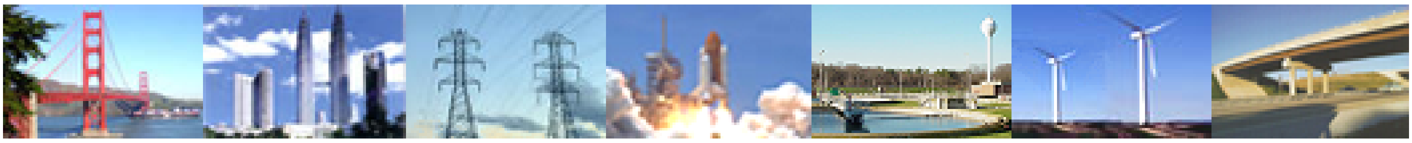

PDHonline Course K105 (2 PDH)

Worst Case Scenario Calculation

Instructor: Robert B. Coulter, PE

2012

PDH Online | PDH Center

5272 Meadow Estates Drive
Fairfax, VA 22030-6658
Phone & Fax: 703-988-0088
www.PDHonline.org
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Worst Case Scenario Calculation

- Calculation of Worst Case Scenario (WCS) required for applicable sources per EPA 40 CFR part 68 (Chemical Accident Prevention rule or CAP)
- WCS is the release of the largest quantity of a listed substance from a process
- Also, the WCS is the release that results in the greatest distance to the endpoint for the listed substance
- This course shows how to calculate WCS using EPA's Risk Management Program Guidance for Offsite Consequence Analysis (referred to as OCAGD in this course)

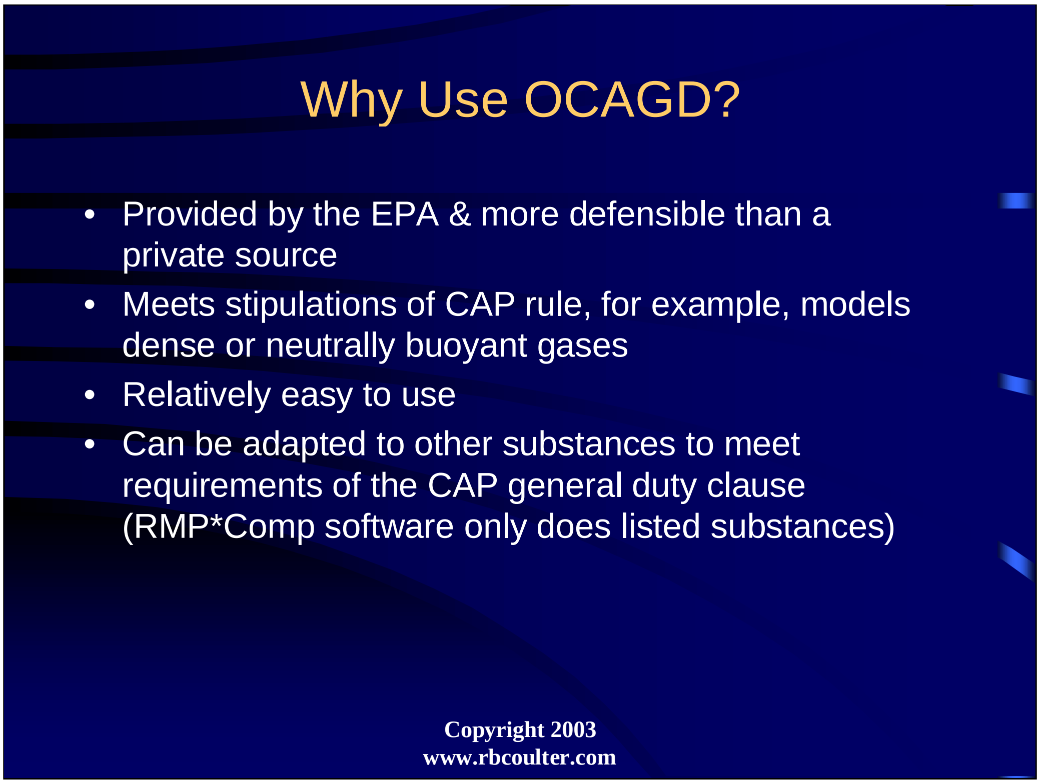
The calculation of Worst Case Scenario (WCS) is required for applicable stationary sources per EPA's rule in 40 CFR part 68 (Chemical Accident Prevention rule or CAP - see the link below)

The WCS for a process or vessel is the release of the largest quantity of a listed substance from that vessel or process.

The WCS for a source is that release from a source process that results in the greatest distance to the endpoint for a listed toxic or flammable substance.

The intent of modeling the WCS is to define the extent, or distance to an endpoint, of a toxic release or explosion. The goal is to aid the owner/operator of the source & local emergency responders in implementing prevention & mitigation measures.

This course shows how to calculate WCS using EPA's Risk Management Program Guidance for Offsite Consequence Analysis (referred to as OCAGD in this course). This document is available, for free, from the EPA. See the link below.



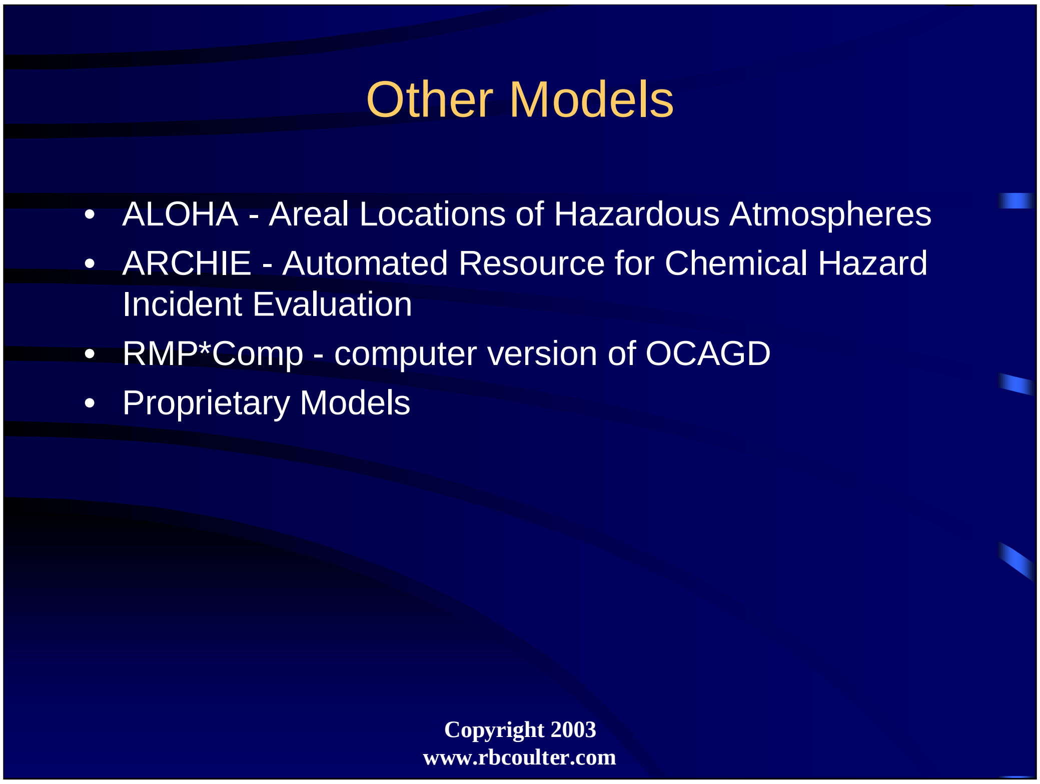
The EPA developed OCAGD specifically for the owners & operators of CAP regulated facilities as a fast & reasonably accurate means of assessing the extent of harm caused by the release of CAP listed substances. Although owners or operators are not required to use this method, OCAGD is more defensible if challenged by another party. (Because it is the EPA supported method.)

The method models neutrally buoyant & dense gases which is a specific requirement of the rule. Some other methods model dense gases as neutrally buoyant which would not be acceptable here.

The model is relatively easy to use. Convenient tables are provided to aid in the calculation of release rates & endpoints.

Also, the method is easily adapted to other substances to meet requirements of the CAP general duty clause. The CAP general duty clause requires all owners (even those without CAP listed substances) to implement CAP measures if they have extremely hazardous substances, if released, could cause harm to the environment or the public. (RMP*Comp software only does listed substances)

See the link below for more information on the CAP general duty clause.



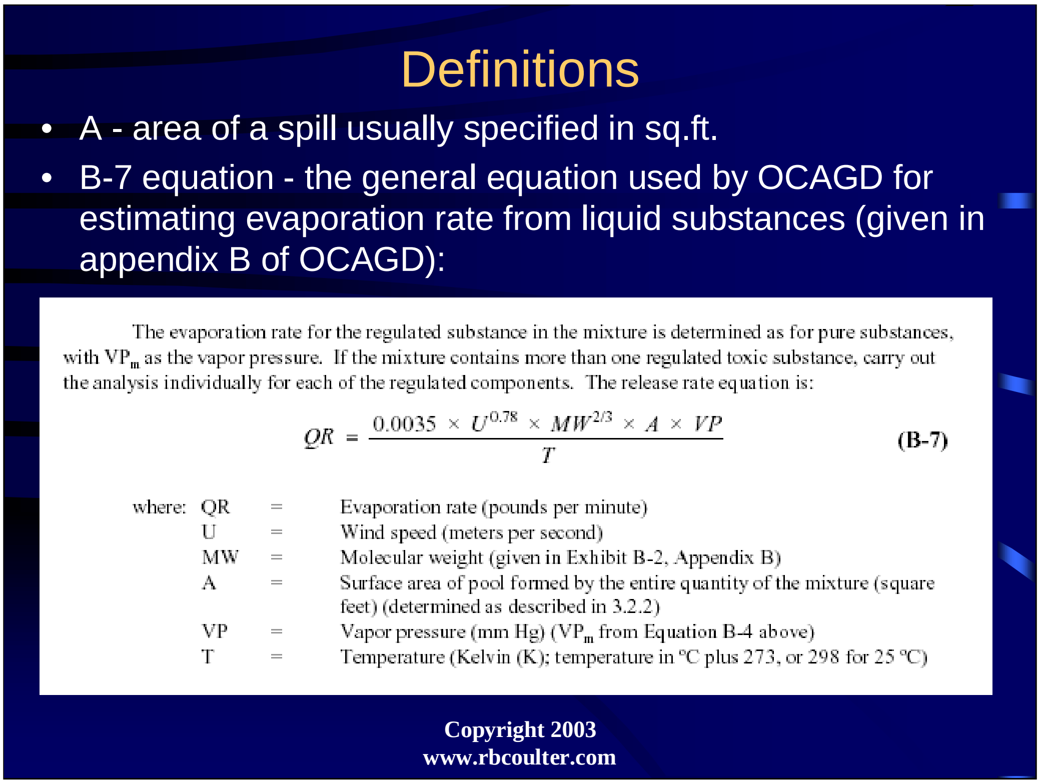
The following are other methods that may be used for WCSs.

ALOHA - This is Areal Locations of Hazardous Atmospheres. It was developed by the NOAA & the EPA and is available for free from the EPA (see link below). Usually included as part of the CAMEO suite of software. Its emphasis is more for emergency response assistance (as opposed to emergency pre-planning). It has a large database of chemicals & is user-friendly. It does not do explosions & only models to endpoints no further than about 6 miles.

ARCHIE - This is the Automated Resource for Chemical Hazard Incident developed by Hazmat America Inc. for FEMA. It's currently available through the DOT. (See the link below.) The software is more than 10 years old & runs under a DOS prompt. It appears suitable for neutrally buoyant toxic release dispersions (not dense) & fire/explosion modeling .

RMP*Comp - This is the programmed version of OCAGD and is a very fast way to model the LISTED substances in the CAP rule (see link below). It does not have much value in complying with the general duty clause.

Proprietary Models - There are a number of software packages available from private companies with varying degrees of sophistication. They can be expensive, and the buyer must assume the responsibility of their suitability for complying with the CAP rule.



A - Is the area of a spill usually specified in sq.ft.

B-7 equation - This is the general equation used by OCAGD for estimating evaporation rate from liquid substances (given in appendix B of OCAGD).

Note: Where examples are used in this course that show calculations, the math notation is given as though it were in a spreadsheet cell or as in most BASIC programming languages. That is * symbol is multiplication, the / symbol is division & the ^ symbol is exponentation.

Definitions

- C-2 equation - the general equation used by OCAGD for estimating the distance to the 1 psi overpressure point resulting from a flammable substance(s) explosion (given in appendix C of OCAGD):

$$D_{mi} = 0.0081 \times \left(0.1 \times W_{lb} \times \frac{HC_f}{HC_{TNT}}\right)^{1/3} \qquad \textbf{(C-2)}$$

where: D_{mi} = Distance to overpressure of 1 psi (miles)
W_{lb} = Weight of flammable substance (pounds)

These equations were used to derive Reference Table 13 for worst-case distances to the overpressure endpoint (1 psi) for vapor cloud explosions.

Hc_f = Heat of combustion of flammable substance (kilojoules per kilogram) (listed in Exhibit C-1)
HC_{TNT} = Heat of explosion of trinitrotoluene (TNT) (4,680 kilojoules per kilogram)

C-2 equation - This is the general equation used by OCAGD for estimating the distance to the 1 psi overpressure point resulting from a flammable substance(s) explosion (given in appendix C of OCAGD):

Definitions

- CAP - EPA's Chemical Accident Prevention Provisions - 40 CFR Part 68
- DF - Density Factor, substance specific parameter used by OCAGD
- Endpoint or Toxic Endpoint - the level of concern (concentration) in the atmosphere (usually expressed as mg/l) of a listed toxic substance
- HC - Heat of combustion usually expressed as KJ/kg
- LFA - Liquid Factor Ambient, substance specific parameter
- LFB - Liquid Factor Boiling , substance specific parameter
- LRG - Liquefied refrigerated gas

CAP - This is the EPA's Chemical Accident Prevention Provisions - 40 CFR Part 68 as mentioned previously

DF - Density Factor, substance specific parameter used by OCAGD. Purpose is to estimate the size of an unmitigated pool.

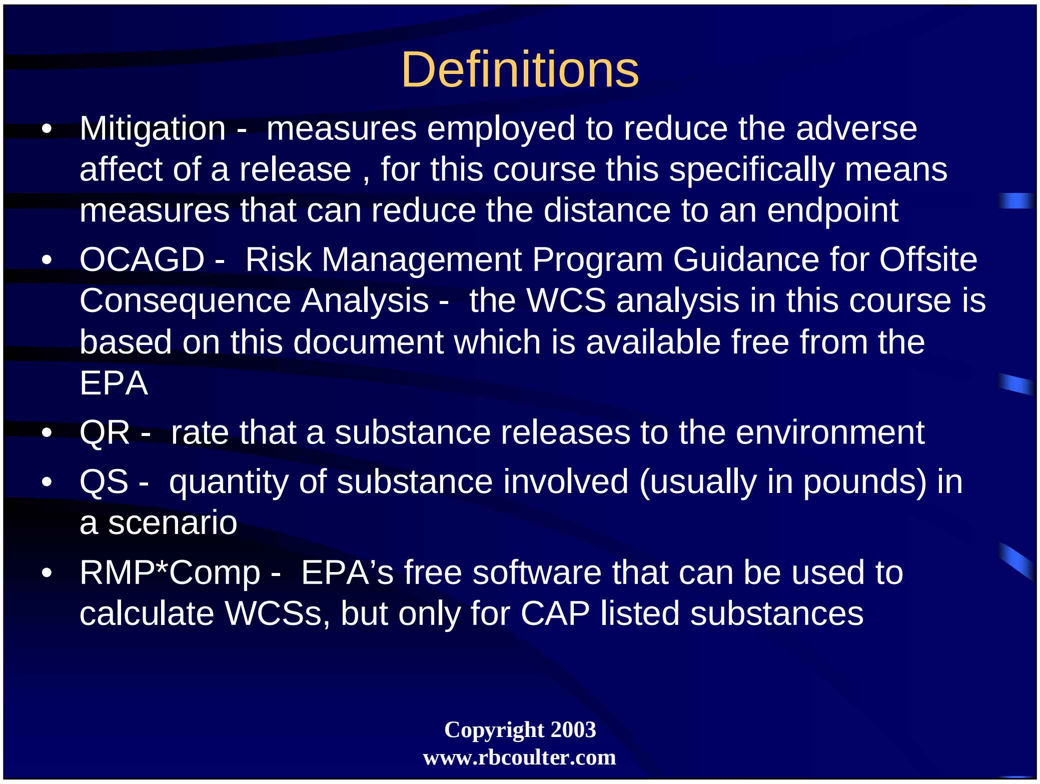
Endpoint or Toxic Endpoint - the level of concern (concentration) in the atmosphere (usually expressed as mg/l) of a listed toxic substance. It represents the outside limit of an impacted (affected) zone of a toxic WCS.

HC - This is the heat of combustion usually expressed as KJ/kg. It's used in explosion modeling.

LFA - Liquid Factor Ambient, substance specific parameter

LFB - Liquid Factor Boiling , substance specific parameter

LRG - Liquefied refrigerated gas - They are specifically noted here because they are usually modeled as liquids (not gases)



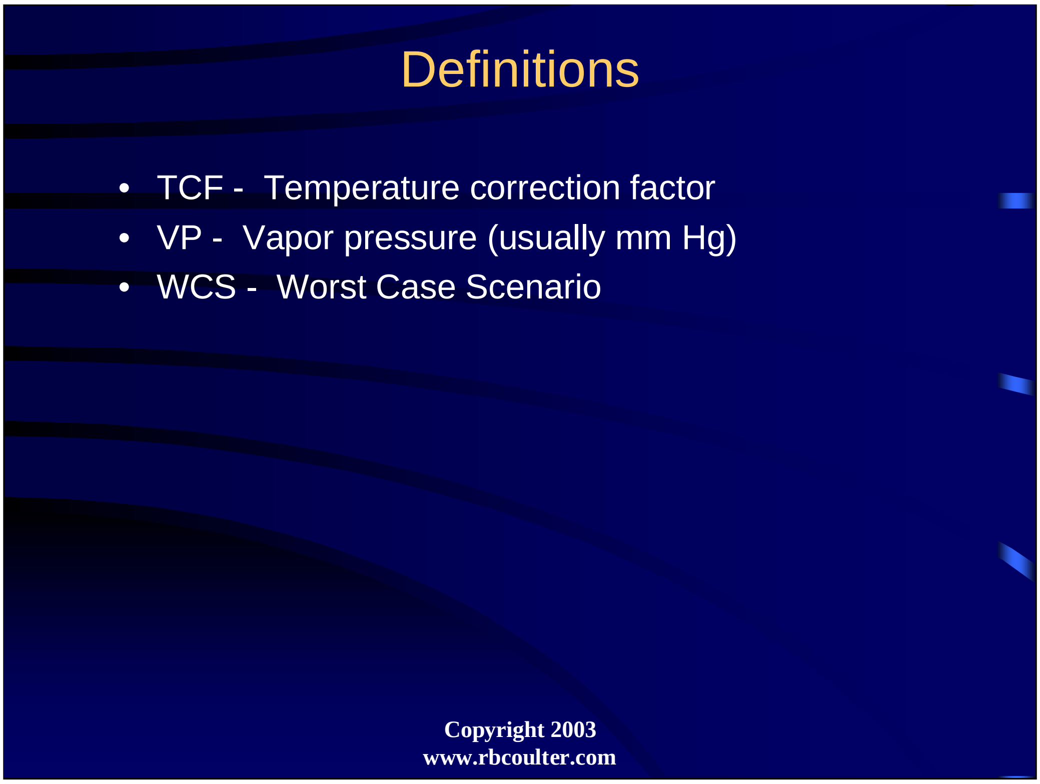
Mitigation - These are the measures employed to reduce the adverse affect of a release , for this course this specifically means measures that can reduce the distance to an endpoint or level of concern. For WCSs, only passive mitigation is considered. Passive mitigation is usually fixed structures, buildings or dikes.

OCAGD - This is EPA's Risk Management Program Guidance for Offsite Consequence Analysis - The WCS analysis in this course is based on this document which is available free from the EPA. See the link below.

QR - This is the rate that a substance releases to the environment.

QS - This is the quantity of substance involved (usually in pounds) in a scenario. Do not confuse this with the release rate (QR). For example, a WCS involving a liquid spill of 20,000 lbs would assume that the 20,000 lbs is spilled IMMEDIATELY. The QR, or release rate, is the evaporation rate from the spill.

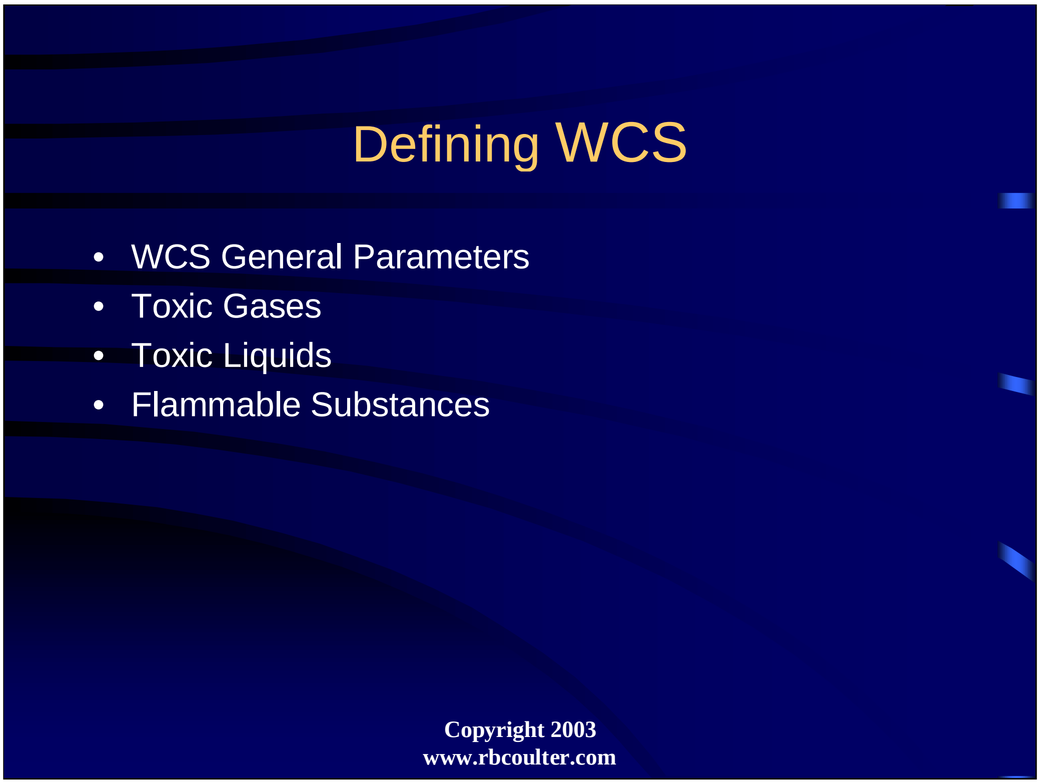
RMP*Comp - EPA's free software that can be used to calculate WCSs, but only for CAP listed substances (as discussed earlier)



TCF - Temperature correction factor - A factor used to correct the release rate (calculated at 25 C) so that it is applicable to the correct release temperature.

VP - This is the vapor pressure (usually mm Hg).

WCS - Worst Case Scenario (as discussed earlier)



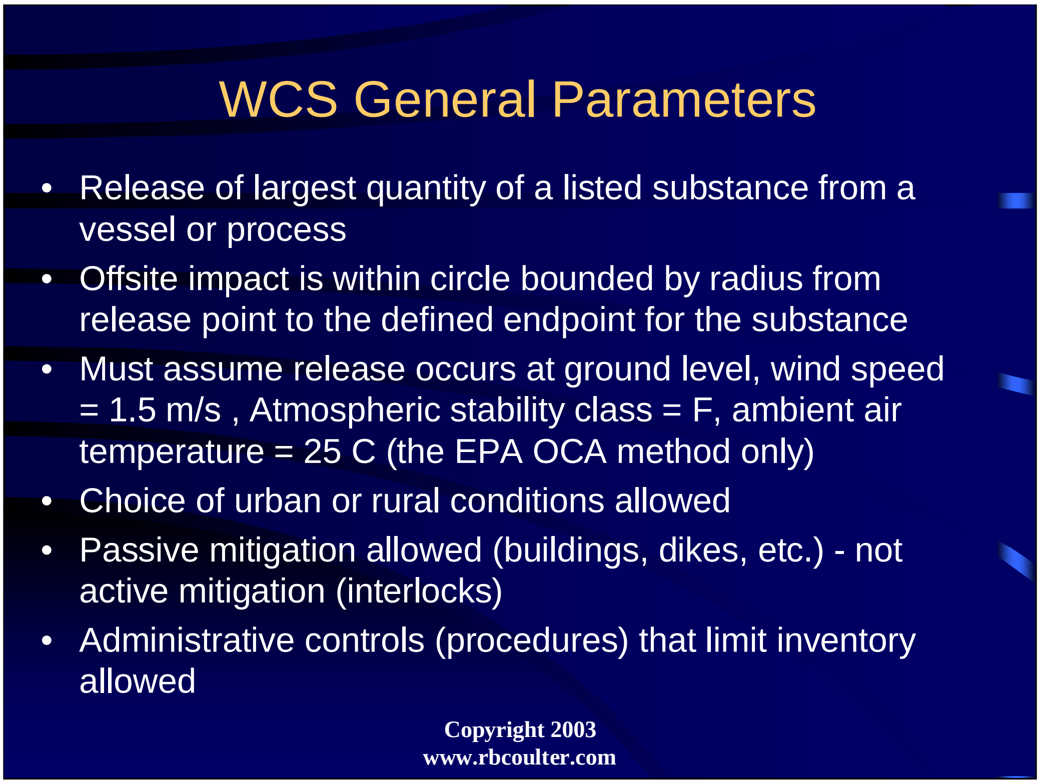
In the next series of slides, we will discuss in more detail the definition of a WCS. The sections to be discussed are:

WCS General Parameters

Toxic Gases

Toxic Liquids

Flammable Substances



As noted earlier, the WCS is the release of the largest quantity of a listed substance from a vessel or process.

The purpose of doing a WCS analysis is to determine the offsite impact “distance to endpoint”. The offsite impact is defined within the circle bounded by the radius starting from the release point to the specified endpoint for the substance.

The WCS analysis must assume the release occurs at ground level, the wind speed = 1.5 m/s & the atmospheric stability class = F. The ambient air temperature = 25 C which is only allowed for the EPA OCA method.

There is a choice of urban or rural conditions. Urban conditions have many obstructions in the way of a plume. Rural conditions have little or no obstructions.

Passive mitigation is allowed (buildings, dikes, etc.). Active mitigation (interlocks) are not allowed. For example, the reduction of the release rate that could occur from the use of an automatic foam blanketing system would not be allowed.

Administrative controls (procedures) that limit inventory are allowed. For example, policies that limit a tank to being stored only half full are acceptable.

Toxic Gases

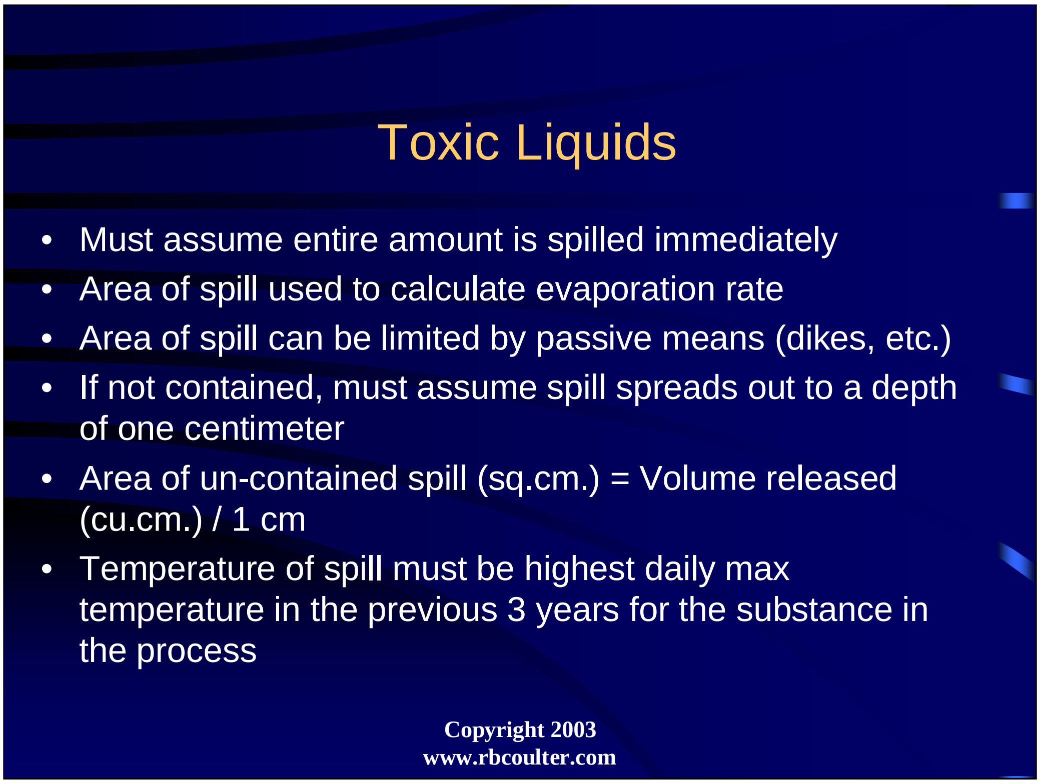
- Listed substances that are gases at 25 C
- However, gases liquefied by refrigeration (LRG) may be modeled as liquids
- Release to atmosphere assumed to occur within 10 minutes (except LRG)
- LRG modeled as liquid releases at normal boiling point

These are listed substances that are gases at 25 C

Also, gases that liquefied by refrigeration (LRG) may be modeled as liquids. This is because these fluids would not be expected to exceed their normal boiling point temperatures if released. Their evaporation rates would be similar to boiling liquids.

Gases are assumed to be released to the atmosphere within 10 minutes (except LRG as noted above)

LRG modeled as liquid releases at normal boiling point (as mentioned)



The WCS analysis must assume the entire amount is spilled immediately.

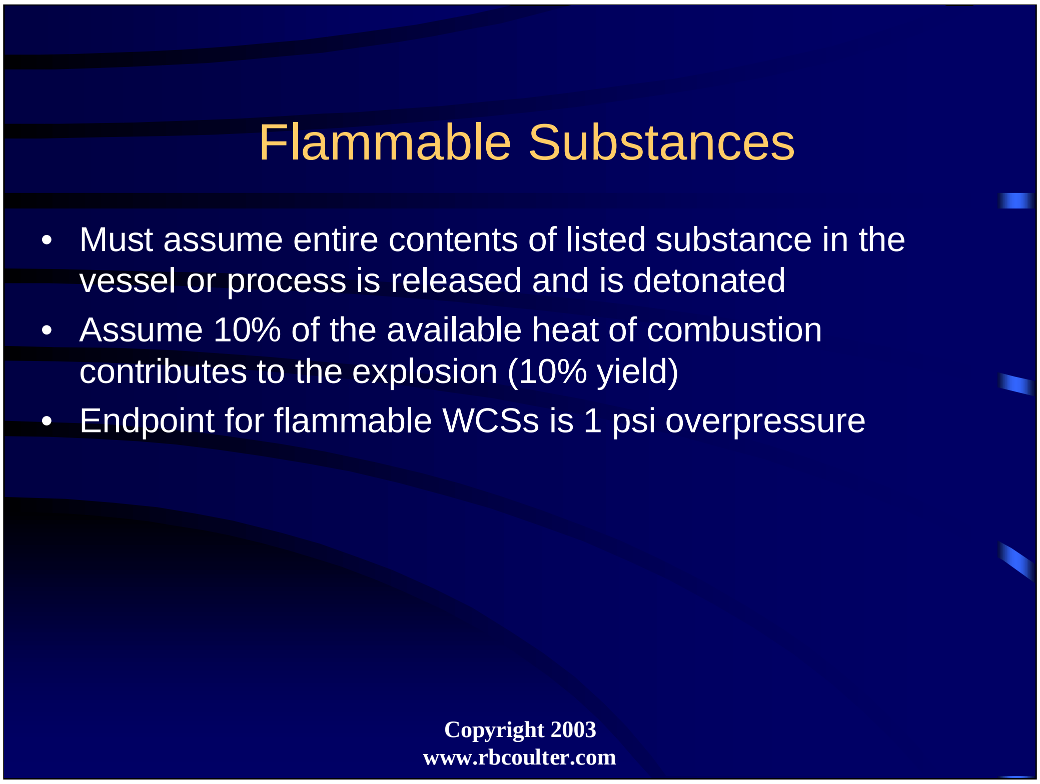
The area of the spill is used to calculate evaporation rate or release rate (QR)

The area of the spill can be limited by passive means (dikes, etc.)

If the spill is not contained, it must be assumed that the spill spreads out to a depth of one centimeter. If this is done then the:

Area of the uncontained spill (sq.cm.) = the Volume released (cu.cm.) / 1 cm

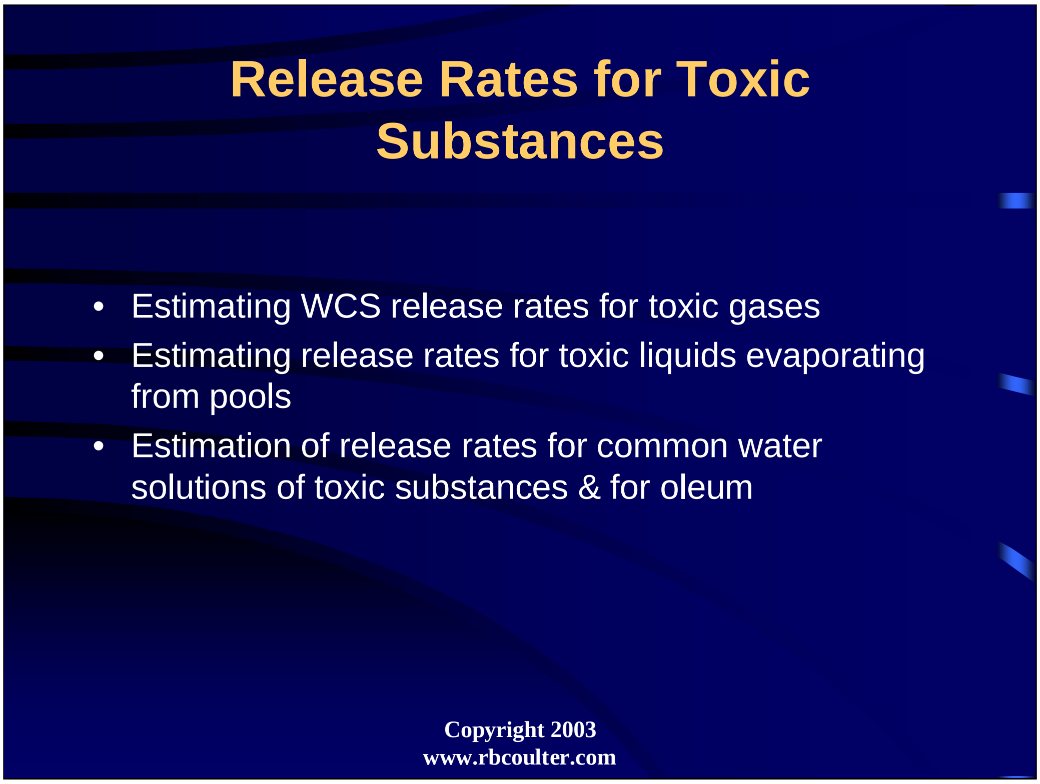
The temperature of the spill must be the highest daily max temperature in the previous 3 years for the substance in the process. Note this is not the outside air temperature which can be assumed to be 25 C.



Flammable listed substances must assume the entire contents of the listed substance in the vessel or process is released and is detonated.

Assume that 10% of the available heat of combustion contributes to the explosion (10% yield)

The endpoint for flammable WCSs is 1 psi overpressure.

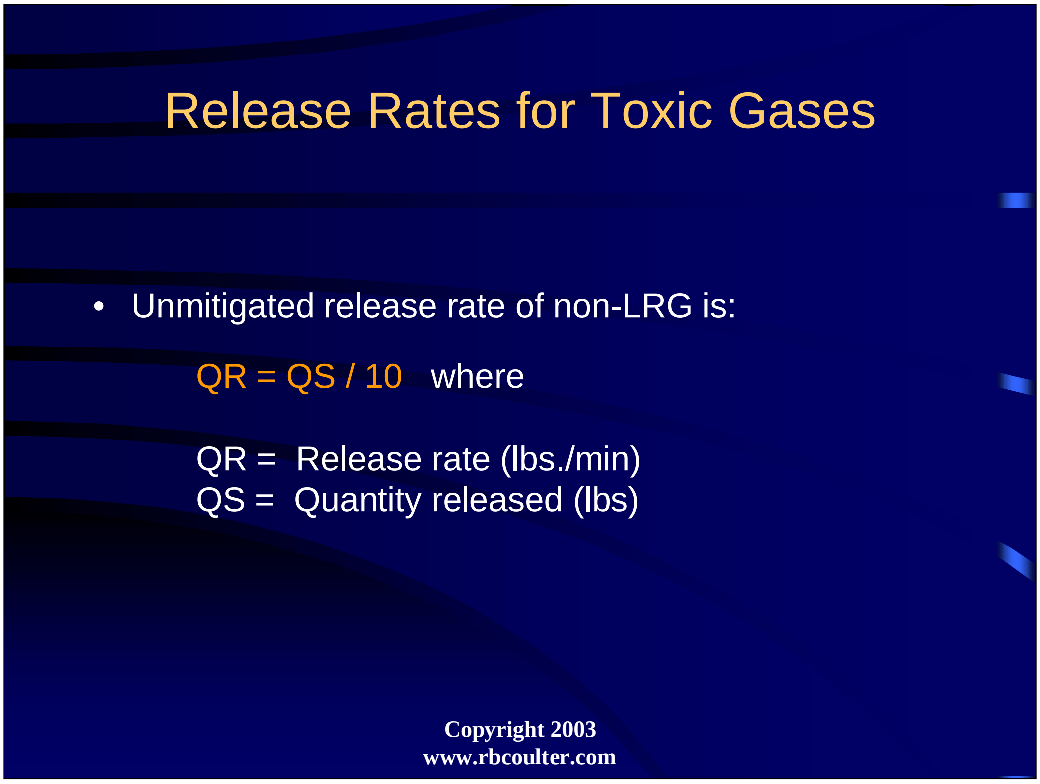


In this section the method for Estimating WCS release rates for toxic substances will be discussed. Release rates for toxic substances need to be determined in order to compute the toxic endpoint distance. Higher release rates increase the distance to endpoint. There are three main categories of toxic substance releases for which a release rates needs to be determined:

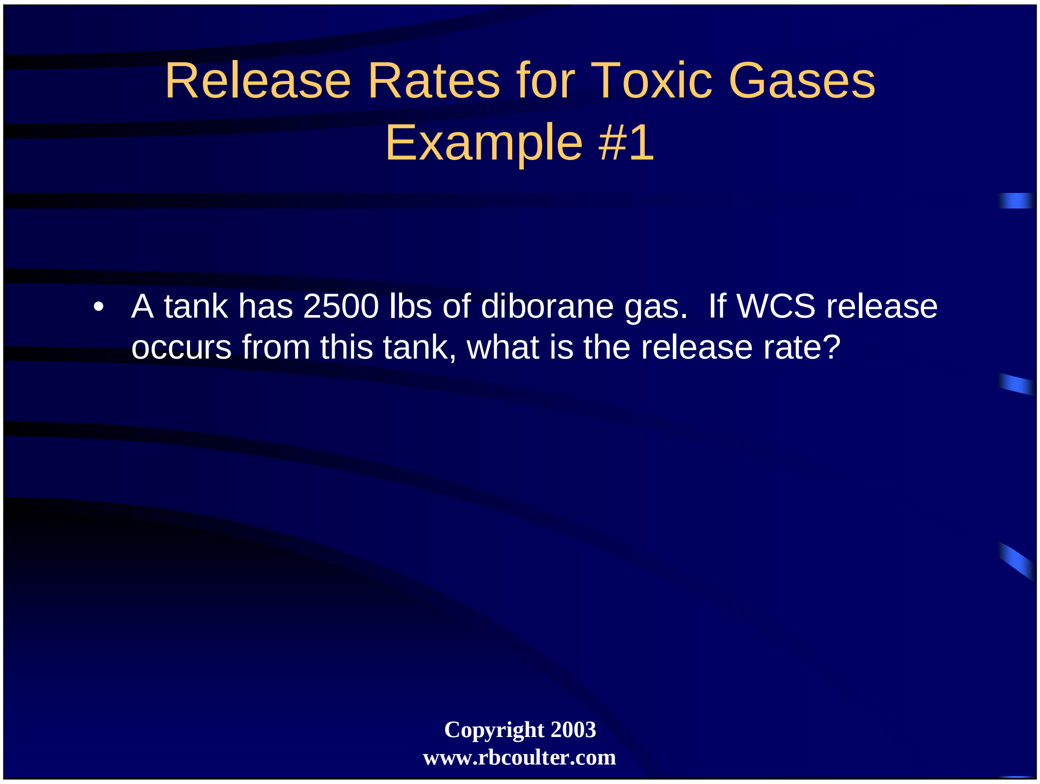
Estimating release rates for toxic gases

Estimating release rates for toxic liquids evaporating from pools

Estimation of release rates for common water solutions of toxic substances & for oleum

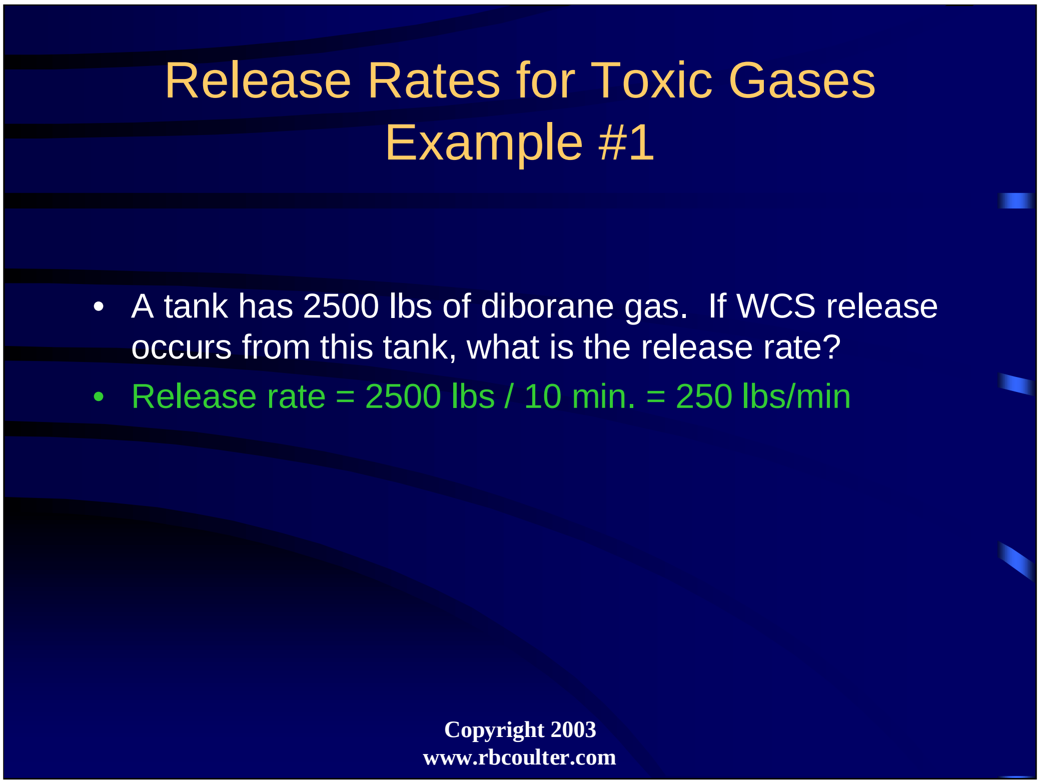


Toxic gases are those substances that would be gases and 25 C & atmospheric pressure. LRG are not included here because they would normally behave as liquids if released. A toxic gas might be stored as a compressed gas, uncompressed gas or compressed liquid. In either of these gases, the guidance requires that the release rate be computed by assuming that the entire contents is released to the environment (atmosphere) in ten minutes. Therefore, the release rate (QR) is the quantity released (QS) divided by 10 minutes.



This can be illustrated with a simple example:

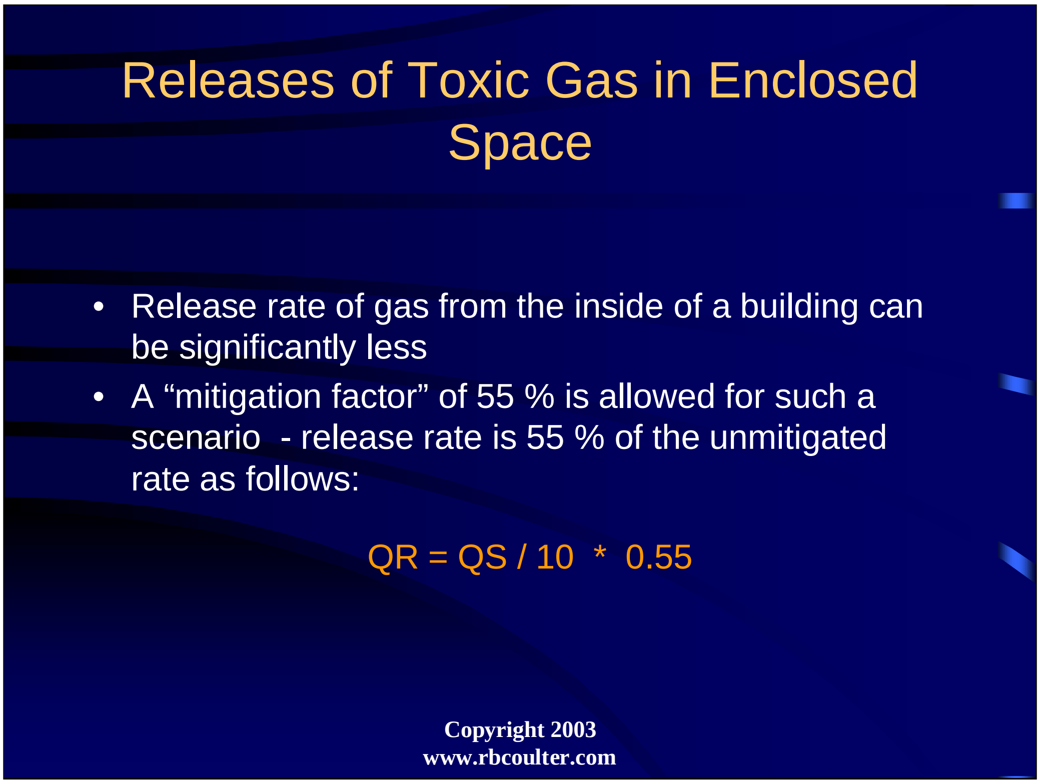
A tank has 2500 lbs of diborane gas. If WCS release occurs from this tank, what is the release rate?



A tank has 2500 lbs of diborane gas. If WCS release occurs from this tank, what is the release rate?

Consulting the OCAGD table exhibit B-1 we find that diborane is listed as a gas. Assuming that it is not stored as an LRG, the release rate must be computed as follows:

Release rate (QR) = 2500 lbs / 10 min. = 250 lbs/min



Release rate of gas from the inside of a building can be significantly less. For this reason the guidance allows for mitigated or reduced release rate if this occurs. The building is assumed to be totally enclosed, that is, windows & doors are not open.

A "mitigation factor" of 55 % is allowed for such a scenario. In other words, the release rate is 55 % of the unmitigated rate as follows:

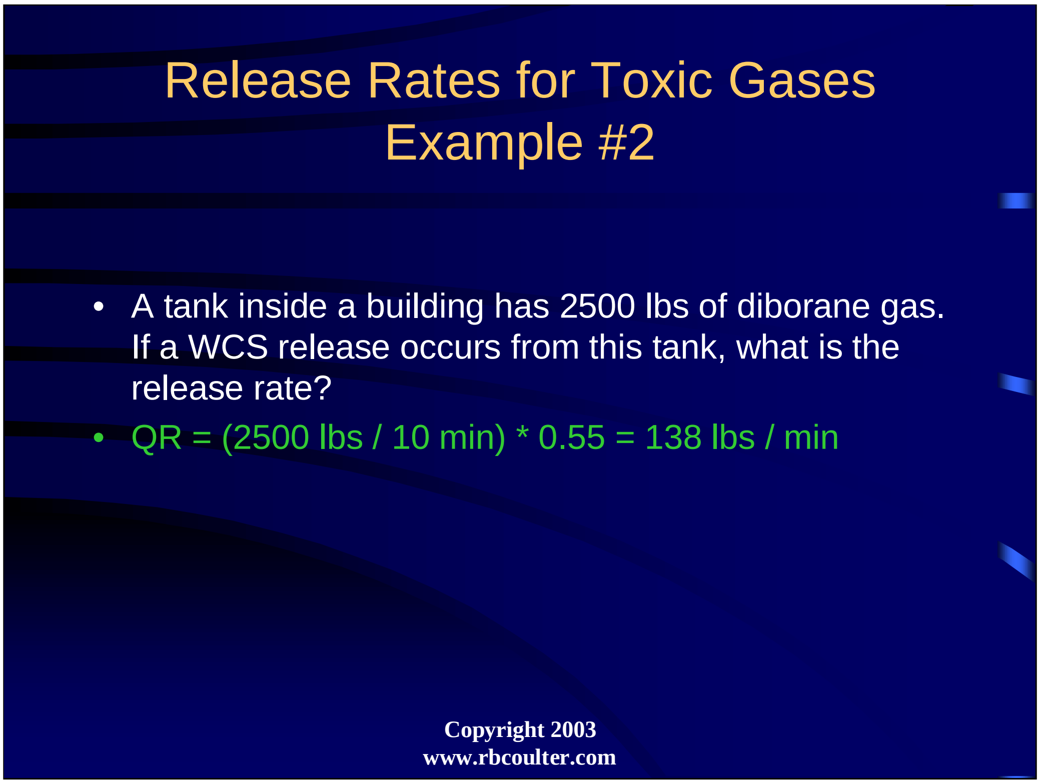
Release rate (QR) = Quantity released / 10 * 0.55

Release Rates for Toxic Gases Example #2

- A tank inside a building has 2500 lbs of diborane gas. If a WCS release occurs from this tank, what is the release rate?

This example illustrates the building mitigation effect of a gas release:

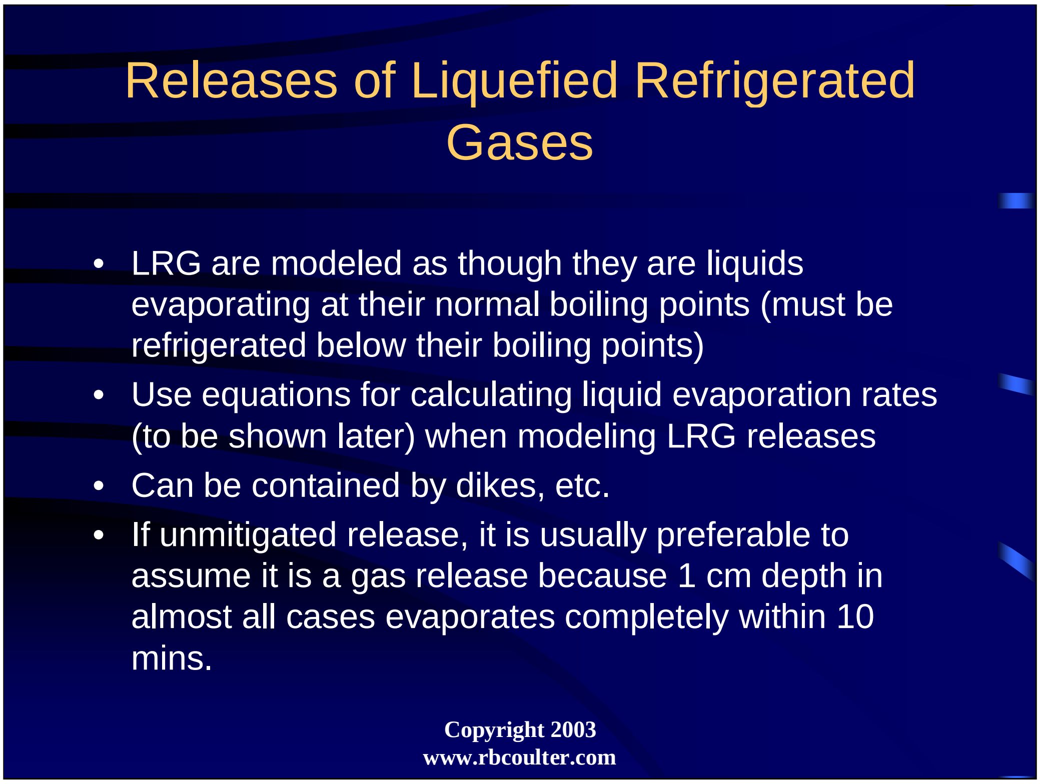
A tank inside a building has 2500 lbs of diborane gas. If a WCS release occurs from this tank, what is the release rate?



A tank inside a building has 2500 lbs of diborane gas. If a WCS release occurs from this tank, what is the release rate?

This is the same as the previous example except that a building mitigation factor is allowed:

QR = (2500 lbs / 10 min) * 0.55 = 138 lbs / min

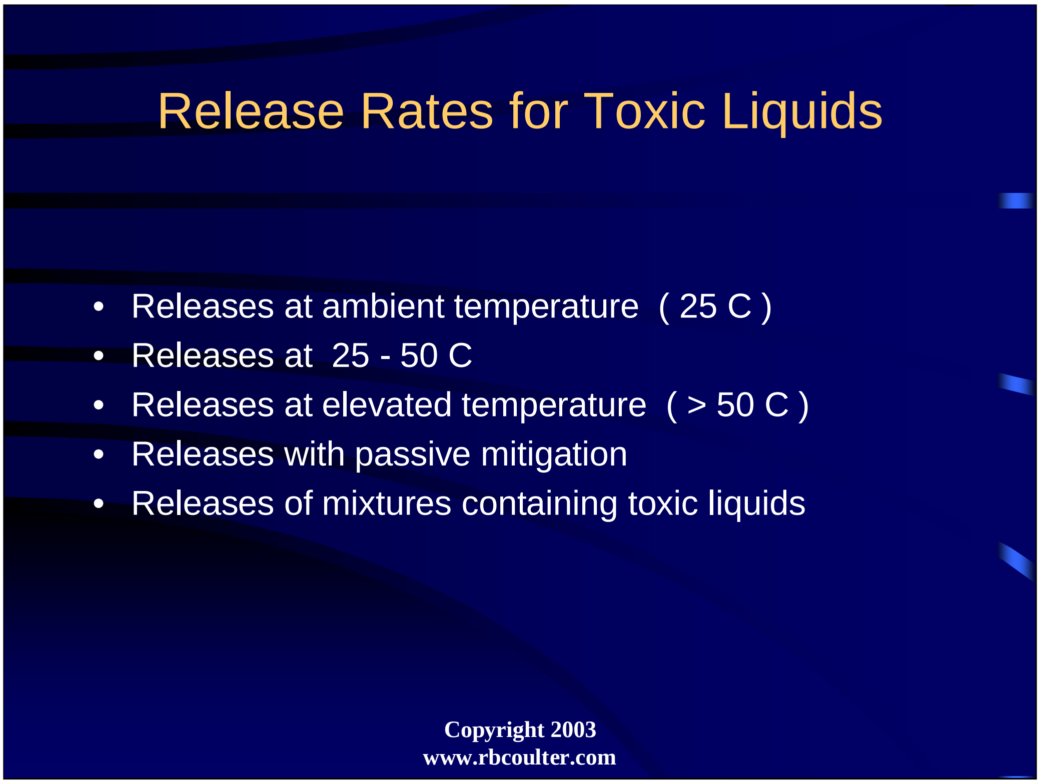


LRG are a treated differently. They can be modeled as though they are liquids evaporating at their normal boiling points (must be refrigerated below their boiling points). To be considered LRG for the purposes of this guidance, the gas must be cooled by refrigeration below its normal boiling point. For example, chlorine stored at - 25 C would not be consider an LRG because it is above its boiling point.

The methods for modeling LRG are similar to liquids. The calculation of the release or evaporation rates from LRG will be shown later when liquid release rates are discussed.

LRG can be contained by dikes and this mitigation effect is allowed.

If unmitigated release, it is usually preferable to assume it is a gas release & simply compute the release rate as though it were a gas (set QR = QS /10) This is because a 1 cm depth of an LRG (in almost all cases) will evaporate completely within 10 mins.



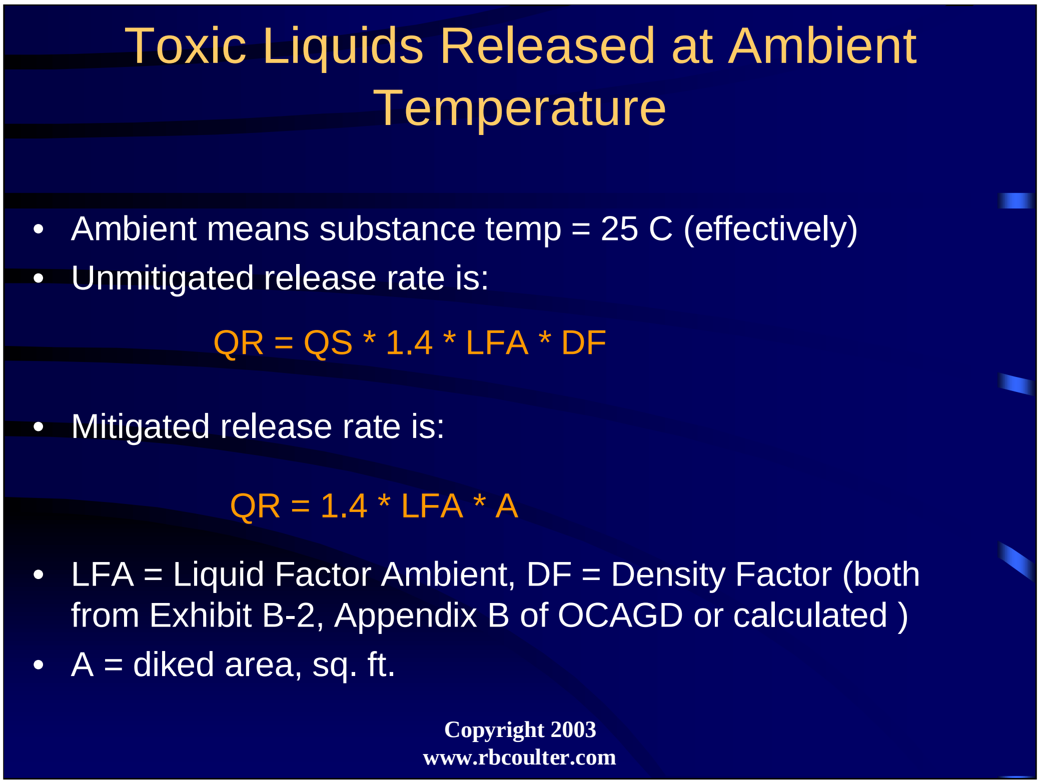
The determination of a WCS toxic liquid release rate is more complicated than that of a non-LRG release.

First we will discuss the calculation of release rates at the substance temperature of 25 C . Later this value is “corrected” to the actual substance temperature by the application of a temperature correction factor for releases that are between 25 - 50 C.

Releases at elevated temperature (> 50 C), boiling liquids and LRGs are modeled with a different equation that employs the use of the substance specific boiling factor (or LFB).

WCS release rates of toxic liquids can be mitigated by dikes and buildings. Mitigation factors for liquids can affect the pool size and the dispersion rate.

Last, we will discuss the calculation of release rates of mixtures containing toxic liquids.



The first step in calculating the release rate from a toxic liquid is to determine the release rate at the ambient substance temp of 25 C . Be sure not to confuse this with the air temperature, which for this guidance method, is assumed to be 25 C. The release rates determined at ambient substance temperature have little use since very few processes would have 25 C as a daily maximum temperature for the past three years. Remember to always correct these release rate values to the actual WCS required temperature.

Unmitigated release rate is determined by the following equation:

QR (release or evaporation rate) = QS (quantity release/spilled) * 1.4 * LFA * DF

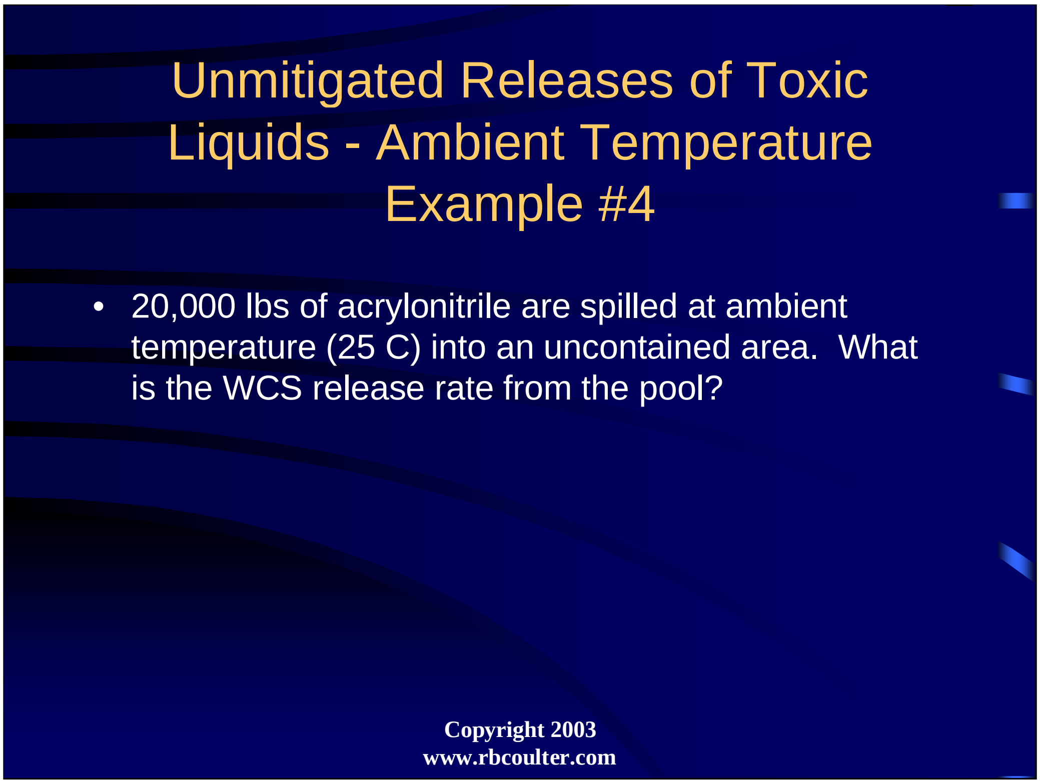
The density factor - QS term is the area of the spill (sq.ft) assuming a 1 cm depth (as previously specified)

Mitigated release rate is:

QR (release or evaporation rate) = A * 1.4 * LFA

The LFA is the Liquid Factor Ambient and DF is the Density Factor (both from Exhibit B-2, Appendix B of OCAGD or calculated per the equations listed in appendix D of OCAGD)

A is the area of the dike in square feet.



This example will show how to calculate the release rate of an unmitigated toxic liquid release.

20,000 lbs of acrylonitrile are spilled at ambient temperature (25 C) into an uncontained area. What is the WCS release rate from the pool?

Unmitigated Releases of Toxic Liquids - Ambient Temperature Example #4

- 20,000 lbs of acrylonitrile are spilled at ambient temperature (25 C) into an uncontained area. What is the WCS release rate from the pool?
- QR = 20,000 * 1.4 * 0.018 * 0.61 = 307 lbs / min
- 0.61 = DF for acrylonitrile
- 0.018 = LFA for acrylonitrile

20,000 lbs of acrylonitrile are spilled at ambient temperature (25 C) into an uncontained area. What is the WCS release rate from the pool?

Since this is an unmitigated release we use the first liquid equation described previously (equation 3-7 in OCAGD).

The QR (release rate) = 20,000 * 1.4 * 0.018 * 0.61 = 307 lbs / min

0.61 = DF for acrylonitrile

0.018 = LFA for acrylonitrile

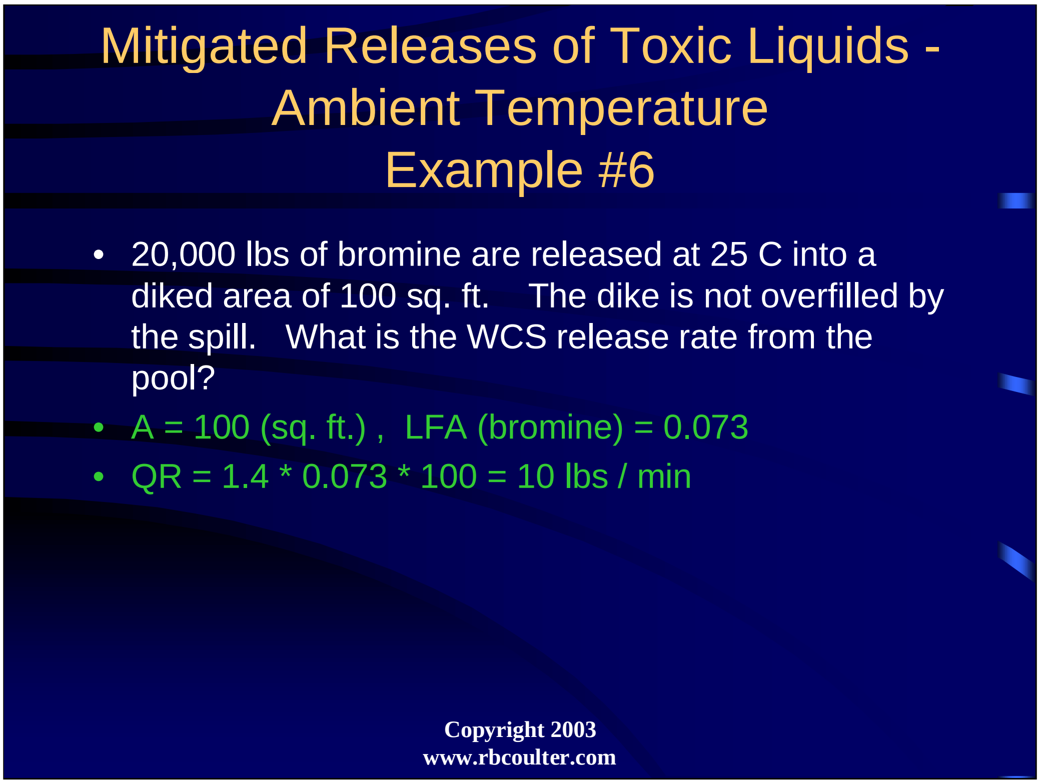
The DF & LFA for acrylonitrile can be found in Exhibit B-2, Appendix B of OCAGD.

Mitigated Releases of Toxic Liquids - Ambient Temperature Example #6

- 20,000 lbs of bromine are released at 25 C into a diked area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate from the pool?

This is an example of a mitigated release of a toxic liquid:

20,000 lbs of bromine are released at 25 C into a diked area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate (or evaporation rate) from the pool?



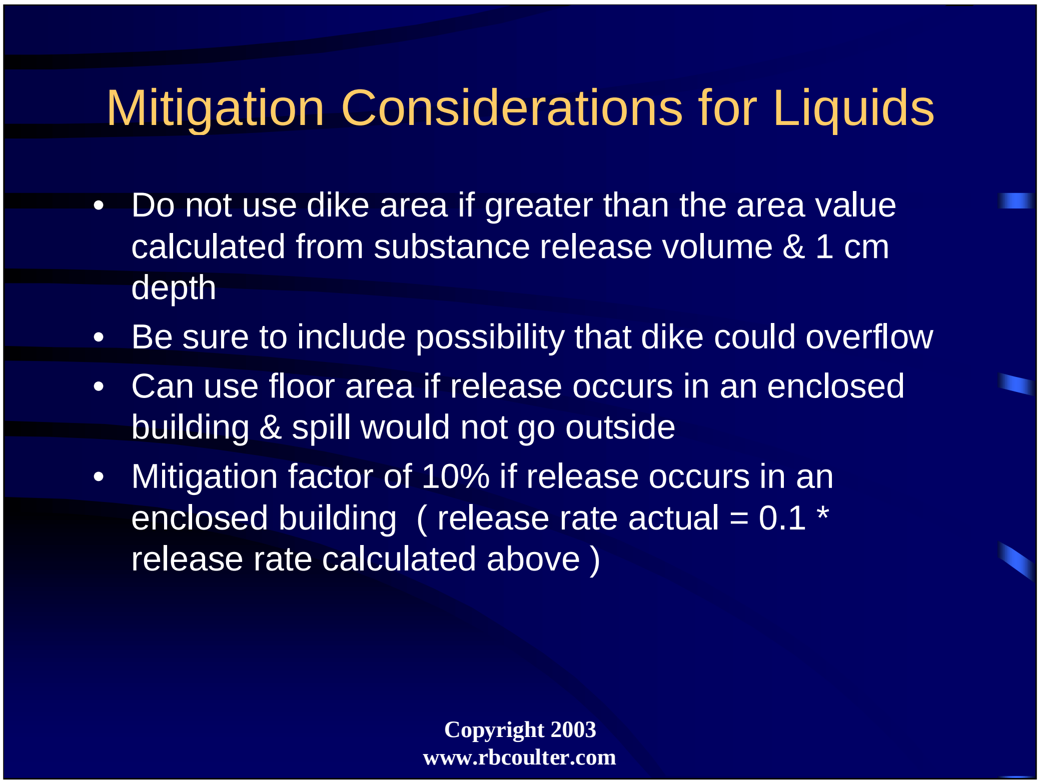
20,000 lbs of bromine are released at 25 C into a diked area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate from the pool?

The area of the dike is given as A = 100 (sq. ft.). The student may want to verify that the depth of the spilled substance is greater than 1 cm.

The LFA for bromine is 0.073 which is obtained from Exhibit B-2, Appendix B of OCAGD. Now use equation 3-8 from OCAGD:

QR (release rate) = 1.4 * 0.073 * 100 = 10 lbs / min

Note: If the substance depth was less than 1 cm then equation 3-7 should be used.

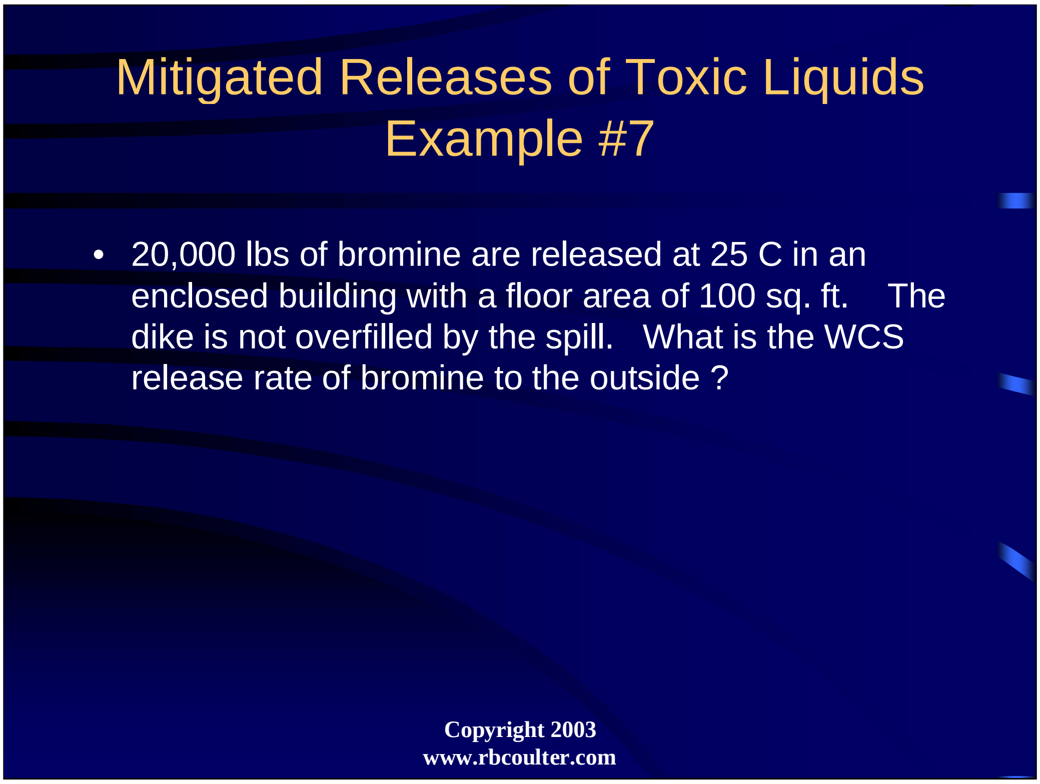


Do not use the dike area if it is greater than the area value calculated from substance release volume & 1 cm depth (In other words if dike area > DF*QS)

Be sure to include the possibility that dike could overflow. If this could happen, be sure to include the area of the spill outside the dike when calculating the spill rate

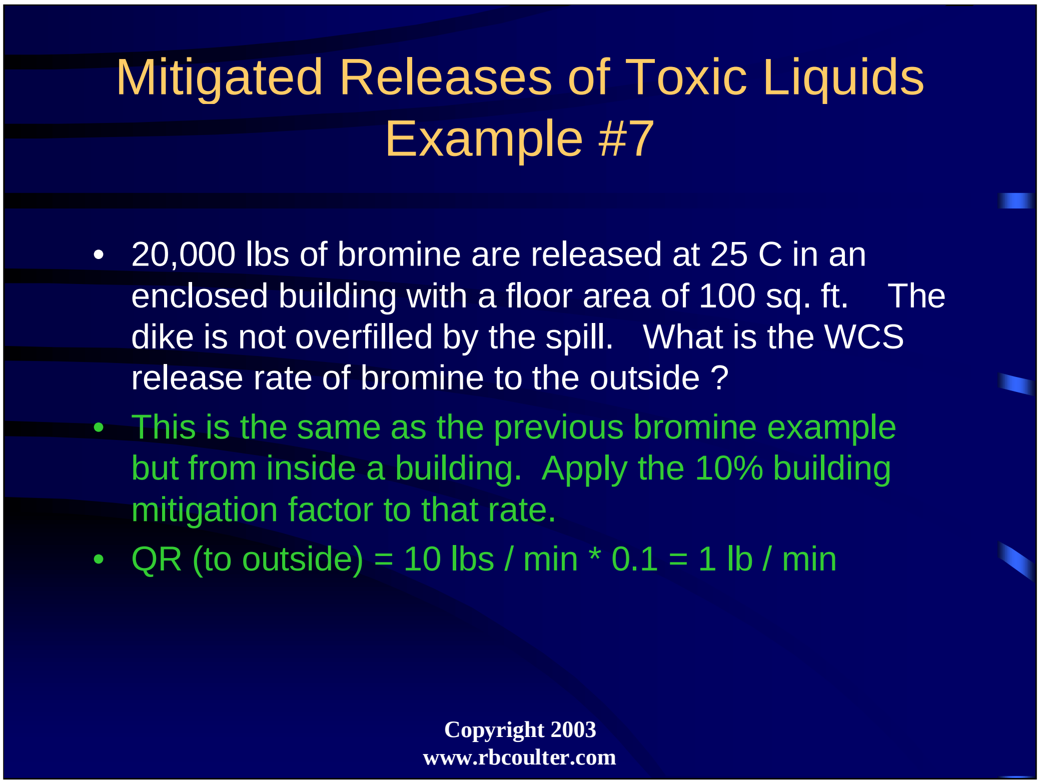
You can use the floor area inside of a building if the release occurs in an enclosed building & the spill would not go outside.

A mitigation factor of 10% can be applied to the release rate calculated for a WCS occurring in an enclosed building. In other words, the actual release rate = 0.1 * release rate as calculated above)



The following example illustrates the mitigation effect of a building:

20,000 lbs of bromine are released at 25 C in an enclosed building with a floor area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate of bromine to the outside ?



20,000 lbs of bromine are released at 25 C in an enclosed building with a floor area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate of bromine to the outside ?

This is the same as the previous bromine example but from it occurs inside a building. Apply the 10% building mitigation factor to the release rate calculated from that example.

QR (to outside) = 10 lbs / min * 0.1 = 1 lb / min

Release Rate Correction for Toxic Liquids Released at Temperatures Between 25 C & 50 C

- If liquid temperature is between 25 C & 50 C then higher temperature must be used - previous examples using ambient temp. not likely to occur
- Temperature Correction Factor (TCF) applied to ambient (25 C) calculated rate values to obtain temp. adjusted values
- TCF given in Exhibit B-4, appendix B of OCAGD or can be calculated (see definitions)
- QRc (temp. corrected) = QR (ambient) * TCF

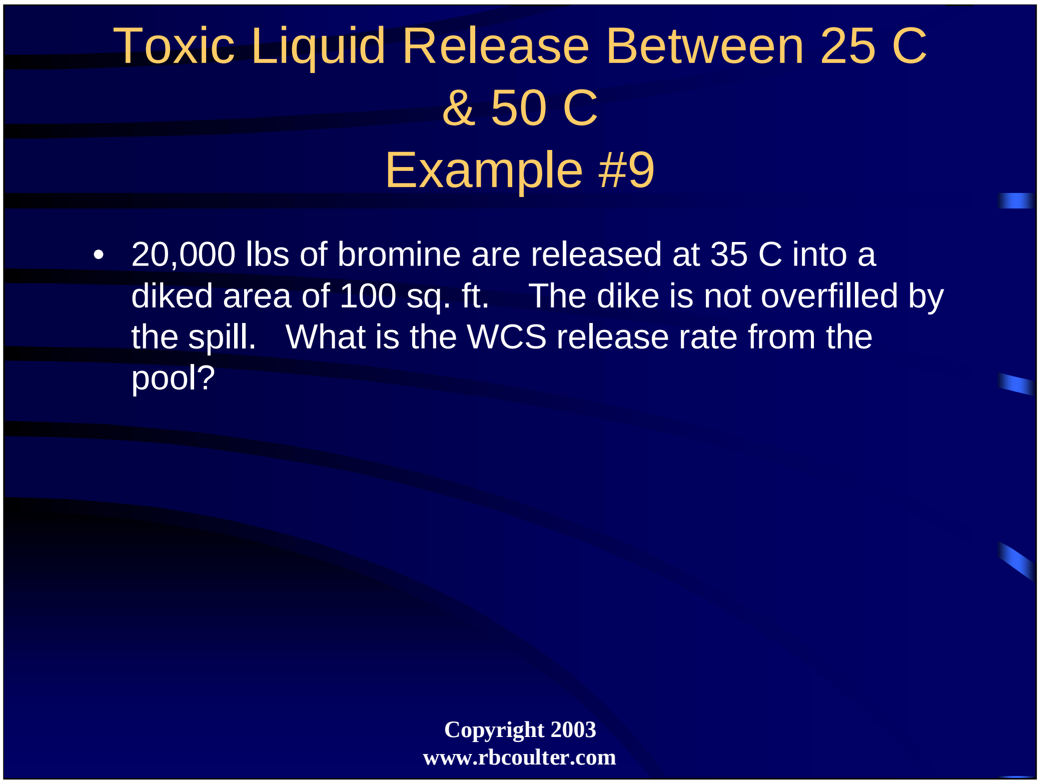
If liquid temperature is between 25 C & 50 C then the higher temperature must be used. The previous examples using the ambient substance temperature of 25 C are, for all practical purposes, academic exercises because relatively few places would have a highest daily maximum temperature over the past three years equal to or less than 25 C.

The temperature corrected release rate is applied by multiplying the ambient release rate by the TCF or temperature correction factor .

The TCFs for various listed substances is given in Exhibit B-4, appendix B of OCAGD. It can also be calculated directly from equation D-5 in appendix D of OCAGD.

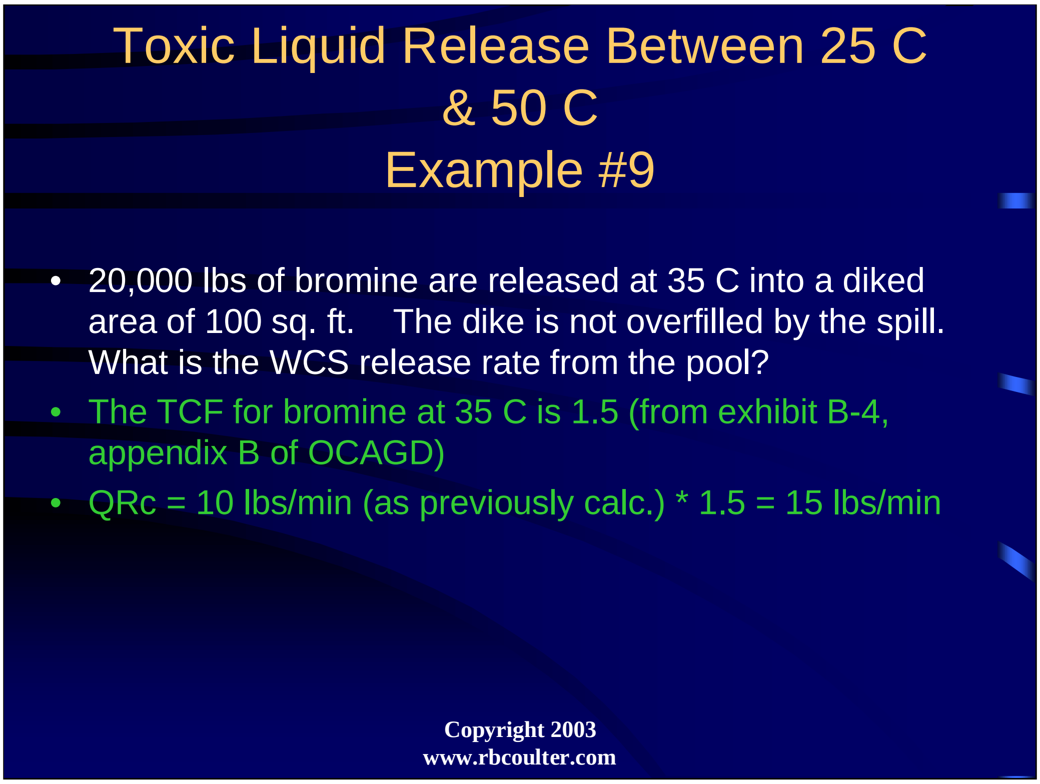
The explicit equation is:

QRc (temp. corrected) = QR (ambient) * TCF



The following example shows how to use the TCF:

20,000 lbs of bromine are released at 35 C into a diked area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate from the pool?

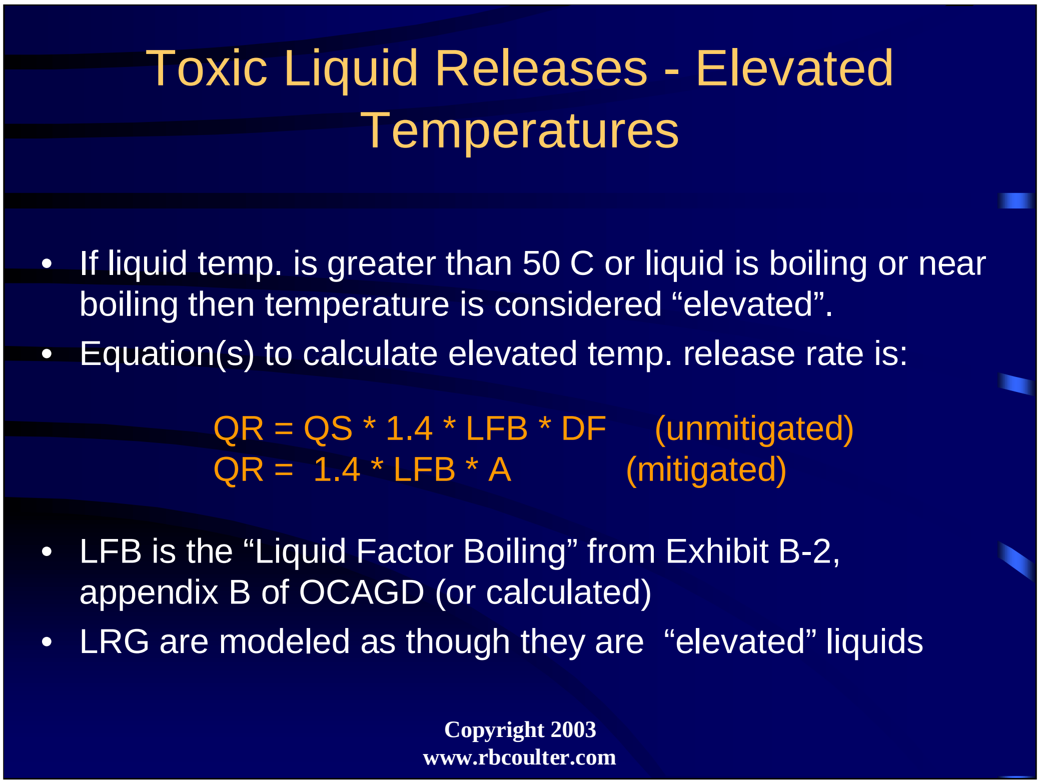


20,000 lbs of bromine are released at 35 C into a diked area of 100 sq. ft. The dike is not overfilled by the spill. What is the WCS release rate from the pool?

Look up the TCF for bromine at 35 C is 1.5 (from exhibit B-4, appendix B of OCAGD) or calculate it directly.

This example is similar to the previous example concerning the spill of bromine into a dike at 25 C. We use the release rate calculated for that example here:

QRc (temperature corrected) = 10 lbs/min (as previously calc.) * 1.5 = 15 lbs/min



If liquid temp. is greater than 50 C or is boiling or near boiling then the temperature is considered “elevated”.

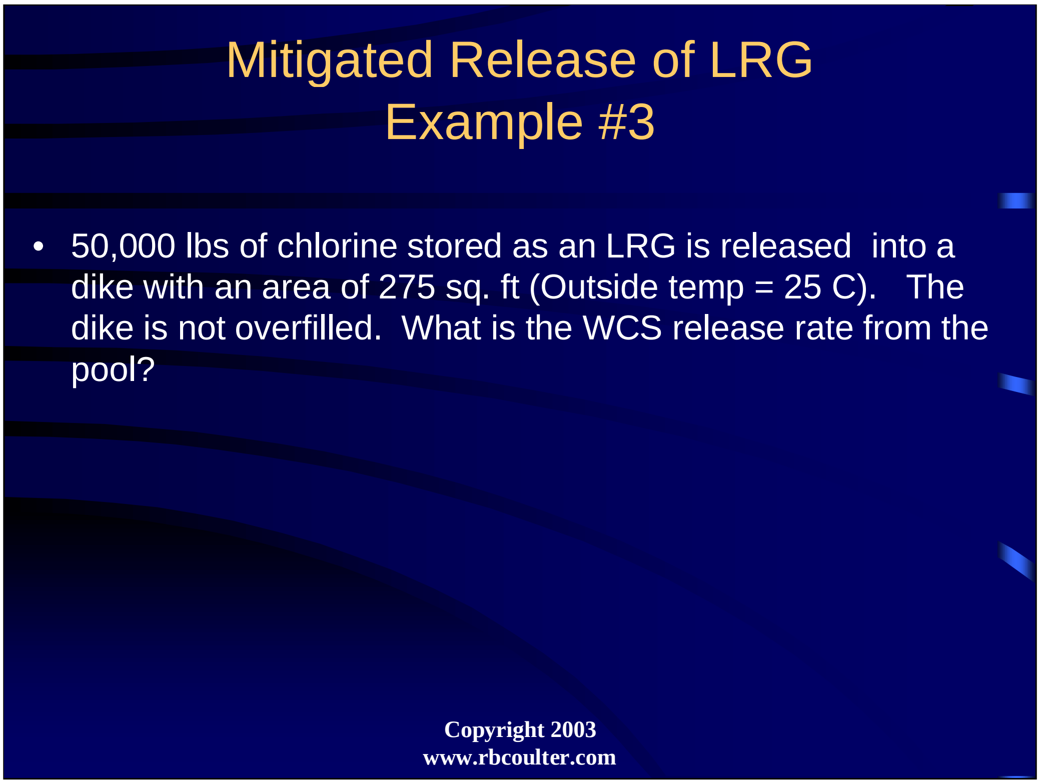
The equation(s) to calculate of elevated temp. substance release rates are as follows:

QR = QS * 1.4 * LFB * DF (unmitigated)

QR = 1.4 * LFB * A (mitigated)

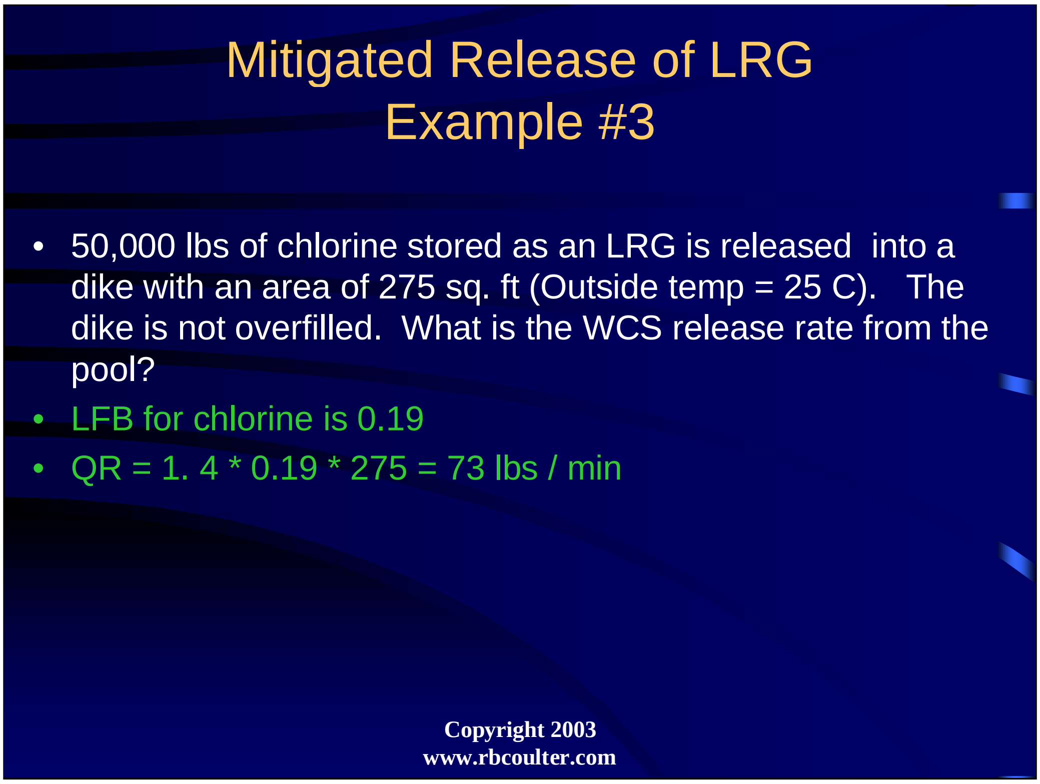
The LFB is the “Liquid Factor Boiling” from Exhibit B-2, appendix B of OCAGD (or calculated). It is a substance specific value like LFA & DF.

Because LRGs would be boiling upon release, they are modeled as though they are “elevated” liquids using the above equations.



The following is an example of how to calculate WCS release rates of LRGs:

50,000 lbs of chlorine stored as an LRG is released into a dike with an area of 275 sq. ft (Outside temp = 25 C). The dike is not overfilled. What is the WCS release rate from the pool?

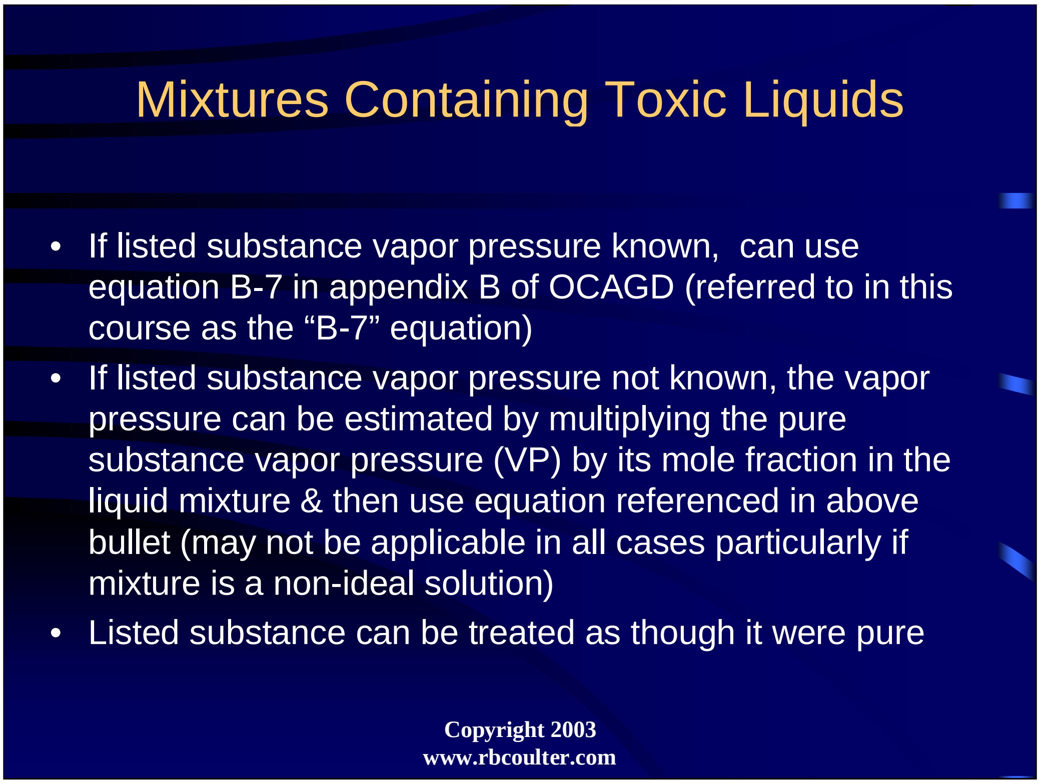


50,000 lbs of chlorine stored as an LRG is released into a dike with an area of 275 sq. ft (Outside temp = 25 C). The dike is not overfilled. What is the WCS release rate from the pool?

Because chlorine is an LRG in this example we look up the LFB for chlorine in exhibit B-1, appendix B of OCAGD. It is 0.19.

We use the mitigated elevated temperature equation mentioned previously:

QR (release rate) = 1. 4 * 0.19 * 275 = 73 lbs / min

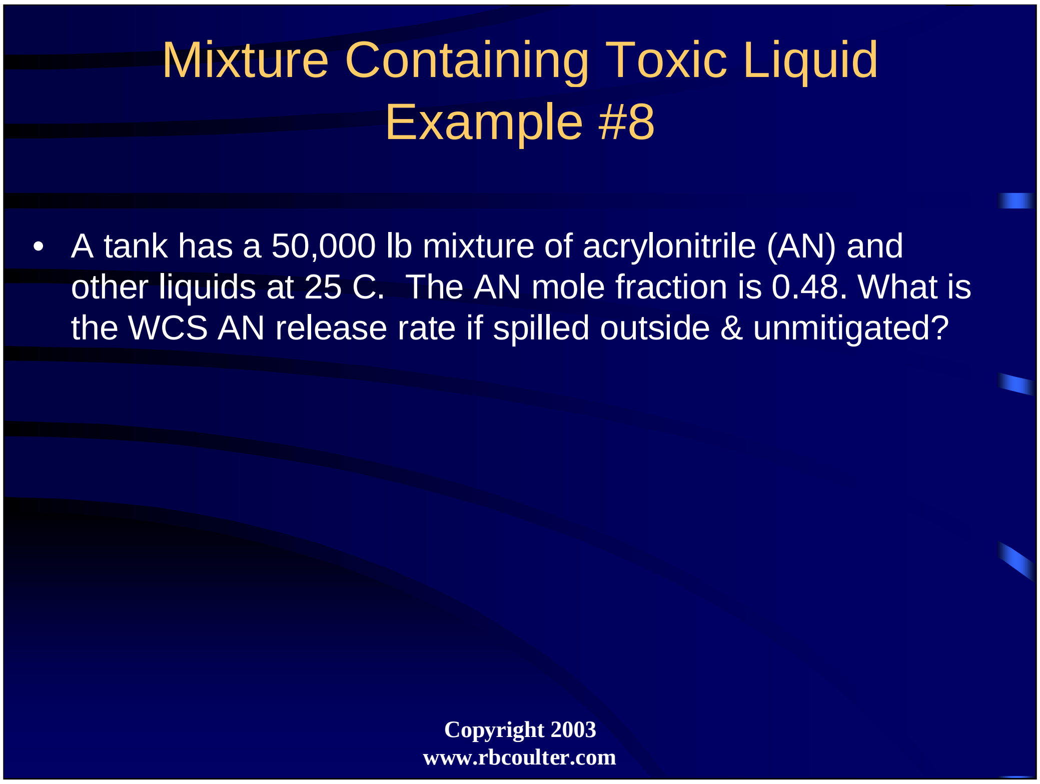


Mixtures containing toxic liquids are more complicated to model. There are several options or methods one may choose if this is the case:

If a listed substance vapor pressure in the mixture is known at the WCS temperature, then equation B-7 in appendix B of OCAGD can be used.

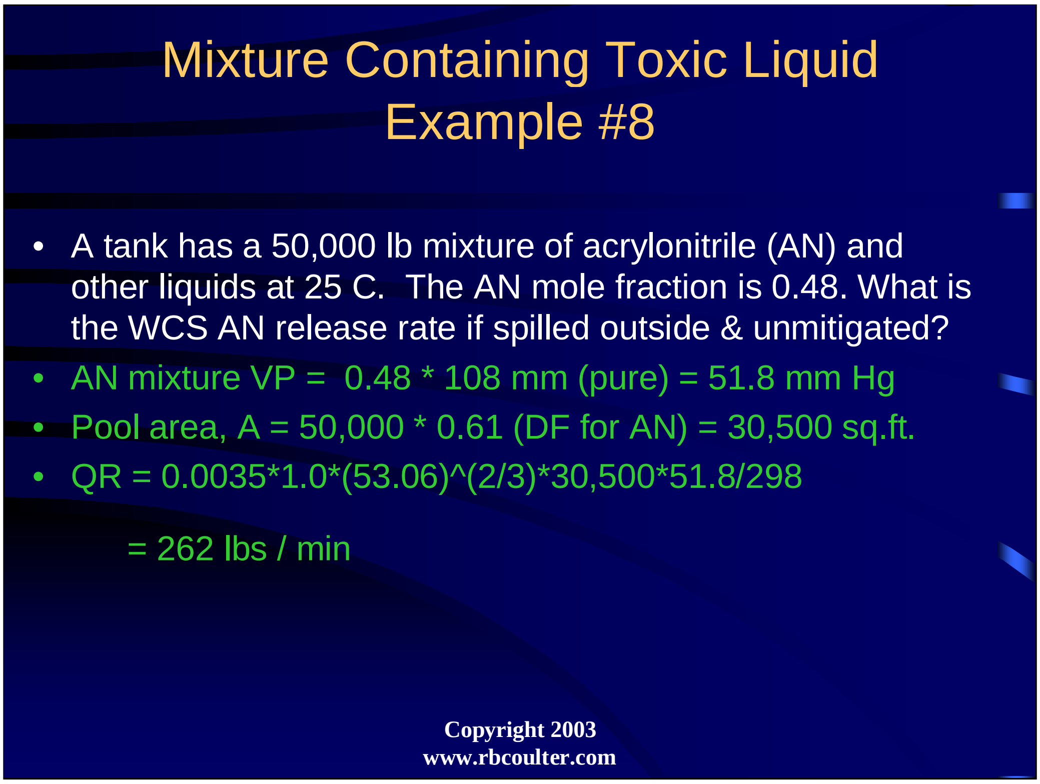
If the listed substance vapor pressure is not known, the vapor pressure can be estimated by multiplying the pure substance vapor pressure (VP) by its mole fraction in the liquid mixture. This needs to be done at the WCS temperature. This value is then used in the B-7 equation. Note that his may not be applicable in all cases. If the solution is not an ideal mixture this may give erroneous results.

The easiest alternative is to treat the listed substance in the mixture as though it were pure. The QS term (or quantity released) can be set equal to the actually amount the listed substance in the mixture (not the mixture amount). The pure substance properties & factors can then be used in the simplified equations mentioned in the previous slides. Although this would be a simpler way to model mixtures the release rates would tend to be over-estimated.



The following is an example of a listed substance in a mixture:

A tank has a 50,000 lb mixture of acrylonitrile (AN) and other liquids. The AN mole fraction is 0.48. What is the WCS AN release rate if spilled outside & unmitigated?



A tank has a 50,000 lb mixture of acrylonitrile (AN) and other liquids. The AN mole fraction is 0.48. What is the WCS AN release rate if spilled outside & unmitigated?

If we assume that this is an ideal mixture then the following approach can be taken. First calculate the vapor pressure (or partial pressure) of acrylonitrile above the liquid by using the following equation:

AN mixture VP = 0.48 * 108 mm (pure AN VP at 25 C) = 51.8 mm Hg

Pool area, A = 50,000 * 0.61 (DF for AN) = 30,500 sq.ft.

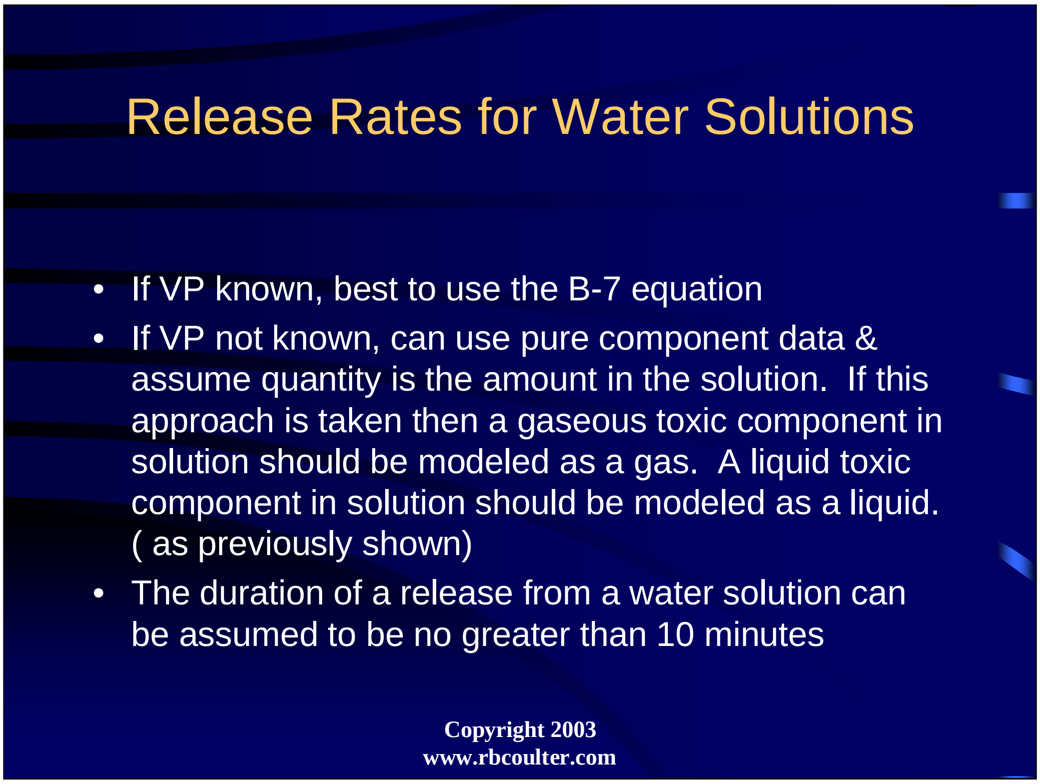
Note: We assume the DF of the mixture is approximately equal to the DF of pure AN.

We then use the B-7 equation to calculate the release rate of AN:

QR = 0.0035*1.0*(53.06)^(2/3)*30,500*51.8/298

53.06 is the molecular weight of AN from Exhibit B-2.

Note that the above example occurs at 25 C. To convert to a higher temperature that is less than 50 C. Use the TCF for AN as show in previous examples.



The class of mixtures that involve a listed substance in water solutions are allowed special considerations. If the VP of the listed substance in the water solution is known, then its best to use the B-7 equation as illustrated previously for non-specific mixtures. In some cases the water / toxic substance solution is has a listed "line item" entry in the CAP rule. This includes aqueous ammonia and aqueous hydrochloric acid. This listed aqueous mixtures have their own factors (for example, LFA, DF, etc.) in exhibit B-3 of the OCAGD. One need only to use the factors as shown in the previous examples for these solutions. To adjust for temperatures between 25 C & 50 C, simply use the TCFs for the pure listed substances.

If the listed substance VP in the solution is not known, then one can use the pure component data & assume quantity is the amount in the solution. If this approach is taken then a gaseous toxic component in solution should be modeled as a gas. A liquid toxic component in solution should be modeled as a liquid.

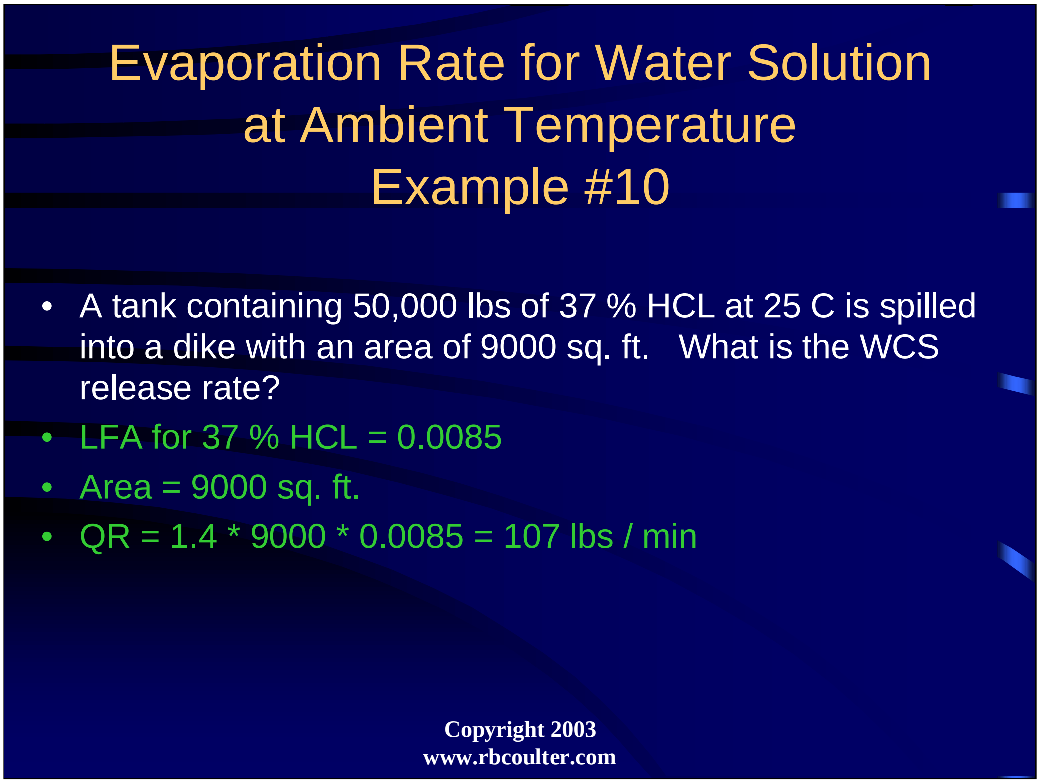
After about ten minutes the release rates of listed substance from water solutions decreases so significantly that the duration of the release can be assumed to be only ten minutes. This affects the distance to endpoint which will be discuss later.

Evaporation Rate for Water Solution at Ambient Temperature Example #10

- A tank containing 50,000 lbs of 37 % HCL at 25 C is spilled into a dike with an area of 9000 sq. ft. What is the WCS release rate?

The following is an example of release rate calculation from an aqueous solution:

A tank containing 50,000 lbs of 37 % HCL at 25 C is spilled into a dike with an area of 9000 sq. ft. What is the WCS release rate?



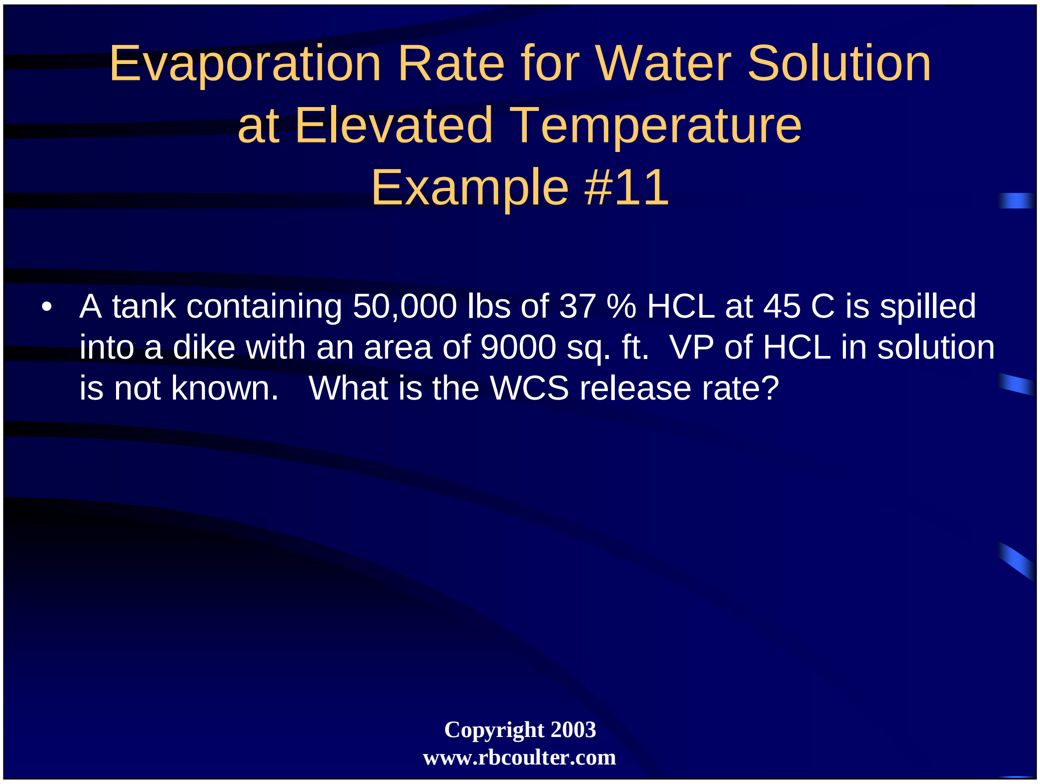
A tank containing 50,000 lbs of 37 % HCL at 25 C is spilled into a dike with an area of 9000 sq. ft. What is the WCS release rate?

37 % HCL acid is a specifically listed aqueous mixture. The appropriate factors for it can be obtained from exhibit B-3.

The LFA for 37 % HCL is 0.0085.

The area = 9000 sq. ft.

QR = 1.4 * 9000 * 0.0085 = 107 lbs / min



Here is an example at an elevated temperature:

A tank containing 50,000 lbs of 37 % HCL at 45 C is spilled into a dike with an area of 9000 sq. ft. VP of HCL in the solution at this temperature is not known. What is the WCS release rate?

Evaporation Rate for Water Solution at Elevated Temperature Example #11

- A tank containing 50,000 lbs of 37 % HCL at 45 C is spilled into a dike with an area of 9000 sq. ft. VP of HCL in solution is not known.   What is the WCS release rate?
- Assume entire quantity of HCL is released as a gas over a 10 minute period.
- QR = 0.37 * 50,000 / 10 = 1850 lbs/min

A tank containing 50,000 lbs of 37 % HCL at 45 C is spilled into a dike with an area of 9000 sq. ft. VP of HCL in the solution at this temperature is not known. What is the WCS release rate?

Since we do not know the VP of HCL at 45 C we will assume the entire quantity of HCL is released as a gas over a 10 minute period.

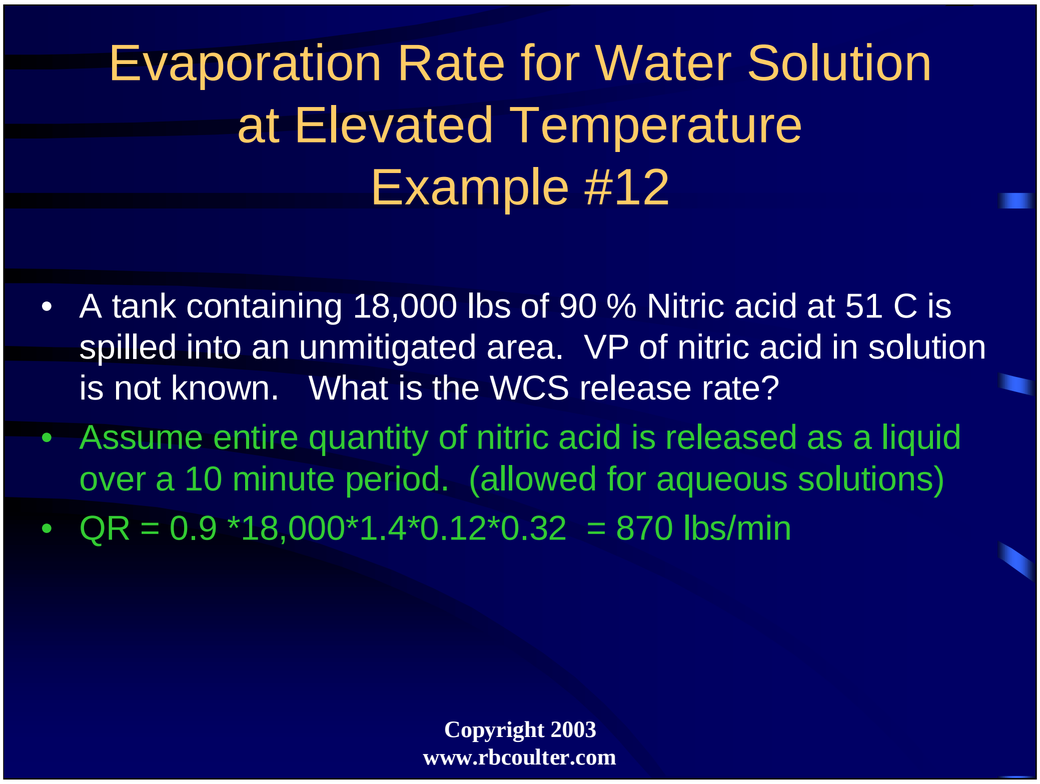
QR = 0.37 * 50,000 / 10 = 1850 lbs/min

Evaporation Rate for Water Solution at Elevated Temperature Example #12

- A tank containing 18,000 lbs of 90 % Nitric acid at 51 C is spilled into an unmitigated area. VP of nitric acid in solution is not known. What is the WCS release rate?

The following example involves a toxic liquid in a water solution:

A tank containing 18,000 lbs of 90 % Nitric acid at 45 C is spilled into an unmitigated area. VP of nitric acid in solution is not known. What is the WCS release rate?



A tank containing 18,000 lbs of 90 % Nitric acid at 45 C is spilled into an unmitigated area. VP of nitric acid in solution is not known. What is the WCS release rate?

Assume the entire quantity of nitric acid is released as a liquid over a 10 minute period. (Remember this is allowed for aqueous solutions.)

Because we do not know the VP of nitric acid in solution we assume that pure nitric acid is released at an elevated temperature:

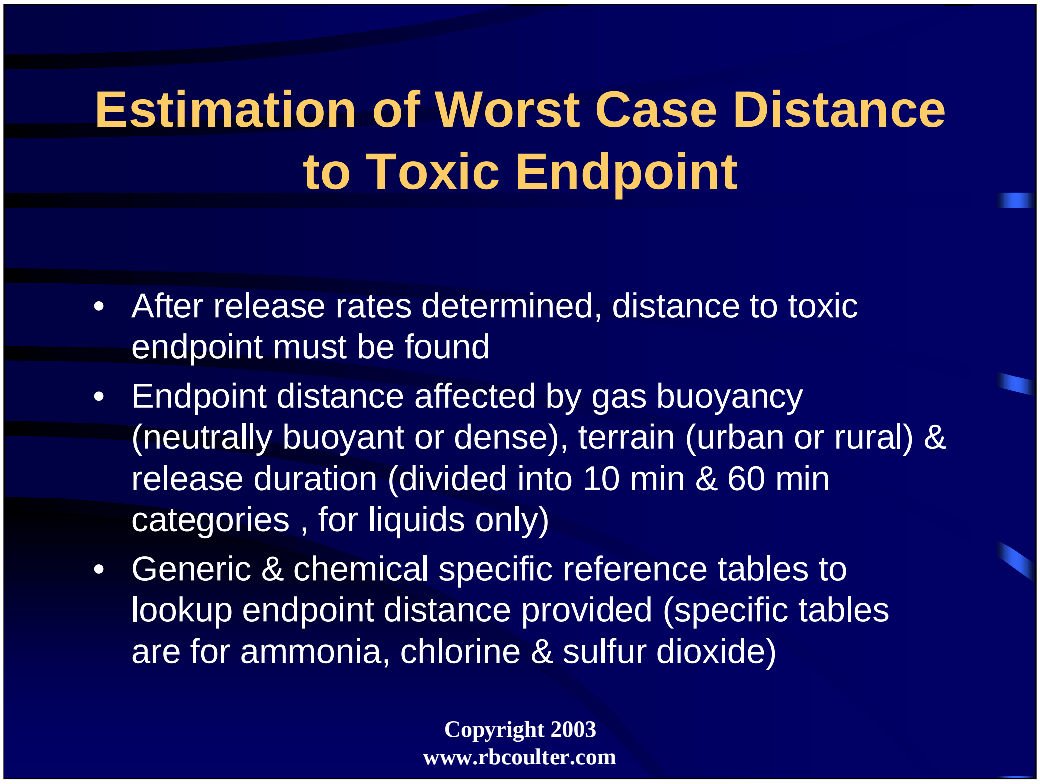
From exhibit B-2 we obtained for nitric acid:

LFB = 0.12

DF = 0.32

Use the equation for pure substances at elevated temperatures & for an unmitigated pool size:

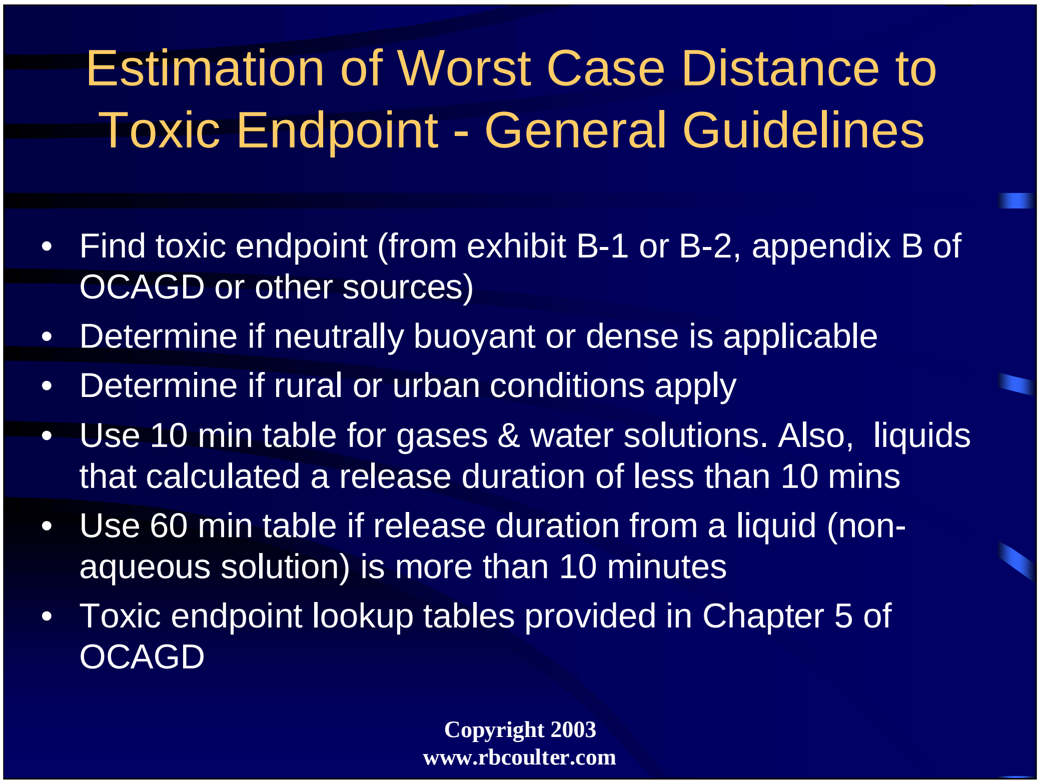
QR = 0.9 *18,000*1.4*0.12*0.32 = 870 lbs/min



The previous discussion focused on the calculation of release rates which is an important value in determining the distance to toxic endpoint. The distance to toxic endpoint is the main goal of modeling a WCS.

Other than release rates endpoint distance can be affected by gas buoyancy (neutrally buoyant or dense), the terrain surrounding the point of release (urban or rural) & the release duration (Which is divided into 10 min & 60 min categories. All gas releases are of 10 minute duration. Liquid releases can be categorized as 10 or 60 minute duration depending on the release rate & the quantity of the release.

Generic & chemical specific reference tables are provided in OCAGD to lookup endpoint distances once the above parameters have been determined. Specific tables provided in OCAGD for ammonia, chlorine & sulfur dioxide.



The general guidelines for finding the distance to the toxic endpoints are as follows:

First, find the toxic endpoint that corresponds to the substance in the WCS. They are listed exhibit B-1 or B-2, appendix B of OCAGD for listed substances. Toxic endpoints are usually the ERPG-2 values developed by the American Institute of Industrial Hygienists or 10% of the IDLH (Immediately dangerous to life & health) values available from the National Institute of Occupational Safety & Health (NIOSH).

Determine if neutrally buoyant or dense is applicable. As a general rule, substances that are heavier than air (MW > 29) are dense and those lighter than air (MW < 29) are neutrally buoyant. However, vapors or gases released as tiny droplets or aerosols may behave as though they are dense.

Also determine if rural or urban conditions apply. Rural conditions have few buildings or obstructions. Urban conditions have many obstructions.

Use the 10 min table for gases, water solutions and liquids that calculated a release duration of less than 10 mins (release duration = QS / QR)

Use the 60 min table if the calculated release duration from a liquid (non-aqueous solution) is more than 10 minutes

The various toxic endpoint lookup tables are provided in Chapter 5 of OCAGD.

Generic Reference Tables of Distances for WCS

Exhibit 2
Generic Reference Tables of Distances for Worst-case Scenarios

Applicable Conditions			Reference Table Number
Gas or Vapor Density	**Topography**	**Release Duration (minutes)**	
Neutrally buoyant	Rural	10	1
		60	2
	Urban	10	3
		60	4
Dense	Rural	10	5
		60	6
	Urban	10	7
		60	8

The following is a table given in OCAGD to outlines the appropriate reference table for looking up distances to endpoints. The three input parameters gas/vapor density, topography & release duration.

Specific Reference Tables of Distances for WCS

Exhibit 3
Chemical-Specific Reference Tables of Distances for Worst-case Scenarios

Substance	Applicable Conditions			Reference Table Number
	Gas or Vapor Density	Topography	Release Duration (minutes)	
Anhydrous ammonia liquefied under pressure	Dense	Rural, Urban	10	9
Non-liquefied ammonia, ammonia liquefied by refrigeration, or aqueous ammonia	Neutrally buoyant	Rural, Urban	10	10
Chlorine	Dense	Rural, Urban	10	11
Sulfur dioxide (anhydrous)	Dense	Rural, Urban	10	12

This chart outlines the appropriate table for the specific listed substances - ammonia, chlorine & sulfur dioxide.

Distance to Toxic Endpoint Lookup

- For neutrally buoyant gases, divide QR (lbs/min) by toxic endpoint (mg/L) & lookup in corresponding table
- Dense gases & vapors must use both endpoint & release rate (QR) in the corresponding tables
- Do not interpolate, round up if equal to or greater than midpoint, otherwise round down
- Specific tables provided for ammonia, chlorine & sulfur dioxide

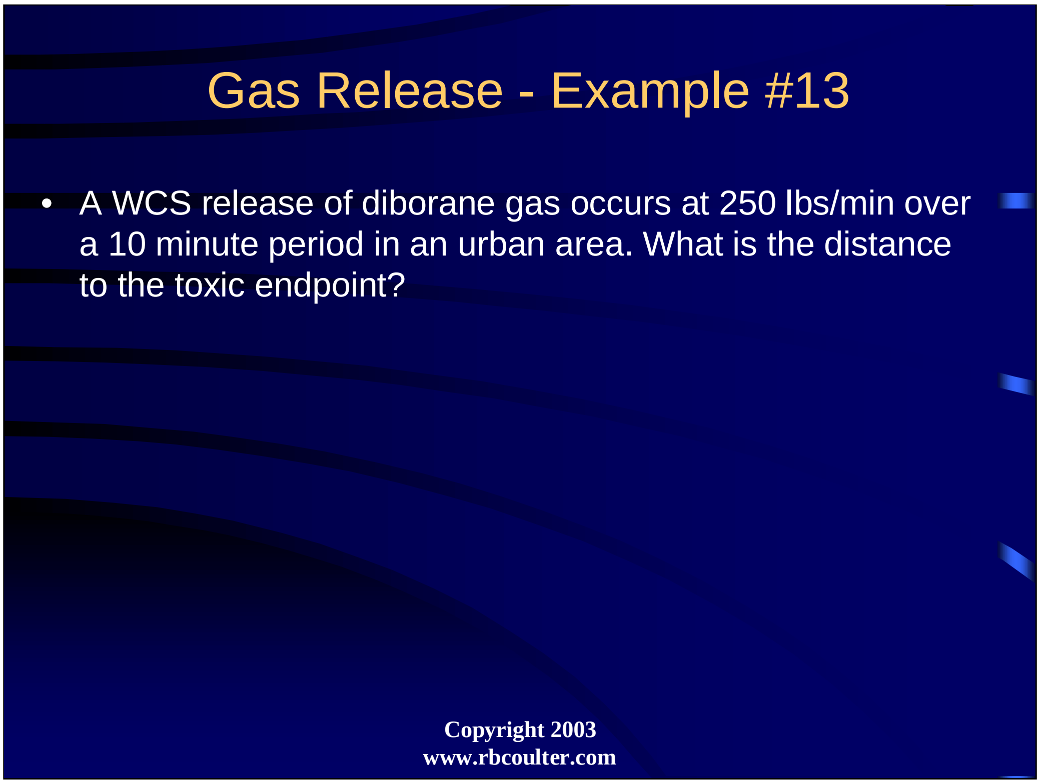
The following is the procedure for using the “distance to toxic endpoint” tables:

For neutrally buoyant gases, divide the release rate QR (lbs/min) by toxic endpoint (mg/L). This quotient is the only value needed. Lookup the distance to endpoint in the corresponding table per the outline charts shown previously.

Dense gases & vapors must use both the endpoint & release rate (QR). The release rates are listed vertically & the endpoints are listed horizontally across the top of each table.

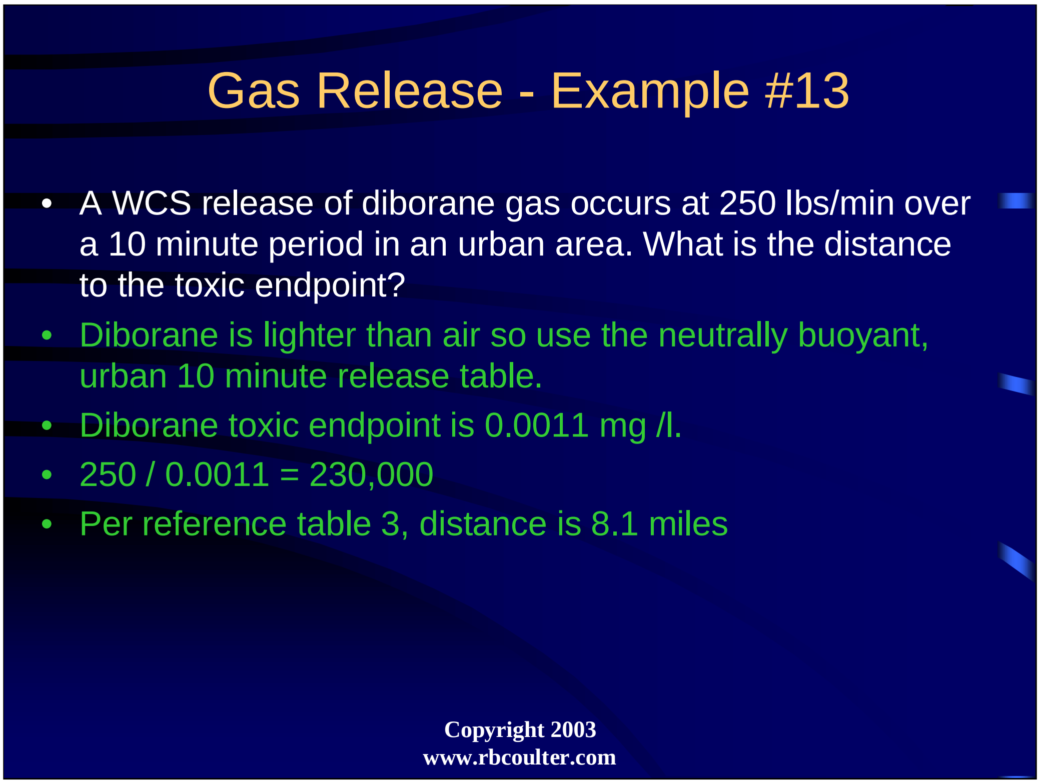
Do not interpolate the values in the table, round up if equal to or greater than midpoint for a particular value (release rate or endpoint), otherwise round down.

If ammonia, chlorine or sulfur dioxide is modeled, use the specific tables for those substances.



The following example illustrates the use of the “distance to endpoint” tables for a neutrally buoyant gas:

A WCS release of diborane gas occurs at 250 lbs/min over a 10 minute period in an urban area. What is the distance to the toxic endpoint?



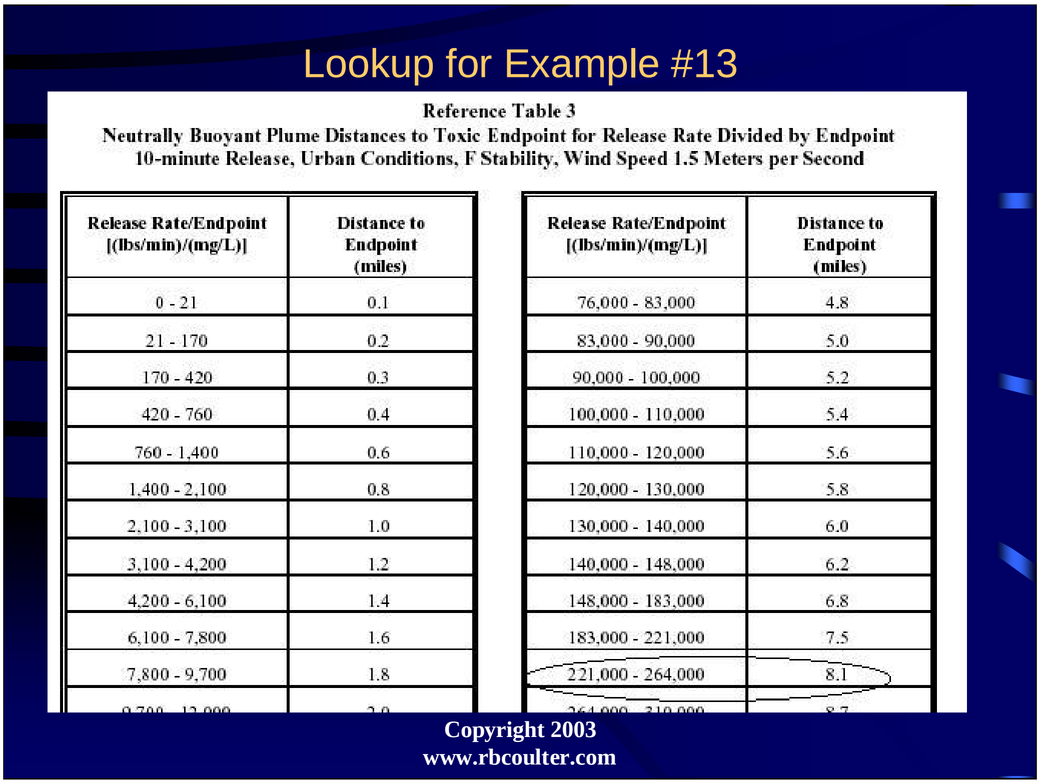
A WCS release of diborane gas occurs at 250 lbs/min over a 10 minute period in an urban area. What is the distance to the toxic endpoint?

Diborane is lighter than air so use the neutrally buoyant, urban 10 minute release table.

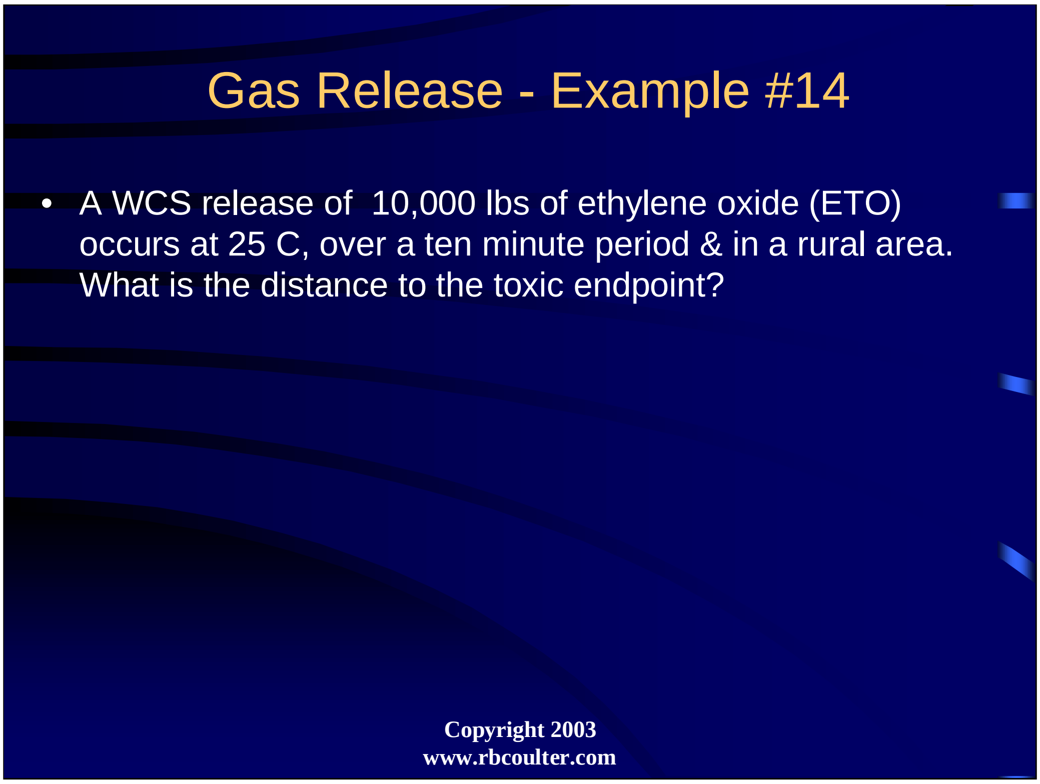
The diborane toxic endpoint is 0.0011 mg /l per exhibit B-1.

Because diborane is neutrally buoyant in this scenario the release rate QR is divided by the toxic endpoint as follows: 250 / 0.0011 = 230,000

The 230,000 quotient value is then used to lookup the distance to toxic endpoint in table 3 . The endpoint distance is 8.1 miles.

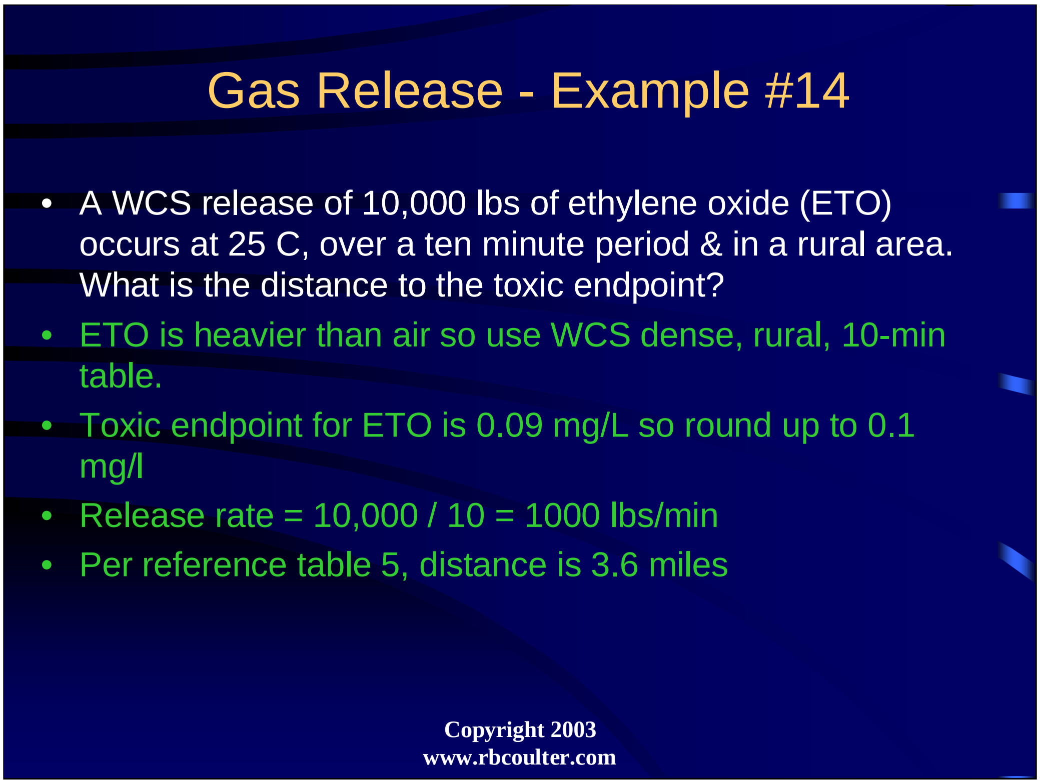


This slide indicates how the quotient value, 230,000 , is used to find the distance to endpoint for example #13. The value is between 221,000 & 264,000 which gives an endpoint distance of 8.1 miles. Note that this is the neutrally buoyant, 10-minute release, urban conditions WCS table. Remember, WCS atmospheric conditions must be F stability class & a wind speed of 1.5 meters / second.



The following is an example of a dense gas release:

A WCS release of 10,000 lbs of ethylene oxide (ETO) occurs at 25 C, over a ten minute period & in a rural area. What is the distance to the toxic endpoint?



A WCS release of 10,000 lbs of ethylene oxide (ETO) occurs at 25 C, over a ten minute period & in a rural area. What is the distance to the toxic endpoint?

ETO is heavier than air so we need to use the WCS dense, rural, 10-min table.

This is reference table #5 in OCAGD (see next slide).

Toxic endpoint per exhibit B-1 for ETO is 0.09 mg/L. Since there is no 0.09 entry in table #5 we must round up to 0.1 mg/l

We calculate the release rate to be 10,000 / 10 = 1000 lbs/min

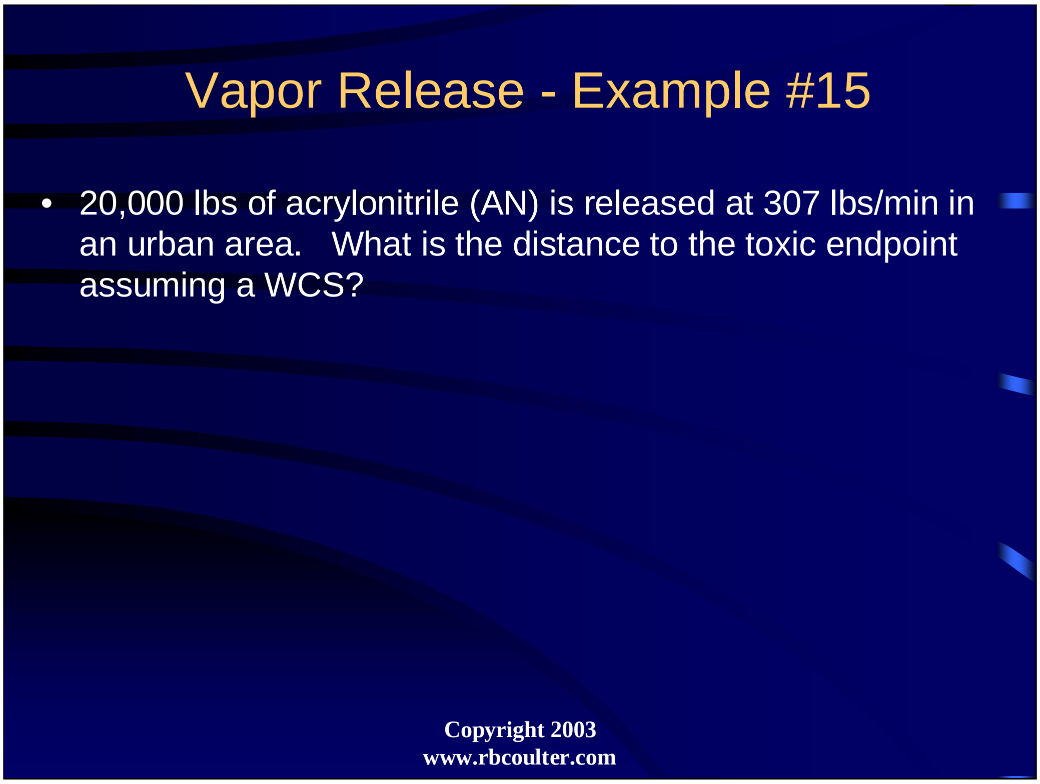
Looking up in reference table 5 we find the distance is 3.6 miles.

Lookup for Example #14

Reference Table 5
Dense Gas Distances to Toxic Endpoint
10-minute Release, Rural Conditions, F Stability, Wind Speed 1.5 Meters per Second

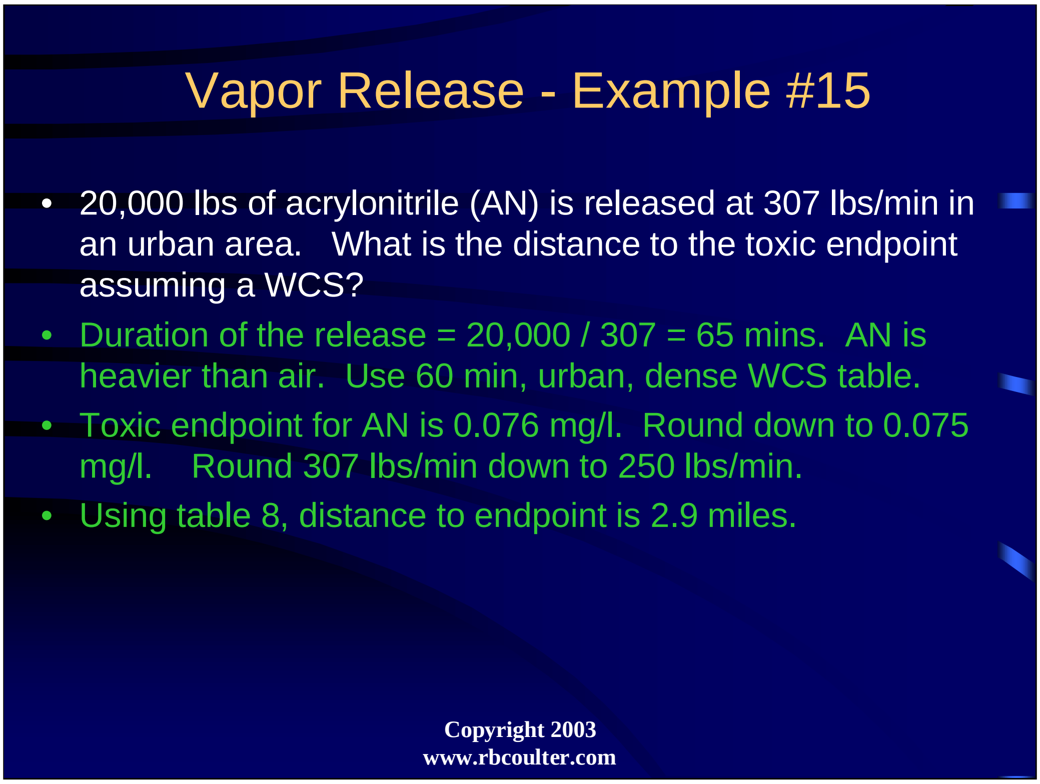
Release Rate (lbs/min)	Toxic Endpoint (mg/L)												
	0.0004	0.0007	0.001	0.002	0.0035	0.005	0.0075	0.01	0.02	0.035	0.05	0.075	0.1
	Distance (Miles)												
1	2.2	1.7	1.5	1.1	0.8	0.7	0.5	0.5	0.3	0.2	0.2	0.2	0.1
2	3.0	2.4	2.1	1.5	1.1	0.9	0.7	0.7	0.4	0.3	0.3	0.2	0.2
5	4.8	3.7	3.0	2.2	1.7	1.5	1.2	1.0	0.7	0.5	0.4	0.3	0.3
10	6.8	5.0	4.2	3.0	2.4	2.1	1.7	1.4	1.0	0.7	0.6	0.5	0.4
30	11	8.7	6.8	5.2	3.9	3.4	2.8	2.4	1.7	1.3	1.1	0.9	0.7
50	14	11	9.3	6.8	5.0	4.2	3.5	3.0	2.2	1.7	1.4	1.1	0.9
100	19	15	12	8.7	6.8	5.8	4.8	4.2	2.9	2.2	1.9	1.6	1.3
150	24	18	15	11	8.1	6.8	5.7	5.0	3.6	2.7	2.3	1.9	1.6
250	>25	22	19	14	11	8.7	7.4	6.2	4.5	3.4	2.8	2.3	2.0
500	*	>25	>25	19	14	12	9.9	8.7	6.2	4.7	3.8	3.1	2.7
750	*	*	*	23	17	15	12	11	7.4	5.5	4.5	3.7	3.2
1,000	*	*	*	>25	20	17	14	12	8.1	6.2	5.2	4.2	3.6
1,500	*	*	*	*	24	20	16	14	9.9	7.4	6.2	5.0	4.3

This is table #5 from OCAGD used for Example #14. The correct value, 3.6 miles, is circled in the lower left corner.



The following is an example of a vapor release from a toxic liquid spill:

20,000 lbs of acrylonitrile (AN) is released at 307 lbs/min in an urban area. What is the distance to the toxic endpoint assuming a WCS?



20,000 lbs of acrylonitrile (AN) is released at 307 lbs/min in an urban area. What is the distance to the toxic endpoint?

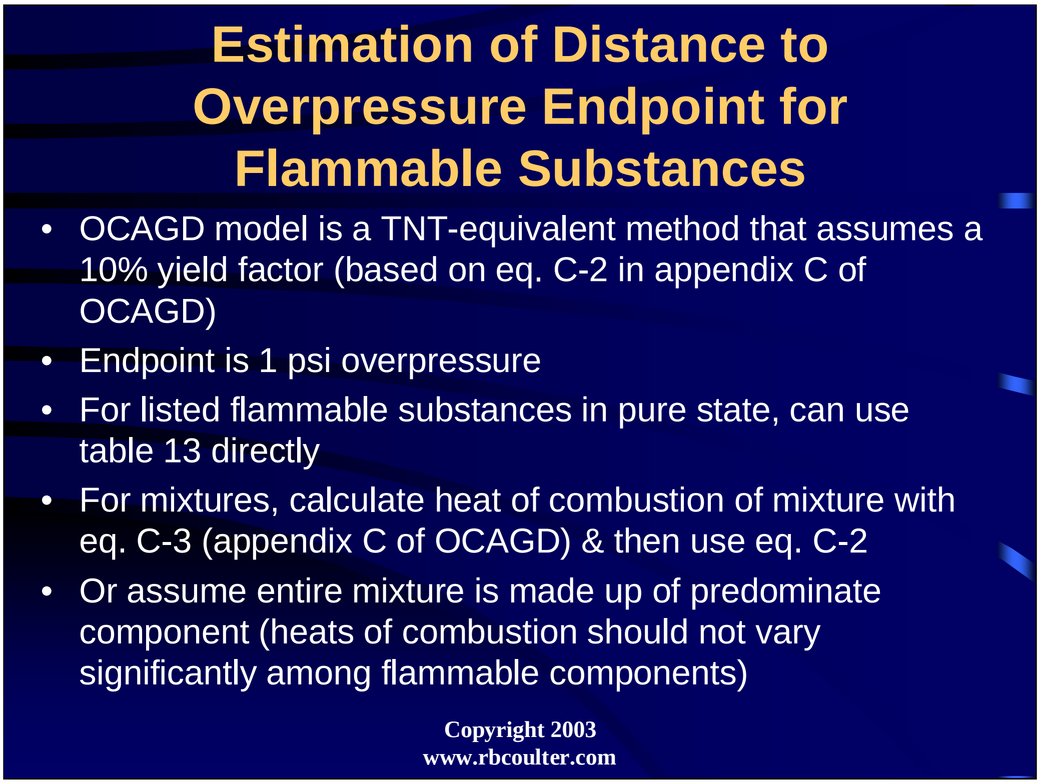
Because this is a liquid release we need to determine if the 10 min or 60 min release duration is appropriate. The duration of the release = 20,000 / 307 = 65 mins.

The rule says that if the release is greater than 10 minutes that the 60 minute duration value must be used..

AN has a molecular weight of 53 so is heavier than air. This means we use the 60 min, urban, dense WCS table. This is table #8.

The toxic endpoint for AN per exhibit B-2 is 0.076 mg/l. We can round down to 0.075 mg/l in table #8. Round 307 lbs/min down to 250 lbs/min.

Using table 8, the distance to the WCS endpoint is 2.9 miles.



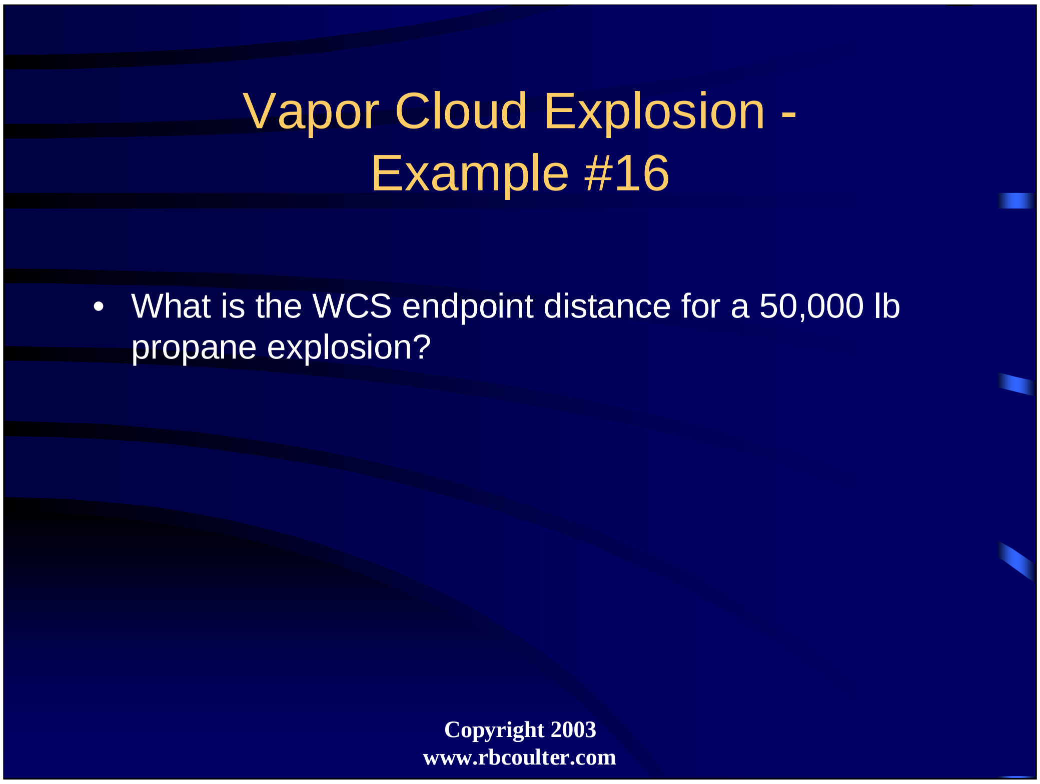
For flammable substances the WCS is the immediate release and detonation of the substance in a process or vessel. The OCAGD model is a TNT-equivalent method that assumes a 10% yield factor. That is, 10% of the theoretical heat of combustion of the amount released is considered to contribute to the explosion. The OCAGD explosion model & tables are based on eq. C-2 in appendix C of the document.

The CAP rule sets and endpoint of 1 psi overpressure for WCS explosions .It is believed that this is a reasonable limit to the negative impact of a WCS blast.

Modeling of flammable WCSs is much easier than toxic WCS. For listed flammable substances in pure state, one need only the identity & quantity of the substance in the process and then lookup the distance to the endpoint in table 13, Chapter 5 of OCAGD.

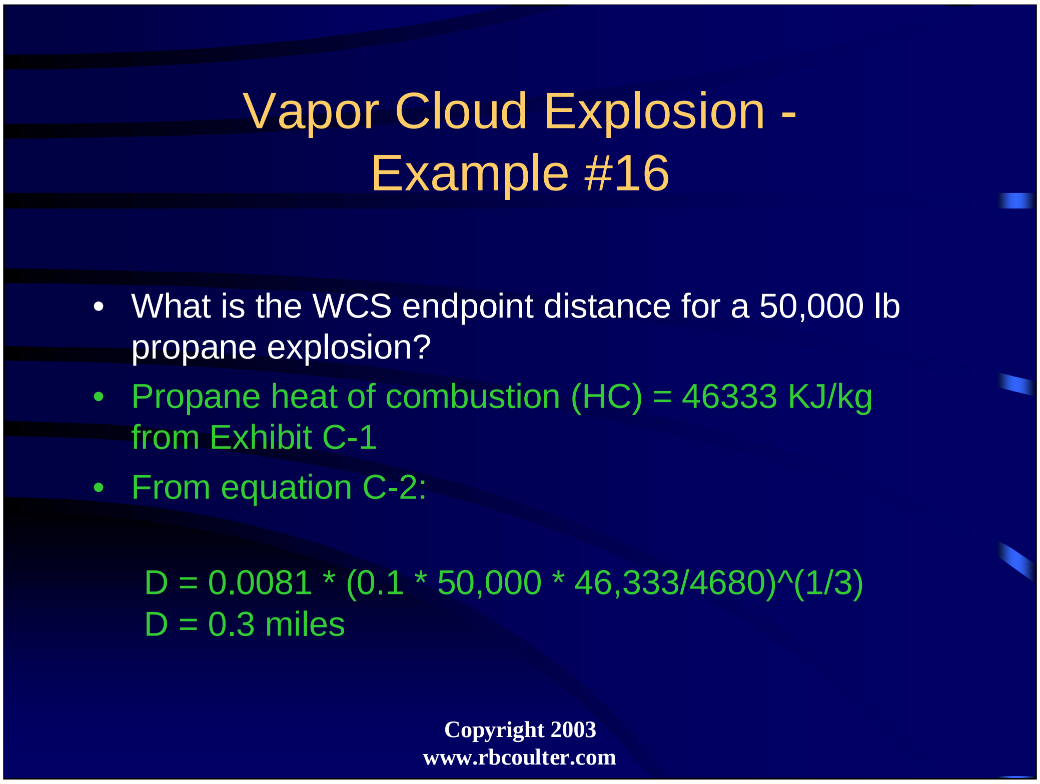
For mixtures, one should calculate heat of combustion of the mixture with eq. C-3 (appendix C of OCAGD) & then use eq. C-2 directly.

One can also assume that the entire mixture is made up of the predominate component and then use table 13. The heats of combustion should not vary significantly among flammable components. For example, a 10,000 lb mixture of 80% butane and 20% propane, one can assume that the entire mixture is butane for modeling purposes.



The following is an example of a flammable WCS:

What is the WCS endpoint distance for a 50,000 lb propane explosion?



What is the WCS endpoint distance for a 50,000 lb propane explosion?

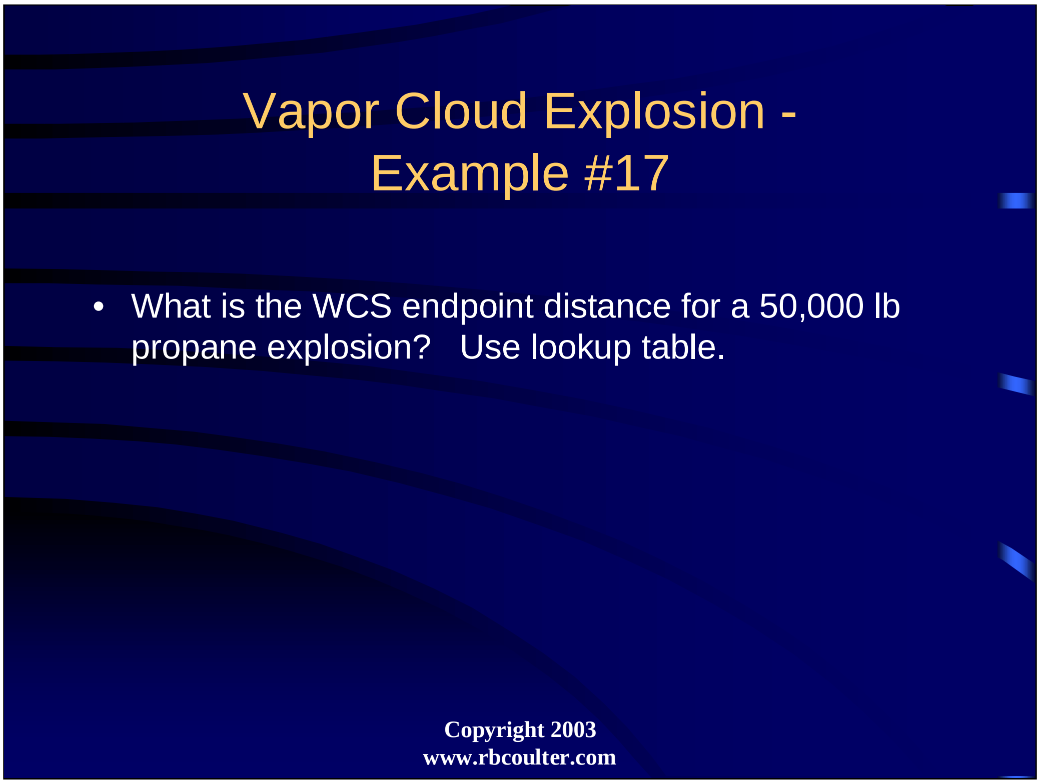
Let's calculate this model based directly on equation C-2:

Propane's heat of combustion (HC) is = 46333 KJ/kg from Exhibit C-1

Now by applying equation C-2:

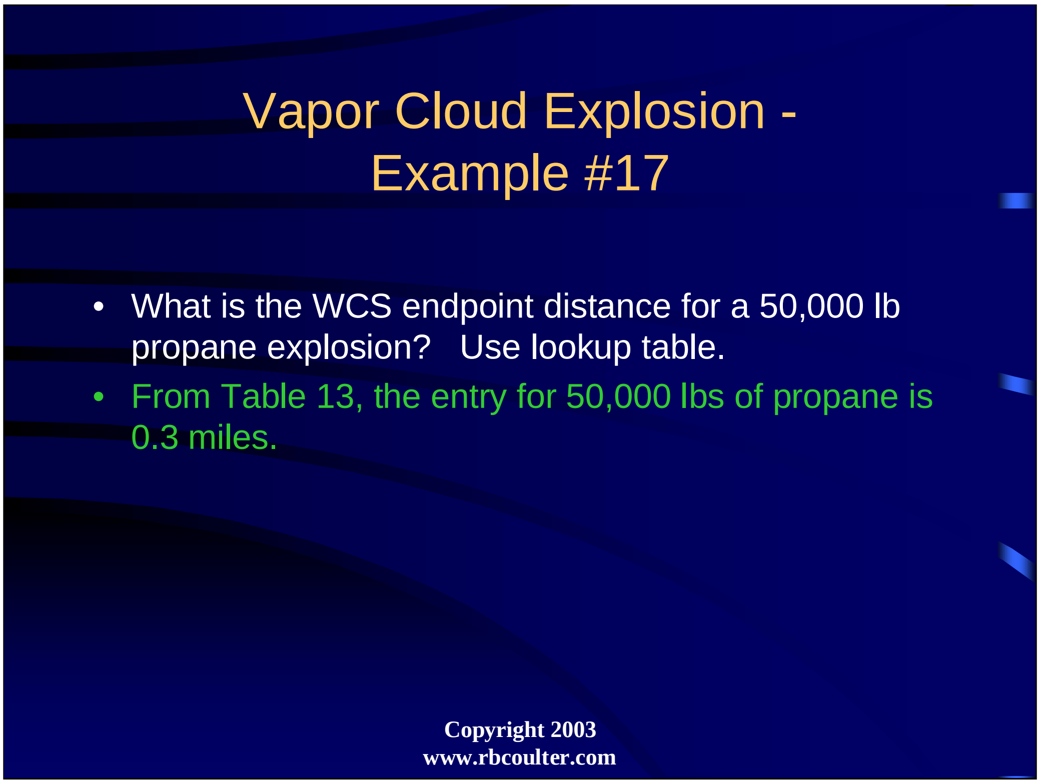
D = 0.0081 * (0.1 * 50,000 * 46,333/4680)^(1/3)

D = 0.3 miles which is the distance to the 1 psi overpressure boundary.



Now do the previous example by using the lookup table:

What is the WCS endpoint distance for a 50,000 lb propane explosion?



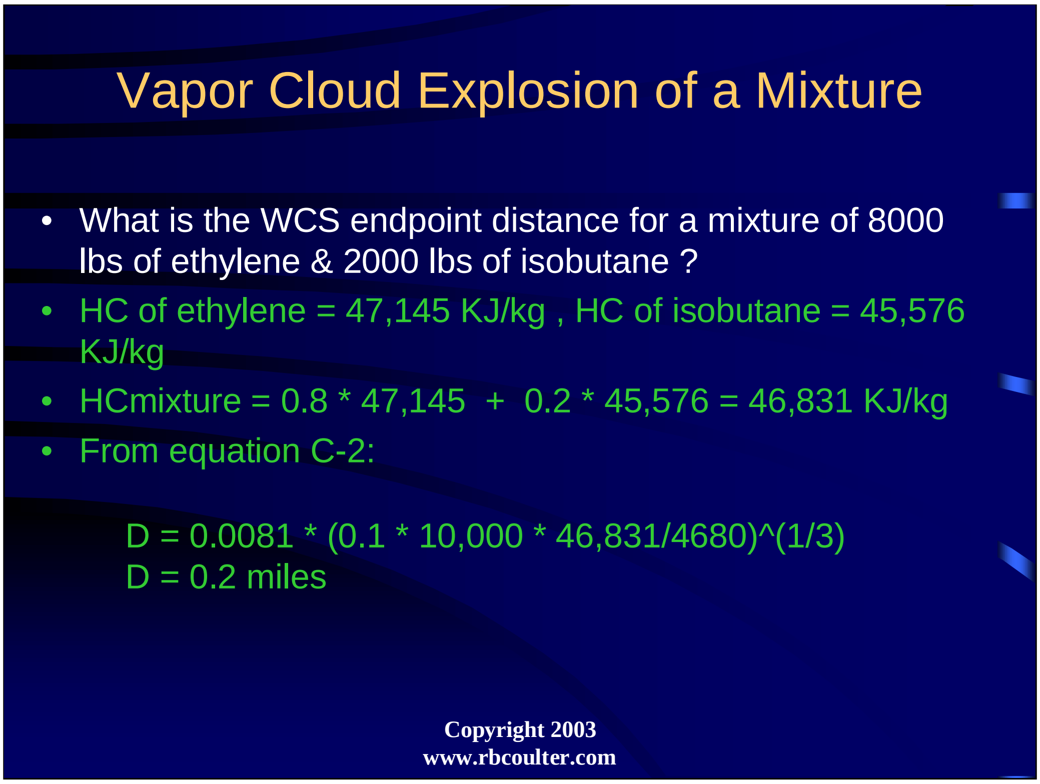
What is the WCS endpoint distance for a 50,000 lb propane explosion? Use lookup table.

After consulting table 13, we find the distance to 1 psi overpressure for 50,000 lbs of propane is 0.3 miles.

Vapor Cloud Explosion of a Mixture

- What is the WCS endpoint distance for a mixture of 8000 lbs of ethylene & 2000 lbs of isobutane ?

The following is an illustration of WCS explosions involving mixtures of flammable substances. What is the WCS endpoint distance for a mixture of 8000 lbs of ethylene & 2000 lbs of isobutane ?



What is the WCS endpoint distance for a mixture of 8000 lbs of ethylene & 2000 lbs of isobutane ?

From exhibit C-1 we find the HC of ethylene is 47,145 KJ/kg & the HC of isobutane is 45,576 KJ/kg

The average HC for the mixture is 0.8 * 47,145 + 0.2 * 45,576 = 46,831 KJ/kg

From equation C-2:

D = 0.0081 * (0.1 * 10,000 * 46,831/4680)^(1/3)

D = 0.2 miles

WCS Calculation for Substances Not Listed in the CAP Rule

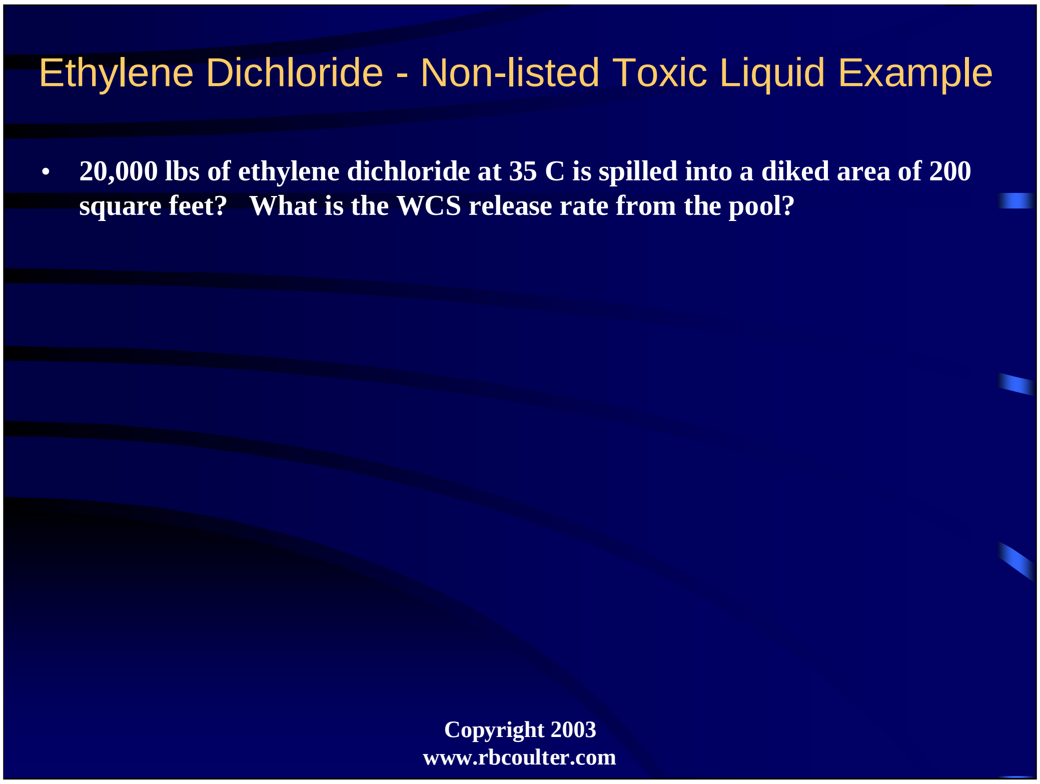
- Facilities should consider general duty clause implications of the CAP rule - may need to model WCSs for non-listed substances
- Need to obtain ERPG-2 or IDLH values for non-listed substances, ERPG-2 from American Industrial Hygiene Association , IDLH from NIOSH - if not available use NIOSH STEL (short term exposure limit) , LOC = ERPG-2 or 10% of IDLH value
- For liquid non-listed substances, will need vapor pressure at release temperature, molecular weight & density
- Heat of combustion values needed for non-listed flammable substances

Owners & operators of facilities should consider the general duty clause implications of the CAP rule. They may need to model WCSs for non-listed substances.

To do a toxic WCS model for a non-listed substance using OCAGD, one will need to obtain ERPG-2 or IDLH values for non-listed substances. The ERPG-2 values are available from the American Industrial Hygiene Association. IDLH values come from NIOSH. If the IDLH or ERPG-2 values are not available, use the NIOSH STEL (short term exposure limit) for the LOC (level of concern or toxic endpoint). Otherwise set LOC = ERPG-2 value or LOC = 10% of the IDLH value.

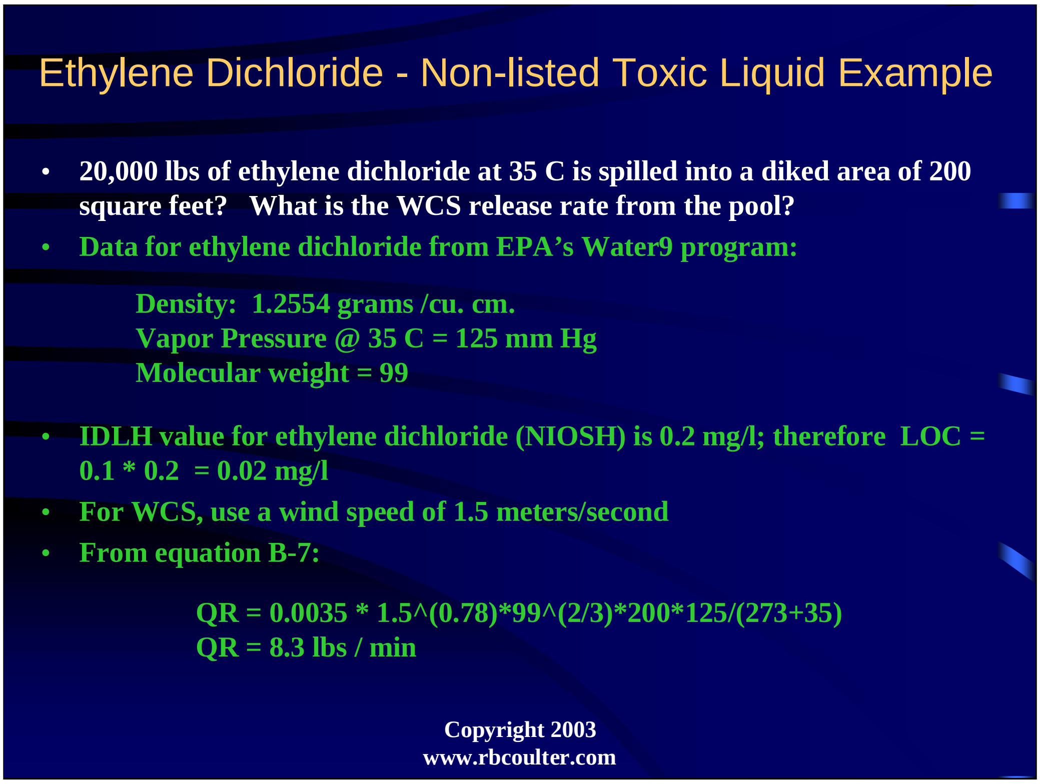
For liquid non-listed substances, one will also need vapor pressure date for the substance at the release temperature, molecular weight & density. One source for this data is EPA’s Water9 program which is available, for free, from their website.

Heat of combustion values will be needed for flammable WCSs involving non-listed substances.



The following example shows how to do a WCS for a non-listed liquid substance:

20,000 lbs of ethylene dichloride at 35 C is spilled into a diked area of 200 square feet? What is the WCS release rate from the pool?



20,000 lbs of ethylene dichloride at 35 C is spilled into a diked area of 200 square feet? What is the WCS release rate from the pool?

Pertinent data for ethylene dichloride can be obtained from EPA's Water9 program:

Density: 1.2554 grams /cu. cm.

Vapor Pressure @ 35 C = 125 mm Hg This vapor pressure value was calculated by using the Antoine equation coefficients provided in Water9 for ethylene dichloride.

Molecular weight = 99

The IDLH value for ethylene dichloride (NIOSH) is 0.2 mg/l. When using IDLH value we set the LOC = 0.1 * 0.2 = 0.02 mg/l.

For a WCS, we must use a wind speed of 1.5 meters/second.

From equation B-7:

QR = 0.0035 * 1.5^(0.78)*99^(2/3)*200*125/(273+35)

QR = 8.3 lbs / min

Ethylene Dichloride - Non-listed Toxic Liquid Example

- **Assuming a rural release, what is the WCS distance to the endpoint for the ethylene dichloride release rate just calculated?**
- **The duration of release is:**

  Duration of release = 20,000 / 8.3 = 2400 minutes

- **The MW of ethylene dichloride (99) is greater than 29, so it is a dense vapor**
- **Duration is greater than 60 minutes, so use the 1.5 meter, rural, 60 minute, dense gas table - Reference Table 6 in OCAGD**
- **Round the release rate of 8.3 lbs/min to 10 lbs/min & lookup the distance to endpoint using the 0.02 mg/l toxic endpoint value**
- **Distance to endpoint for the WCS is 1.4 miles**

20,000 lbs of ethylene dichloride at 35 C is spilled into a diked area of 200 square feet? What is the WCS release rate from the pool?

Calculate the duration of the release as follows:

Duration of release = 20,000 / 8.3 = 2400 minutes

The MW of ethylene dichloride (99). This greater than 29, so it is a dense vapor.

Because the duration of the release is greater than 60 minutes, we use the 1.5 meter, rural, 60 minute, dense gas table which is reference table 6 in OCAGD.

Round the release rate of 8.3 lbs/min to 10 lbs/min & lookup the distance to endpoint using the 0.02 mg/l toxic endpoint value.

The distance to the endpoint for the WCS is 1.4 miles.