Review Comment Form (RCF)			Page 1 of 11
Document Title: BGCAPP GB Hydrolysate Transportation Risk Assessment BGCAPP VX Hydrolysate Transportation Risk Assessment			**Version/Draft (# or date):** GB Hydrolysate TRA (Final, Rev.5, April 2021) VX Hydrolysate TRA (Final, Rev. 1, February 2021)
Reviewer(s)/Date: KDEP, 5/10/2021			**Originator:** Leidos
			Document Number: RM-20-008 (GB); RM-20-013 (VX)
Cmt #	**Applies to**	**Comment**	**Proposed Resolution**
1	GB Hydrolysate TRA – Table 4-3	Hazard Severity Definition Used for TRA Page 13, Negligible, Level IV, Rationale, Part a: It appears that the term "hazard distance" was used in error. Please replace "hazard distance" with "concentration" if this is the correct term.	The term "hazard distance" is correct as used. As explained in Section 4.2, page 11, "the hazard is characterized in terms of hazard distances, which are the distances necessary for the chemical concentration to fall below specific concentration levels, as it disperses. For GB, the concentration levels are based on established Acute Exposure Guideline Levels (AEGLs). For example, the 30-minute AEGL-1 hazard distance is the distance required for the GB concentration to fall below the 30-minute AEGL-1 concentration. Hazard distances are calculated using a plume dispersion model, specifically, the Army-sponsored D2PC software (Whitacre et al. 1987)."
2	GB Hydrolysate TRA – Section 6.1	Exposure via Vapor Inhalation from Spill,Page 20, Equation 1.: The variable *d* is listed as *the length of spill surface in the downwind direction (meters)*, which would appear to be the radius of the spill from the source to the edge of the spill. The referenced document (SAIC 2011) for the source of Equation 1 states that *d* equals the spill diameter. Please specify the values used for *d* in Equation 1 and revise the definition of *d* as needed.	The phrase "length of spill surface in the downwind direction" refers to the entire spill surface , not just the portion starting from the center to the edge of the spill. The value of *d* was in fact calculated by the model as the diameter of the circular spill. For example, for a 5,000 gallon (18.927 cubic meter) spill with a spill depth of 1 cm (0.01 m), $18.927 = \prod d^2/4 \times 0.01$ $d = 49.08$ m We will add the above calculation in the text in Section 6.1.

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3	GB Hydrolysate TRA – Section 6.1	Exposure via Vapor Inhalation from Spill, Page 20, Equation 3 description: In the description of Equation 3, the following sentence is included: "Pv in Pascals is converted to millimeters of mercury [mm Hg] by dividing by 133." It is unclear why this conversion factor is included. Equation 3 is used to find a Pv value which is used in Equation 1: however, the Pv input for Equation 1 should be in atmospheres, not mm Hg. Please explain the reasoning for the sentence explaining the conversion from Pascals to mm Hg and verify that the value for Pv used in Equation 1 was in atmospheres.	We understand the confusion. We will change the statement as follows: "Pv in Pascals is converted to atm by dividing by 101,325". Similarly, for the VX Hydrolysate TRA, we will change it to "Pv in mm Hg is converted to atm by dividing by 760." (The reason for the statement regarding conversion to mm Hg was because the model spreadsheet is currently set up to receive the vapor pressures in mm Hg. The spreadsheet then converts these values to atmospheres and uses those values in Equation 1.)
4	GB Hydrolysate TRA – Section 6.1	Exposure via Vapor Inhalation from Spill, Page 23, Table 6-1: As we do not have access to the models that were used, please rovide the calculations used to derive mass of chemical released due to evaporation from a 5,000-gallon hydrolysate spill.	Two example calculations (non-agent and agent) are provided. See continuation sheet for Comment #4. We will include these example calculations in the TRA report as an appendix.

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5	VX Hydrolysate TRA – Section 2	Description of Waste to Be Shipped, Page 2: This section states that the samples discussed in the VX Hydrolysate Characterization memo were well-mixed samples taken from a reactor; however, when not being mixed, the hydrolysate is said to divide into an upper organic layer rich layer and a denser lower layer. Please discuss how this separation may affect the potential hazard during a spill. How will the evaporation rate be affected? Is direct contact more of a concern?	The hydrolysate is likely to be well-mixed initially, but would eventually separate with an organic mixture potentially forming a thin layer on the surface of the spill. Of the compounds in the organic layer (mainly disulfides and DIPA, only DIPA is highly volatile. We have done a bounding calculation that assumes all of the DIPA is released – see response to comment #8. At the time of the spill, when drivers may still be present at the scene, the hydrolysate will be well-mixed and may not have separated into layers. Section 6.3 of the TRA addresses dermal impacts of the hydrolysate. The drivers are equipped with respirators, googles, chemical-resistant gloves, coveralls, and booties. The driver training and spill/safety equipment will reduce the probability or severity of any dermal exposure.
6	VX Hydrolysate TRA –Table 4-3	Hazard Severity Definitions Used for TRA, Page 14, Negligible, Level IV, Rationale, Part a: It appears that the term “hazard distance” was used in error. Please replace “hazard distance” with “concentration” if this is the correct term.	The term “hazard distance” is correct as used. As explained in Section 4.2, page 12, “the hazard is characterized in terms of hazard distances, which are the distances necessary for the chemical concentration to fall below specific concentration levels, as it disperses. For VX, the concentration levels are based on established Acute Exposure Guideline Levels (AEGLs). For example, the 30-minute AEGL-1 hazard distance is the distance required for the VX concentration to fall below the 30-minute AEGL-1 concentration. Hazard distances are calculated using a plume dispersion model, specifically, the Army-sponsored D2PC software (Whitacre et al. 1987).”

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7	VX Hydrolysate TRA – Section 6.1	Exposure Via Inhalation from Spill, Page 21: The variable *d* is listed as *the length of spill surface in the downwind direction (meters)*, which would appear to be the radius of the spill from the source to the edge of the spill. The referenced document (SAIC 2011) for the source of Equation 1 states that *d* equals the spill diameter. Please specify the values used for *d* in Equation 1 and revise the definition of *d* as needed.	The phrase "length of spill surface in the downwind direction" refers to the entire spill surface , not just the portion starting from the center to the edge of the spill. The value of *d* was in fact calculated by the model as the diameter of the circular spill. For example, for a 5,000 gallon (18.927 cubic meter) spill with a spill depth of 1 cm (0.01 m), $18.927 = \prod d^2/4 \times 0.01$ d = 49.08 m We will add the above calculation in the text in Section 6.1.
8	VX Hydrolysate TRA – Section 6.1	Exposure via Vapor Inhalation from Spill, Page 22,Equations 5 and 6: As discussed in Section 2, the VX hydrolysate divides into layers when not being mixed. In addition, VX is not as water soluble as GB. Raoult's Law (Equation 5) is generally used fro ideal mixtures of liquids. Please explain why it is appropriate to use Raoult's Law (Equation 5) & Equation 6 for VX hydrolysate, which divides into layers when settled.	The commenter is correct that Raoult's Law assumes ideal mixture. Non-ideal solutions produce partial pressures that may be greater than or less than the partial pressure calculated based on Raoult's Law. In the absence of any information on non-ideality of the mixture, we felt that Raoult's Law was a reasonable approximation. Nonethless, we are supplementing our response by providing a demonstration of worst-case estimates. (See continuation sheet for Comment #8.) We will revise the TRA to include these worst-case estimates in an appendix.
9	VX Hydrolysate TRA – Section 6.1	Exposure via Vapor Inhalation from Spill, Page 22, Equation 5 & 6: As we do not have access to the models that were used, please provide the cvalculations that led to the calculated mass of chemical released due to evaporation from a 5,000-gallon hydrolysate spill.	One example calculation is provided. See continuation sheet for Comment #9. We will include this example calculation in the TRA report as an appendix.

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Cmt #	Applies to	Comment	Proposed Resolution
10	VX Hydrolysate TRA – Section 6.4	Aquatic Impacts: This section suggests that, while perhaps unlikely, a large-scale release of hydrolysate to a smaller, low flow stream or river may result in significant impact to aquatic life. This being the case, the Division suggests avoiding routes that parallel such waterways to the extent practicable.	We will add the following sentence to the end of the Aquatic Impacts section: “It is suggested that the transporter avoid routes that parallel smaller, low-flow stream or river waterways to the extent practicable.”

GB Hydrolysate TRA – Calculation of TBA Evaporated Mass

NOTE: Manual calculation will involve rounding errors. It is recommended that these calculation steps be performed sequentially using a spreadsheet.

Temp = 41.7 C

Amt spilled = 5000 gal = 18.927 m3

Spill depth = 1 cm = 0.01 m

Spill area = 5000*0.0037854/0.01 = 1892.7 m2

Spill diameter = SQRT(1892.7*4/∏) = 49.08 m

Calculation of mole fractions from given wt fractions using Equation 5:

MW	Chemical	wt frac	Moles (wt frac/MW)	mole frac (moles/total moles)
140.1	O-isopropyl methylphosphonofluoridate (GB)	5.20E-08	3.71E-10	7.13E-09
160.1	Sodium O-isopropyl methylphosphonate (NaIMPA)	4.15E-02	2.59E-04	4.99E-03
140.0	Disodium methylphosphonate (Na2MPA)	2.91E-03	2.08E-05	4.00E-04
180.2	O,O'-diisopropyl methylphosphonate (DIMP)	1.64E-03	9.09E-06	1.75E-04
120.0	Sodium methylphosphonofluoridate (NaFA)	6.55E-04	5.46E-06	1.05E-04
42.0	Sodium fluoride	2.52E-02	5.99E-04	1.15E-02
185.4	Tributylamine (TBA)	2.51E-03	1.35E-05	2.60E-04
60.1	Isopropanol	3.48E-04	5.79E-06	1.11E-04
144.2	N,N'-diisopropylurea (DIU)	1.69E-04	1.17E-06	2.25E-05
40.0	Sodium Hydroxide	7.64E-03	1.91E-04	3.67E-03
18.0	Water	9.17E-01	5.09E-02	9.79E-01
		1.00E+00	5.20E-02	

Moles = wt frac/MW = 2.51E-03/185.4 = 1.35E-05

Mole frac = moles/total moles = 1.35E-05/5.2E-02 = 2.6E-04

Calculation of TBA vapor pressure at 41.7 deg C using Equation 4:

Boiling point = 488 K

Pv = Exp(19*(1-488 K/314.7 K)+8.5LN(488 K/314.7 K)) = 1.19E-03 atm

Calculation of TBA Partial Pressure in the mixture using Equation 6:

Partial Pressure TBA = 1.19E-03 atm x 2.60E-04 = 3.09E-07 atm

Calculation of Diffusivity using Equation 2:

Diffusivity of water = 2.4E-05 m2/s

Diffusivity (D) of TBA = 2.4E-05 * SQRT(18/185.4) = 7.48E-06 m2/s = 7.48E-02 cm2/s

Calculation of Schmidt Number for Equation 1:

Sc = μ/(D*density of air) or kinematic viscosity of air(μ/density of air)/D = (0.1516 cm2/s)/(7.48E-02m2/s) = 2.0

Calculation of Evaporation Rate using Equation 1:

E = 3530*3.1 m/s^0.78*185.4*3.09E-07 atm/2.0^(2/3)/49.08 m^0.11/1/(273 C+41.7 C) = 6.36E-04 g/min/m2
(Note: The correct units for E are g/min/m2. We will correct it in the TRA report)

Calculation of Evaporated Mass:

Evap Mass = 6.36E-04 g/min.m2*spill area*120 min

= 6.3E-04 g/min-m2*18.927m3/0.01m*120 = 145 g

GB Hydrolysate TRA – Calculation of GB Evaporated Mass

Temp = 41.7 C

Amt spilled = 5000 gal = 18.927 m3

Spill depth = 1 cm = 0.01 m

Spill area = 5000*0.0037854/0.01 = 1892.7 m2

Spill diameter = SQRT(1892.7*4/∏) = 49.08 m

Calculation of mole fractions from given wt fractions using Equation 5:

MW	Chemical	wt frac	Moles (wt frac/MW)	mole frac (moles/total moles)
140.1	O-isopropyl methylphosphonofluoridate (GB)	5.20E-08	3.71E-10	7.13E-09
160.1	Sodium O-isopropyl methylphosphonate (NaIMPA)	4.15E-02	2.59E-04	4.99E-03
140.0	Disodium methylphosphonate (Na2MPA)	2.91E-03	2.08E-05	4.00E-04
180.2	O,O'-diisopropyl methylphosphonate (DIMP)	1.64E-03	9.09E-06	1.75E-04
120.0	Sodium methylphosphonofluoridate (NaFA)	6.55E-04	5.46E-06	1.05E-04
42.0	Sodium fluoride	2.52E-02	5.99E-04	1.15E-02
185.4	Tributylamine (TBA)	2.51E-03	1.35E-05	2.60E-04
60.1	Isopropanol	3.48E-04	5.79E-06	1.11E-04
144.2	N,N'-diisopropylurea (DIU)	1.69E-04	1.17E-06	2.25E-05
40.0	Sodium Hydroxide	7.64E-03	1.91E-04	3.67E-03
18.0	Water	9.17E-01	5.09E-02	9.79E-01
		1.00E+00	5.20E-02	

Moles = wt frac/MW = 5.2E-08E-03/140.1 =3.71E-10

Mole frac = moles/total moles = 3.71E-10/5.2E-02 = 7.13E-09

Calculation of GB vapor pressure at 41.7 deg C using Equation 3:

Pv = 2.718^[22.72-4320.8/(-41.245+314.7)] = 1010.81 Pascals

Pv= 1010.81/101325 = 9.97E-03 atm

Calculation of GB Partial Pressure in the mixture using Equation 6:

Partial Pressure GB = 9.97E-03 x 7.13E-09 = 7.13E-11 atm

Calculation of Diffusivity using Equation 2:

Diffusivity of water = 2.4E-05 m2/s

Diffusivity (D) of GB = 2.4E-05 m2/s * SQRT(18/140.1) = 8.6E-06 m2/s = 8.6E-02 cm2/s

Calculation of Schmidt Number for Equation 1:

Sc = μ/(D*density of air) or kinematic viscosity of air(μ/density of air)/D = (0.1516 cm2/s)/(8.6E-02m2/s) = 1.74

Calculation of Evaporation Rate using Equation 1:

E = 3530*3.1 m/s^0.78*140.1*7.13E-11 atm/2.0^(2/3)/49.08 m^0.11/1/(273 C+41.7 C) = 1.22E-07 g/min/m2

Calculation of Evaporated Mass:

Evap Mass = 1.22E-07 g/min.m2*spill area*120 min

= 1.22E-07 g/min-m2*18.927m3/0.01m*120 = 2.77E-02 g

(Note: The model had previously used the starting GB mass fraction as 5.5E-08 (an earlier value) instead of 5.2E-08 as shown in Table 2-1 of the TRA. This has been corrected. The mass changed from 2.93E-02 to 2.77E-02. There is little to no effect on the hazard distances.)

Worst-case estimates

Case 1: DIPA

DIPA is the only highly volatile chemical in the top layer. Instead of using the evaporation model to estmate the mass evaporated, it is assumed that all of the DIPA present is evaporated, which is conservative.

For a 5,000 gallon spill, the total mass of the spill = 5000 gal x specific gravity x 3.785 kg/gal = 5000*1.087*3.785 = 20,571.475 kg

Mass of DIPA = wt. frac x 20571.475 kg = 0.0053 x 20571.475 kg = 109 kg or 1.09E+05 g.

This mass was then used in the D2PC model to predict the hazard distances for the worst case (Temp = 41.7 deg C, Stability D). It should be noted that D2PC calculations assume a point source, therefore, the estimate is conservative. The results are as follows:

2-hr PAC-1 distance = 33 meters (versus 29)

30-min PAC-1 distance = 11 meters (versus 10 m [recalculated – previously 9m - see VX example calculation last line])

For 29 deg C, Stability F:

2-hr PAC-1 distance = 47 meters (versus 30 m [recalculated – previously 29])

30-min PAC-1 distance = 13 meters (versus 7)

Case 2: VX

For VX – Assume all of the VX is the sole liquid in the spill

Siimilarly, results are as follows for both 41.7 deg C and 20 deg C:

2-hr AEGL-1 distance = 0 meters (versus 0)

30-min AEGL-1 distance = 0 meters (versus 0)

Case 3: Disulfide – Assume it is the sole liquid in the spill.

Similary, results are as follows for both 41.7 deg C and 29 deg C:

2-hr AEGL-1 distance = 0 meters (versus 0)

30-min AEGL-1 distance = 0 meters (versus 0)

All of the distances above are compared to those estimated from the evaporation model (in parenthesis), and also meet the “Negligible” hazard severity level shown in Table 4-3.

VX Hydrolysate TRA – Calculation of DIPA Evaporated Mass

NOTE: Manual calculation will involve rounding errors. It is recommended that these calculation steps be performed sequentially using a spreadsheet.

Temp = 41.7 C

Amt spilled = 5000 gal = 18.927 m3

Spill depth = 1 cm = 0.01 m

Spill area = 5000*0.0037854/0.01 = 1892.7 m2

Spill diameter = SQRT(1892.7*4/∏) = 49.08 m

Calculation of mole fractions from given wt fractions using Equation 5:

MW	Comp	wt frac (mixture)	Mmoles (wt frac/MW)	mol frac (moles/total moles)
267.4	VX	8.00E-08	2.99E-10	6.48E-09
239.3	EA 2192	1.00E-06	4.18E-09	9.05E-08
124.1	EMPA	7.70E-02	6.20E-04	1.34E-02
145.0	MPA	9.70E-03	6.69E-05	1.45E-03
161.3	Thiolamine	6.30E-02	3.91E-04	8.45E-03
320.0	Disulfide	1.40E-02	4.38E-05	9.47E-04
101.0	DIPA	5.30E-03	5.25E-05	1.14E-03
46.1	Ethanol	1.60E-03	3.47E-05	7.51E-04
40.0	NaOH	3.50E-02	8.75E-04	1.89E-02
18.0	Water	7.94E-01	4.41E-02	9.55E-01
		1.00E+00	4.62E-02	

Moles = wt frac/MW = 5.3E-03/101 = 5.25E-05

Mole frac = moles/total moles = 5.25E-05/4.62E-02 = 1.14E-03

Calculation of DIPA vapor pressure at 41.7 deg C using Equation 4:

Boiling point = 355 K

Pv = Exp(19*(1-355K/314.7K)+8.5LN(355K/314.7K)) = 0.2444 atm

Calculation of DIPA Partial Pressure in the mixture using Equation 6:

Partial Pressure TBA = 0.2444 x 1.14E-03 = 2.78E-04 atm

Calculation of Diffusivity using Equation 2:

Diffusivity of water = 2.4E-05 m2/s

Diffusivity (D) of TBA = 2.4E-05 * SQRT(18/101) = 1.01E-05 m2/s = 1.01E-01 cm2/s

Calculation of Schmidt Number for Equation 1:

Sc = μ/(D*density of air) or kinematic viscosity of air(μ/density of air)/D = (0.1516 cm2/s)/(1.01E-01 m2/s) = 2.0

Calculation of Evaporation Rate using Equation 1:

E = 3530*3.1 m/s^0.78*101*2.78E-04 atm/2.0^(2/3)/49.08 m^0.11/1/(273 C+41.7 C) = 3.82E-01 g/min/m2

Calculation of Evaporated Mass:

Evap Mass = 3.82E-01 g/min.m2*spill area*120 min

= 3.82E-01 g/min-m2*18.927m3/0.01m*120 min

= 8.67E+04 g

(Note: We fixed a small discrepancy in a cell reference of the model, which results in a small difference (8.67E+04 g versus 8.33E+04 g). There is little to no effect on the hazard distances.