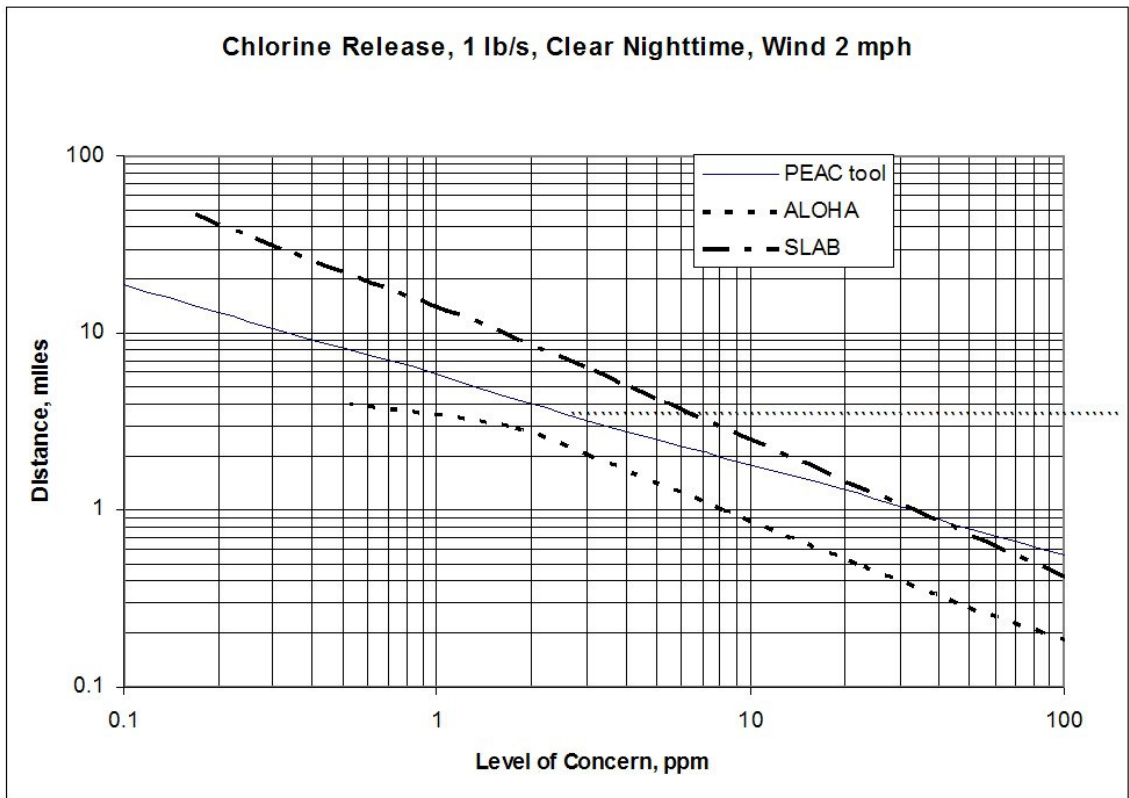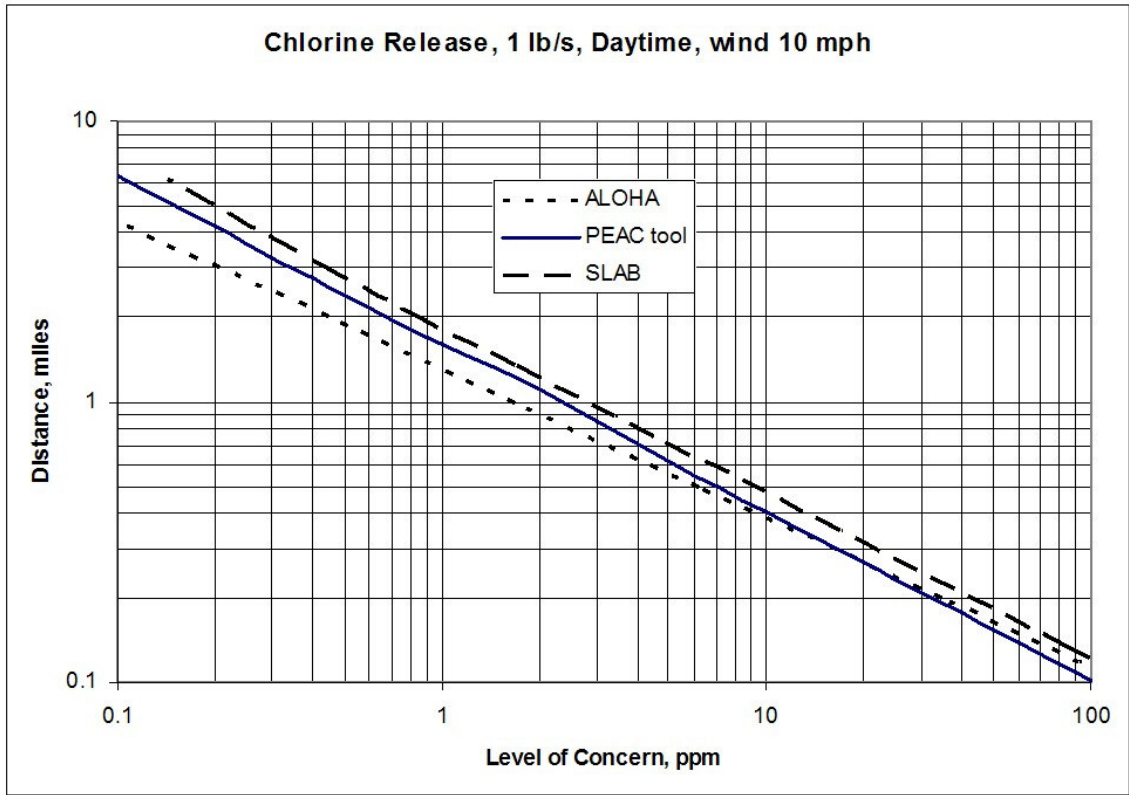
What is a large spill and what is a small spill? For most hazardous chemicals, the Emergency Response Guidebook considers anything greater than 55 or 60 gallons as a large spill. A 90-ton rail car is a large spill, but a breach in a one-ton chlorine tank would also be considered a large spill. We will discuss the Emergency Response Guidebook further, but first let's consider gas dispersion modeling.

Gas dispersion models ask the user basic information such as (1) the chemical itself, or at least information about the chemical such as molecular weight and boiling point; (2) amount of chemical released, (3) information about the terrain, which is usually expressed in terms of a "surface roughness", and (4) meteorology. The user then specifies a location downwind, and the model predicts a concentration at that location. Alternatively, the user may specify a concentration representing a "level of concern", and the model predicts a distance downwind corresponding to that concentration. Information requested on meteorology could include (1) wind speed and direction, and (2) atmospheric stability (estimated from time of day, geographical location, date, percent cloud cover, etc.).

What model should the responder use? Some popular models in the public domain are ALOHA and SLAB. Chlorine is a dense gas which tends to "hug" the ground as it travels downwind until either solar heating creates atmospheric instability or turbulence from wind eventually disperses the gas. Therefore any model selected should have a "dense gas" component, which both ALOHA and SLAB have. The model in the PEAC tool also has a dense gas component.

Let us do a model comparison for a chlorine release rate of 1 lb/second under daytime and nighttime conditions. We don't know the release rate but need to proceed with a reasonable guess.

Chlorine Release, 1 lb/s, Daytime, wind 10 mph

Legend:
- ALOHA
- PEAC tool
- SLAB

X-axis: Level of Concern, ppm
Y-axis: Distance, miles

Chlorine Release, 1 lb/s, Clear Nighttime, Wind 2 mph

Legend:
- PEAC tool
- ALOHA
- SLAB

X-axis: Level of Concern, ppm
Y-axis: Distance, miles

The ALOHA model is available at no cost from the U.S. Environmental Protection Agency. Version 5.3.1 of the ALOHA model can be downloaded at http://www.epa.gov/ceppo/cameo/aloha.htm. The PEAC tool is available from AristaTek, at http://www.aristatek.com/. SLAB is a dense gas model developed by Lawrence Livermore National Laboratories under U.S. Dept. of Energy contract. SLAB is available from a number of sources such as http://www.weblakes.com/lakeepa4.html.

The models shown above were compared at a surface roughness of 0.1 meters (cropland, light residential terrain), and the wind speed was measured at a 2 meter height.

Usually, the Emergency Response Planning Guideline Level 2 (ERPG-2) is used as the Level of Concern for public evacuation distance. The ERPG-2 is also used in the 2004 Emergency Response Guidebook for their Protective Action Distance. ERPG-2 is established by the American Industrial Hygiene Association and is defined as the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. For chlorine, the ERPG-2 is 3 ppm. For the daytime condition at 10 mph wind, the corresponding distance ranges from 0.7 to 1 miles (1.1 to 1.6 km) depending upon what model is used. For nighttime conditions at 2 mph wind, the distances corresponding to 3 ppm varied from 2 to 7 miles (3.2 to 11.3 km) depending upon the model.

The lethal concentration of chlorine (LC50) for a one-hour exposure based on rat studies is just under 300 ppm.

Note that the model comparisons are plotted logarithmically. The level of concern represents the ground level, plume cloud centerline concentration for different distances (in miles) downwind. The models agree fairly close to each other under windy or overcast conditions as represented by the top graph, but depart from each other under the low-wind, clear nighttime condition. The first graph represents a neutral, or "D" atmospheric stability; "neutral" meaning that there is little ground cooling or solar heating resulting in a minimal temperature gradient in the air. The second graph represents a "stable" nighttime atmospheric condition where the cooler air tends to sink to the ground, sometimes referred to as the "F" atmospheric stability. The toxic gas cloud is not readily dispersed under stable, nighttime conditions, and as a consequence, the distances matching up with Levels of Concern are much greater.

Why are the models predict essentially the same results under "neutral" conditions but depart under the stable, nighttime, "F" stability condition? Models in their development require data sets for calibration. The data sets allow development of algorithms which predict how the chemical cloud will spread and disperse as it travels downwind. For example, the ALOHA model uses Briggs' dispersion algorithms (called "sigmas") which were developed from sulfur dioxide releases tests in a Kansas field in the 1960's. SLAB used some data sets for chemical releases done at the Nevada Test Site near Mercury, Nevada. There are many data sets developed under "D" or neutral stability conditions; the data sets can easily be done in a wind tunnel under controlled conditions. But data sets are few and far between under the stable, nighttime "F" stability condition. Consequently the models differ depending upon what data sets are used.

Aristatek, Inc., completed a series of chemical releases at the Nevada Test Site under a variety of meteorological conditions ranging from the neutral "D" to the stable "F" stability. The chemical was released and the air concentrations in the chemical cloud was measured by a complex array of sensors placed downwind. Various structures were in the cloud path mimicking conditions which might occur at an industrial complex such as a refinery. Data sets taken under neutral or "D" stability conditions were easy to characterize. The "F" nighttime stability was much more difficult, the data collected was very much dependent upon micrometeorology. There can be a "near F" condition where there was enough local turbulence to disperse the chemical cloud, and a "far F" condition where the chemical cloud remained. Also, meteorological conditions were not uniform as the cloud moved from the source.

Therefore, it should not come as a surprise if available models differ under the "F" stability condition. The discrepancy becomes worse as the wind speed decreases. Available models cannot handle the "zero" wind condition.

A small chlorine release incident occurred in Springfield, MA during June 1988 under calm and overcast nighttime conditions. Based on odor reports, the chlorine cloud appeared to move in all directions from the site, bypassing some locations, with no discernable pattern. People within about ¼ mile from the site were evacuated. A couple of days later, on June 19, the release was much greater with an accompanying fire. Under a daytime 8 mph wind condition, the chemical cloud was described as several miles long and only a few city blocks wide.

The concentrations graphed are maximum, centerline concentrations. If a person moves crosswind from the chemical cloud centerline, the concentrations will usually rapidly drop off. But if conditions are calm or a very low wind speed, especially after sunset, conditions are often unpredictable. If the chemical is a dense gas such as chlorine and there is no fire, the person may be advised to seek higher ground.

What can we conclude from this?
- In real accidents responders rarely have all the necessary information required to run a gas dispersion model. Reasonable guesses must be made. One of the biggest unknowns is the release rate to the atmosphere. Usually first responders can't even get close to the site to determine exactly what is happening.
- Reasonable guesses must be made as to the release rate and meteorology. If the responders guess too conservatively (e.g. all of the chemical released at once or within a short period of time), critics may say that the model is too conservative.
- The available popular models generally give similar results under "neutral" atmospheric conditions or under light or moderate wind conditions. There may be major differences under low wind, clear, nighttime conditions.

Modeling the Potential Terrorist Incident

Back to the suspicious package at the sports stadium: The package at a distance looks like an explosive device attached to a bottle containing a liquid. The stadium is emptied. A sensitive gamma radiation counter is available, but there is no elevation in radioactivity as the package is approached. The possibility that package might contain nitroglycerine was brought up. The web site,

lists safe outdoor evacuation distances for explosives taking into account fragmentation from shrapnel or glass. Judging from the size of the bottle and the package, there could be up to 2 kg of explosives, or a safe outdoor evacuation distance of almost 1000 feet. Under protection of a vehicle, responders might safely approach up to 100 feet. But what if the bottle contained a chemical warfare agent Sarin? What is the safe evacuation distance for Sarin, if the bottle explodes releasing all of its contents at once?

1 kg Sarin Release, daytime, 10 mph wind

1 kg Sarin Release, nighttime, low wind, clear skies
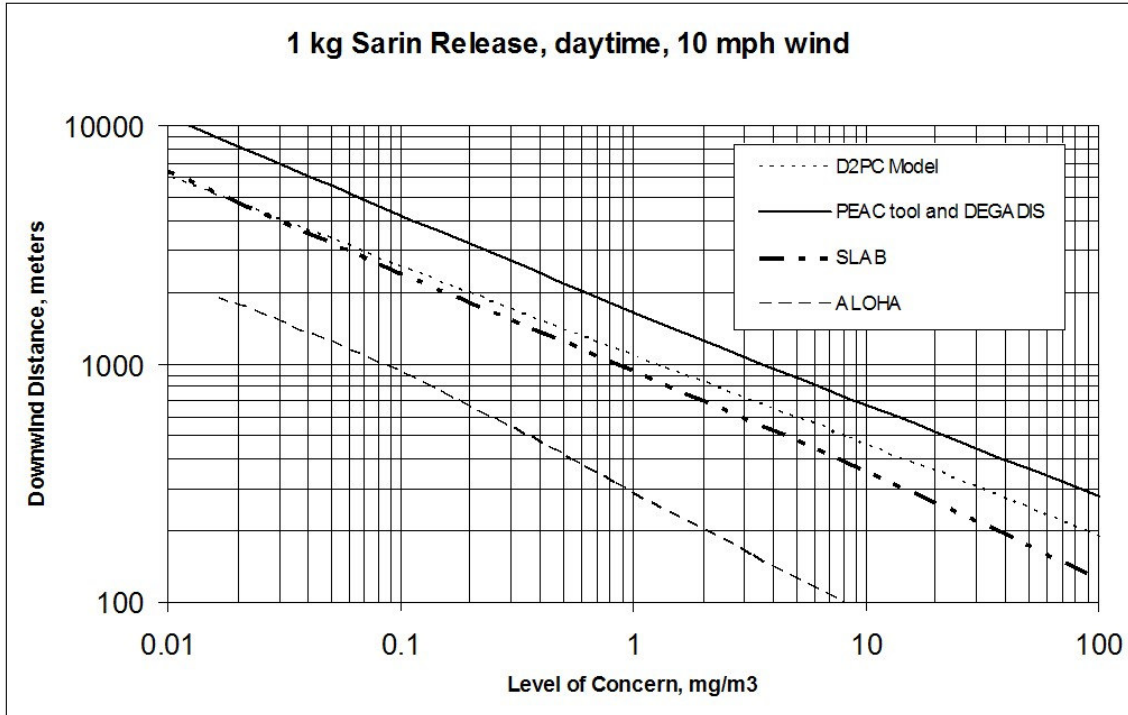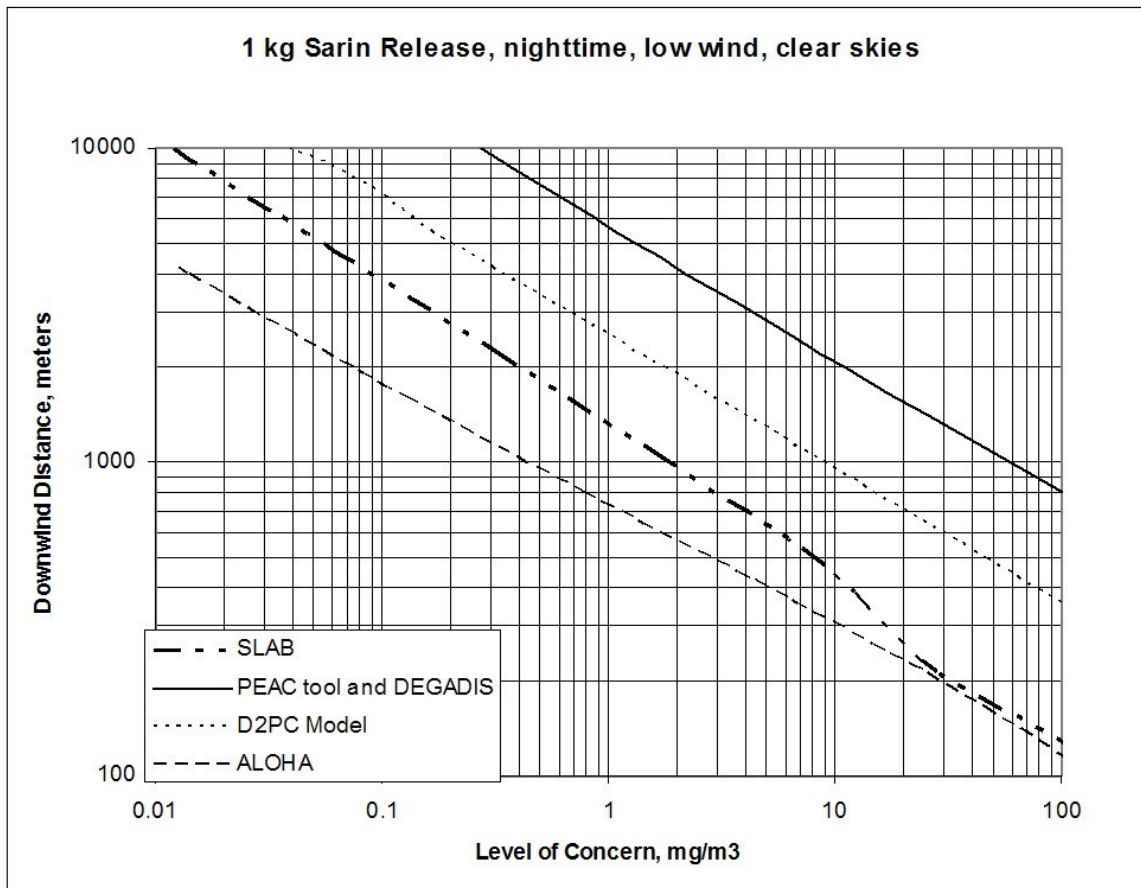
All of the above models were executed in a passive (Gaussian) mode (as opposed to a dense gas mode). The D2PC Model is a Gaussian dispersion model developed by the military for gas dispersion of chemical warfare agents, especially if released from munitions. The reference citation is C. Glenvil Whitacre et al, 1987, Personal Computer Program for Chemical Hazard Prediction (D2PC), CRDEC-TR-87021, U.S. Army Armament Munitions Chemical Command, Aberdeen Proving Ground, MD. The DEGADIS model is documented in an EPA publication, Spicer, T.O., and J.A. Havens, Users Guide for the DEGADIS 2.1 Dense Gas Dispersion Model, EPA-450/4-89-019. 1989.

The models do not predict the same results. The major reason for the differences is in how the models average concentrations when dealing with an instantaneous release, as in an explosion. At one end of the spectrum is the ALOHA model which treats the release as lasting one minute. The other models treat an instantaneous release as lasting a much shorter period, and as such, the peak concentrations within the toxic cloud as it travels downwind are greater. There are also differences in the concentration averaging time, and what data sets are used to calibrate the models.

The 2004 Emergency Response Guidebook lists initial isolation zones and protective action distances for small and large spills of Sarin (when used as a weapon), under daytime and nighttime conditions. For the purpose of the ERG, a small spill is 2 kg and a large spill is 100 kg. "When used as a weapon" implies an instantaneous release as in this example. The initial isolation zone for small spills is defined by a radius of 150

meters in all directions from the incident. The protective action distance (PAD) s 1.7 km (1 mile) downwind for daytime conditions, and 3.4 km (2.1 miles) for nighttime conditions.

What concentration of Sarin should be used as the Level of Concern? An ERPG-2 has not been established for Sarin. The 2004 ERG uses 0.01 times the 1-hour LC_{50} for rats as their Level of Concern, or 0.001 ppm (0.006 mg/m^3). Perhaps most suitable would be the Acute Exposure Guideline Levels (AEGLs are published at the EPA Website, http://www.epa.gov/oppt/aegl/). The U.S. Military with some exceptions has adopted the AEGLs for their military exposure limits for chemical warfare agents. These numbers used by the military are available at:
http://chppm-www.apgea.army.mil/imo/ddb/DMD/TG/TECHGUID/Tg230.pdf . Perhaps most appropriate for a PAD is the Level 2 AEGL, or AEGL-2, defined as:

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.

The AEGLs are exposure time dependent. AEGLs are available for various exposure times (5 minute, 10 minute, 30 minute, 1 hour, 4 hours, and 8 hours). Considering that Sarin was modeled here as an instantaneous release, the toxic cloud is expected to pass quickly. Shelter in place is a viable option. Therefore a 5-minute or 10-minute AEGL-2 is appropriate. The 10-minute exposure time as used by the military is 0.087 mg/m^3 for Sarin. Referring to the graphs presented above, the daytime downwind distance corresponding to 0.087 mg/m^3 Level of Concern ranges from 1 to 4 km depending upon what model is selected, or 2 to over 10 km for clear, low wind, nighttime conditions.

Fortunately, Sarin will hydrolyze with water vapor in the air. None of the models available consider the destruction of Sarin by water vapor or sunlight. Therefore the concentrations far downwind from the incident should be less than that predicted by any of the models. How much less is difficult to say, but this should be taken into consideration for any model predictions over a couple of miles.

Shelter in place is certainly an option and should be considered for distances away from the stadium location.

Protective foams and bleach solutions may be a viable action to mitigate or reduce the dispersal of the liquid in the container if an explosion takes place.

What can we conclude from the Sarin example?
- There are many unknowns when confronting a suspicious package. Responders must consider all possible situations and develop a plan for possible situations which may occur.
- Instantaneous or sudden releases are more difficult to model than the constant release rate situation. The release time, how the material is dispersed at the source, and downwind concentration averaging times all come into play when using a model. Default situations may be built into the model. Therefore available models will give different answers depending upon how the model is structured.

- Levels of Concern will be different for an instantaneous or short duration release compared with a steady state, continuous release. If there is any wind, the toxic cloud will travel downwind and pass quickly. Similarly if there is solar heating of the ground the toxic cloud will rapidly disperse.. Therefore, the Level of Concern can be based on a short exposure time, for example, the 10-minute AEGL-2. For steady state conditions, or any release under clam nighttime conditions with a clear sky, an ERPG-2 (or 1-hour AEGL-2 if ERPG-2 is unavailable) may be more appropriate. Shelter-in-place may be a viable option for short duration releases.