U.S. Army
Chemical Materials Agency

Bounding Transportation Risk Assessment for > 1 Vapor Screening Level (VSL) Waste

FINAL

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FOREWORD

This Programmatic Bounding Transportation Risk Assessment (TRA) has been prepared to define the conditions under which all sites and activities can safely ship greater than 1 Vapor Screening Level (VSL) agent-contaminated secondary waste to offsite treatment, storage, and disposal incineration facilities. Offsite shipment is proposed as an alternative to onsite treatment in order to expedite the destruction of the chemical agent stored onsite and thereby reduce the risk to the public and workers from potential accidents during storage of that agent. Offsite shipment of secondary waste generated during closure operations will also greatly reduce the risk to workers that would otherwise be involved in treatment of that waste onsite.

The U.S. Army Chemical Materials Agency (CMA) feels strongly that continued safe shipment of secondary waste will ensure the highest level of protection for the workers, communities, and the environment.

CONRAD F. WHYNE
Director
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EXECUTIVE SUMMARY

Secondary waste is generated during disposal of the Army's stockpile of chemical agents and munitions. Management and disposal of this waste is a growing concern at the Army facilities, in large part because of the limited capacity for treating this waste onsite. In addition, the equipment used to treat the waste onsite is generally being used for disposal of chemical agent and munitions; thus, devoting time to secondary waste disposal increases the time required for destruction of the chemical stockpile. Increasing the time required for destruction of the stockpile increases the risks to members of the public near the site.

Offsite treatment of the secondary waste at a commercial treatment, storage, and disposal facility (TSDF) is being considered as an alternative to onsite disposal. Shipment of the waste to a TSDF is a viable option because the secondary waste has very low levels of chemical agent contamination, so the potential risk to members of the public in the event of a transportation accident is small. The National Research Council has recently recommended that the Army pursue offsite shipment and disposal of secondary waste if it can be accomplished safely.

To ensure protection of the public during transport of hazardous materials, the TSDF and waste shipper are required to follow Department of Transportation regulations outlined in 49 CFR parts 100 to 185. The regulations protect the public by specifying packaging, loading, and marking requirements for the waste, mandating requirements for vehicle maintenance and driver training, and dictating procedures to be used when transporting the waste.

A transportation risk assessment (TRA) is performed to identify and assess the potential risks to members of the public due to accidents during transport of hazardous waste. TRAs have traditionally not been required for hazardous waste transport. This includes transport of wastes that are comparable to or more hazardous than the secondary wastes generated at the Army's chemical agent disposal facilities (for example, chlorine in tanker trucks). Although a TRA is not required, the Army previously has completed TRAs to support planned shipment of certain types of agent-contaminated secondary waste from specific Army facilities to a permitted TSDF. These shipments were subsequently completed safely and without incident.

Rather than continuing to perform waste-specific and site-specific TRAs, this TRA was conducted to determine bounding conditions for shipment of secondary waste. This bounding TRA is to be used in support of transportation of secondary waste streams from any stockpile or non-stockpile site. It specifically addresses public risk due to an accident during transport of secondary wastes contaminated with sarin (GB), O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothioate (VX), or mustard (H, HD, and HT, hereafter collectively referred to as 'H') . The potential risks from transporting lewisite (L)- or tabun (GA)-contaminated wastes were not specifically modeled in this analysis. However, because the Acute Exposure Guideline Levels (AEGLs) for GA are higher than or equal to those for GB, the GB calculations are bounding for GA. Sites with Lewisite-contaminated waste will address the transportation risks for that waste in site-specific TRAs.

The bounding TRA assesses the risk to the public from an accident during transport of secondary waste items to an offsite TSDF. It does not consider risk from potential accidents during handling, loading, or unloading the wastes at the originating facility/storage area or at the TSDF. Documents that address hazards during these activities, such as job hazard analyses or monitoring plans, will be developed independently from this bounding TRA.

The objectives of the bounding TRA are 1) to evaluate the conditions under which the waste may be shipped with acceptable risk and 2) to provide a detailed assessment of the public risk associated with an accident during shipment of this waste to a TSDF. This is accomplished using standard risk assessment methods coupled with conservative (pessimistic) assumptions regarding the likelihood of the accident and the severity of the resulting downwind hazard. It is likely that these methods greatly overestimate the public risk due to offsite shipment.

The bounding TRA specifies limits on the level of agent contamination in the waste and the total number of shipments that can be completed. The limits on agent contamination are provided to limit downwind hazard to a level that would result in little or no health impact. The limits on total number of shipments are provided to limit the probability of an accident during the life of the shipment operation. If a site that would like to ship secondary and/or closure wastes can show that their waste is within the conditions analyzed in the bounding TRA, then the risks associated with shipping their waste would be acceptable and no site-specific TRA would be needed.

It should be noted that this bounding TRA is just one element of the Army's program to ensure protection of the public, workers, and the environment during shipment operations. Other documents are prepared to cover 1) monitoring and characterization of the waste, 2) packaging and segregation of the waste, 3) loading and unloading operations, 4) transportation planning and procedures, and 5) emergency response planning and procedures.

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SECTION 1
INTRODUCTION

1.1 Background

Agent-contaminated secondary waste is generated as a result of chemical agent storage, disposal, and decommissioning operations. This waste must be disposed of in a safe and environmentally sound manner. The Army's chemical agent disposal facilities have systems that are capable of disposing of these wastes, but at very limited throughput rates. For that reason, the Army is pursuing off-site shipment of these wastes to a commercial treatment, storage and disposal facility (TSDF).

In their *Review of Chemical Agent Secondary Waste Disposal and Regulatory Requirements* (National Research Council, 2007), the National Research Council (NRC) made the following recommendation to the Chemical Materials Agency (CMA) on the management of secondary waste:

> Recommendation 3-3. The committee encourages the CMA to continue the pursuit of off-site shipment and disposal of > 1 STL [short-term limit][1] secondary waste....

As part of CMA's continuing effort to handle secondary waste safely and effectively, offsite shipment has moved to the forefront for management of secondary waste.

To ensure protection of the public during transport of hazardous materials, the TSDF and waste shipper are required to follow all applicable Department of Transportation regulations outlined in 49 CFR parts 100 to 185 (Federal Register, 2007). These regulations protect the public by specifying packaging, loading, and marking requirements for the waste, mandating requirements for vehicle maintenance and driver training, and dictating procedures to be used when transporting the waste.

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[1] STL refers to an agent concentration measured in milligrams per cubic meter.

Transportation risk assessments (TRAs) have traditionally not been required for hazardous waste transport. This includes transport of wastes comparable to or more hazardous than the secondary wastes generated at the Army's chemical agent disposal facilities (e.g., chlorine transported in tanker trucks). Although a TRA is not required, the Army previously has completed TRAs to evaluate the risk due to postulated accidents during shipment of agent-contaminated secondary waste materials to an offsite TSDF. These TRAs have been prepared for shipment of greater than one vapor screening level (> 1 VSL[2]) wastes, including VX-, GB-, and H-contaminated waste. The VSL levels for VX, GB, and H are 0.00001 mg/m^3, 0.0001 mg/m^3, and 0.003 mg/m^3, respectively. For these previous TRAs, such as the *Transportation Risk Assessment for Secondary Waste from the Newport Former Production Facility* [FPF] (SAIC, 2007), the specific waste streams to be transported were characterized based on drum headspace monitoring data and/or generator knowledge.

Rather than continuing to write TRAs tailored to specific sites and specific waste profiles, an effort to streamline the TRA process by completing a bounding TRA was proposed. The bounding TRA may be applied to secondary or closure waste leaving any chemical agent stockpile or non-stockpile site, thus creating continuity in the criteria applied to shipment of secondary waste. Creating a bounding TRA also complies with the following recent recommendation from the NRC:

> Recommendation 2-5. The Chemical Materials Agency should establish consistent and detailed criteria for conducting whatever transportation risk assessments are required to ensure accuracy and uniformity in the expression of results.

The bounding TRA will be part of a package of information required prior to shipment of > 1 VSL agent-contaminated wastes to an offsite TSDF. Additional documentation (e.g., a Monitoring Plan and a Health and Safety Approach Document) will be included in the information package. Table 1-1 lists the various documents to be included and describes what each document will address.

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[2] VSL usually references an agent concentration in the air above agent-contaminated material. Here, VSL and STL are equivalent in meaning.

1.2 Scope

The bounding TRA will determine the bounding conditions under which secondary waste or closure shipment can be completed with acceptable risk. The bounding conditions to be determined include 1) the maximum permissible agent concentrations and/or agent quantity per drum and 2) the maximum permissible number of shipments during the shipment operation. The bounding TRA can then be used as the basis for determining whether shipment of various wastes from a site to a TSDF will involve acceptable risk. It is recognized that there will be instances when assumptions made in the bounding TRA conflict with procedures or other protocols employed by the generator of the waste. In these instances, a site-specific addendum to the TRA may be prepared to show that the waste still falls within the bounds of this TRA.

Table 1-1. Information Package Required for Off-Site Shipment

Document	Contents
Waste Profile	Description of waste to be shipped. Agent content based on headspace monitoring or generator knowledge.
Monitoring Plans and SOPs	Description of monitoring procedures employed.
Waste Segregation and Packaging SOPs	Description of how waste is segregated and packaged for shipment.
Transportation Plans	Description of packaging and containment of waste during transport, driver training, route and emergency response planning.
Health and Safety Approach	Description of the approach to ensuring protection of workers involved in loading, unloading, and shipment operations.
Bounding Transportation Risk Assessment and Site-Specific Addendum (if needed)	This document and any addendum required to address site-specific factors not covered in the Bounding TRA

Before discussing the methodology and technical approach to the bounding TRA, it is useful to review the types of waste to be shipped, how these wastes are packaged, and the procedures to be employed in the event of an accidental release during transport. This background information is provided in sections 2 and 3. The overall methodology used in the TRA is then outlined in section 4, followed by a more detailed discussion of the analysis and results in sections 5 and 6. Section 7 then provides a brief discussion of how these results would be used by a site to obtain approval for a secondary waste shipment operation.

SECTION 2
DESCRIPTION OF WASTE TO BE SHIPPED

2.1 Waste Description

Waste items for shipment will vary from site to site. However, it is anticipated that the waste streams from each of the sites will be fairly similar in makeup. The waste streams addressed in this TRA include all porous and non-porous wastes except agent-contaminated spent carbon filters or carbon filter media, which will be addressed in a separate TRA. The waste items will be dismantled and have no occluded spaces. Ultimately, the waste items that will be shipped offsite must comply with the requirements set forth by the TSDF that will receive the waste materials.

Waste information profiles, describing each waste stream, will be prepared in compliance with United States Environmental Protection Agency (USEPA) and state permit requirements. All > 1 VSL wastes proposed for shipment to a TSDF must meet all established acceptance criteria of the facility and the site desiring to ship the waste.

2.2 Waste Packaging

Waste items will be placed into containers meeting Department of Transportation (DOT) packaging requirements. It is anticipated that most waste will be shipped in polyethylene drums, though the use of metal drums is not precluded. Polyethylene drums are preferred because they can be fed directly to the TSDF incinerator. Metal drums must have the lids loosened before they can be fed in order to prevent pressure excursions inside the incinerator. Loosening the lids provides an additional worker exposure hazard that is not present if polyethylene drums are used. In addition, the feed rate to the incinerator is much slower for metal drums compared to the polyethylene drums.

It is assumed that the container will be sealed with a lid. Waste items also may be placed in bags and/or into lined drums to provide additional containment; however, to be conservative in this analysis, the TRA does not give credit to use of bags or liners to contain waste materials inside the drum. The drum with a secured lid is the primary source of protection for the waste materials.

2.3 Transport Truck Capacity

Both 55-gallon and 95-gallon drums were assumed to be used for shipment of waste items. Based on trucks that have been used to ship waste in the past, one truck can accommodate 80 55-gallon drums or 51 95-gallon drums if stacked one high. Drums will be loaded onto pallets and the pallets placed in the transport truck. For the purpose of this TRA, it is assumed that the trucks will be loaded with one size drum on each pallet, with no stacking of the pallets. Stacking is not allowed in order to make inspection easier. It was also assumed in this TRA that only one agent type was present in each drum and on each shipment. Drums containing multi-agent wastes or shipments containing more than one agent type may be acceptable for shipment, but will be addressed on a site-specific basis.

SECTION 3
MITIGATION MEASURES DURING TRANSPORT

In order to limit the potential for accidents resulting in human health or environmental impacts, several safety measures are to be taken during shipment of the waste. These measures include the following.

- Two drivers per vehicle with both drivers trained in Hazardous Waste Operations and Emergency Response (HAZWOPER)
- Multiple vehicle caravans
- Global positioning satellite (GPS) tracking of the vehicles
- Frequent contact with the vehicle dispatcher
- Emergency response teams available along the route for environmental remediation following the initial response by the driver teams and local emergency responders.

A site-specific Health and Safety Approach document will be prepared that will describe these measures in greater detail.

Drivers will participate in appropriate safety briefings before shipment. They will receive a copy of any applicable safety documents (e.g., safety plans, MSDS, etc.) before commencing transportation of the waste.

The TSDF that is receiving the waste will have emergency response coordinators and response teams on standby throughout the transportation operation in the event of an emergency along the planned route. All TSDF personnel on standby will be specifically trained in emergency response procedures for the waste shipments, and will be qualified as emergency responders per 29 CFR 1910.120 (HAZWOPER) (Federal Register, 1989). Emergency response teams will be capable of responding to and mitigating any accident along the route within two hours.

The trucks that transport the waste will use a driver team and "visual" caravan[3] approach to such shipments. The use of a visual caravan along a pre-approved route adds an additional level of safety and security. The drivers will be in routine contact with each other, their dispatch, and the appropriate authorities from the TSDF.

Should an accident occur while material is being shipped, drivers are instructed to communicate immediately with 911, their dispatch, and emergency response coordinators from the TSDF, and to establish an initial isolation zone at a minimum of 25 meters from the accident site. The TSDF will be prepared to provide on-site emergency responders, with additional assistance available via telephone.

The TSDF will make preparations to mobilize emergency response teams to complete all necessary cleanup activities. Local responders will be instructed to:

- Provide immediate medical aid to persons who may have been injured.
- Establish isolation distances around the incident scene in accordance with the DOT Emergency Response Guidebook recommendations for placarded shipments and the emergency response instructions that the drivers of the trucks provide.

Transport personnel will assist the on-scene Incident Commander (IC) in establishing site isolation and control zones. The IC is typically an official from the jurisdiction having authority over the event (e.g., local hazardous material unit chief). First responders will establish a secondary boundary at a minimum of 50 meters from the accident site. They will evacuate this area and take actions to terminate the agent

[3] In a "visual" caravan, each team of drivers maintains line-of-sight visual contact with other trucks in the caravan.

vapor release. Site control zones will be demarcated using barricades, barriers or hazard tape. All spilled waste material will be collected for appropriate disposition. The decontamination process will be managed by the IC in concert with local and state environmental offices should there be any environmental impacts associated with the response.

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SECTION 4
METHODOLOGY

4.1 Overview of the Methodology

The general methodology used in the bounding TRA relies on the traditionally-accepted Army risk management approach. The methodology is similar to that used in the Newport FPF TRA (SAIC, 2007), but has been modified to meet the specific needs of the bounding TRA.

Historically, Department of the Army Pamphlet (DA PAM) 385-61 has been the basis for Army risk management program for chemical agent-related hazards (DA, 2002). Appendix F of DA PAM 385-61 provides an overview of the Army strategy for a risk management program. It states in part:

> Risk assessment, as a part of risk management, provides a useful tool for estimating the effectiveness of existing and proposed safeguards against chemical agent mishaps. The potential for and consequences of mishaps must be carefully analyzed. The risk assessment must consider not only the traditional MCEs [Maximum Credible Events] and resulting consequences, but also the probabilities and consequences of any realistic accident scenario that could present a risk to worker, the environment or the public.

DA PAM 385-61 has recently been replaced by a more generally applicable document, DA PAM 385-30, entitled *Mishap Risk Management* (DA, 2007). DA PAM 385-30 outlines a risk management approach that is consistent with that outlined in DA PAM 385-61.

As outlined in DA PAM 385-30, the risk assessment is used to establish priorities for corrective action and resolution of identified hazards. Consistent with these objectives, the bounding TRA evaluated the risk of the potential accident and release scenarios based on the combination of hazard probability and severity.

Figure 4-1 provides the Department of the Army model for risk acceptance according to DA PAM 385-30. Risk categories range from *Low* to *Extremely High*. *Low* risks are generally considered to be acceptable without mitigation, whereas higher risk categories generally require mitigation. The decision on whether or not to mitigate or accept specific hazards is left to the discretion of Army authorities.

Hazard Severity	**Hazard Probability**				
	A Frequent	**B Likely**	**C Occasional**	**D Seldom**	**E Unlikely**
I - Catastrophic	Extremely High				
II – Critical		High			
III - Marginal			Medium		
IV - Negligible				Low	

Figure 4-1. Qualitative Risk Evaluation Matrix per DA PAM 385-30

The probabilities and severities in the matrix above may be categorized using schemes provided in DA PAM 385-30 and Army Regulation, AR 385-61 (DA, 2001). These categorization schemes are shown in tables 4-1 and 4-2, respectively. In the bounding TRA, a set of accidents was selected and evaluated to determine the risk level for each accident scenario.

In the bounding TRA, it is assumed that only *Low* risk is allowable because *Low* risk hazards are generally deemed acceptable without mitigation. As shown in figure 4-1, if the hazard severity is *Negligible*, *Low* risk is achieved with hazard probabilities ranging from *Likely* to *Unlikely*. If, however, the hazard severity is *Marginal*, *Low* risk is achieved only if the hazard probability is *Seldom* or *Unlikely*. Based on accident frequencies presented later in this document, it is not expected that frequencies will be

Table 4-1. Probability Categories per DA PAM 385-30

Description	Level	Single Item or Activity
Frequent	A	Likely to occur often in the life of an item, with a probability of occurrence greater than 10^{-1} in that life.
Probable or Likely	B	Will occur several times in the life of an item, with a probability of occurrence less than 10^{-1} but greater than 10^{-2} [1 time/100 opportunities] in that life.
Occasional	C	Likely to occur some time in the life of an item, with a probability of occurrence less than 10^{-2} but greater than 10^{-3} [1 time/1,000 opportunities] in that life.
Seldom or Remote	D	Unlikely but possible to occur in the life of an item, with a probability of occurrence less than 10^{-3} but greater than 10^{-6} [1 time/1,000,000 opportunities] in that life.
Unlikely or Improbable	E	So unlikely, it can be assumed occurrence may not be experienced, with a probability of occurrence less than 10^{-6} in that life.

Table 4-2. Hazard Severity Descriptions in AR 385-61 and DA PAM 385-30

Hazard Severity	Level	Description
Catastrophic	I	AR 385-61: Fatality or injury resulting in permanent total disability; agent release in which the 1% lethality extends beyond the installation boundary. DA PAM 385-30: One or more deaths or permanent total disabilities.
Critical	II	AR 385-61: Serious or partially disabling injury; agent release in which the 1% lethality extends outside the limited area but within the installation boundary or, agent concentrations outside the limited area but within the installation boundary that exceed the AEL. DA PAM 385-30: One or more permanent partial disabilities or temporary total disability resulting in more than 3 months lost time.
Marginal/ Moderate	III	AR 385-61: Minor injury; agent release in which the 1% lethality does not extend beyond the limited area, or agent release above the worker AEL outside of engineering controls that does not extend beyond the limited area. DA PAM 385-30: One or more injuries or illnesses resulting in less than 3 months lost time.
Negligible	IV	AR 385-61: Agent release within engineering controls or agent release beyond engineering controls but not exceeding the AEL. DA PAM 385-30: One or more injuries or illnesses requiring first aid or medical treatment.

Notes:

AEL = airborne exposure limit (As used in AR 385-61, the AEL is the 8-hr worker population limit for unmasked workers.)

below 10^{-6} per year, so hazard probabilities of *Unlikely* are not anticipated. For that reason, a hazard severity of *Critical* is not likely to be acceptable.

Because the bounding TRA seeks to determine the bounding waste characteristics that can be shipped with acceptable (*Low*) risk, it is necessary to more clearly define what constitutes a hazard with *Negligible* or *Marginal* severity. Although *Critical* hazards are not likely to be acceptable, it is worthwhile to define *Critical* hazards as a basis for comparison to hazards that are deemed acceptable.

4.2 Hazard Definition

The approach outlined below defines hazard severity based on two response zones: 1) the initial isolation zone and 2) the secondary control zone. In the event of an accident, personnel involved in the convoy will isolate and evacuate the area within 25 meters of the site, as recommended by the Emergency Response Guidebook (ERG 2008). In the TRA, it was assumed this could be accomplished within 30 minutes of the accident. It was also assumed that the secondary control zone will be established at a minimum of 50 meters from the accident site and that it may take up to 2 hours for first responders to arrive at the accident scene, evacuate the secondary zone, and terminate the vapor release. It should be noted that the Emergency Response Guidebook specifies that emergency responders should consider evacuation out to at least 100 meters depending on the hazardous material involved. Assuming a secondary control zone of only 50 meters results in a higher calculated exposure to a hypothetical individual at the secondary control zone boundary, and is therefore is conservative.

The hazard is characterized in terms of hazard distances. The hazard distances are the distances necessary for the agent concentration to fall below specific concentration levels. The concentration levels used in the bounding TRA are based on established Acute Exposure Guideline Levels (AEGLs) for the chemical agents. For example, the 30-minute AEGL-1 hazard distance is the distance required for the agent 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, 1987).

Table 4-3 presents a set of hazard severity definitions that provide the same acceptable exposure levels both inside and outside the initial isolation zone, the only difference being the duration of the exposure in these two areas. The hazard severity definitions reference AEGL-1, -2, and -3 concentrations for 2-hour and 30-minute exposures. Exposures at greater than the AEGL-3 concentration could lead to life-threatening effects or death for susceptible receptors. Exposures at greater than the AEGL-2

Table 4-3. Hazard Severity Definitions Used in the Bounding TRA

Hazard Severity	Level	Proposed Definition and Rationale
Negligible	IV	2-hr AEGL-1 hazard distance < distance to nearest member of the public 30-min AEGL-1 hazard distance < distance to boundary of the initial isolation zone Rationale: a. Ensuring that the 2-hr AEGL-1 hazard distance does not reach the nearest member of the public ensures that there are negligible health effects. b. Ensuring that the 30-min AEGL-1 hazard distance does not extend beyond the initial isolation zone would likely ensure negligible health effects for bystanders.
Marginal	III	2-hr AEGL-2 hazard distance < distance to nearest member of the public 30-min AEGL-2 hazard distance < distance to boundary of the initial isolation zone Rationale: a. Ensuring that the 2-hr AEGL-2 concentration does not reach the nearest member of the public ensures that injuries are minor. b. Ensuring that 30-min AEGL-2 hazard distance does not extend beyond the initial isolation zone would likely ensure only minor injuries for bystanders.
Critical	II	2-hr AEGL-3 hazard distance < distance to nearest member of the public 30-min AEGL-3 hazard distance < distance to boundary of the initial isolation zone Rationale: a. Ensuring that the 2-hr AEGL-3 concentration does not reach the nearest member of the public ensures that injuries are not fatal, although they may be serious. b. Ensuring that the 30-min AEGL-3 hazard distance does not extend beyond the initial isolation zone would likely ensure that injuries are not fatal, although they may be serious.

concentration, but less than the AEGL-3 concentration, could result in long-lasting and irreversible health effects. Exposures at greater than the AEGL-1 concentration, but less than the AEGL-2 concentration, could result in non-disabling and reversible health effects. The 30-minute AEGL concentrations (NRC, 2003) are presented in table 4-4 for each agent type. Since 2-hour AEGL concentrations are not available, the existing values were interpolated to obtain the 2-hour values presented in table 4-4. This interpolation is discussed in Appendix C.

Table 4-4. AEGL Concentrations

Agent	AEGL-1	AEGL-2	AEGL-3
		30-minute	
VX	0.00033 mg/m^3	0.0042 mg/m^3	0.015 mg/m^3
GB	0.0040 mg/m^3	0.050 mg/m^3	0.19 mg/m^3
H	0.13 mg/m^3	0.20 mg/m^3	2.7 mg/m^3
		2-hour[a]	
VX	0.00013 mg/m^3	0.0019 mg/m^3	0.0070 mg/m^3
GB	0.0019 mg/m^3	0.023 mg/m^3	0.094 mg/m^3
H	0.033 mg/m^3	0.051 mg/m^3	1.07 mg/m^3

Notes:

[a] Derived values. See discussion in Appendix C.

mg/m^3 = milligrams per cubic meter

4.3 Technical Approach

A brief discussion of the methodology for this TRA was presented in the previous section. This section describes the specific steps taken to complete this assessment and identifies key assumptions made in the analysis. A more detailed discussion of the analysis approach is provided in sections 5 and 6.

4.3.1 Steps for Determining Bounding Conditions. The following steps were completed to determine the bounding conditions for shipment.

- Determine the hazard probability by estimating the truck accident probability using available data for hazardous material transportation accidents.

- Based on the hazard probability, determine the corresponding hazard severity that would result in *Low* risk.

- Develop a set of bounding transportation accident scenarios to be assessed.

- Characterize the hazard distances for these accident scenarios using the Army's atmospheric dispersion model, D2PC.

- Iteratively determine the maximum agent concentration and/or agent mass in the waste that could be transported while remaining within the hazard severity constraints.

- Determine the maximum number of shipments that could be completed while ensuring *Low* total risk.

4.3.2 Assumptions. Several assumptions were made in support of this assessment. These assumptions were developed based on consideration of the chemical, physical, and toxicological properties of the waste and how it would be shipped. The following are considered the key assumptions for this analysis:

- There is no neat agent present in the drums of secondary waste. Any chemical agent present is in a diluted form.

- Although precautions have been taken to ensure that there are no free liquids in the drums (for example, the use of absorbents and spill pads), it is conservatively assumed in the TRA that liquid is present on the surface of all waste materials. The liquid is assumed to coat the surface of the packaged waste materials with a thin film. The liquid film is assumed to evaporate from the surface of the solid waste items. In reality, the agent contaminated liquid is absorbed/adsorbed into the waste materials, limiting the rate at which vapor would be released to the atmosphere.

- It has been assumed that waste drum pallets will be loaded into an enclosed box type trailer for shipment. The rear of the trailer box will be closed and the doors secured during transport. The trailer will be climate controlled with an interior temperature at 70°F or lower.

4.3.3 Accident Scenarios Assessed. Two bounding accident scenarios were assessed in this TRA: a bounding evaporative release scenario and a bounding fire scenario.

- The bounding evaporative release scenario is one in which 50 percent of the drums have been breached and have dispersed their contents. This scenario would require an extremely violent crash and was therefore considered to be conservative. As will be shown in section 5, the probability that this large a fraction of the drums is involved in the release is very small. In addition, it is extremely unlikely that the drums would be breached and disperse their contents in the manner assumed.

- The bounding fire scenario is one in which all of the drums are involved in the fire. Involving all of the drums in the fire bounds the potential release.

SECTION 5
WASTE TRANSPORT TRUCK ACCIDENT PROBABILITY

5.1 Mode of Transportation

The mode of transport to be utilized for shipment of the waste will be in compliance with TSDF handling standards and will be provided by a commercially licensed DOT hazardous material (HAZMAT) waste hauler. In accordance with DOT requirements, all vehicles (tractors and trailers) to be used for waste transport must be thoroughly evaluated for road worthiness and safety prior to transport. Drivers are also required to prepare a Daily Vehicle Inspection Report at the end of each workday. In addition, maintenance logs must be maintained current and any recent major repairs and preventative maintenance on transport vehicles must be documented by the transporter and available for review prior to transport.

It has been assumed for the purposes of this analysis that the trailer will be an enclosed semi-tractor trailer with rear doors that are closed and secured during transport. If the trailer box is longer than the number of pallets loaded, the load will be positioned and secured to prevent shifting during transit. The transport convoy will be subjected to routine inspection for regulatory compliance by the hauler. All DOT transport rules and regulations will apply, including rest periods and daily driver road limits.

5.2 Waste Transportation Routing

It is anticipated that transportation routes will be chosen to avoid major population centers to the extent practicable, although still primarily using public highways or interstates. The convoy will be expected to comply with all DOT and state regulations for transport. In addition, the generator of the waste, shipper, and the TSDF will work together to select a shipment route that ensures adequate emergency response capabilities.

5.3 Truck Accident Scenarios

The bounding TRA investigated truck accident scenarios that could cause potential release of agent from the waste drums. Accidents with and without fire were considered because the fire could significantly affect the magnitude and duration of the release. The following sections discuss how accident probabilities were determined for a truck accident resulting in an agent release.

5.4 Truck Accident Probability Estimation

A baseline probability for truck accidents was obtained from a Battelle study of hazardous material truck shipments (Battelle, 2001). The data from this study was collected from the Hazardous Materials Information System (HMIS), supplemented by the Motor Carrier Management Information System (MCMIS) accident database, as well as Commodity Flow Survey (CFS) data from the U.S. Department of Commerce, the Federal Highway Administration's (FHWA) Highway Statistics, and the Research and Special Program Administration's (RSPA) Office of Hazardous Materials Safety 1998 study on *Hazardous Materials Shipments*.

The accident rate from the Battelle study that was determined to be most applicable to this waste transport study was the accident rate of 2.29×10^{-7} accidents per mile applicable during transport of Class 6 materials. Class 6 materials include toxic materials and infectious substances and were, therefore, considered relevant to the potentially chemical agent-containing wastes to be transported.

As a comparison, data were obtained on the accident rate associated with shipments of radioactive waste to the Waste Isolation Pilot Plant (WIPP) from the various national laboratories and other facilities that generated the waste. WIPP shipments are closely monitored via a tracking system called TRANSCOM and could, therefore, be considered reflective of the type of shipment monitoring and safety precautions implemented during waste transport. Based on the WIPP accident data shown in table 5-1, an accident rate of 2.59×10^{-7} accidents per mile was calculated. This value is very close to the accident

Table 5-1. Waste Isolation Pilot Plant Shipment Data
(reference: http://www.wipp.energy.gov/shipments.htm)

Site	Shipments[a]	Miles
Argonne National Laboratory	14	23,453
Hanford Site	402	726,816
Idaho National Laboratory	2,820	3,924,048
Lawrence Livermore National Laboratory	18	24,804
Los Alamos National Laboratory	388	132,696
Nevada Test Site	48	57,312
Rocky Flats Environmental Technology Site	2,045	1,446,444
Savannah River Site	899	1,384,460
Total to WIPP	**6,634**	**7,720,033**
Total Vehicle Accidents = 2		
Accident rate per mile = 2.59×10^{-7} accidents per mile		

Notes:

[a] As of April 21, 2008

WIPP = Waste Isolation Pilot Plant

rate of 2.29×10^{-7} estimated from the Battelle study. This indicates that the TRA data are consistent with accident experience for closely tracked hazardous waste shipments.

Data were also obtained from Tri-State Motor Transit Company, a trucking company used in several previous Army secondary waste shipments. Tri-State reported one accident in 4,032,486 miles of escorted hazardous waste shipments. This is equivalent to an accident rate of 2.48×10^{-7}. This value is very close to the value reported in the Battelle study. Because the Battelle value is based on a much larger data sample, it will be used in the bounding TRA.

As discussed previously, waste transport will involve significant safety precautions beyond those of a general shipment and even beyond those of many Class 6 HAZMAT shipments. For example, it is planned that shipments will occur in convoys that will travel at posted speeds, with dual drivers per truck, and with "hot button" emergency notification[4] available in case of an unsafe condition.

The DOT's National Highway Transportation Safety Administration (NHTSA) and the Federal Motor Carrier Safety Administration (FMCSA) funded a Large Truck Crash Causation Study or LTCCS (DOT, 2005) that looked into various causal factors for large truck accidents. This study was thorough in its evaluation of historical truck accidents and evaluated the driver and environmental factors contributing to large truck crashes. The use of multiple-truck convoys with two drivers in each truck is expected to reduce or eliminate some of these causal factors, which would reduce the overall accident rate. However, because it is not possible to determine what fraction of the Class 6, WIPP, or Tri-State shipments used these precautions, it is not possible to determine the appropriate accident rate reduction. Consequently, no accident rate reduction was applied in the TRA model.

Accidents during hazardous waste transport do not always involve a hazardous material release to the environment. Since the TRA is concerned only with accidents in which a release occurs, it was necessary to determine the probability of a release given that an accident occurs. The Battelle study (Battelle, 2001) indicated that a release occurs in 30 percent of the transportation accidents. This value is considerably greater than the 15 percent probability estimated by Harwood and Russell (1990) based on DOT data from 1984 and 1985.

In addition, data from Tri-State indicate that there were no hazardous material releases in over 16.6 million miles of hazardous waste transport in drums similar to what will be used for the Army's secondary waste. Common statistical techniques can be used to estimate a release probability based on this data even though no releases have occurred. Bailey recommends using the following equation to estimate the probability (Bailey, 1997):

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[4] Activation of the "hot button" immediately notifies the transporter's central dispatch that there is an emergency.

$$P = 1 - 0.5^{\frac{1}{n}} \quad (5\text{-}1)$$

where n is the number of trials without an observed occurrence (i.e., the total shipment miles). Welker and Lipow recommend the following equation (Welker and Lipow, 1974):

$$P = \frac{1/3}{n} \quad (5\text{-}2)$$

Accident release rates calculated using these two equations are 4.1×10^{-8} per mile (from equation 5-1) and 2.0×10^{-8} (equation 5-2). Given the assumed accident rate of 2.29×10^{-7} per mile, these values would correspond to release probabilities of 0.179 and 0.087, respectively.

In keeping with the conservative approach taken throughout the rest of the analysis, a conservative release probability of 0.30 from the Battelle study is used in the bounding TRA.

A baseline accident release rate was determined by taking the original Battelle accident rate of 2.29×10^{-7} and then multiplying by the probability of a release as a result of the accident (0.30). The resulting accident release rate was 6.87×10^{-8} releases per mile. Next, the probabilities of the two bounding accident scenarios were estimated.

The bounding evaporative release scenario is one in which 50 percent of the drums on the truck are breached and release their contents. Such an accident would require a very violent collision and is therefore expected to be rare. A national transportation risk assessment performed by Argonne National Laboratory (ANL) included a review of historical accident data to determine the fraction of the transported hazardous material likely be involved in the release (Brown, 2000). The ANL study showed that, in those accidents in which a release occurred during shipment of polyethylene drums, there was a 50 percent chance that the release involved fewer than 5 percent of the drums and only a 10 percent chance that the release involved 50 percent or more of the drums. For metal drums, there was a 50 percent chance that the release involved fewer than 8 percent of the drums and only a 17 percent chance that the release involved 50 percent or more of the drums. For the bounding TRA, it is conservatively assumed that 50 percent of the drums are involved in the release 50 percent of the time. The calculated probability of the large evaporative release scenario is shown in table 5-2. Probabilities are calculated per mile and per shipment, where the latter are calculated assuming a 2,000 mile transport distance.

Table 5-2. Truck Shipment Accident Data Estimates

Basis for Probability	Truck Accident Probability (per mile or shipment)
Accidents per mile [from Battelle study data; HAZMAT transporters of Class 6 materials (poisons)]	2.29×10^{-7}
Hazmat releases per mile (Multiply by 30% - maximum release probability from the Battelle study)	6.87×10^{-8}
Large evaporative hazmat releases per mile (Multiply non-fire release probability[a] by 50% - conservative estimate of the probability that 50% of the drums are involved)	3.14×10^{-8}
Fire releases per mile (Multiply by 8.5% - maximum probability from Battelle study)	5.84×10^{-9}
Example Accident Release Probability per Shipment	
Miles per shipment	2,000
Accidental release probability per shipment	1.37×10^{-4}
Large evaporative release probability (per shipment)	6.29×10^{-5}
Accidental release involving fire (per shipment)	1.17×10^{-5}

Notes:

[a] The non-fire release probability is the hazmat release probability minus the fire release probability.

HAZMAT = hazardous material

A small percentage of truck accidents result in a fire. A fire that spreads to the waste drums could cause a release of agent vapor that would have adverse health consequences. For that reason it is important to consider fire scenarios separately.

The 2001 Battelle study reports that a fire occurs in approximately 8.5 percent of all accidents in which a release occurs during transport of hazardous materials. This fire probability is multiplied by the overall accident release rate to determine the rate of accidents involving fire. The resulting probabilities per mile and per 2,000-mile shipment are shown in table 5-2.

The accident rates discussed previously are per shipment. In order to determine the total probability of an accidental release during waste transport from a given site or facility, it is necessary to multiply the total number of planned shipments from that site/facility. For example, if a given site has 100 waste shipments and is transporting waste 2,000 miles to a TSDF, the total probability of the large evaporative release scenario would be approximately 0.006. This would place the total probability for this accident scenario in the *Occasional* range based on the definitions in table 4-1. Under these conditions, an overall risk level of *Low* could only be achieved if the hazard severity is *Negligible*. Similarly, if 100 total shipments are assumed, the total probability for a truck accident with fire would be approximately 0.0012, which would again place the total probability in the *Occasional* range so only a hazard with *Negligible* severity would result in an overall risk level of *Low*.

The tables below illustrate the acceptable number of shipments that can be made based on maintaining an overall risk category of *Low*. Table 5-3 displays the transportation options for 55-gallon drums, assuming that 80 drums can be transported in each truck. Table 5-4 shows the transportation options for 95-gallon drums, assuming that 51 drums can be transported in each truck.

Tables 5-3 and 5-4 show a range of shipment limits based on the hazard severity and shipping distance. For example, a site may ship up to 71,520 55-gallon drums (assuming 80 per truck) over a total of 894 3,000-mile shipments when the hazard severity for those drums is *Negligible*. However, if the hazard severity for the drums is *Marginal*, only 640 drums and 8 shipments would be allowed. Therefore, these tables should be used in conjunction with the hazard severity tables shown in section 6 when determining shipment limits.

Table 5-3. Shipping Criteria for 55-gallon Drums

Shipping Distance	Severity Category	Total Number of Shipments	Total Number of Drums for Shipment	Hazard Probability	Overall Risk Category
3,000 miles	Negligible	894	71,520[a]	Likely	Low
	Negligible	89	7,120	Occasional	Low
	Negligible	8	640	Seldom	Low
	Marginal	8	640	Seldom	Low
2,000 miles	Negligible	1,341	107,280	Likely	Low
	Negligible	134	10,720	Occasional	Low
	Negligible	13	1,040	Seldom	Low
	Marginal	13	1,040	Seldom	Low
1,000 miles	Negligible	2,683	214,640	Likely	Low
	Negligible	268	21,440	Occasional	Low
	Negligible	26	2,080	Seldom	Low
	Marginal	26	2,080	Seldom	Low
500 miles	Negligible	5,366	429,280	Likely	Low
	Negligible	536	42,880	Occasional	Low
	Negligible	53	4,240	Seldom	Low
	Marginal	53	4,240	Seldom	Low

Notes:

[a] Values in this column are calculated by dividing the upper bound probability for the probability category (e.g., 0.1 for the *Likely* category) by the sum of the per shipment probabilities for a large evaporative release and a fire release (per shipment probabilities calculated as in table 5-2).

Table 5-4. Shipping Criteria for 95-gallon Drums

Shipping Distance	Severity Category	Total Number of Shipments	Total Number of Drums for Shipment	Hazard Probability	Overall Risk Category
3,000 miles	Negligible	894	45,594	Likely	Low
	Negligible	89	4,539	Occasional	Low
	Negligible	8	408	Seldom	Low
	Marginal	8	408	Seldom	Low
2,000 miles	Negligible	1,341	68,391	Likely	Low
	Negligible	134	6,834	Occasional	Low
	Negligible	13	663	Seldom	Low
	Marginal	13	663	Seldom	Low
1,000 miles	Negligible	2,683	136,833	Likely	Low
	Negligible	268	13,668	Occasional	Low
	Negligible	26	1,326	Seldom	Low
	Marginal	26	1,326	Seldom	Low
500 miles	Negligible	5,366	273,666	Likely	Low
	Negligible	536	27,336	Occasional	Low
	Negligible	53	2,703	Seldom	Low
	Marginal	53	2,703	Seldom	Low

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SECTION 6
HAZARD ASSESSMENT

Any release of agent-contaminated material during transport could result in a release of agent vapor to the atmosphere. Exposure of unprotected people, that is, the general public, to any accidental release would be dependent upon the nature of the accident, the amount of material exposed to the atmosphere, atmospheric or meteorological conditions, the distance to local population centers, and response time by local response agencies.

Previous TRAs [e.g., the Newport FPF TRA (SAIC, 2007)] have evaluated a range of potential evaporative release scenarios from the breach of one drum with no dispersal of its contents to the breach of half of the drums on the shipment with dispersal of their contents. These release scenarios were selected to illustrate the range of potential hazards.

In this bounding TRA, only the accident scenarios resulting in the greatest downwind hazard are modeled. Therefore, for the evaporative release scenario, an accident involving breach of 50 percent of the drums followed by dispersal of their contents was selected for analysis. Such a large release could occur only in an extremely violent accident and is therefore very unlikely. It is conservatively assumed in this TRA that the bounding evaporative release occurs in half of the accidents not involving a fire.

Similarly, the bounding fire release scenario was assumed to be a fire that involved all of the drums on the truck. Because 100 percent of the drums are involved in the fire, this scenario bounds the amount of agent that could be released during the accident.

6.1 Release of Agent Due to Evaporation

All drums will be shipped in an enclosed trailer. While the trailer will not be air tight, it will be sufficiently sealed to prevent free exchange of its atmosphere with the outside air. For the bounding evaporative release scenario to occur, the following would be required:

- The trailer box would have to be breached. Without breaching the trailer, there would be no pathway for release to the environment.

- The accident would have to be sufficiently violent to cause half of the drums to be breached, dispersing their contents and exposing the agent-contaminated contents to the outside air.

If the contents of the drums are dispersed, the exposed surface area could be substantial. The air flow across these contents would be at the local wind velocity and the agent vapor would freely evaporate from the surface.

The bounding evaporative release scenario is one in which 50 percent of the drums on a truck are breached but no fire occurs. Agent is released from the drums as an initial puff of vapor from the drum headspace followed by an evaporative release. The evaporative release is assumed to occur for two hours, at which time emergency responders are able to terminate the release.

6.2 Release of Agent During a Fire

If a fire occurs, all of the containers in the truck are assumed to be involved in the fire. Agent in containers engulfed by the fire is likely to be consumed by the fire since the agent itself is combustible. Depending on the availability of oxygen to feed the fire, the fraction of agent consumed could exceed 90 percent (SAIC, 2002). Drums that are not engulfed in the fire may release a portion of their contents by evaporation and, depending on the location of the drum relative to the fire, the evaporated agent may escape the fire without being consumed.

In this TRA, it was assumed that 50 percent of the drums are engulfed by the fire and that 90 percent of the agent in these drums is destroyed by the fire. For the remaining 50 percent of the drums (those not engulfed by the fire), it is assumed that only half of the agent is destroyed by the fire. The net agent result from these two assumptions is that 30 percent of the agent is released during the fire.

A 30 percent release fraction is conservative relative to the values typically used in the analysis of fires at chemical warehouses or storage facilities. For example, in the *Safety Report Assessment Guide: Chemical Warehouses* published by the United Kingdom Health and Safety Executive (HSE, 2002) [the British equivalent of the U.S. Environmental Protection Agency (USEPA), Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH)] a 10 percent release fraction for toxic organic compounds is recommended as a conservative value for well-ventilated chemical warehouse fires. The HSE report notes that larger release fractions of around 30 percent can occur for under-ventilated fires (e.g., fires inside buildings with restricted air flow). Because truck fires occur outdoors rather than inside a building, air flow should be sufficient to ensure a well-ventilated condition; thus a release fraction of 10 percent could be justified. However, to maintain a high level of conservatism in the analysis, a 30 percent release fraction is assumed in the analysis.

The agent is released over the duration of the fire, which is assumed to be 30 minutes. A 30-minute fire duration was selected because it is commonly used in the analysis of fires during hazardous material transport [see for example, Code of Federal Regulations (CFR), 10 CFR 71.73 (Federal Register, 2004)].

6.3 Calculation of the Bounding Puff and Evaporative Release

The releases of agent vapor during the puff and subsequent evaporation were determined and downwind hazard due to exposure to these releases was then evaluated. The next two sections discuss the puff and evaporative release calculations.

6.3.1 Puff Release Calculation. The puff release was calculated assuming that the entire interior volume of the drum is filled with vapor at the drum headspace concentration. This assumption is conservative because the volume occupied by the waste is neglected. The agent vapor in the headspace of 50 percent of the drums is assumed to be released over one minute.

6.3.2 Evaporative Release Calculation. If the level of agent-contamination in the waste is characterized based on a headspace concentration, then the agent concentration in the liquid waste[5] can be determined based on the headspace concentration using the following form of Raoult's Law:

$$x_a = 10^{-3} \frac{C_H}{P_v} \frac{RT}{MW_a} \qquad (6\text{-}1)$$

where

x_a	=	the mole fraction of agent in the liquid (moles agent/mole liquid)
C_H	=	the headspace concentration (milligrams [mg] agent/cubic meter [m^3] headspace)
P_v	=	the vapor pressure of pure agent at temperature T (atmosphere [atm])
R	=	the Universal Gas Constant (8.2056×10^{-5} atm-m^3/mole K)
T	=	the temperature of the waste when the headspace sample is taken (K), assumed to be 298 K
MW_a	=	the molecular weight of agent (grams [g] agent/mole agent).

5 Here, liquid waste refers to any agent-containing liquid or liquid absorbed into other materials such as spill pads or PPE. There are no free liquids in the drum.

Henry's Law may be used when organic compounds are present in aqueous solutions, particularly when the organic compound is present at low concentrations. Henry's Law accounts for the solubility of the agent in the aqueous solution and the relative tendency of the compound to partition between the headspace and the aqueous liquid. The following form of the Henry's law equation is analogous to equation 6-1:

$$x_a = 10^{-6} \frac{C_H}{H} \frac{RT}{MW_a} \frac{MW_{soln}}{\rho_{soln}} \qquad (6\text{-}2)$$

where H is the agent-specific Henry's law constant (atmosphere [atm]-m3 liquid/mole agent), MW_{soln} is the molecular weight of the solution (g liquid/mole liquid) (approximately 18 g/mole), and ρ_{soln} is the density of the solution (kilograms [kg] liquid/m^3 liquid) (approximately 1,000 kg/m^3), and all other terms are as defined above.

Analyses performed using Raoult's and Henry's Laws showed that both give approximately the same release by evaporation, but that Raoult's Law gives a significantly higher agent concentration in the liquid. This higher liquid concentration results in a greater release due to fire. For that reason, Raoult's Law was used to calculate the evaporative release from the waste.

In equation 6-1, the vapor pressure of pure agent, P_v, is calculated using the Antoine equation, which has the following form:

$$P_v = \frac{10^{A+\left(\frac{B}{T-273.15+C}\right)}}{760} \qquad (6\text{-}3)$$

where A, B, and C are the agent-specific Antoine coefficients and the number in the denominator is a conversion factor representing 760 mm Hg per atmosphere. The Antoine coefficients used in the analysis are shown in table 6-1.

Table 6-1. Antoine Coefficients for the Chemical Agents

Agent	Antoine Coefficient A	Antoine Coefficient B	Antoine Coefficient C
VX[a]	8.1761	-2673.04	212.99
GB[b]	8.5797	-2348.32	261.9
HD[c]	7.4709	-1935.47	204.2

Notes:

[a] Values derived from Buchanan, et al., 1999.
[b] Values taken from Penski, 1994.
[c] Values taken from DDESB, 1980.

Based on discussions with representatives from the stockpile sites, it was assumed that there is as much as 0.5 liter of liquid in a drum. The same liquid amount was assumed for both 55-gallon and 95-gallon drums. Although the liquid is assumed to be fully absorbed onto the materials within the drums (in other words, there would be no free liquids in the drum), it was conservatively assumed in the TRA that the liquid would evaporate at the same rate as a free liquid.

The mole fraction of agent in the waste drum is converted to a mass fraction to determine the total agent mass in the drum. This is accomplished using equation 6-4 below,

$$w_a = x_a \cdot \frac{MW_a}{MW_{liq}} \qquad (6\text{-}4)$$

where

w_a = the mass fraction of agent in the liquid (gram of agent per gram of liquid)

x_a = the mole fraction of agent in the solution (moles of agent per moles of liquid)

MW_a = molecular weight of agent (grams of agent per mole of agent)

MW_{liq} = molecular weight of liquid, assumed to be water (grams of liquid per mole of liquid).

The mass fraction is then used to determine the mass of agent in each drum, by multiplying by the total volume of liquid available, as shown in equation 6-5,

$$m_a = 1 \times 10^3 w_a V_{liq} \rho_{liq} \qquad (6\text{-}5)$$

where

m_a	=	the mass of agent (g)
w_a	=	the mass fraction of agent in the liquid (gram of agent per gram of liquid)
V_{liq}	=	volume of liquid (liters [L])
ρ_{liq}	=	density of liquid (grams per milliliter [g/mL]).

Evaporative release of chemical agent vapor from an outside spill can be calculated using the following equation (Rife, 1981)[6].

$$E_m = \frac{3.53 \times 10^3 \ u^{0.78} \, MW_a P_v}{Sc^{0.67} \ d^{0.11} P_{amb} \ T} A_{spill} \qquad (6\text{-}6)$$

where

E_m	=	evaporation rate (grams per minute [g/min])
Sc	=	Schmidt number = $\mu/(D\rho)$ (dimensionless)
D	=	diffusivity of the agent vapor in air (square centimeter per second [cm^2/s])
	=	0.24 (MW_{liq}/MW_a) (Thibodeaux, 1979)
μ	=	dynamic viscosity of air (grams per centimeter second [g/cm s])
	≈	1.85×10^{-4} g/cm s at ambient temperature
ρ	=	density of air (grams per cubic centimeter [g/cm^3])
	≈	1.2×10^{-3} g/cm^3 at ambient temperature

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[6] This equation has a slightly different form from the equation used in the D2PC model. It was selected because it compares well to other commonly accepted evaporation models such as the one used in the EPA's ALOHA® software (USEPA, 2007). It generally predicts evaporation rates that are slightly higher than predicted by the D2PC equation.

u	=	wind speed (meters per second [m/s])
d	=	length of spill surface in the downwind direction (m)
P_v	=	vapor pressure of the agent at temperature T (atm)
T	=	temperature at the surface of liquid (K)
P_{amb}	=	total ambient pressure at the liquid surface (atm)
MW_a	=	molecular weight of the agent
MW_{liq}	=	molecular weight of the solution (assumed to be 18 g/mole)
A_{spill}	=	surface area for evaporation (m^2).

This equation applies to liquid spills but can be used for evaporation from liquid-contaminated waste, where *d* in the denominator of this equation represents the downwind dimension of the waste, and the term A_{spill} represents the total surface area of the liquid-contaminated waste (that is, the area available for evaporation).

When applying equation 6-6 to the evaporative release of agent from a dilute solution, the partial pressure of agent should be used in place of the vapor pressure of pure agent, $P_{v,a}$. The partial pressure of agent in a dilute solution can be calculated using the following form of Raoult's Law:

$$P_{v,a} = P_{vp,a}\, x_a \qquad (6\text{-}7)$$

where $P_{v,a}$ is partial pressure of the agent in the solution, $P_{vp,a}$ is the vapor pressure of the agent in pure form, and x_a is the mole fraction of agent in the solution. The evaporation rate would be greatly overestimated unless the inputs to the model are adjusted to account for dilution of the agent in the liquid.

If the container contents have been dispersed, the exposed surface of the waste will vary greatly, depending on the type of waste material in the container. However, it is possible to bound the surface area using some simplifying assumptions. One way to estimate the surface area for evaporation is to assume that the liquid is spread to a uniform thickness on the exposed surface of the solid waste material. For this TRA, it is assumed that the liquid is spread to a uniform thickness of 0.1 millimeter. This thickness is conservative[7], especially in the case of porous waste material. Using this assumed depth along with the assumed volume of liquid in a drum (0.5 L), the estimated surface area is approximately 5.0 m^2.

Equations 6-1 through 6-7 were solved for a range of assumed headspace concentrations to determine the resulting evaporative releases. In these calculations, worst-case daytime or nighttime conditions were assumed. For the worst case daytime conditions, the ambient temperature was 95°F (35°C) and the wind velocity was 1 meter per second (m/s). When combined with the worst-case atmospheric stability for daytime conditions [stability class D (Hanna, 1982)], these conditions were found to yield the highest downwind hazard. Similarly, studies showed that the highest nighttime evaporative release occurs when the ambient temperature is 75°F (24°C) and the wind velocity is 1 m/s. These conditions yielded the highest downwind hazard for the worst-case nighttime atmospheric stability (stability class F) (USEPA, 1999). Appendix D provides some sample calculations illustrating how the preceding methodology is used to calculate evaporative release for a given headspace concentration.

It should be noted that no attempt was made to determine the likelihood of these conditions. In reality, most daytime or nighttime releases would occur when the atmosphere is much more unstable than the conditions assumed. For example, Chemical Stockpile Emergency Preparedness Program (CSEPP) studies using actual meteorological data from three of the chemical stockpile sites showed that a 95°F ambient temperature, D weather stability, and 1 m/s wind speed occur much less than 1 percent of the time during the day (see appendix E). More unstable conditions would result in more rapid dispersion of the agent plume and lower downwind hazard.

6.3.3 Downwind Hazard Assessment. To determine the potential health effects from exposure to a vapor release, the characteristics of the agent release are entered in an

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[7] For most solid surfaces and liquids of interest, a balance between surface tension and gravitational forces would indicate a thickness of greater than 1 mm. For porous materials, the liquid would penetrate into the material, thus further reducing the surface area for evaporation.

atmospheric dispersion model, such as D2PC (Whitacre, 1987). D2PC is a Gaussian plume model that calculates the distance to specified agent exposures or concentrations.

As with any computer model, there are a number of variables that must be input in order to model a specific accident scenario. In D2PC, these inputs are referred to as *dispersion control characteristics.* Table 6-2 provides a list of the control characteristics that must be specified for each accident scenario.

Table 6-2. D2PC Dispersion Control Characteristics for Evaporative Releases

Control Characteristic	Input Values Used	Description of Characteristic
Mixing Layer Height	400 meters (daytime) 250 meters (nighttime)	Mixing layer height based average conditions for summer
Release Type	Semi-continuous – outdoor	Specifies the nature of the release from the waste
Atmospheric Stability	D stability for worst case daytime release (used for VX and H) F stability for worst case nighttime release (used for GB)	Characterizes the degree of dispersion due to atmospheric mixing and turbulence
Wind Speed	1 m/s for outdoor release	A factor in the evaporative release calculation for outdoor releases; also determines the rate of downwind transport
Agent Mass Released	Iterated to determine maximum acceptable agent release	Agent mass that evaporates as determined from spreadsheets using the equation from evaporation from a liquid spill
Release Duration	120 minutes	Duration of the release and exposure; determined by the availability of emergency responders; varies by release location: urban, suburban, or rural

As noted earlier, the initial puff release was modeled as a semi-continuous release over a one minute period and the subsequent evaporative release was modeled as a semi-continuous release over the assumed 2-hour time release duration. Due to limitations in the D2PC model, it was necessary to perform separate calculations for the puff and evaporative releases. In addition, it was necessary to model the releases as point-sources, rather than as area sources, which would be much more realistic. Because a point-source produces a more concentrated agent plume than an area source, the downwind hazard is overestimated by D2PC. Thus, the current downwind hazard analysis is conservative.

As noted in table 6-2, calculations were performed for both daytime and nighttime weather conditions. Nighttime conditions result in lower evaporation, but less dispersion of the agent plume than daytime conditions. Calculations with D2PC showed that daytime conditions always results in a higher downwind hazard for releases of VX and H, but that nighttime conditions result in higher downwind hazard for GB releases. Therefore, all VX and H calculations reported below were run assuming daytime conditions and all GB calculations were run assuming nighttime conditions.

Calculations were performed using D2PC to determine the downwind hazard for a given release scenario. The puff and evaporative release calculations and D2PC calculations were repeated in an iterative manner to determine the maximum headspace concentration that would result in severity categories of *Negligible* or *Marginal* as defined in table 4-3. The procedure was as follows:

1. For a given headspace concentration, determine the magnitude of the puff release from 50 percent of the drums.

2. Based on this puff release, calculate the dose 25 and 50 meters downwind using D2PC.

3. Compare this dose to the, 10-minute AEGL-1 and AEGL-2 doses[8] to determine the fraction of the AEGL dose resulting from the puff release. Reduce the allowable 30-minute and 2-hour AEGL concentrations by this fraction. The reduced concentrations will be used in the evaporative release calculations.

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[8] The 10-minute AEGL doses are used because 10 minutes is the shortest exposure duration for which health effects were determined (NRC, 2003).

4. For a given headspace concentration, determine the evaporative release from 50 percent of the drums.

5. Based on this evaporative release, calculate the hazard distances to the reduced 30-minute and 2-hour AEGL-1 and AEGL-2 concentrations using D2PC.

6. Repeat steps 1 through 5 to determine the headspace concentration that results in AEGL hazard distances of 25 meters for a 30-minute exposure and 50 meters for a 2-hour exposure.

The D2PC calculations for the puff release indicated that the puff results in less than 2 percent of the 10-minute AEGL dose. Thus, essentially the same results are calculated if the puff release is ignored.

The results from this analysis are the headspace concentrations that would result in 30-minute AEGL hazard distances of 25 meters and headspace concentrations that would result in 2-hour AEGL hazard distances of 50 meters. The limiting headspace concentration for a *Negligible* hazard is the smaller of the two concentrations that would give the AEGL-1 hazard distance (25 meters for a 30-minute exposure or 50 meters for a 2-hour exposure). The limiting headspace concentration for a *Marginal* hazard is the smaller of the two concentrations that would give the AEGL-2 hazard distance. The results from these iterations are discussed in the next section.

6.4 Bounding Results for the Evaporative Release Scenario

Hazard distances were determined based on the agent mass released from a breach of 50 percent of the drums. Table 6-3 shows the limiting agent headspace concentrations that would result in *Negligible* or *Marginal* downwind hazard.

Table 6-3. Hazard Distances from Evaporation of 50 Percent of 55-gallon Drums

Agent	Headspace Concentration	Hazard Severity	2-hr Hazard Distance (m)			30-minute Hazard Distance (m)		
			AEGL-3	AEGL-2	AEGL-1	AEGL-3	AEGL-2	AEGL-1
VX	240 VSL	Negligible	4	9	43	3	6	**25**
	3,000 VSL	Marginal	19	31	181	12	**25**	107
GB	250 VSL	Negligible	3	7	41	2	4	**25**
	3,100 VSL	Marginal	16	42	237	10	**25**	142
H	290 VSL	Negligible	10	39	**50**	4	18	23
	440 VSL	Marginal	13	**50**	64	5	23	29

Table 6-3 shows that for headspace concentrations up to 240 VSL for VX waste, the hazard severity is *Negligible*, because the 30-minute AEGL-1 hazard distance extends to 25 meters at that concentration (the distance to the initial isolation zone). As defined in table 4-3, *Negligible* hazards are those in which the AEGL-1 hazard distance is less than the distance to the boundary of the initial isolation zone. Since the 30-minute AEGL-1 hazard distance reached 25 meters before the 2-hour AEGL-1 hazard distance reached 50 meters, the 30-minute AEGL-1 case is bounding. Further, for VX headspace concentrations greater than 240 VSL but less than 3,000 VSL, the hazard severity is *Marginal*, because the 30-minute AEGL-2 hazard distance reaches 25 meters at the 3,000 VSL level.

The hazard severity for GB is *Negligible* for headspace concentrations up to 250 VSL, and *Marginal* for headspace concentrations greater than 250 VSL but less than 3,100 VSL. The hazard severity for H is *Negligible* for headspace concentrations up to 290 VSL and *Marginal* at headspace concentrations greater than 290 VSL but less than 440 VSL. Unlike the VX and GB cases where the 30-minute AEGLs were bounding, the 2-hour AEGLs are bounding for H.

Tables 6-4 through 6-6 present the waste characteristics, drum and truck agent masses, and evaporative release masses calculated based on the limiting headspace concentrations presented in table 6-3.

The preceding calculations were performed assuming 80 55-gallon drums on a shipment. A similar set of calculations was performed assuming the shipment contains 51 95-gallon drums. Since fewer drums are transported when 95-gallon drums are used but the amount of liquid in each drum is assumed to be the same, the agent concentration in each drum may be higher than when 55-gallon drums are used and still achieve the same downwind hazard. The limiting headspace concentrations for 95-gallon drums can be determined by multiplying the limiting headspace concentration for 55-gallon drums by the ratio of the number of 55-gallon drums to the number of 95-gallon drums. This ratio is 80/51 or 1.57. Table 6-7 shows the adjusted headspace concentrations and corresponding mole fractions for shipment of 95-gallon drums.

Table 6-8 shows the resulting agent mass per 95-gallon drum and total mass per shipment. At the assumed headspace concentrations, the mass of agent vapor released from 50 percent of the 95-gallon drums is the same as the mass released from 50 percent of the 55-gallon drums (shown in table 6-6)

Table 6-9 presents a summary of the limiting headspace concentrations for shipments of both 55-gallon drums and 95-gallon drums.

The hazard severities shown in table 6-9 should be used in conjunction with the hazard probability in order to remain within the *Low* risk category. For example, if a site has numerous shipments to make and the hazard probability is in the *Occasional* range, then the site may only transport waste with a *Negligible* severity to ensure the risk from transporting the waste is *Low*.

Table 6-4. Limiting Headspace Concentration and Mole Fraction for 55-gallon Drums

Agent	Headspace Concentration	Headspace Concentration (mg/m^3)	Mole Fraction in the Liquid
VX	240 VSL	0.0024	1.9×10^{-4}
	3,000 VSL	0.030	2.4×10^{-3}
GB	250 VSL	0.025	1.3×10^{-6}
	3,100 VSL	0.31	1.7×10^{-5}
H	290 VSL	0.87	9.7×10^{-4}
	440 VSL	1.3	1.5×10^{-3}

Table 6-5. Calculated Agent Masses per 55-gallon Drum and Truck Shipment

Agent	Headspace Concentration	Mass Fraction	Total Agent Mass per Drum (g)	Total Agent Mass per Shipment[a,b] (g)
VX	240 VSL	2.8×10^{-3}	1.4	110
	3,000 VSL	3.6×10^{-2}	18	1,440
GB	250 VSL	1.0×10^{-5}	0.0053	0.42
	3,100 VSL	1.3×10^{-4}	0.065	5.2
H	290 VSL	8.6×10^{-3}	4.3	340
	440 VSL	1.3×10^{-2}	6.6	530

Notes:

[a] The total agent mass per shipment assumes 80 drums.
[b] The slight differences between the values shown in this table and in table 6-8 result from rounding the headspace concentration down to two significant figures.

Table 6-6. Agent Mass Released from Evaporation of 50 Percent of 55-gallon Drums

Agent	Headspace Concentration	Agent Mass Released (g)
VX	240 VSL	0.024
	3,000 VSL	0.30
GB	250 VSL	0.12
	3,100 VSL	1.5
H	290 VSL	8.1
	440 VSL	12

Table 6-7. Limiting Headspace Concentration and Mole Fraction for 95-gallon Drums

Agent	Headspace Concentration	Headspace Concentration (mg/m^3)	Mole Fraction in the Liquid
VX	380 VSL	0.0038	3.1×10^{-4}
	4,700 VSL	0.047	3.8×10^{-3}
GB	390 VSL	0.039	2.1×10^{-6}
	4,900 VSL	0.49	2.6×10^{-5}
H	460 VSL	1.4	1.5×10^{-3}
	690 VSL	2.1	2.3×10^{-3}

Table 6-8. Calculated Agent Masses per 95-gallon Drum and Truck Shipment

Agent	Headspace Concentration	Mass Fraction	Total Agent Mass per Drum (g)	Total Agent Mass per Shipment[a,b] (g)
VX	380 VSL	4.5×10^{-3}	2.3	120
	4,700 VSL	5.5×10^{-2}	28	1400
GB	390 VSL	1.6×10^{-5}	0.008	0.41
	4,900 VSL	2.0×10^{-4}	0.10	5.1
H	460 VSL	1.3×10^{-2}	6.5	330
	690 VSL	2.0×10^{-2}	10	510

Notes:

[a] The total agent mass per shipment assumes 51 drums.
[b] The slight differences between the values shown in this table and in table 6-5 result from rounding the headspace concentration down to two significant figures.

Table 6-9. Limiting Headspace Concentrations Corresponding to Hazard Severity Levels for Evaporative Releases

Agent	Headspace Concentrations (55-gallon drums)	Headspace Concentrations (95-gallon drums)	Hazard Severity Category
VX	< 240 VSL	< 380 VSL	Negligible
	240 VSL < X < 3,000 VSL	380 VSL < X < 4,700 VSL	Marginal
GB	< 250 VSL	< 390 VSL	Negligible
	250 VSL < X < 3,100 VSL	390 VSL < X < 4,900 VSL	Marginal
H	< 290 VSL	< 460 VSL	Negligible
	290 VSL < X < 440 VSL	460VSL < X < 690 VSL	Marginal

6.5 Bounding Fire Release Results

Separate D2PC analyses were performed to assess fire scenarios. As a starting point in the fire analysis, it was assumed that the masses of agent per drum were the same as those shown in tables 6-5 and 6-8. If the calculated hazard distances for the fire releases are greater than the corresponding hazard distances for the evaporative releases, then the fire scenarios would entail greater risk and the limiting headspace concentrations would have to be recalculated based on a fire release.

As discussed in section 6.2, the fire was conservatively assumed to involve all of drums in the truck. All of the agent in these drums was assumed to be released during the 30-minute fire and 70 percent of the released agent was assumed to be consumed by the fire. Therefore, 30 percent of the agent in the drums is assumed to be released to the atmosphere.

The D2PC calculations assume a fuel tank ruptures, releasing diesel fuel, which then ignites. The model considers the energy release rate of the fire and calculates the plume rise based on that energy release. A range of fuel levels and resulting energy release rates were considered and, in all cases, the plume rose a considerable distance into the air, in some cases approaching the height of the mixing layer [assumed to be either 400 meters (daytime releases) or 250 meters (nighttime releases) in the D2PC simulations].

Nighttime conditions represent the worst-case atmospheric conditions for fire release because the air is more stable and there is less downwind dispersion of the plume. For that reason, all D2PC fire accident simulations were performed assuming F atmospheric stability and 1 m/s windspeed.

Because the hot gases from the fire carry the plume up into the air, downwind transport and dispersion occurs before the plume reaches ground level. In all cases involving GB and H releases, the ground level agent concentration was below the AEGL-1 concentration so the hazard severity was always *Negligible*. Because the hazard severity for the evaporative releases is greater than for fire releases, the evaporative release scenarios were used as the basis for the bounding headspace concentrations of GB and H.

With accidents involving VX wastes, the D2PC calculations indicated that the AEGL-1 hazard distance extended well beyond the distances shown in table 6-3. For a total VX mass on the truck of 150 grams (from table 6-5), the AEGL-1 hazard distance was calculated to be greater than 10 kilometers. Because the hazard distance for the fire release is greater than the corresponding distance for the evaporative release, the fire scenario is a more severe hazard. Thus, a new limiting VX headspace concentration must be calculated based on the fire release scenario. This was accomplished by adjusting the headspace concentration in the drum until the ground level concentration for the nighttime fire scenario remained below the AEGL-1 level. The resulting headspace concentration for a 55-gallon drum was determined to be 32 VSL. At this headspace concentration, the ground level concentration remains below the AEGL-1 level so the hazard would be categorized as *Negligible.* The corresponding value for a 95-gallon drum was 50 VSL[9]. Adjusted VX limits per shipment have been calculated based on these new headspace concentrations. The new limits are shown in table 6-10

Table 6-10. Shipment Limits for VX-Contaminated Waste Based on Fire Scenario

Agent	Drum Size	Hazard Severity	Headspace Concentration	Total Agent Mass per Drum (g)	Total Agent Mass per Shipment[a] (g)
VX	55 gal	Negligible	32 VSL	0.19	15
VX	95 gal	Negligible	50 VSL	0.29	15
VX	55 gal	Marginal	390 VSL	2.3	180
VX	95 gal	Marginal	620 VSL	3.6	180

[9] This value is determined such that the total mass of agent on the truck with 95-gallon drums is the same as the total mass of agent on a truck with 55-gallon drums.

A similar analysis was performed to determine the maximum headspace concentration of a drum that would result in a downwind concentration that is always below the AEGL-2 level. This maximum headspace concentration for a 55-gallon drum was determined to be 390 VSL. At this drum concentration, the downwind hazard for the nighttime fire scenario would be categorized as *Marginal*. The corresponding value for a 95-gallon drum was 620 VSL. New mass limits for VX-contaminated waste have been calculated based on these new headspace concentrations. The new limits are shown in table 6-10.

The fire-based headspace concentrations for VX would be limiting unless the probability of a fire involving the drums is significantly reduced. This could be accomplished by including with the convoy a reliable fire fighting capability so that the fire could be extinguished before spreading to the drums. Another option would be to transport the drums in a fire-resistant container, such as the International Organization for Standardization (ISO) shipping containers that are commonly used to transport hazardous materials by land, sea, or rail. Testing has shown that these containers can withstand intense fires without losing their structural integrity (SNL, 1997).

It should be noted that the downwind hazard for the fire scenarios was evaluated for ground-level receptors, but there may be instances in which people are located at an elevated location relative to the accident site. The worst-case exposure would occur for someone located at the elevation of the fire plume. However, calculations performed using D2PUFF showed that the downwind concentration drops off rapidly with a change in elevation. (These calculations are summarized in appendix F.) Therefore, the higher agent concentration would be experienced only by individuals located directly downwind from the accident and over a relatively narrow range of elevations. At any given point along the transportation route, the probability of individuals being located in these areas would be very small.

SECTION 7
SITE-SPECIFIC APPLICATIONS

The previous sections have detailed the approach taken for determining the maximum agent concentration in the waste and maximum number of shipments that could be completed while ensuring an acceptable level of risk. Although secondary waste shipments from a given site may fall within the bounds established by this TRA, additional information is required from the site in order to commence offsite shipment of the waste. This TRA establishes guidelines for waste shipments, but it is the responsibility of the site to prove that their waste meets these guidelines.

In addition to meeting the constraints of the headspace concentrations specified previously, the sites must demonstrate that their waste falls within the bounds established by this document by providing details on the waste for shipment. The site must provide the following information with appropriate sources in order for the initial waste shipments to be approved by CMA management per the CMA Director's memo, *Guidance for Development of Site-Specific Plans for Shipment of Chemical Agent Contaminated Secondary Wastes* (2007):

- Details of the waste streams in the form of documented waste profiles. The waste profiles will be based on generator knowledge or analytical data (including headspace monitoring).

- In the absence of adequate generator knowledge, monitoring data to confirm the headspace concentration of the waste materials.

- Details on methods of waste segregation and packaging (i.e., SOPs for packaging).

- Number, capacity (e.g., 55-gallon, 95-gallon, etc.), and type of drum (e.g., polyethylene, steel overpacked in polyethylene, etc.) for shipment.

- Truck capacity and total number of shipments required.

- TSDF to be receiving the waste and distance to the TSDF (miles).

CMA staff will review this information and determine whether the proposed shipment conditions (e.g., waste type, shipment distances, etc.) are bounded by those evaluated in this bounding TRA. If so, then the information package will be provided to the CMA director for his review and approval. If not, then the site will be asked to provide an addendum to the bounding TRA that demonstrates the risk acceptability of any such site-specific conditions. CMA staff will review the addendum and, if it is determined to be acceptable, will provide the addendum along with the rest of the information package to the CMA director for review and approval.

SECTION 8
SUMMARY AND CONCLUSIONS

This report has presented a bounding TRA that was prepared to characterize the risk associated with an accident during offsite shipment of agent-contaminated secondary waste. The objectives of the bounding TRA were 1) evaluate the conditions under which the waste may be shipped with acceptable risk and 2) provide a detailed assessment of the public risk associated with shipping the waste to a TSDF. These objectives were met through development of a methodology based on the Army's established risk management procedures. The bounding TRA methodology included conservative assumptions to ensure the safety of the public during transport of the waste.

The bounding TRA streamlines the approach to assessing the risk from an accident during shipment of secondary waste by determining the maximum agent concentration in the waste that would be acceptable for shipment. In so doing, it establishes guidelines for shipment of > 1 VSL secondary waste from any site to an offsite TSDF.

The underlying assumption in the bounding TRA was that shipment of secondary waste must meet an overall risk category of *Low,* which means that the risk is acceptable without mitigation. The requirements for *Low* risk were defined based on the overall accident probability and downwind hazard. Accident rates were determined based on historical data, and an accident probability per shipment was calculated assuming a maximum shipping distance of 3,000 miles. Based on the agent concentration in the waste, downwind hazard distances were calculated. The agent concentration was varied in order to determine the maximum permissible agent concentration in the waste that would lead to an acceptable downwind hazard.

A substantial number of conservative assumptions were used throughout the bounding TRA analysis. Key conservatisms are outlined in table 8-1.

Table 8-1. Conservative Assumptions Used in the Bounding TRA

Conservative Assumption	Part of the Analysis	Nature of the Conservatism
Neglect impact of dual drivers and convoys	Accident Probability	Would lower the overall accident rate.
30 percent probability of a release	Accident Probability	Data indicate a much lower release probability.
50 percent probability that half of the drums release their contents	Accident Probability	Data indicate a much smaller probability that this number of drums is involved.
Using Raoult's Law rather than Henry's law	Headspace Analysis and Release	Maximizes the agent content in the drums and the release during a fire.
Drums are breached and disperse their contents over a wide area	Evaporative Release	Increases the calculated evaporation.
Assuming 95°F for all daytime releases and 75°F for all nighttime releases.	Evaporative Release	Ambient temperature would usually be much lower during most of the year. Also, neglects the lower starting temperature of the waste due to its initial climate-controlled condition.
All of the drums on the truck are involved in the fire and 30 percent of the agent is released	Fire Release	Assuming all of the drums are involved maximizes the potential agent release. A 30 percent release fraction is greater than the recommended value of 10 percent.
Agent release treated as a point source rather than an area source	Downwind Hazard	Concentrates the initial agent plume and increases the downwind hazard.
50 meter secondary control zone assumed rather than the larger zones identified in the ERG	Downwind Hazard	Placing individuals nearer the source increases the calculated downwind hazard.
Using worst case weather conditions for all daytime and nighttime releases	Downwind Hazard	Using these very rare conditions maximizes the downwind hazard. More probable conditions yield much lower hazard.

Tables 8-2 through 8-4 summarize the maximum agent headspace concentrations and maximum number of shipments that were calculated to result in acceptable (*Low)* risk. The values shown in the tables define the bounding waste characteristics and maximum number of shipments allowed as a function of the shipment distance.

There are a number of different ways in which a site can use these tables to manage the risk associated with secondary waste shipments. The results from the Bounding

TRA can be used in several different ways to manage risk. For example, a site may have some shipments that would be classified as having *Marginal* hazard based on the VSL limits shown in tables 8-2 through 8-4, and others that would be classified as having *Negligible* hazard. The allowable number of *Marginal* and *Negligible* hazard shipments is easily determined based on the tables. The approach outlined below ensures that the total risk from all shipments is less than or equal to that characterized in the Bounding TRA.

For example, let's say that a site requires 4 shipments containing 55-gallon drums with VX-contaminated waste at greater than 32 VSL, but less than 390 VSL. These would be classified as *Marginal* hazard shipments. For a TSDF that is 2,000 miles away, table 8-2 indicates that 13 total *Marginal* hazard shipments would be allowed. The required 4 shipments would be 31 percent of the total. Thus, the available number of *Negligible* hazard shipments listed in table 8-2 would be reduced by 31 percent for a total of 925 shipments.

Within the *Marginal* or *Negligible* hazard shipment classifications, it is acceptable to mix higher VSL waste with lower VSL wastes while ensuring that the total agent mass on the shipment is lower than or equal to the limits established in tables 6-5. 6-8 and 6-10. In effect, the inventory of drums on the shipment would be managed such that the average VSL level for the drums on the shipment is less than or equal to the VSL limits specified in tables 6-9 and 6-10. This simple approach to managing shipment risk is possible because the agent release (either evaporative or fire) is directly proportional to the total agent load on the truck, which is then directly proportional to the average headspace concentration in the drums on the truck. In order to limit the potential exposure of workers that may be involved in the initial emergency response or subsequent cleanup, the VSL limit for any drum be capped at the *Marginal* hazard limit (e.g., 390 VSL for VX).

As an example, consider a shipment of VX-contaminated waste that will include 4 drums with 360 VSL waste. In order to ensure that the total agent mass on the truck is less than the total for a *Negligible* hazard shipment, the remaining drums on the truck must average 14.7 VSL or lower. The following calculation illustrates how this value was determined:

80 drums × 32 VSL/drum = 2560 VSL available

4 drums × 360 VSL/drum = 1440 VSL in the high drums

(2560 VSL – 1440 VSL)/76 drums = 14.7 VSL average per remaining drum

Table 8-2. Summary of Bounding Conditions for Shipment of VX

Shipping Distance	Hazard Severity	55-gallon Drum Shipments		95-gallon Drum Shipments		Risk Level
		Headspace Concentration[a]	Number of Shipments	Headspace Concentration[a]	Number of Shipments	
3,000 miles	Negligible	< 32 VSL	894	< 50 VSL	894	Low
	Marginal	32 to 390 VSL	8	50 to 620 VSL	8	Low
2,000 miles	Negligible	< 32 VSL	1,341	< 50 VSL	1,341	Low
	Marginal	32 to 390 VSL	13	50 to 620 VSL	13	Low
1,000 miles	Negligible	< 32 VSL	2,683	< 50 VSL	2,683	Low
	Marginal	32 to 390 VSL	26	50 to 620 VSL	26	Low
500 miles	Negligible	< 32 VSL	5,366	< 50 VSL	5,366	Low
	Marginal	32 to 390 VSL	53	50 to 620 VSL	53	Low

Note:
[a] As discussed in section 6.5, the limiting headspace concentrations for VX are based on the bounding fire scenario. If the probability of a fire involving the waste drums can be sufficiently reduced, the limiting headspace concentrations for evaporative releases would be used (see table 6-8).

Table 8-3. Summary of Bounding Conditions for Shipment of GB

Shipping Distance	Hazard Severity	55-gallon Drum Shipments		95-gallon Drum Shipments		Risk Level
		Headspace Concentration	Number of Shipments	Headspace Concentration	Number of Shipments	
3,000 miles	Negligible	< 250 VSL	894	< 390 VSL	894	Low
	Marginal	250 to 3,100 VSL	8	390 to 4,900 VSL	8	Low
2,000 miles	Negligible	< 250 VSL	1,341	< 390 VSL	1,341	Low
	Marginal	250 to 3,100 VSL	13	390 to 4,900 VSL	13	Low
1,000 miles	Negligible	< 250 VSL	2,683	< 390 VSL	2,683	Low
	Marginal	250 to 3,100 VSL	26	390 to 4,900 VSL	26	Low
500 miles	Negligible	< 250 VSL	5,366	< 390 VSL	5,366	Low
	Marginal	250 to 3,100 VSL	53	390 to 4,900 VSL	53	Low

Table 8-4. Summary of Bounding Conditions for Shipment of H

Shipping Distance	Hazard Severity	55-gallon Drum Shipments		95-gallon Drum Shipments		Risk Level
		Headspace Concentration	Number of Shipments	Headspace Concentration	Number of Shipments	
3,000 miles	Negligible	< 290 VSL	894	< 460 VSL	894	Low
	Marginal	290 to 440 VSL	8	460 to 690 VSL	8	Low
2,000 miles	Negligible	< 290 VSL	1,341	< 460 VSL	1,341	Low
	Marginal	290 to 440 VSL	13	460 to 690 VSL	13	Low
1,000 miles	Negligible	< 290 VSL	2,683	< 460 VSL	2,683	Low
	Marginal	290 to 440 VSL	26	460 to 690 VSL	26	Low
500 miles	Negligible	< 290 VSL	5,366	< 460 VSL	5,366	Low
	Marginal	290 to 440 VSL	53	460 to 690 VSL	53	Low

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APPENDIX A
ACRONYMS/ABBREVIATIONS

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ACRONYMS/ABBREVIATIONS

AEGL	Acute Exposure Guideline Level
AEL	airborne exposure limit
ANL	Argonne National Laboratory
AR	Army Regulation
atm	atmosphere
CDF	chemical agent disposal facility
CFR	Code of Federal Regulations
CFS	Commodity Flow Survey
cm^2/s	square centimeter per second
CMA	Chemical Materials Agency
D2PC	Personal Computer Program for Chemical Hazard Prediction
DA PAM	Department of the Army Pamphlet
DOT	Department of Transportation
FHWA	Federal Highway Administration
FMCSA	Federal Motor Carrier Safety Administration
FPF	Former Production Facility
ft^3	cubic feet
g	gram
g/cm s	grams per centimeter second
g/cm^3	grams per cubic centimeter
g/s	grams per second
GA	tabun
GB	sarin
GPS	global positioning satellite

HAZMAT	hazardous material
HAZWOPER	Hazardous Waste Operations and Emergency Response
H, HD, HT	mustard
HMIS	Hazardous Material Information System
hr	hour
HSE	Health and Safety Executive
IC	incident commander
ISO	International Organization for Standards
K	Kelvin
L	lewisite
LTCCS	Large Truck Crash Causation Study
m	meter
m/s	meters per second
m^2	square meter
m^3	cubic meter
MCMIS	Motor Carrier Management Information System
mg	milligram
mg/m^3	milligram per cubic meter
MIL-STD	military standard
min	minute
MSDS	material safety data sheet
NHTSA	National Highway Transportation Safety Administration
NIOSH	National Institute for Occupational Safety and Health
NRC	National Research Council
OSHA	Occupational Safety and Health Administration

PPE	personal protective equipment
RSPA	Research and Special Program Administration
SAIC	Science Applications International Corporation
SNL	Sandia National Laboratories
SOP	Standing Operating Procedure
STL	short-term limit
TRA	transportation risk assessment
TRANSCOM	Transportation Command
TSDF	treatment, storage, and disposal facility
USEPA	United States Environmental Protection Agency
VSL	vapor screening level
VX	O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothioate
WIPP	Waste Isolation Pilot Plant

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APPENDIX B

REFERENCES

APPENDIX B
REFERENCES

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APPENDIX C

DERIVATION OF 2-HOUR AEGL CONCENTRATIONS

APPENDIX C

DERIVATION OF 2-HOUR AEGL CONCENTRATIONS

AEGL concentrations are provided for several discrete exposure durations ranging from 10 minutes to 8 hours (NRC, 2003). For the bounding TRA, AEGL concentrations were needed for two exposure durations: 30 minutes and 2 hours. Only the 30 minute AEGL values were available in the published literature. Consequently, it was necessary to derive 2-hour AEGL concentrations based on the AEGL concentrations listed for other exposure durations.

Data for chemical toxicity of hazardous compounds often can be plotted using an equation of the following form:

$$C^n t = k \qquad \text{(C-1)}$$

where

C	=	the concentration for an observed toxic endpoint
t	=	the exposure duration (minutes)
n	=	an exponent determined based on the toxicity data
k	=	a constant

The constants, *n* and *k* are determined by fitting the available AEGL concentration data to equation C-1.

It was possible to fit the AEGL concentration data very closely if the data were broken up into two intervals: one for exposure durations up to 1 hour and one for exposure durations of greater than 1 hour. For GB and VX, the value for *n* that gave the best comparison to the greater than 1 hour AEGL concentrations was 2.29. For H, a value for *n* of 1 gave the best comparison to the AEGL-1 and AEGL-2 concentrations, and for greater than 1 hour AEGL-3 concentrations, but a value of 3 gave the best comparison to the less than 1 hour AEGL-3 concentrations.

These values for *n* were used along with the AEGL concentrations and exposure durations to determine an average value for the constant *k*. This value for *k* was then used with the value for *n* listed above to determine the 2-hour AEGL concentrations. The calculated values are listed in table C-1 along with the published AEGL concentrations.

Table C-1 Published and Calculated AEGL Concentrations

Agent	AEGL Concentration (mg/m^3)	Exposure Duration					
		10 minutes	30 minutes	1 hours	Derived Value for 2 hours	4 hours	8 hours
VX	AEGL-1	0.00057	0.00033	0.00017	0.00013	0.0001	0.000071
VX	AEGL-2	0.0072	0.0042	0.0029	0.0019	0.0015	0.001
VX	AEGL-3	0.029	0.015	0.01	0.0070	0.0052	0.0038
GB	AEGL-1	0.0069	0.004	0.0028	0.0019	0.0014	0.001
GB	AEGL-2	0.087	0.05	0.035	0.023	0.017	0.013
GB	AEGL-3	0.38	0.19	0.13	0.094	0.07	0.051
HD	AEGL-1	0.4	0.13	0.067	0.033	0.017	0.008
HD	AEGL-2	0.6	0.2	0.1	0.051	0.025	0.013
HD	AEGL-3	3.9	2.7	2.1	1.07	0.53	0.27

APPENDIX D

SAMPLE CALCULATIONS OF LIQUID CONCENTRATION AND EVAPORATION RATE BASED ON HEADSPACE CONCENTRATION

APPENDIX D

SAMPLE CALCULATIONS OF LIQUID CONCENTRATION AND EVAPORATION RATE BASED ON HEADSPACE CONCENTRATION

This appendix provides an example of how equations 6-1 through 6-6 are used to calculate the evaporative release of agent from waste at a given headspace concentration. In this calculation, it is assumed that VX-contaminated waste is being shipped and the headspace concentration in each drum on the truck is less than or equal to 240 VSL. A bounding evaporative release will be calculated by assuming that all drums have a measured headspace concentration of 240 VSL (0.0024 mg/m^3).

Equation 6-1 is used to determine the concentration of agent in the liquid based on the concentration in the headspace.

$$x_a = \frac{10^{-3}\,\text{g/mg} \times 0.0024\ \text{mg/m}^3 \times (8.2056 \times 10^{-5}\,\text{atm} - \text{m}^3\,/\,\text{mole K}) \times 298.15\ \text{K}}{1.16 \times 10^{-6}\ \text{atm} \times 267\ \text{g/mole}}$$

$$x_a = 1.90 \times 10^{-4}\ \text{moles VX/mole liquid}$$

where the value for P_v of 1.16 × 10^{-6} atm is determined using equation 6-2 and the Antoine coefficients in table 6-1.

Based on this mole fraction, the mass fraction of agent and total mass of agent in each drum can be calculated using equations 6-3 and 6-4.

$$w_a = \frac{1.90 \times 10^{-4} \times 267\ \text{g/mole}}{18\ \text{g/mole}} = 2.81 \times 10^{-3}\ \text{g VX/g liquid}$$

$$m_a = 1 \times 10^3\,\frac{\text{mL}}{\text{L}} \times 2.81 \times 10^{-3}\,\frac{\text{g VX}}{\text{g liquid}} \times 0.5\text{L} \times 1\frac{\text{g}}{\text{mL}} = 1.4\ \text{g VX}$$

Next, equation 6-5 can be used to calculate the agent evaporation rate from the contaminated waste.

$$E_m = \frac{3.53 \times 10^3 \times (1\,m/s)^{0.78} \times 267\,g/mole \times 6.2 \times 10^{-10}\,atm}{2.4^{0.67} \times 2.4^{0.11} \times 1\,atm \times 308.15\,K} \times 5\,m^2$$

$$E_m = 4.8 \times 10^{-6}\ g/min$$

where the agent partial pressure in the numerator of this equation is calculated using equation 6-6 with the mole fraction calculated above and the agent vapor pressure at 35°C calculated using the Antoine equation (3.3×10^{-6} atm).

The amount of agent vapor released from each breached drum during the 120 minute release period is therefore 0.58 mg and the amount of agent vapor released by 40 breached drums is approximately 24 mg.

APPENDIX E
PROBABILITY OF WORST CASE WEATHER CONDITIONS ASSUMED IN THE BOUNDING TRA

APPENDIX E
PROBABILITY OF WORST CASE WEATHER CONDITIONS ASSUMED IN THE BOUNDING TRA

A study was performed to determine the likelihood of the worst-case daytime and nighttime weather conditions assumed in the bounding TRA. This study used meteorological data taken at three stockpile sites over a two year period. The three sites included Anniston Army Depot, Blue Grass Army Depot, and Umatilla Army Depot. The weather conditions at these sites were judged to be representative of weather conditions across the country.

Tables E-1 through E-3 present a summary of the meteorological data. The tables show the atmospheric stability conditions determined during daytime and nighttime hours at the three sites. In all cases, the worst-case daytime condition was D stability and the worst-case nighttime condition was F stability. The tables also show the fraction of the time that the wind speed was above and below 1.5 meters per second, and the fraction of the time that the weather conditions were characterized by the worst-case conditions assumed in the bounding TRA. In all cases, the assumed worst-case conditions were extremely rare. The worst-case daytime conditions occurred much less than 1 percent of the time, whereas the worst-case nighttime conditions occurred less than 4 percent of the time.

Table E-1: Probabilities of Worst Case Weather Conditions for Anniston Army Depot (Tower 1 Data from 30 November 2005 - 30 November 2007)

Stability Class Incidence: Daytime Hours

Stability Class	Incidences[a]	%
A	1,619	4.68
B	7,156	20.66
C	6,120	17.67
D	19,735	56.99
Total	34,630	

Daytime Incidences of Wind Speeds less than or equal to 1.5 m/s

	Incidences	%
Wind Speed ≤ 1.5 m/s	10,621	30.67
Wind Speed > 1.5	24,009	69.33
Total	34,630	

Temperatures During Stability Class D, with Wind Speeds less than or equal to 1.5 m/s

	Incidences	% of D	% of all
75° to 84.99° F	1,356	6.87%	3.92%
85° to 94.99° F	647	3.28%	1.87%
≥ 95°F	104	0.53%	0.30%

Stability Class Incidence: Night time Hours

Stability Class	Incidences	%
D	15,988	45.52
E	2,646	7.53
F	16,486	46.94
Total	35,120	

Nighttime Incidences of Wind Speeds less than or equal to 1.5 m/s

	Incidences	%
Wind Speed ≤ 1.5 m/s	24,619	70.1
Wind Speed > 1.5	10,501	29.9
Total	35,120	

Temperatures During Stability Class F, with Wind Speeds less than or equal to 1.5 m/s

	Incidences	% of F	% of all
65° to 74.99° F	3,999	24.26%	11.39%
75° to 84.99° F	1,221	7.41%	3.48%
≥ 85°F	219	1.33%	0.62%

Note:
[a] Incidences are hours during which the listed conditions were observed.

Table E-2: Probabilities of Worst Case Weather Conditions for Blue Grass Army Depot (Tower 1 Data from 30 November 2005 - 30 November 2007)

Stability Class Incidence: Daytime Hours

Stability Class	Incidences[a]	%
A	1,431	4.05
B	8,008	22.66
C	9,962	28.19
D	15,938	45.10
Total	35,339	

Daytime Incidences of Wind Speeds less than or equal to 1.5 m/s

	Incidences	%
Wind Speed ≤ 1.5 m/s	9,124	25.82
Wind Speed > 1.5	26,215	74.18
Total	35,339	

Temperatures During Stability Class D, with Wind Speeds less than or equal to 1.5 m/s

	Incidences	% of D	% of all
75° to 84.99° F	663	4.16%	1.88%
85° to 94.99° F	57	0.36%	0.16%
≥ 95°F	9	0.06%	0.03%

Stability Class Incidence: Night time Hours

Stability Class	Incidences	%
D	7,756	22.44
E	5,071	14.67
F	21,730	62.88
Total	34,557	

Nighttime Incidences of Wind Speeds less than or equal to 1.5 m/s

	Incidences	%
Wind Speed ≤ 1.5 m/s	19,567	25.82
Wind Speed > 1.5	14,990	74.18
Total	34,557	

Temperatures During Stability Class F, with Wind Speeds less than or equal to 1.5 m/s

	Incidences	% of F	% of all
65° to 74.99° F	4,452	20.49%	12.88%
75° to 84.99° F	696	3.20%	2.01%
≥ 85°F	15	0.07%	0.04%

Note:
[a] Incidences are hours during which the listed conditions were observed.

Table E-3: Probabilities of Worst Case Weather Conditions for Umatilla Army Depot (Tower 1 Data from 30 November 2005 - 30 November 2007)

Stability Class Incidence: Daytime Hours

Stability Class	Incidences[a]	%
A	512	1.43
B	6,989	19.54
C	7,675	21.46
D	20,585	57.56
Total	35,761	

Daytime Incidences of Wind Speeds less than or equal to 1.5 m/s

	Incidences	%
Wind Speed ≤ 1.5 m/s	5,040	14.09
Wind Speed > 1.5	30,721	85.91
Total	35,761	

Temperatures During Stability Class D, with Wind Speeds less than or equal to 1.5 m/s

	Incidences	% of D	% of all
75° to 84.99° F	74	0.36%	0.21%
85° to 94.99° F	44	0.21%	0.12%
≥ 95°F	3	0.01%	0.01%

Stability Class Incidence: Night time Hours

Stability Class	Incidences	%
D	21,472	62.68
E	7,188	20.98
F	5,596	16.34
Total	34,526	

Nighttime Incidences of Wind Speeds less than or equal to 1.5 m/s

	Incidences	%
Wind Speed ≤ 1.5 m/s	5,730	16.73
Wind Speed > 1.5	28,526	83.27
Total	34,256	

Temperatures During Stability Class F, with Wind Speeds less than or equal to 1.5 m/s

	Incidences	% of F	% of all
65° to 74.99° F	172	3.07%	0.50%
75° to 84.99° F	91	1.63%	0.26%
≥ 85°F	25	0.45%	0.07%

Note:
[a] Incidences are hours during which the listed conditions were observed.

APPENDIX F
CHANGE IN CONCENTRATION WITH ELEVATION FOR FIRE SCENARIOS

APPENDIX F

CHANGE IN CONCENTRATION WITH ELEVATION FOR FIRE SCENARIOS

Agent vapor released during a fire is carried upward by the heated gases from the fire. The elevation to which the heated plume is carried depends on several different factors such as the rate of heat produced by the fire, the ambient temperature, and wind speed. Under most conditions, the fire would carry the agent vapor hundreds of meters into the air.

The agent plume disperses both vertically and laterally as it moves downwind. A substantial reduction in the agent concentration occurs before the plume reaches the ground. It was recognized, however, that the potential exists for an individual at an elevated location relative to the site of the accident to receive a greater exposure than someone at ground level. A study was performed to determine how the downwind concentration of agent varies with elevation of the receptor.

The analysis shows that, for the nighttime weather conditions of greatest interest in the current study (F stability and 1 m/s wind speed), limited vertical dispersion occurs as the plume moves downwind and the agent concentration decreases rapidly with vertical distance from the plume centerline. For example, table F-1 shows that at 100 meters downwind from the accident site, the concentration decreases by 90 percent at a distance of only 6 meters from the plume centerline and by 99 percent at a distance of only 8 meters from the centerline. Therefore, only individuals located downwind in a narrow range of elevations would the experience higher agent concentrations found near the plume centerline.

Table F-1 Effect of Elevation Change on Agent Vapor Concentration

Nighttime Conditions (F stability, 1 m/s)

Concentration Reduction (%)	Downwind Distance (meters)		
	25	100	500
	Vertical Distance to Produce Given Percent Reduction		
50	2 m	3 m	10 m
90	3 m	6 m	18 m
99	4 m	8 m	25 m

Daytime Conditions (D stability, 1 m/s)

Concentration Reduction (%)	Downwind Distance (meters)		
	25	100	500
	Vertical Distance to Produce Given Percent Reduction		
50	2 m	5 m	20 m
90	4 m	10 m	40 m
99	6 m	14 m	60 m