NRT Quick Reference Guide: Sulfur Mustard (HD)



GHS: Acute Toxicity, Category 1 H310 – Fatal in contact with skin H330 – Fatal if inhaled



GHS: Eye Damage/Irritation, Category 1 H318 – Causes serious eye damage

1. Agent Characteristics

Agent Characteristics

Agent Classification: Schedule 1 Chemical Warfare Blister (Vesicant) Agent; Sulfur Mustard (HD); CAS 505-60-2 **Description:** Sulfur mustard, Bis-(2-chloroethyl) sulfide, is sometimes called "mustard gas" but is actually a yellow to brown oily liquid with a garlic, onion, horseradish, or mustard-like odor. It is a blister (vesicant) agent that will have delayed health effects on the order of hours, and is reported to be a known human carcinogen. It can be manufactured at different concentrations; with impurities, additives, or thickening materials that will all affect physical properties, appearance, persistence, and analytical detection limits. Distilled mustard (HD) is considered the most toxic form and is the basis of this QRG. Because HD evaporates slowly, HD is primarily a liquid hazard – or dermal (contact) hazard – under temperate conditions, although aerosols and vapors can be generated under proper conditions and would present an ocular or inhalation hazard. Environmental breakdown (hydrolysis) products of HD, including thiodiglycol (TDG) [CAS 111-48-8] and hydrochloric acid (HCl), are relatively non-toxic, but some combustion and decontamination byproducts can be toxic (e.g., sulfur oxides, sulfones).

Other Sulfur Mustard Agents:

- Agent H (CAS 505-60-2): H is Levinstein mustard, from a production process that originated during WWI and contains about 30% impurities. The reported physical and chemical properties, and toxicity, are essentially the same as those reported for HD.
- Agent HT (CAS: 101-77-9): HT is a mixture of 60% Agent HD and 40% Agent T ((bis (2-chloroethylthio) diethyl ether)), a vesicant that is a byproduct of certain methods of manufacturing mustard. Agent T is intentionally included to lower the freezing point of HT (32-34.3°F (0-1.3°C)), lower the volatility, and increase the persistence of sulfur mustard. The reported toxicity and remaining physical and chemical properties of HT are similar to those of HD.

Persistence: HD is considered a "persistent or semi-persistent" chemical warfare agent with liquid deposition on surfaces lasting for hours to days. Persistence will depend upon the amount and purity of the agent, method of release, environmental conditions, and the types of surfaces and materials impacted. HD can be 2 to 5 times more persistent in winter than in summer due to lower winter temperatures. Under certain environmental conditions, HD liquid may go through a partial hydrolysis that results in an outer protective coating around "globules" that are resistant to further hydrolysis and can persist for decades if not physically disturbed. This is often the case in aqueous systems where HD, with a liquid density greater than water (>1), will sink to the bottom of water systems, and persist for considerable periods of time (years, decades), while retaining its vesicant properties. Porous, permeable, organic, or polymeric materials such as carpets, vinyl tiles, and painted surfaces can accumulate HD vapors and liquids, acting as "sinks," thereby prolonging persistence.

2. Physical Properties

P	hysical Properties
Molecular Weight: 159.08 g/mol	Formula: C ₄ H ₈ Cl ₂ S
Vapor Density: 5.4 (air = 1)	Flash Point: 219-221°F/104-105°C
Vapor Pressure: 0.072 mm Hg (68°F/20°C)	Liquid Density: 1.27 g/mL (68°F/20°C)
Volatility: 610 mg/m ³ (68°F/20°C)	Melting/Freezing Point: 55-57°F/13-14°C
Boiling Point: 419-423°F/215-217°C	Non-aqueous Solubility: Common organic solvents, alcohols, gasoline, oils, fats
Hydrolysis ($t_{1/2}$): The rate of HD hydrolysis is controlled by the speed of dissolution of the HD into water, which is typically very slow especially if "globules" are formed (see	Aqueous Solubility: HD is practically insoluble in water and is limited by the rate of dissolution (mass transfer) of HD into the bulk water. After HD is dissolved, the solubility of HD in distilled water is $0.92 \text{ g/L} (72^{\circ}\text{F}/22^{\circ}\text{C}).$
Aqueous Solubility). Once HD is dissolved in bulk water, hydrolysis proceeds rapidly.	HD is heavier than water (Liquid density > 1) and if released in or on top of the water, will sink to the bottom of waterbodies where it can
In distilled water, $t_{1/2} = 5-8.5$ minutes (77°F/25°C). In salt water, $t_{1/2} = 60$ minutes (77°F/25°C).	form a protective coating around "globules" (see Persistence in AGENT CHARACTERISTICS section above) and resist further dissolution and persist for considerable periods of time (years, decades) while retaining its vesicant properties.
Note: physical properties are listed at/near STP un	less otherwise indicated. The reported Physical Properties for H and HT

are similar to the reported physical properties for HD. **Conversion Factors for HD:** $ppm = mg/m^3 \times 0.1538$; $mg/m^3 = ppm \times 6.503$

3. Release Scenarios

Release Scenarios

AIR RELEASE SCENARIOS ARE ASSUMED MOST PROBABLE; HOWEVER, OTHER RELEASE SCENARIOS AND EXPOSURE ROUTES SHOULD BE CONSIDERED.

Open Areas: HD is difficult to disperse in air due to low volatility; however, it may be possible to disperse HD as a vapor/aerosol plume or liquid droplets if an appropriate heat/explosive device is employed. The low volatility of HD would limit the size and extent of plume dissipation, posing localized hazards. **HD has a melting/freezing point at 55-57°F/13-14°C.** Frozen HD can easily melt as ambient temperatures rise, and may present a continued dermal (contact) hazard. The vapor hazard of HD increases with increasing temperature; HD is a definite vapor hazard (i.e., ocular or inhalation hazard) at temperatures above 100°F (38°C). HD vapors are heavier than air, so vapors can accumulate in lower terrains.

- **Water/Water Systems:** If released into natural waters or water systems, HD may sink to the bottom, then slowly dissolve. Some release conditions may be conducive for enhancing the dissolution rate, such as agitation and dispersion as fine droplets. Once dissolved, the HD hydrolyzes with a half-life dependent on the composition of the water, ranging from 5-8.5 minutes (at 77°F/25°C in distilled water) to 60 minutes (at 77°F/25°C in high chloride waters, such as seawater). In sufficient amounts (relative to water volume) and under certain environmental conditions (low temperature and oxygen levels), HD may also form globules surrounded by a protective outer layer resistant to hydrolysis. These globules may settle out or be entrapped, persisting for decades, and posing a contact hazard to anyone disturbing them. Areas in which the globules may persist include stagnant volumes of water as small as puddles formed by precipitation events. Water systems, plumbing, surfaces, and equipment that have contacted HD globules should be evaluated for decontamination.
- **Indoor Facility:** HD is a semi-persistent agent with low to moderate volatility and would be difficult to distribute effectively throughout a building or facility from a point source. Liquid HD will result in localized areas of surface contamination. However, HD vapors can be generated if conditions are right. HD vapors are heavier than air so vapors can accumulate in lower levels, basements, floor drains, or utility corridors inside the buildings.
- **Other:** HD will decompose when heated or when combusted in a fire to form highly toxic fumes of sulfur oxides and hydrochloric acid. If HD is released into the air as a liquid spray (aerosol), it has the potential to contaminate agricultural products. If HD is released as a vapor, it is unlikely to contaminate agricultural products, since it will likely recondense as a liquid soon after release, presenting a potentially short- or long-term secondary dermal (contact) hazard.
- **Military Munitions:** Information for OSCs on military munitions found in the civilian sector (e.g., recovery of seadisposed discarded HD munitions during diving or commercial fishing, clamming, and dredging) is available on <u>nrt.org</u> (scroll to or click on military munitions hazards).

4. Health Effects

Health Effects

4.1. Onset: Onset of symptoms is dose and route dependent. Onset and severity of effects depend on dose, duration, and route of exposure (not all signs/symptoms may develop). The effects caused by HD are not typically fatal immediately, but can require substantial supportive medical care as there is no antidote, and secondary infections from blisters/tissue damage may also be fatal. HD produces effects by causing DNA damage/cell death in seconds (this is not like an acid burn). Despite the immediate DNA damage actual **signs/symptoms may be delayed 1-48 hours** after exposure, so those exposed may not be aware.

4.2. Signs/Symptoms: Initial symptoms will vary depending on dose and exposure route (see EXPOSURE ROUTES section below). The following is a general list of possible symptoms. The severity of effects depends upon the dosage.Mild: Effects delayed 1-48 hours (severity depends on dose): Eye irritation (tearing, grittiness), runny nose, sneezing, nosebleed, hoarseness, hacking cough.

Moderate: Effects delayed 1-24 hours: Mild effects plus reddening and swelling of eyelids, severe cough, shortness of breath, reddening of skin.

Severe: Effects delayed 1-24 hours: Upper respiratory/lung damage may occur at high concentrations and longer exposure durations.

4.3. Exposure Routes:

- **Inhalation:** Airway injury develops slowly, within 2-6 hours after severe exposure or within 12-24 hours after mild exposure and intensifies over several days. Airway injury begins with the upper airways and descends to the lower airways. Vapor exposure is absorbed in mucous membranes (e.g., mouth, throat, lungs).
 - Mild exposure: Runny nose, sneezing, nosebleed, hoarseness, hacking cough, wheezing, and difficulty breathing.
 - Severe exposure: Same as above, plus acute inflammation of upper and lower airways, tissue death of airway lining, airway blockage from inflamed and dead (necrotic) cells, and death due to lung inflammation (pneumonia).

Skin: Direct contact with HD liquid can cause redness or blisters in 2-24 hours. Some skin injury may appear as late as 48 hours after exposure. Warm and sweaty skin areas (e.g., underarms, groin) are most susceptible to exposure. Skin effects of HD liquid occur sooner than skin effects of HD vapor.

• Mild exposure: Redness (erythema) within 1-24 hours, blistering (vesication) within 2-18 hours after onset of redness, itching, and burning pain.

• Severe exposure: All of the above, with more severe blistering (vesication) with areas of tissue death (necrosis) along with whole-body (systemic) effects including weakness, vomiting (emesis), fever, exhaustion. Skin exposure to HD can be fatal: an area of redness (erythema), with or without blistering (vesication), which covers 25% or more of the body's surface area, suggests a lethal exposure.

Eyes: Eyes are the most sensitive to HD vapors; effects occur after 1-2 hours after severe exposure or within 3-12 hours after a mild to moderate exposure.

- Mild/Moderate exposure: Lacrimation (tear production), irritation, burning, dryness or gritty feeling, itching, weeping, reddening, lid swelling (edema in eyelids), and moderate pain.
- Severe exposure: Severe pain and additional effects include increased lid swelling (edema in eyelids), light sensitivity, corneal injury, and blindness and generally require extended medical treatment.

Ingestion: Consumption of contaminated food or drink could cause nausea, vomiting (emesis), pain, and possible chemical burns of gastrointestinal (GI) tract.

5. Effect Levels

Effect Levels

Air (inhalation vapor hazard): Acute Exposure Guideline Levels (AEGLs) for general population one-time exposure emergency scenarios for HD (complete definitions are available at: <u>https://www.epa.gov/aegl</u>).

AEGL Level in mg/m ³ , at various exposure durations for HD. (Note: AEGL values for H and HT are not available)	10 min.	30 min.	1 hr.	4 hr.	8 hr.
AEGL 1: Threshold mild effects	0.40	0.13	0.067	0.017	0.008
AEGL 2: Potentially irreversible effects or impaired ability to escape	0.60	0.20	0.10	0.025	0.013
AEGL 3: Threshold for severe effects/medical needs/increasing potential for lethality	3.9	2.7	2.1	0.53	0.27

American Industrial Hygiene Association (AIHA) Emergency Response Planning Guidelines (ERPGTM) are not established/determined for HD.

6. Exposure Guidelines

Exposure Guidelines

6.1. Airborne Exposure Limits (AELs): CDC has issued recommendations for protecting human health from potential adverse effects of exposure to this agent. The reported AELs for H and HT are the same as those for HD. (refer to: NIOSH ERSH-DB, <u>https://www.cdc.gov/NIOSH/ershdb/EmergencyResponseCard_29750008.html</u>)

[original source: CDC, National Center for Environmental Health (NCEH), Interim Recommendations for Airborne Exposure Limits for Chemical Warfare Agents H and HD (Sulfur Mustard), 69 FR 24164-24168 (May 3, 2004)]

CDC/National Center for Environmental Health (NCEH) IDLH = 0.7 mg/m^3 ; workers should remove themselves immediately from exposure if the concentration is reached at any point in time

CDC/NCEH STEL = 0.003 mg/m^3 (3 × 10⁻³); exposure at the STEL should be as short as practical (but no longer than 15 minutes) and should not occur more than once per day

CDC/NCEH Worker Population Limit (WPL) = $0.0004 \text{ mg/m}^3 (4 \times 10^{-4})$

CDC/NCEH General Population Limit (GPL) = $0.00002 \text{ mg/m}^3 (2 \times 10^{-5})$

6.2. Occupational: (NA = not available)

NIOSH IDLH = NA	OSHA PEL = NA
NIOSH REL-TWA $=$ NA	ACGIH TLV-TWA = NA
NIOSH REL-STEL = NA	ACGIH TLV-STEL = NA

6.3. Population:

Soil: USAPHC Health Based Environmental Screening Levels (HBESL) = TBD. The US Department of Defense (DOD) will be issuing new HBESL values for both industrial and residential soil after DOD completes a reevaluation of toxicological information related to liquid mustard skin exposure and vesication (blistering). Until DOD releases these new HBESL values to the public, DO NOT use current values available from websites and other resources.

Drinking Water: EPA Provisional Advisory Levels (PALs): see below for more information.

EPA Provisional Advisory Level (PAL): PALs represent chemical concentrations in air or drinking water above which varying health effects (PAL1, PAL2, PAL3) are expected. They are developed for 24-hour, 30-day, and 90-day exposure durations. In the event of a nationally significant or large-scale chemical release, EPA can provide PALs, if available, to appropriate end-users and stakeholders as needed (PALs are not currently available to the public) to assist in response decision-making. Contact: <u>PALs@epa.gov</u>, for information on and access to the PALs. (Note: PALs are not intended to define cleanup levels.)

7. Personnel Safety

Personnel Safety

Note: Personal Protective Equipment (PPE) selection (Levels A-D), medical surveillance requirements, First Aid options, and personnel decontamination may vary depending upon the amount and purity of agent, site conditions, and the release scenario. Additional information on personnel safety and PPE selection criteria can be found at:

www.cdc.gov/niosh/ershdb. We also recommend that responders check their own internal procedures (i.e., SOPs), if applicable.

7.1. Medical:

Pre-incident: Must have current medical and respiratory clearances as part of an Occupational Medical Surveillance Program according to OSHA HAZWOPER and Respiratory Protection Program, as per 29 CFR 1910.

During Incident: Conduct periodic on-site medical monitoring, observe for any signs and symptoms as per HEALTH EFFECTS section above and treat accordingly as per First Aid section below.

Post-incident: Perform post-incident medical surveillance, as per 29 CFR 1910. Because health effects may not occur until several hours after exposure, patients/victims should be under medical surveillance for at least 24-48 hours.

7.2. First Aid: Immediately remove person from affected area and remove contaminated clothing and articles. Wash bare skin immediately with water, or warm, soapy water if available, at normal household pressures (~50-60 psi) for three minutes, ensure thorough soaking. Rinse eyes exposed to agent (liquid or vapor; eyes are especially sensitive to HD) with potable water for at least 15 minutes. If irritation or pain is severe or persists, prolonged eye washing is advised. Do not cover eyes with bandages. Seek immediate medical attention.

Antidote: NO ANTIDOTE AVAILABLE.

Other: RSDL (Reactive Skin Decontamination Lotion), an FDA-cleared kit with a sponge impregnated with a lotion to remove or neutralize chemical warfare agents from contaminated skin. Apply RSDL immediately to area of skin with suspected exposure to a chemical warfare agent (do not wait for symptoms) and wipe affected area using a scrubbing action, rinse with water when time permits.

After administering first aid, send person for follow-up medical attention and evaluation. If cleared to resume work, continue to monitor for signs/symptoms and treat accordingly.

7.3. Personal Protective Equipment (PPE):

GENERAL INFORMATION: NIOSH Approved® Chemical, Biological, Radiological, Nuclear (CBRN) Self Contained Breathing Apparatus (SCBA), NIOSH Approved Air Purifying Respirators (APR) or Powered Air Purifying Respirators (PAPR), full-face masks, and protective clothing should be used. Level A protection should be used until monitoring results confirm identity and concentration of contaminant. Pre-incident training and exercises on the proper use of PPE are recommended.

Per NIOSH guidance -

- **LEVEL A:** Recommended for the initial response to an HD incident. NIOSH Approved CBRN full-face-piece SCBA operated in pressure-demand mode with Level A suit that provides protection against CBRN agents. Level A provides the greatest level of skin (totally-encapsulating chemical protective suit and chemical-resistant inner and outer gloves, along with chemical-resistant boots with steel toe and shank), respiratory (SCBA), and eye protection when the contaminant identity or concentration is unknown. Select Level A when the HD concentration is unknown or above the IDLH or AEGL-2, and when there is a potential of ocular or dermal exposure.
- **LEVEL B:** Pressure-demand SCBA (NIOSH Approved CBRN full-face-piece SCBA) with Level B protective suit that provides protection against CBRN agents. Level B provides the highest level of respiratory protection (SCBA) when a lesser level of skin protection is required. Select Level B when the HD concentration is unknown or above the IDLH or AEGL-2, and when dermal exposure is less of a risk. Level B differs from Level A in that it typically incorporates a non-encapsulating, splash-protective, chemical-resistant outer suit that provides protection against most liquids but is not vapor tight (hooded chemical-resistant outer suit and chemical-resistant inner and outer gloves, along with chemical-resistant boots with steel toe and shank).
- **LEVEL C:** May be selected when the contaminant identity and concentration are known and the respiratory protection criteria factors for the use of APR or PAPR (i.e., < IDLH, warning properties) are met. Level C may be appropriate when decontaminating personnel or equipment. Level C still incorporates hooded chemical-resistant outer suit that provides protection against CBRN agents, chemical-resistant inner and outer gloves, and chemical-resistant boots with steel toe and shank.
 - For air levels greater than AEGL-2: NIOSH Approved CBRN tight-fitting PAPR with a filter or a combination organic vapor, acid gas, and particulate cartridge/filter combination or a continuous flow respirator.
 - For air levels greater than AEGL-1: NIOSH Approved CBRN tight-fitting APR with a canister-type gas mask or CBRN PAPR.
- **LEVEL D:** Select Level D when the contaminant is known and the concentration is below the appropriate occupational exposure limits or less than AEGL-1 for the stated duration times. PPE includes coveralls or other work clothes, boots, and gloves.

Downgrading PPE levels can be considered only by the site Health and Safety Officer when the identity and concentration of the contaminant and the risks of dermal exposure are known, and must be accompanied by on-site

monitoring. The on-site availability of any applicable medical countermeasures should also be considered when deciding to downgrade PPE during a CBRN response.

8. Personnel Decontamination

Personnel Decontamination

8.1. Personnel Decontamination Procedure:

Tents, berms, and collection vessels should be able to maintain copious amounts of wastewater in a contained and safe manner. Procedures should be in place to treat and replace contaminated materials used during the decontamination process as well as replace necessary chemicals and decontamination solutions.

Prior to entering the hot zone, all personnel are required to familiarize themselves with the site-specific personnel decontamination procedures.

Personnel decontamination should take place in a decontamination area comprised of two decontamination corridors (one for entering and one for exiting). Position corridors upwind and uphill of release area; exit should be upwind and uphill of entrance. Detergent and water solution (pH>8, but <10.5), soft brushes, and durable 6-mil polyethylene bags should be provided.

Personnel decontamination area workers need to wear appropriate PPE as indicated below. Be aware that absorbed agent can be released from clothing and skin as a vapor.

Conduct personnel decontamination per NIOSH ERSH-DB: https://www.cdc.gov/NIOSH/ershdb/EmergencyResponseCard_29750008.html

- Emergency Responders: Use soft brush to wash PPE with soap and detergent solution in a downward motion, getting into all folds. Repeat washing and rinsing until thoroughly clean. Remove PPE by rolling downward from head; avoid pulling PPE over the head. Remove SCBA last, and place all PPE in polyethylene bags.
- Patient/victim: Remove all clothing down to at least undergarments, and place in polyethylene bags. Thoroughly wash and rinse skin with soap and water solution, taking care not to break the skin and covering all open wounds. Cover patient/victim (e.g., blanket, towels, Tyvek) and move to treatment area. If available in decontamination kit, apply RSDL immediately to area of skin with suspected exposure to a chemical warfare agent (do not wait for symptoms) and wipe affected area using a scrubbing action, rinse with water when time permits.

8.2. Personnel Decontamination Procedures by Zone/Step: (attendants will verbally direct personnel through each step)

Conducted in Hot Zone (exclusion zone)

1	Equipment	Place equipment taken into the Hot Zone on a plastic covered table or container provided prior to entering
	Drop	the contamination reduction corridor. Equipment will either be reused if more than one entry is planned or
		will be decontaminated later.

Conducted in Warm Zone (contamination reduction zone)

2	Sample Drop	Place samples in a container provided for sample decontamination. Care needs to be taken to ensure that workers maintain chain-of-custody of samples. It is recommended that samples are decontaminated in a separate decontamination line.
3	Outer Boot and Glove Wash	The purpose of this step is to enable physical removal of gross contamination if contamination is visible. If gross contamination is not visible, this step may be skipped. Wash outer boots and then outer gloves using designated decontaminating agents as specified in HASP (e.g., soap and water, trisodium phosphate substitute, or diluted bleach).
4	Glove, Boot, and Suit Wash	Wash all outer surfaces in a contained area (e.g., kiddie pool) using a pressurized spray with designated decontamination solution. Start with decontaminating boots and gloves, then work on suit from the top down, including SCBA/PAPR casing. Decontamination personnel should conduct this step. Care should be taken to ensure that all areas are decontaminated, including around zipper, arms, front torso, and any other area that could have come in contact with contamination. The solution used for decontamination should be contained, collected, and disposed of properly from the decontamination line.
5	Outer Glove, Boot, and Suit Removal	While sitting on a stool, remove outer boots and outer gloves. Undo the SCBA/PAPR belt and hold in hand. While touching only the inside of suit, carefully roll suit in an outward motion from shoulders down to feet. Dispose of boots, gloves, and suit in a designated container. This step may require decontamination personnel to assist either by holding SCBA/PAPR unit or assisting in suit removal.
6	Mask Removal	With inner gloves, remove the mask. Remove cartridge filters and place into designated container. Put mask into mask wash. Decontamination personnel will clean each mask and SCBA/PAPR assembly prior to return to service.
7	Inner Glove Removal	Remove inner gloves by only touching outside of first glove and then only inside of second glove. Place gloves into designated container.

Conducted in Cold Zone (support zone)

8	Quadrant	Using appropriate HD air monitoring equipment, screen personnel for residual contamination by dividing
	Monitoring	body into 4 sections: upper right and left sides of the body, and lower left and right sides. If positive, perform
		spot decontamination immediately and direct person to showers.

9	Personal Shower	Personnel should shower using copious quantities of soap and water for a minimum of 5 minutes and change into clean clothes. If a personal shower is not immediately available then, at the minimum, hands and face should be washed thoroughly.
10	Medical	Report to medical monitoring station for post-entry monitoring and report to appropriate personnel for
	Monitoring	debriefing. Observe for any obvious sign of HD exposure. Using criteria listed above in PERSONNEL
		SAFETY section of this ORG, administer RSDL and notify site Health and Safety officer.

Emergency Egress Corridor: Establish an emergency egress line to use for quickly decontaminating personnel who have medical emergencies while in the hot zone. Personnel must be decontaminated prior to receiving treatment from emergency medical technicians or transported to a hospital.

Hand-Wash Station: A hand-wash station with soap and water should be available for personnel to clean up or physically remove any residual decontaminant following entry. If a hand-wash station is not initially available or weather conditions prohibit its use, personnel should wash their hands and face as soon as possible.

Caution: Avoid waterless hand cleaners, which contain solvents (alcohols) that could increase risk of dermal exposure to HD.

9. Field Detection

Field Detection

Real-time field screening tools (results not confirmatory or quantitative): Caution should be given to equipment that has not been properly evaluated. False positive and false negatives may occur in the presence of interferents common in the environment. The following is a summary of minimum screening concentration ranges or levels for equipment procured by many EPA and HAZMAT response teams. Other screening tools may be used by these teams and other agencies and responders, some with similar capabilities and limitations.

9.1. Minimum Screening Ranges/Levels for Air/(Vapor):

Field Equipment:	ppm	mg/m ³	
JCAD M4A1, at 10 secs [30 mins/pre-concentrator]	8 [0.003]	50 [0.02]	
AP2C / AP4C	0.08	0.5	
MX-908 Vapor Mode	1.2	7.8	
Dräger (CDS Kit)	0.15	1.0	
MINICAMS [™] (Near real-time; at 5 minutes)	0.0005	0.003	

9.2. Minimum Screening Ranges/Levels for Vapor/Liquid:

Field Equipment:	ppm (vapor)	mg/m ³ (vapor)	mL (liquid)
M256 / M256A1 (13 mins)	0.46	3.0	0.02 (via M8 paper)
M8	NA	NA	0.02

Note: M256 is combined 2 kits with 12 disposable sampler/detectors for vapors and a booklet of M8 paper for liquids. NA = not applicable

9.3. Minimum Screening Ranges/Levels for Water:

Field Equipment:	mg/L
M272	0.02

10. Environmental Sampling

Environmental Sampling

Note: This section on sampling contains general guidelines and does not replace the need for a site-specific sampling plan

10.1. Sampling Concerns: Detection, sampling equipment and procedures, and analytical techniques will be site-specific and depend on: 1) physical state of the agent; 2) type of surfaces contaminated (e.g., porous vs. non-porous); 3) the purpose of sampling (e.g., characterization, decontamination efficacy, and clearance); and 4) specific laboratory requirements. The U.S. Environmental Protection Agency (EPA) has set up mobile and fixed labs and analytical assets for chemical agent analysis of environmental samples under their Environmental Response Laboratory Network (ERLN), see ANALYSIS section below, (https://www.epa.gov/emergency-response/environmental-response-laboratory-network). For questions on environmental sampling for HD call EPA/HQ-EOC at 202-564-3850.

10.2. Sample Locations and Planning: Initially consider air monitoring to ensure worker safety and to determine if there is a vapor plume that could impact other areas. Characterization sampling is initiated by targeted or judgmental sampling to identify "hot spots," potential agent flow paths, and media or objects potentially acting as sinks. Additional biased or random sampling can be used to determine the extent of potential contamination or to verify the efficacy of decontamination. More thorough probabilistic sampling (e.g., grid, statistical approach) may be required for the clearance phase or if there are large uncertainties about the area impacted or the amount released. Because HD is a semi-persistent liquid, sample priorities should include surfaces that are potentially contaminated with liquid (e.g., release site, low lying areas, HVAC, utility corridors) and areas that people are likely to contact or where food or agricultural products are present.

Note: HD breaks down in most environmental and decontamination conditions to numerous breakdown products, especially TDG, which may be used as a marker to determine the extent of contamination of the parent HD. See

ANALYSIS section below to ensure sampling procedures are compatible with all analytes. Some preparation techniques for both HD and its breakdown products are available in EPA's Sample Information Collection Documents (<u>https://www.epa.gov/esam/sample-collection-information-documents-scids</u>). These provide general information regarding sampling procedures for different media, sampling supplies, sample size, container, holding time, preservation, packaging, and shipping, supporting collection of samples.

10.3. Types of Samples:

- **Air** (Vapors are heavier than air): Samples are collected using appropriate solid phase absorbent media (tubes) or air sampler (e.g., SUMMA canister) at breathing zone level (~5 ft.) to assess inhalation exposure. To assess off gassing from surfaces and at ground levels, collect air samples at ~6 in. above the ground. Concurrent air monitoring for HD is recommended.
- **Water:** Water should be collected in appropriate containers with addition of appropriate de-chlorinating agents and preservatives to minimize HD degradation and hydrolysis prior to analysis. Concurrent air monitoring for HD is recommended.
- **Soil:** For localized "hot spot" areas where soil deposition may occur (i.e., neat liquid, aerosol or liquid droplets), surface soil samples should be taken from a non-vegetated area to a depth of less than one inch. Sub-surface soil samples are typically not necessary unless a large amount of liquid was poured on the ground, or if an underlying aquifer is endangered. Concurrent air monitoring for HD is recommended.
- **Surface Wipes:** Wipe samples are often desired to indicate absence of HD on non-porous surfaces. Concurrent air monitoring for HD is recommended.
- **Bulk:** For hot spot areas where liquid HD deposition may occur on porous surfaces (e.g., concrete, asphalt), actual pieces (chips) or cores of contaminated surface may be obtained using appropriate tools (scabbling, coring, or drills) for subsequent laboratory extraction analysis. Bulk samples of suspected sink materials may be recommended to rule out secondary vapor phase disposition or absorption of HD into these materials. Concurrent air monitoring for HD is recommended.

Other Sample Matrices: Contact EPA/HQ-EOC at 202-564-3850 for sampling instructions.

11. Packaging/Shipping: CWA Environmental Samples for Site Characterization

Packaging and Shipping: CWA Environmental Samples For Site Characterization

The packaging and shipping of environmental samples potentially contaminated with a chemical warfare agent (CWA) would be subject to complex and restrictive regulations established primarily by DOT for ground transportation (49 CFR Parts 171-180), and by DOT, ICAO, and IATA for air transportation (in addition to other regulations by CDC, USPS, OSHA). Transportation of HD-contaminated waste for treatment and disposal is covered under the WASTE MANAGEMENT section below.

Samples can be collected from environmental media that include surface and subsurface soil, groundwater, surface water, drinking water, dust, air, and solids other than soil (e.g., building materials). Given the wide range of potential environmental media and complex regulatory requirements, the approach would likely be situationally dependent.

CAUTION: Environmental samples potentially contaminated with CWA should not be introduced into commercial transportation as an undeclared hazardous material. Hazard classification, packaging, and hazard communication are the shipper's responsibility under DOT's Hazardous Materials Regulations (49 CFR Parts 171-180).

A summary of key packaging and shipping considerations for environmental samples with unknown concentrations of a potential unknown CWA is:

- Transport of pure HD is forbidden other than via military (Technical Escort Unit) transport in accordance with 49 CFR \$173.7.
- If the collected sample contains or is suspected to contain hazardous materials, as defined in 49 CFR §171.8, the shipper must determine the appropriate UN ID Number, the Proper Shipping Name (PSN), and the Packing Group (PG) from the Hazardous Materials Table in 49 CFR §107.101. The table will then direct the shipper to the type of hazard and handling labels needed, the appropriate packaging (inner and outer packaging), and any special provisions.
- The designated shipper (EPA personnel or contractors) must be trained and certified according to the requirements found in 49 CFR §172.704 (a)(2) and/or by IATA Dangerous Goods (DG) 1.5 requirements for shipments by air.
- Contact the sample-receiving laboratory to determine if they have additional packaging, shipping, or labeling requirements.

Note that there is no UN ID for HD listed in the Hazardous Materials Table (49 CFR §172.101). Therefore, the most likely classification would be UN3381, Toxic by inhalation liquid, n.o.s. with an LC50 lower than or equal to 200 mL/m³ and saturated vapor concentration greater than or equal to 500 LC50, PG I. In the US, non-bulk packaging would then be in accordance with 49 CFR §173.226.

Use of Mobile labs: Another consideration would be use of an on-site mobile laboratory for CWA analysis. This could eliminate the shipper's responsibility for transporting the collected samples containing a substance that might be considered forbidden for transport by air or a hazardous material or DG by ground or air transport to an off-site laboratory. In addition, there may be public concern about shipping samples off-site, or reluctance of commercial shipping companies to accept and transport samples from a known CWA-contaminated site. EPA maintains mobile laboratory assets (PHILIS mobile laboratories: https://www.epa.gov/emergency-response/philis-portable-high-

throughput-integrated-laboratory-identification-system) in NJ and CO that are capable of analyzing CWAs, including HD, in environmental matrices, down to health-based risk clearance levels. Access to the PHILIS mobile labs for a CWA incident can be obtained from EPA HQ/EOC at 202-564-3850. EPA also has access to the US Army CBRNE assets, including shipping and analysis, through inter-agency agreements as described in the COORDINATION WITH OTHER AGENCIES section below.

12. Analysis

Analysis

CAUTION: Many labs may not be able to perform analysis on all matrices (e.g., wipes and soil). Few laboratories currently have the capability to determine HD, particularly for large numbers of samples and for the various types of environmental media. EPA's ERLN labs (https://www.epa.gov/emergency-response/environmental-response-laboratory-network) that are specially trained and equipped for the analysis of HD, will use sample prep and analytical methods from EPA's Environmental Sampling and Analytical Methods (ESAM) Programs (https://www.epa.gov/esam). For access to the nearest ERLN laboratory specially trained and equipped for HD analysis, and methods provided in EPA's ESAM, contact EPA/HQ-EOC at 202-564-3850. The ERLN also maintains EPA's Compendium of Environmental Testing Laboratories (CETL), a database of commercial, federal, state, and academic laboratories, which can be queried for specific analyses and matrices. Analysis on environmental matrices for toxic organics, metals, biological and radiological agents, as well as several of the CWAs, including HD and its breakdown products, can be obtained by querying the database of laboratories listed in EPA's CETL (https://cfext.epa.gov/cetl/lblogin.cfm?action=None); prior registration for access to CETL website is necessary.

13. Coordination with Other Agencies: CWA Field Activities

Coordination With Other Agencies: CWA Field Activities

Numerous agencies other than EPA may be involved in a chemical agent response incident. Every attempt should be made to integrate assets and design a uniform approach to sampling procedures, quality assurance, and data sharing. Every attempt should be made to coordinate activities, share data, and maintain chain-of-custody integrity throughout all phases of the response, amongst all agencies involved.

Civilian: The National Guard Civil Support Team (CST) and the U.S. Coast Guard "Strike Teams" deploy survey teams, response vehicles, and mobile labs to hazardous chemical incidents throughout the United States. Many CSTs and Strike Teams have the capabilities to sample, prepare, and analyze certain types of environmental samples for CWA analysis. CSTs have analytical equipment that can provide screening or presumptive data results for CWAs. The OSC should discuss site-specific types of samples, data quality, and chain-of-custody requirements with Strike Teams and CSTs before integrating their capabilities into the overall CWA response. Other agencies, such as the FBI, may be present on-site performing tasks, such as evidence retrieval, which are specific for their agency.

Military: EPA's Special Teams (ERT and CMAD) have access to Department of Defense (DOD) assets through Inter-Agency Agreements (IAA) with the US Army's Combat Capabilities Development Command, Chemical Biological Center (CBC) at Aberdeen Proving Ground, MD. The CBC has expertise and deployable assets for CWA air monitoring (i.e., MINICAMSTM), sampling, analysis, decontamination, and waste transport and disposal through their ongoing demilitarization activities at former chemical agent munitions facilities in the US and abroad.

Access to EPA's IAA for support to Federal OSCs at a CBRN response or incident can be arranged through EPA/HQ-EOC at 202-564-3850. Consultation or training for EPA personnel and partners that do not need to go through EPA/HQ-EOC can be arranged via the IAA with EPA's ERT-Special Team at 732-321-6660. Additional CBRNE support can be obtained via the IAA with EPA's CMAD-Special Team, including support for chemical, biological, and radiological agent response through EPA/HQ-EOC at 202-564-3850.

14. Environmental Decontamination/Cleanup

Environmental Decontamination/Cleanup

14.1. Decontamination/Cleanup Planning:

Once site controls are in place, develop a site-specific decontamination/cleanup plan. Environmental decontamination may require a "tiered approach" using a variety of techniques and products. Call EPA/HQ-EOC at 202-564-3850 for more information.

General Considerations: A cost vs. benefit evaluation should be undertaken for each decontamination strategy and approach that considers public safety, total cost, impact on the area, wastes generated, time the area or item will be inaccessible and/or out of service, as well as any socio-economic, public health, and/or security impacts that may result. Large volumes of decontamination wastes may be generated that will need to be collected, treated, and disposed of properly. Waste handling and disposal must be addressed as early in the decontamination and cleanup process as possible (see WASTE MANAGEMENT section below).

Disposal Option: The urgency to restore an area or item as quickly as possible may result in the outright and timely removal and disposal of contaminated materials. Certain materials may be impacted by the decontamination products, and/or may be cheaper to discard and replace than to decontaminate and restore.

Monitored Natural Attenuation: HD degrades via natural processes. Environmental monitoring must be maintained during decontamination and recovery phases. Monitored natural attenuation may require institutional controls (e.g., access restriction and contaminant containment measures). The time to achieve clearance must be considered in the overall cost/benefit evaluation. This option is more passive than other options but is non-destructive to materials.

Fix-in-Place Option: The contaminated area may be resistant to decontamination products or may be unable or impractical to be treated. Physical barriers can be used to immobilize the contamination and prevent it from coming into contact with the environment or the public. This can be a temporary or permanent solution.

14.2. Decontamination Strategy:

A decontamination strategy can be developed by designating contaminated areas into five broad categories: 1) surfaces or hot spots, 2) large volumetric spaces, 3) sensitive equipment or items, 4) aqueous solutions, and 5) water systems. Areas in each category may be treated using one or more unique decontamination processes in a tiered approach to the overall site-specific decontamination strategy. The described strategy is for HD; strategies for other sulfur mustard agents (H, HT; see AGENT CHARACTERISTICS section) are expected to be similar.

Cautions:

- Decontamination products may have unique safety/PPE requirements due to their own toxicity or that of breakdown products during use (e.g., use of bleach results in release of chlorine vapors). Strong oxidizers, such as hypochlorite, may react violently with organics.
- Under oxidizing conditions (particularly for household chlorine bleach or other hypochlorite-containing solutions), **HD can break down into several toxic byproducts, such as mustard and vinyl sulfones.** Decontamination formulations and conditions should be chosen as to minimize or eliminate the formation of these toxic breakdown products.
- Hydrolysis of HD produces HCl. Situation-specific tolerance to potentially altered pH and corrosiveness should be evaluated when developing a decontamination strategy.
- Dirt, grime, and other coatings (organic load) can reduce the efficacy of decontamination; pre-cleaning surfaces with soap and water may be needed before the application of decontamination formulations, but resulting pre-cleaning rinsates require containment to avoid agent spread.

For additional information, contact the EPA/HQ-EOC at 202-564-3850.

Surfaces/Hot Spots: This category is for areas smaller in size but with higher levels of agent contamination. They may require more rigorous decontamination products and methods. Excess HD liquid should be absorbed using, e.g., vermiculite or dry sand, and transferred into a sealed container and disposed of according to WASTE MANAGEMENT section below. In contrast to the rapid hydrolysis when HD is dissolved in water, the hydrolysis of HD on surfaces is generally slower since it is limited by the amount of available moisture. Application of the following oxidative decontamination solutions and formulations may be efficacious by following applicable manufacturers' directions.

- Hypochlorite-containing solutions: Hypochlorite can be corrosive to certain surfaces and materials and should be rinsed thoroughly afterwards. Household bleach solutions (≥5% sodium hypochlorite) are effective for HD with efficacy achieved with contact time of 15-60 minutes depending on surface material. Calcium hypochlorite, present in commercial products, such as HTH (10% hypochlorite solution), is better for surfaces with high concentrations of liquids in localized areas. Note that lowering the pH of hypochlorite solutions is not required and may be counterproductive. If inadequate amount of oxidant is used, toxic byproducts will likely accumulate.
- 2) Proprietary decontamination technologies such as EasyDecon DF-200®, Decon7 (D7), Dahlgren Decon®, CASCAD®, Decon Green®, or L-Gel® have been shown to be effective against HD (and may be less corrosive than hypochlorite-containing solutions) on the order of minutes to hours, but not all have been thoroughly tested. Availability, cost, and the need for specialized equipment to apply the decontaminant may limit their use early in the response.

Large Volumetric Spaces: This category is for areas larger in size but with lower levels of agent contamination. These areas may require less aggressive, but more broadly applied, decontamination products and methods.

- 1) Monitored Natural Attenuation is more passive than other decontamination options and is non-destructive to materials. This option may be preferable depending on the scope and severity of contamination.
- 2) Forced or Hot Air ventilation methods are recommended for vapor plume contamination or low surface concentration of HD in large volumetric spaces, including HVAC systems, or open areas; efficacy may be typically achieved in hours to days with less waste and adverse impacts to materials. Capture technologies, such as activated carbon-containing air filters, would be required to prevent transfer of the HD vapor to the outside environment or prevent recirculation into other surrounding spaces.
- 3) Funigations with modified vaporous hydrogen peroxide (mVHP®; a combination of ammonia and hydrogen peroxide vapor) or chlorine dioxide (ClO₂) have been reported to be effective against HD. Prolonged hydrogen peroxide funigation (up to 24 hours) at lower vapor concentrations (≤75 ppmv) was found to be non-efficacious.
- 4) Steam application has been reported to effectively degrade HD on surfaces with no HD found in the condensate. Condensate may contain HCl.
- **Sensitive Equipment or Items:** Forced or Hot Air ventilation may be used for HD and can be used either in-situ or exsitu to decontaminate these items. Capture technologies using activated carbon air filters would be required to prevent transfer of the HD vapor to the outside environment or prevent recirculation into other surrounding spaces. Fumigation

with mVHP® is another option that could be efficacious with no or minimal impact on materials. Use of steam can be considered if presence of condensate (likely containing HCl) is not detrimental to the equipment or item.

- Aqueous Solutions: HD degrades via hydrolysis but may persist in aqueous solutions, depending on initial concentration and environmental conditions, such as pH and temperature. Also contributing to persistence is that hydrolysis products of HD may accumulate at the interface between the HD liquid and the water, forming a protective coating around HD "globules" that are resistant to further hydrolysis and can persist for decades if not physically disturbed. The amount of disturbance required is unknown, so simple mixing of containerized HD solution may not suffice. Hydrolysis of HD produces HCl. If the aqueous solutions result from decontamination operations involving bleach or other high pH conditions, significant HD degradation into toxic byproducts may occur (see toxic byproducts statement under Cautions above). Avoid any additional release and/or inappropriate disposal to water systems, drains, or sewers. Contain or transfer liquid to appropriate containers and dispose of according to WASTE MANAGEMENT section below.
- **Water Systems:** Hydrolysis and removal of contaminated water will lessen HD contamination in water systems, but HD may persist in hydraulic dead ends and via sorption to system components (e.g., plastics) that act as sinks for HD. It may be necessary to isolate potentially affected portions of the system to evaluate them and implement decontamination. A contaminated water system may transfer HD to building and premise plumbing, which then may also require decontamination. As HD is denser than water, it may sink and accumulate in low lying areas, such as the bottom of pipes and tanks. Hydrolysis of HD in water produces HCl.

Verification of Decontamination: Site and situation specific. Please contact EPA/HQ-EOC at 202-564-3850 for further assistance.

15. Waste Management

Waste Management

15.1. Transportation:

Federal requirements for the commercial transport of hazardous materials and procedures for exemptions are specified in How to Comply with Federal Hazardous Materials Regulations, available at:

https://www.fmcsa.dot.gov/regulations/hazardous-materials/how-comply-federal-hazardous-materials-regulations.

Sulfur Mustard (HD) should not be offered for commercial transportation without being rendered safe by neutralization. Contact the PHMSA Hazardous Materials Information Center at 1-800-467-4922 or <u>infocntr@dot.gov</u> to discuss specific cases. Additional resources on packaging, labeling, and shipping are available at: <u>https://www.phmsa.dot.gov/standards-rulemaking/hazmat/hazardous-materials-regulations</u>. Detailed state regulations can be found at <u>www.envcap.org/</u>.

This QRG is intended to apply to Federal OSCs in the first 24-48 hours of a response. Once determined, the concentrations of HD in individual waste streams should be used to determine which transportation requirements apply. For instance, certain requirements may apply to waste streams with concentrated agent, but may not apply to waste streams such as soil containing dilute concentrations of agent.

15.2. Waste Management:

Under the Resource Conservation and Recovery Act (RCRA), waste is classified as hazardous waste (subtitle C) or solid waste (subtitle D). The RCRA regulations generally define a waste to be hazardous if it is: (1) a listed waste (40 CFR §261.31-§261.32); (2) exhibits specific characteristics (40 CFR §261.21-§261.24); or (3) is a discarded commercial chemical product, off specification species, container residue, or spill residue listed in 40 CFR §261.33. Sulfur Mustard (HD) is not listed under 40 CFR §261.31-33, but HD-contaminated waste may be considered reactive hazardous waste, D003, if, when mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment (40 CFR §261.23(a)(4)) or if it is a sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment (40 CFR §261.23(a)(5)). It is the responsibility of the waste generator to make a hazardous waste determination (40 CFR §261.23(a)(5)).

The states (except for Alaska and Iowa) have the primary responsibility to implement the hazardous waste regulations and can impose more stringent requirements or requirements broader in scope than the federal program. Several states, including CO, IN, KY, MD, OR, and UT, have their own waste designations for chemical agents, which may be applicable for the cleanup of HD-contaminated residues, decomposition products, soils, and debris. It is critical to open a dialogue with state regulators as early as possible.

Management of toxic decomposition products, associated residual decontamination solutions, local waste acceptance criteria, and transportation and handling requirements should be considered. High pH aqueous decontamination solution waste may be considered corrosive hazardous waste, chemical code D002, if it has a pH greater than or equal to 12.5 (40 CFR §261.22).

EPA/CMAD can provide Federal OSCs with information and support to address knowledge gaps for dealing with wastes contaminated with dilute concentrations of CWA; contact EPA/HQ-EOC at 202-564-3850.

EPA also recommends the creation of pre-incident waste management plans as a preparedness measure for chemical agent releases, and has created an **All-Hazards Waste Management Planning Tool** to help state, local, territorial, and tribal

waste management officials coordinate and prepare these plans. Access to the All-Hazards Waste Management Planning Tool requires pre-registration (<u>https://wasteplan.epa.gov/</u>).

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