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Composition of CBRN Decontamination Effluent and Development of Surrogate Mixtures for Testing Effluent Treatment Technologies

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and Lawrence Procell

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Composition of CBRN Decontamination Effluent and Development of Surrogate Mixtures for Testing Effluent Treatment Technologies

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Abstract

Decontamination efforts after a chemical, biological, radiological, or nuclear (CBRN) event require large quantities of water and produce correspondingly large volumes of highly hazardous waste. This water use and production can be problematic in terms of logistics, safety, and liability during and after a domestic or military event. The U.S. Army Engineer Research and Development Center (ERDC) is developing a deployable effluent treatment system that could be used to treat the waste from decontamination operations for responsible discharge or potential reuse in decontamination activities. In order to develop such a system, it is important to understand and characterize the water that will be treated. Fortunately, there has been an absence of CBRN events to collect samples for analysis; so, the best alternative is to estimate the composition and concentration of components likely to be found in decontamination after such an event. This report summarizes our effort to provide that analysis, including the contribution of the CBRN agents, decontaminating agents, and additional materials produced as a result of washing (e.g., oil, dirt, hair, etc.). An estimate of the makeup and relevant concentrations of decontamination effluent is provided to enable testing of treatment technologies, which ensures complete removal of contaminants from decontamination effluent.

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Preface

The study reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL, Vicksburg, MS), the Construction Engineering Research Laboratory (CERL, Champaign, IL), and the Edgewood Chemical & Biological Center (ECBC, Aberdeen Proving Ground, MD). The study resulted from the findings of Task 1 of the Rapid Treatment of Decontamination Effluents project, which was funded by the Direct Allotted Environmental Quality/Installations program.

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Acronyms

ADP	Army Doctrine Publication
AERTA	Army Environmental User Requirements and Technology Assessments
AR	Action Required
ARCIC	Army Capabilities Integration Center
CBR(N)(E)	Chemical, Biological, Radiological,(Nuclear), (Explosive)
CBRND	CBRN Defense
CERCLA	Comprehensive Environmental Response, Compensation, Liability Act
CDD	Capability Development Document
CM	Consequence Management
CFR	Code of Federal Regulations
CSTA	Civil Support Training Activity
CWA	Clean Water Act
DCM	Domestic Consequence Management
DECON	Decontamination
DHS	Department of Homeland Security
DOA	Department of the Army
DOD	Department of Defense
DS2	Decontamination Solution 2
DTRA	Defense Threat Reduction Agency
ECBC	Edgewood Chemical/Biological Center
EL	Environmental Laboratory
ERDC	Army Engineer Research and Development Center

CERL	Construction Engineering Research Laboratory
FM	Field Manual
FOC	Full Operational Capacity
HAZMAT	Hazardous Materials
HTB	High-test Bleach
HTH	High-test Hypochlorite
ICD	Initial Capabilities Document
JCB	Joint Capabilities Board
JRO	Joint Requirements Office
JRP	Joint Research Project
JSTDS-SS	Joint Service Transportable Decontamination System – Stainless Steel
LNO	Liaison Officer
MCD	Mass Casualty Decontamination
MIL	Military Specification
MOPP	Mission-Oriented Protective Posture
MSCoE	(Army) Maneuver Support Center of Excellence
NATO	North Atlantic Treaty Organization
NFPA	National Fire Protection Agency
NGB	National Guard Bureau
NOM	Natural Organic Matter
NPDES	National Point Discharge Elimination System
OCONUS	Outside the Continental United States
PPE	Personal protective equipment
RCRA	Resource Conservation and Recovery Act

RDD	Radiological Dispersion Device (common – dirty bomb)
STB	Supertropical Bleach
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
USACE	United States Army Corps of Engineers
USEPA, EPA	United States Environmental Protection Agency
W/W	Weight to Weight ratio
WEST	Waste Estimation Source Tool
WWI	World War I

Chemical Warfare Agents

CA	Industrial bromine
CG	Phosgene
CK	Cyanogen chloride
CL	Chlorine
CX	Phosgene oxmine
DM	Adamsite
DP	Diphosgene
GA	Tabun
GB	Sarin
GD	Soman
H	Mustard/Sulfur Mustard
HL	Mustard/Lewisite
HN	Nitrogen Mustard
L	Lewisites

Simulants

DEVX	Diethoxyphosphate-VX
DFP	Diisopropyl fluorophosphate
DPCP	Diphenyl chlorophosphate (simulant for soman)
TEP	Triethyl phosphate

Radiological elements

Am	Americium
Co	Cobalt
Cs	Cesium
I	Iodine
Ir	Iridium
Pu	Plutonium
Sr	Strontium
Th	Thorium
U	Uranium

Other Elements

Cl	Chloride
Cr	Chromium
Cu	Copper
Na	Sodium
Ni	Nickel
TN	Total nitrogen
TP	Total phosphorus
Pb	Lead

Zn Zinc

Units

g, Kg grams, kilograms

L Liters

lbs pounds

m meters

1 Purpose

Decontamination following a Chemical, Biological, Radiological, Nuclear (CBRN) event requires large amounts of water (see examples below: ARCIC Deep Futures Exercise and Liberty RadEx simulation). These events can stress supply and transport logistics, and create large amounts of highly contaminated waste effluent. This contaminated effluent poses significant hazard for troops, local populations, and the environment, creates further logistic issues for storage, transport, and eventual treatment, and is a liability until final treatment and/or disposal. Therefore, technologies are needed to treat this contaminated effluent—to decrease liability through safe disposal and potentially decrease logistics by enabling water recycling. However, evaluating technologies developed for treating this contaminated water requires at least a qualitative understanding of the likely composition of decontamination effluents, the volumes of effluent to be treated, and the concentrations of agents that must be removed. Additionally, due to the toxic nature of the CBRN agents, laboratory evaluation of treatment technologies must either take place in specialized facilities, or utilize suitable surrogate materials to safely simulate the contaminants to be removed. This report seeks to fill these knowledge gaps by providing a preliminary estimate of the range, type, and approximate concentration of materials likely to be found in decontamination effluent, while also providing several potential simulant chemicals to enable development of a surrogate CBRN effluent for safe laboratory evaluation of proposed treatment technologies.

2 Background

Decontamination is the process of removing or neutralizing CBRN materials from people, equipment, or the environment following an accidental or purposeful release. Military decontamination became a priority following introduction of large-scale chemical warfare during WWI (Hauver 2002), and the U.S. military continues to maintain extensive decontamination capabilities to remove contaminants from personnel, vehicles, and equipment. This decontamination can be accomplished through physical removal (e.g., spraying, washing, or wiping to physically dislodge contaminants), neutralization (i.e., addition of reactive chemicals or enzymes), or often a combination of physical removal and chemical and/or biological neutralization. While effective, these processes generally require large amounts of water, which can strain supply lines and logistics. Furthermore, collection and storage of the water used for decontamination—into which the CBRN contaminants are transferred during decontamination—becomes a logistical issue and must eventually be removed and/or treated to avoid reintroducing contaminants to troops, civilians, or local ecosystems and water supplies.

Drivers

Army Doctrine, Policy, and Directives

The U.S. Army has doctrine, policies, and directives that support the treatment of decontamination effluent. The Joint Initial Capabilities Document (ICD) for CBRN Contaminant Mitigation states, “The [response] capabilities should result in safe effluents and by-products from the decontamination process” (JCB 2011). In addition, both ICDs for mitigation and for CBRN consequence management specify that CBRN activities should limit migration of contaminants associated with these activities (JCB 2010, 2011). Protecting soldier health has always been a top priority for the Army as documented in FOC-09-08 (Soldier Support) and DOD Directive 4715.1E (Environmental, Safety, and the Environment). In addition, the Army is increasingly emphasizing environmental protection from military activities and contaminants, including AR 200-1 (Environmental Protection & Enhancement), 32 CFR (formerly AR 200-2, Environmental Analysis of Army Actions), and AERTA-R-07-04 (Avoidance of Environmental Risk during Contingency Operations). Decontamination effluent treatment is consistent with all of these goals, and it is an area requiring future study.

Furthermore, if treatment allows for water recycling, it would reduce logistics associated with DECON. This is consistent with the mitigation ICD, with a stated goal to “reduce decontamination logistical requirements and the need for dedicated organization and personnel” (Arcilesi and Hessian 2012, JCB 2011).

U.S. Laws and Regulations

The Army has a critical mission in decontamination operations for CBRN attacks or accidental releases in the United States. The Joint Capabilities Board (JCB) indicated in 2010 that CBRN consequence management (CM) can include all deliberate or inadvertent CBRN releases with potential to cause mass casualties, including (but not limited to) intentional or accidental releases of hazardous materials (HAZMAT), and it includes a sub-activity in Domestic Consequence Management (DCM) (JCB 2010). Similarly, Army Doctrine Publication (ADP) 3-0 indicates, “the homeland is a distinct part of the operational environment for Army forces” (DOA 2011). Operations to support CBR decontamination in the United States would fall under “defense support of civil authorities.” In these cases, federal laws would apply for the discharge of decontamination effluents into the environment, into storm-water drains, and into sanitary sewers. Key laws include:

- The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), found in 40 CFR. These regulations focus on the uncontrolled discharge of hazardous materials. Contaminants from decontamination effluents discharged on soils and sediments could be a CERCLA issue.
- The Resource Conservation and Recovery Act (RCRA). RCRA indicates that hazardous wastes must be managed in a manner to prevent contamination of soil and groundwater resources.
- The Clean Water Act (CWA). The CWA limits the discharge of chemicals and other materials into surface waters (National Point Discharge Elimination System – NPDES).

An efficient and effective decontamination effluent treatment system could assist the Army in complying with these laws within the United States.

Debris/Residuals Management

The U.S. Army Corps of Engineers (USACE) has a mission regarding handling debris and residuals from disasters involving U.S. cities. This also includes the management of hazardous materials. Although it is not explicitly delineated, organizations such as the U.S. Environmental Protection Agency (EPA) have interpreted this to include wastewater from decontamination operations.

Water Based DECON

Water is a very effective solution for decontamination, and as such, it will continue to be a part of decontamination approaches in the foreseeable future, particularly for large events. The majority of CBRN agents are at least partially soluble in water, and washing with water can be very effective at removing them. U.S. Army Field Manual FM 3-11.5 focuses largely on aqueous-based decontamination (U.S. Army 2006). In addition to water, mild detergent, bleach, or caustic materials can be added to aid removal as well as to neutralize the constituents (Liberty Chemical 2014). In a recent exercise evaluating the Army's role in mass casualty decontamination (MCD) in an attack on an American city, the primary means of decontamination was the M26 Joint Transportable Decontamination System-Small Scale (JSTDS-SS), an aqueous based shower system, and it was recommended that this system be adopted by the U.S. Army Reserves for MCD purposes (Lanphere et al. 2014). Similarly, a Department of Homeland Security (DHS) study recognizes that aqueous showering is a standard means for mass personnel decontamination; however, the report suggests that assessments be conducted to determine if milder decontamination methods might be more effective in some situations. A review of decontamination equipment indicates an emphasis on aqueous approaches (including the M26 small-scale system, the M12 large decontamination system, and the Simer small submersible pump). The capability development document (CDD), a document that focuses on decontaminant for hardened military equipment, indicates that the material be compatible with the M26 JSTDS-SS (JRO-CBRND 2013b). In a slide document titled "Decontamination – Planning Factors," water requirements for Army decontamination varied from 40 (MOPP Gear Exchange for 40 men) to 4700 gallons (Detailed Heavy Equipment Decontamination, Platoon). These factors did not consider civilian support missions.

Aqueous wastewater from decontamination has been recognized as an important issue in several Army documents. Lanphere et al. (2014) states, “Material developers should address contaminated water runoff when using various showering systems.” The National Fire Protection Association (NFPA) focuses on aqueous solutions for decontamination of chemicals (the focus is on industrial accidents) and indicates that runoff control should be exercised, if at all possible, to prevent decontamination runoff from entering sewer drains, groundwater, streams, and watershed areas (NFPA 2008). In another exercise conducted by the Army Capabilities and Integration Center (ARCIC) that included a chemical attack and associated DECON, it was determined that water availability and disposal of contaminated fluids were critical shortcomings (ARCIC 2013). The exercise indicated that the development of “portable water purification or reclamation facilities” was desirable.

Appendix K of FM3-11.5 discusses means of dealing with decontamination effluent, and it acknowledges that “wastewater poses significant challenges” (U.S. Army 2006). Appendix K of FM3-11.5 discusses two methods of dealing with decontamination effluent. The first method is to construct and use evaporation ponds and/ or lagoons to evaporate contaminated water and reduce its volume. The second method discussed is to collect solutions and containerize them with the goal of shipping them to another location where they can be treated or disposed. A treatment system would significantly reduce risks and effort compared to these activities.

ARCIC Deep Future Exercise

ARCIC’s 2013 Unified Quest Deep Futures Wargames presented a scenario in which a series of chemical attacks took place in a water-stressed environment located in a fictitious African setting that also served as a good example of a military mission application. One of the results from this exercise was identification that decontamination required larger volumes of water than could be supplied, and that the water required for decontamination would hamper other aspects of the mission (ARCIC 2014). Management of the effluent from the decontamination operations was identified as a major logistical burden as well.

Liberty RadEx

In another example, the Liberty RadEx simulation included a large, but conceivable, radiological event in which a 2300 curie (Ci) source

consisting of Cs-137 in the form of finely milled CsCl was detonated in a large truck bomb in Philadelphia (USEPA 2012). Modeling predicted a plume with high radioactivity (≥ 1000 uCi/m²) about one mile long and about 0.2 miles in its widest portion (estimated from Figure 3 of the report). A more diffuse plume of deposited radioactivity (≥ 112 uCi/m², level equivalent to the 50-year Protective Action Guide and a likely evacuation threshold) stretched for close to nine miles in length with a thickness of more than one mile. Using the Waste Estimation Source Tool (WEST), the water needed to clean up the highly concentrated zone was approximately 14 million gallons (53 million liters), while the amount of water needed to decontaminate and clean up the entire area was approximately 10.9 billion gallons (41.5 billion liters). These large volumes underscore the need to address CBRN decontamination effluent to both mitigate release and decrease logistical demands for decontamination.

3 CBRN Effluent Composition

The first step in understanding the decontamination process is to understand the contaminants involved, including not only the contaminants being removed, but also the other constituents likely carried in the effluent, such as decontamination agents, dirt, and other debris.

CBRN Constituents

Chemical Warfare Agents

Chemical warfare agents are defined based on their source or on their method of toxicity. Table 1 summarizes the primary types and examples. This is certainly not exhaustive, as many industrial materials could be improvised for use as a chemical weapon. One and two letter codes shown in parentheses are NATO codes.

Table 1. Chemical Warfare Agents (adapted from CDC 2013).

Type	Description	Chemicals
Blister Agents	Chemical that severely blisters skin, eyes, lungs, and respiratory organs on contact	Mustards Mustard gas/Sulfur Mustard (H) Mustard/Lewisite (HL) Nitrogen Mustard (HN-1, -2, -3) Sesqui Mustard (Q) Lewisites/chloroarsine agents Lewisite (L, L-1, -2, -3) Phosgene oxime (CX)
Blood Agents	Poisons that affect the body via blood absorption	Arsine Carbon monoxide Cyanide Cyanogen chloride (CK) Hydrogen cyanide (AC) Potassium cyanide Sodium cyanide Sodium monofluoroacetate
Corrosives (Caustics/Acids)	Chemical that burns or corrodes skin, eyes, or mucus membranes	Hydrofluoric acid Hydrogen chloride

Type	Description	Chemicals
Choking/Lung/Pulmonary Agents	Chemical that causes severe irritation or swelling of the respiratory tract.	Various industrial chemicals including ammonia, bromine (CA), hydrogen chloride, methyl bromide, osmium tetroxide, phosphine, phosphorus (elemental, white, or yellow), sulfuranyl fluoride Chlorine (CL) Phosgene Diphosgene (DP) Phosgene (CG)
Long acting anticoagulants	Poisons that prevent blood from clotting properly, leading to uncontrolled bleeding	Super warfarin
Metals	Metallic poisons	Arsenic, Barium, Mercury, Thallium
Nerve agents	Highly poisonous chemicals that work by attacking the nervous system	G agents Sarin (GB), Soman (GD), Tabun (GA) V Agents VX
Organic Solvents	Agents that dissolve fats and oils, damaging tissue	Benzene
Riot control agents/Tear Gas	Highly irritating agents normally used by law enforcement for riot control	Various
Toxic alcohols	Poisonous alcohols that can damage various organs	Ethylene glycol
Vomiting agents	Chemical that causes severe nausea & vomiting	Adamsite (DM)

Biological Agents

Biological agents are microorganisms or biotoxins that are capable of inflicting highly contagious and lethal disease and infection. Potential microorganisms include Botullism, Ebola, Small Pox (widely believed to have been preserved and weaponized by the former Soviet Union), and Anthrax (*Bacillus anthracis*), although there are literally hundreds of possibilities. Anthrax is believed to be the most readily available agent, as it can be stored as a highly resistant spore, which can be very effectively dispersed. Potential biotoxins include ricin, strychnine, and botulism toxins. Biological agents are commonly deactivated by bleach and other chemical processes.

Radiological Agents

Radiological agents are materials or particles that emit harmful radiation to injure or kill exposed people. The most likely means of exposure is via a radiological dispersion device (RDD), which is commonly referred to as a dirty bomb (Ford 1998). However, radiological materials could be dispersed using much cruder methods, including a sacrificial person, or placing high-energy materials in a high-traffic location. Table 2 lists radionuclides considered likely to be components of a dirty bomb. Cesium 137 is probably the greatest threat because it has many uses, and is therefore relatively easy to obtain or steal; it can be milled into a fine powder allowing for effective dispersement, and it is a high-energy gamma emitter, which can penetrate skin and most clothing. Additionally, any nuclear detonation results in the dispersement of radioactive particles into the environment. Radioactive materials cannot be rendered inert through chemical deactivation, but must be physically removed during decontamination. Furthermore, any potential effluent treatment system would involve concentrating radioactive materials (i.e., through filtration) that must be properly contained, stored, and eventually disposed of.

Table 2. Radionuclides considered possible components of a dirty bomb.

Alpha particle emitters	Beta particle emitters	Gamma ray emitters
Americium-241 (²⁴¹ Am)	Phosphorus-32 (³² P)	Cobalt-60 (⁶⁰ Co)
Plutonium-239/238 (²³⁹ Pu and ²³⁸ Pu)	Strontium-90 (⁹⁰ Sr)	Iodine-131 (¹³¹ I)
Uranium (U-235)		Cesium-137 (¹³⁷ Cs)
Thorium (Th-232)		Iridium-192 (¹⁹² Ir)

Adapted from Zimmerman and Loeb (2004)

Types of Decontamination

Decontamination processes can be divided into three broad categories: (1) Personnel Decontamination, (2) Equipment/Vehicular Decontamination, and (3) Wide Area Decontamination.

Personnel Decontamination

Personnel decontamination involves removing contamination from troops, civilians, and decontamination workers. Treatment of contaminated people is the highest priority because it involves the greatest risk to life and health.

There are two kinds of personnel decontamination. The first, MCD, involves removal of threat agents from non-protected people after exposure. It is the most critical form of decontamination for saving lives, and is of the highest priority. Because of the sensitivity of skin and eyes, this approach must focus on mild soaps and detergents with the primary goal of simply removing the contaminant; however, plain water (without decontaminant agents) is sometimes considered the best option (Lake et al. 2013). The wastewater effluent from this process would contain active agents, human skin cells and hair, and possibly surfactants or other decontamination agents. MCD is generally accomplished by setting up triage stations where individuals are moved from hot zones as they are rinsed, have contaminated clothing removed, and are further cleaned to remove as much of the CBRN agent as possible (Figure 1). Clothing and other items that have been decontaminated must also be contained and eventually disposed of.

Figure 1. Soldiers setting up water and power lines in the Interior of a personnel decontamination tent. Figure courtesy of Massachusetts National Guard.



A second form of personnel decontamination focuses on people who are properly protected using appropriate protective clothing, eye, and breathing apparatuses. In this case, the decontamination is very similar to that of a person leaving a hazardous waste site – the protective clothing is cleaned using water and brushes. After the cleaning has occurred, the person can remove the protective clothing and safely transition into the safe zone.

Vehicle Decontamination

Vehicle decontamination includes removing contamination from troop transports, armored vehicles, support vehicles, and other large equipment. Although not as high-priority as personnel decontamination, vehicular decontamination is still mission critical because soldiers can come into contact with the vehicles during combat and become exposed to the threat agent. Priority is focused on areas with frequent human contact. In addition, vehicles can be a vector for migration of the threat agents into non-contaminated areas, increasing the scope of the attack. Vehicle decontamination is usually accomplished with high-pressure spraying wands and brushes (Figure 2).

Figure 2. An Exercise in Vehicular Decontamination using the M26 mobile sprayer.



Wide Area Decontamination

Wide area decontamination involves cleaning ground surfaces, buildings, and other large structures. This is usually considered lowest priority, but could be important if it involves a valuable asset, such as an airfield. It is generally accomplished with vehicle-based spray systems, such as the one shown in Figure 3. Wide area decontamination is generally a lower priority during initial response and decontamination compared to personnel and equipment decontamination.

Figure 3. Area decontamination is usually accomplished by spraying the area with chemical decontamination agents.



Decontamination

Decontamination missions are divided into those supporting military missions (green) and those supporting civilian decontamination (white). Following an attack on a U.S. city, a terrorist event, or an accidental chemical release, the United States focuses on civilian decontamination. In white missions, it is assumed that significant exposures will occur involving the unprotected population; so, a large emphasis is placed on MCD. However, vehicle and equipment decontamination is also conducted to minimize off-site migration of the threat agents. In these missions, a key goal is to collect effluent to prevent contamination of the surrounding environment (e.g., streets, buildings, sewers, water treatment facilities, soil, plants, and animals), in an attempt to minimize off-site migration, long-term exposure issues, and environmental damage.

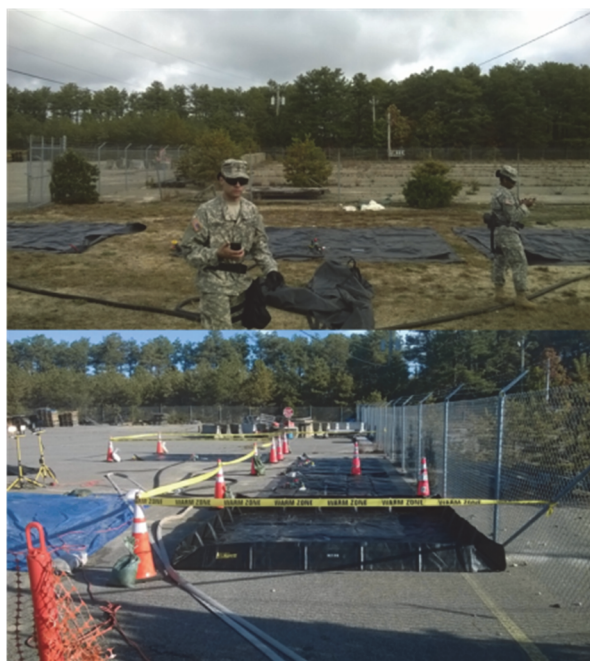
Green missions are decontamination operations in settings outside the continental United States (OCONUS), particularly involving combat operations. Although unprotected human exposure is expected, green missions generally assume that most soldiers will be able to deploy their personal protective equipment; Therefore, human decontamination is more focused on removing agents from protective clothing. In addition, there is a greater emphasis on equipment and vehicular decontamination. Management of effluent is less emphasized; although as mentioned previously, this is likely to change in the future and could be an important liability issue.

Decontamination effluent collection

White Mission Effluent Collections

Collection of waste effluent from white missions is accomplished using portable, high-density plastic berms (Figure 4). Then, the water is moved by gravity or pumped into 1500 to 3000 gallon water blivets (Figure 4). According to the Massachusetts National Guard 272nd Chemical Company CBRN response team, domestic CBRN response procedures call for three of these blivets (plus one for backup) to collect and store waste effluent during a personnel decontamination procedure. However, at peak operational capacity (225 ambulatory patients or 75 non-ambulatory patients per hour), usage rates can be 3,000 gallons per hour. This storage volume will be exceeded in 2-4 hours, resulting in direct release of waste into the environment (Medeiros 2015).

Figure 4. Massachusetts National Guard 272nd Chemical Company CBRN Response Team's effluent collection blivets. Each of the three active blivets holds up to 1500 gallons of effluent waste, with one reserve blivet on hand to extend capacity.



Green Missions

During military response, waste collection priority is secondary to the decontamination mission itself, and therefore waste effluent may not be a priority. For small-scale events (<50 effected individuals) in a mobile

environment, it may make sense to provide no collection. Similarly, when under fire, setting up collection may not be practical. The Defense Threat Reduction Agency (DTRA) to Maneuver Support Center of Excellence (MSCoE) provided the following description of a general decontamination setup in an operational environment. Typically, vehicles are decontaminated in a line. A vehicle will drive up to the first station, where it is scrubbed with soap and rinsed. Then, it will drive to a second station, where it is washed with a bleach (typically STB) solution. If possible, the site around the wash stations is graded to allow the wash water to run off to a pit, where it can seep into the earth or be collected.

Table 3 summarizes key water usage rates for various DECON operations expected in green missions.

Table 3. Planning Factors of Operational DECON (Army G3/5/7 Decontamination Planning Factors).

Mission	Coverage	Water required (gal)	STB* required (lbs)	Time (min)
Detailed troop DECON	40 man unit	318	600	40
Supported Operational DECON	Wheeled Platoon (10 vehicles)	1500	0	30
Detailed Equipment DECON (Heavy decontamination)	Wheeled Platoon (10 vehicles)	4700	600	75
Terrain Decontamination	500 m x 30 m area	1500	300	40

*STB is Supertropical bleach

Troop DECON assumes troops were adequately protected (as opposed to mass casualty)

Decontamination agents

Water by itself can decontaminate equipment, vehicles and people through dissolution, physical removal, and hydrolysis. However, additives have been used to assist in decontamination, including bleach, surfactants, oxidation chemicals, and enzymes. For the purpose of this study, we focus on the two most common classes of decontamination agents, bleach and surfactants.

Bleach

Bleach is an umbrella term for an oxidative process involving hypochlorite – a powerful oxidant. For early disinfection, shovels were used to spread bleach powder (calcium hypochlorite) over infected areas (Hauver 2002). Common, domestic bleach, used for normal household disinfection, is generally a sodium hypochlorite solution, while chlorine dioxide gas, used for industrial disinfection, was used October 2001 to disinfect U.S.

government buildings after anthrax was distributed through a letter. (Fitch et al. 2003). Because many of the chlorine-based decontamination agents did not store well in tropical climates, the Army helped develop a form of bleach that would withstand warm, humid climates called super tropical bleach (STB). STB is a mixture of calcium chloride, calcium hydroxide, and calcium hypochlorite with about 35 percent available chlorine. Another Army-adopted bleach agent, high-test hypochlorite (HTH), is a concentrated calcium hypochlorite solution with 70 percent available chlorine, but it is generally too corrosive for use as a decontamination agent. Although many bleaching agents can be used, including the ones listed here, STB is the most common bleaching decontaminant utilized based on information provided by the MSCoE, the Army North Civil Support Training Activity (CSTA), the Massachusetts National Guard, and the National Guard Bureau (NGB).

Surfactants

A surfactant (surface active agent) is a material that decreases the surface tension between two materials enabling increased mixing. Usually surfactants are molecules in which one side is hydrophobic and the other is hydrophilic, allowing the surfactant to bridge the gap between hydrophobic (contaminants) and hydrophilic (water) materials and enabling increased physical removal. Concentrated surfactants can also cause cells to lyse (i.e., burst open and die), thus acting as a disinfectant. Types of surfactants used in decontamination include:

- Triton-X 100, 0.1-1% v/v
- Tergitol 15-S-9, 1% (Dow Chemical)
- Synthetic nonionic detergent 0.1 - 1 oz/gal.; Military Specification MIL-D-16791
- Triethanolamine, 3-5% (commonly found in laundry detergent)
- Sodium lauryl sulfate, 1-30% (commonly found in dish detergent)

Dawn dish detergent is commonly used for both human and vehicle decontamination (Medeiros 2015). Dish detergent has many advantages. It is a very effective degreasing agent, inexpensive, readily available, mild to human and animal cells, and safe for skin contact (Mootz et al. 2013). However, its disadvantage is that it can create significant foaming.

Common Formulations

Table 4 summarizes decontamination formulations, as communicated by the 272nd Massachusetts National Guard (Medeiros 2015).

Table 4. Ranked Decontamination Formulations based on Threat Agent.

Threat Agent	Decontamination formulations
G series nerve agents	<ol style="list-style-type: none"> 1. Caustic soda solution (Sodium Hydroxide) 2. Washing soda solution (sodium carbonate) 3. STB slurry 4. Hot soapy water
Blister/mustard agents	<ol style="list-style-type: none"> 1. HTH-HTB calcium hypochlorite 2. DS2 3. STB Slurry 4. Household bleach solution
VX nerve agent	<ol style="list-style-type: none"> 1. HTB-HTH 2. DS2 3. STB 4. Household Bleach
Choking agents (phosgene, chlorine)	<ol style="list-style-type: none"> 1. DS2 2. Caustic soda solution
Radioisotopes/Nuclear Residuals	Soap with warm water

DS2 = Decontamination Solution 2

STB = Super Tropical bleach

HTH = High-Test Hypochlorite

HTB = High Test Bleach

While the goal of each of these decontamination categories is the same—removal of the contaminating materials—each has unique requirements and limitations. MCD requires the use of gentle chemicals in small doses to avoid damaging the skin and eyes of the subject, with the goal of removing the contaminants. Since the goal is removal and not degradation of agents, live agent is expected to be found when treating contaminated people; however, uncontaminated people are also expected to be treated. The effluent would also have soap and human materials (e.g., skin, hair, blood, materials from wounds, and even pieces of clothing).

Decontamination of protected personnel would similarly use surfactants, but could also include a bleach component, which would reduce the expected amounts of live agent.

Decontamination of vehicles would likely use a combination of soap and strong bleach. For the soap treatment, it would be expected that the

contaminant concentration could be quite high, and there could be dirt and debris in the effluent. For bleach treatments, the bleach would be expected to reduce the contaminant concentration; however, the bleach could also be a material that would have to be treated or removed prior to further effluent treatment due to the caustic effects of bleach on many types of membranes. Furthermore, bleach can cause corrosion of metal components and could cause paint to fade or strip from surfaces, all of which would be captured in the effluent.

Decontamination additives are valuable in increasing removal of CBRN agents and may deactivate their toxic effects; however, they can also be harmful to human health (Altmann and Richardt 2008). Bleach and caustic solutions can have a corrosive effect on skin, eyes, lungs, and even surfactants; particularly strong ones can be harsh and cause reactions to skin.

Residue

This category consists of all the other materials that could be in the water from washing off humans, vehicles, equipment, buildings, etc., and would include all water constituents not associated with the CBRN release or the products added during decontamination. This could also include contaminants present in the initial water used for decontamination: natural organic matter, residual chlorine from drinking water sources, salts with scaling potential, etc.

Brown (2002) detailed the contents of effluent water from more than thirty commercial car washes in several U.S. cities (e.g., Phoenix, Orlando, and Boston). This information can be used to predict concentrations of residue contaminants in an urban environment (white mission) (Table 5). Green mission concentrations could be similar if in an urban environment or largely on roads, but off road missions could have concentrations on the order of 10 to 100 times higher.

Table 5. Concentrations and ranges of various contaminant classes in car wash effluents from a study of thirty commercial car washes in three U.S. cities (Brown 2002).

Contaminant	Concentration in mg/L	
	Average	Range
Oil & grease	22.8	6.7-60
Total nitrogen (TN)	4.17	0.2-5.6
Total phosphorus (TP)	4.61	0.3-12.1
Chromium (Cr)	0.045	0.006-0.072
Copper (Cu)	0.163	0.095-0.235
Lead (Pb)	0.051	0.016-0.070
Nickel (Ni)	0.028	0.020-0.037
Zinc (Zn)	0.49	0.22-0.98
Sodium (Na)	218.6	43-602
Chloride (Cl)	245.5	34-851
Total Suspended Solids (TSS)	42.14	6-117

4 Concentration Estimation

Testing effluent treatment technologies requires some knowledge of the concentration of the various constituents identified in Table 5. Determining concentrations of CBRN contaminants experimentally is difficult due to the rare occurrence of CBRN incidents. Therefore, it is necessary to estimate concentrations based on possible exposure and decontamination procedures in order to establish a range of contaminant concentrations to test. Table 6 presents this estimation process for two types of vehicles and provides a guide for estimating contaminant concentrations for any decontamination effort. The total surface area can be determined from the vehicle's specifications, and the water required to wash the vehicle can be estimated based on the surface area, or determined from other sources. To estimate the amount of contaminant on a given surface, initial focus is directed toward the surface loading used during testing of aircraft decontamination for the U.S. Air Force (Heater et al. 2011), which ranges from 1-10 g/m². The Edgewood Chemical Biological Center (ECBC) used this loading concentration during testing of a new decontamination agent (Decon Green), identifying 10 g/m² as a representative CWA nominal loading (Wagner et al. 2010). For a sense of scale, this loading (10 g/m²) corresponds to 50 kg of material spread out over an area the size of an American football field (about 5200 m²). Lastly, most chemical or biological contaminants will degrade somewhat during the decontamination process due to hydrolysis, oxidation, cell lysing, etc. Depending on the susceptibility of the contaminant, the concentration in the effluent could be reduced significantly, compared to the total amount removed during decontamination. As a conservative estimate, these processes will be ignored at present, but could be calculated based on the properties of a specific agent for a specific test.

The same principles can be applied to personnel decontamination. For example, the average surface area for a human is 1.5-2.0 m², and the required wash volume ranges from 35 L per person for an ambulatory patient to 100 L for a non-ambulatory patient; an ambulatory person is easier to wash and therefore uses less water (Mediero 2015). Table 7 shows the results of this calculation.

Table 6. Parameters used to estimate the potential overall concentration of CBRN contaminants in vehicle decontamination effluent.

Vehicle Type	Dimensions (m) ¹		Approximate Surface Area (m ²)	Water Volume Required to Clean (L) ²	Max Concentration in Effluent (g/L) ³
Transport (Jeep)	Length	1.798	28.698	227	1.264
	Width	1.615			
	Height	3.353			
Armored vehicle (Tank)	Length	9.43	153.874	673	2.286
	Width	3.63			
	Height	3.27			

¹Dimensions taken from (Carpenter and Reidy 1987) and http://www.militaryfactory.com/armor/detail.asp?armor_id=28

²Volumes from Fileccia et al. 1981

³Contaminant loading 10 g/L from (Heater et al. 2011, Wagner et al. 2010)

Table 7. Parameters used to estimate the potential overall concentration of CBRN contaminants in personnel decontamination effluent.

Patient type	Gender	Approximate Surface Area (m ²)	Water Volume Required to Clean (L)	Max Concentration in Effluent (g/L)
Ambulatory	Male	1.9	35	0.543
	Female	1.6		0.457
Non-Ambulatory	Male	1.9	100	0.190
	Female	1.6		0.160

The worse case is to assume that the concentrations of decontamination agents is identical to their concentrations in the decontamination solutions. According to the Massachusetts National Guard (Medeiros 2015), the concentrations are as follows:

- STB: 40% STB (W/W) for chemical decontamination, 7% STB (W/W) for biological decontamination
- DS2: 20% DS2 (W/W as reported by Medeiros, but reportedly used neat by ECBC. It also appears to be retired)
- Sodium Hypochlorite (household bleach): 50% (V/V) for chemical, 20% (V/V) for biological
- HTH: 5 lbs mixed into 6 gallons water (~100 g/L or 10%)
- Sodium hydroxide (lye): 10 lbs mixed into 12 gallons water (~100 g/L)
- Surfactant: 20% (V/V), but could be significantly less based on communication with ECBC.

5 Simulating Decontamination Effluent

The hazardous nature of CBRN contaminants can make evaluation of treatment technologies difficult, since some compounds require special permits, personal protective equipment (PPE), other equipment, and infrastructure to safely handle them. Therefore, it is advantageous to identify compounds that can be used to simulate CBRN contaminants for initial evaluation of new treatment methods. Likewise, judicious choice of simulant material can significantly decrease the cost of evaluation tests. Preliminary evaluation tests can be conducted with commonly accepted filtration probe compounds, including dyes (e.g., methylene blue or methyl orange) and metal salts (e.g., magnesium chloride). These provide a rough approximation of molecular size and weight. As evaluation tests progress, it is important to use simulants that have similar physical, chemical, and solution characteristics to the target compounds to ensure that results can reasonably be correlated to CBRN compounds. Once preliminary evaluations using simulants is completed, the technology must be verified with the CBRN contaminants. Focus in this section will be devoted to simulants of chemical agents.

Requirements for simulants

As stated above, to be an effective simulant, a material must meet several requirements, including:

- The simulant must be safer than actual agents. Preferably, the simulant should be safe enough to be able to evaluate in a laboratory setting with only moderate safety precautions (e.g., PPE, fume hood, etc.).
- The simulant should have characteristics similar to the contaminant it is simulating, e.g., similar chemical structure, size, hydrodynamic radius, and hydrophobicity. If the removal strategy relies on size exclusion, for example, then the size and solution behavior must be carefully matched. For chemical removal, the simulant must have similar reaction kinetics to the contaminant. If the removal mechanism is by sorption, the hydrophobicity and sorption kinetics must match, etc.
- Choice of simulant must also be guided by cost and availability, so that acquiring the simulant material is feasible within project budget and time constraints.

Chemical Warfare Agent Simulants (VX and Soman)

As a demonstration of the process of selecting a suitable simulant, Tables 8 and 9 show several possible options to simulate the chemical agents VX and soman, respectively. The tables show the materials along with their chemical structure and pros and cons for their use as simulants. Based on these pros and cons, Malathion appears to be a suitable choice for VX, and Diphenyl chlorophosphate (DPCP) serves as a suitable simulant for soman; however, individual test circumstances may lead researchers to choose alternative simulant compounds. For example, in some cases, choices may be dictated by chemical price and availability, while in other cases, it may be more important to choose a simulant based on physical or chemical similarity. Computational methods can be employed in some instances to help with these decisions (see Lavoie et al. 2011).

Triethyl phosphate (TEP) is another chemical commonly used as a chemical warfare agent simulant. It is a readily available chemical that is used in a variety of industrial processes, including as a plasticizer, a resin modifier, and as a solvent. TEP is relatively safe to use in a laboratory setting, but it is an intermediate in the production of many organophosphate pesticides and warfare agents. TEP has a molecular weight of 182 g/mol and a density of 1.072 g/mL. It is miscible in water, and Gas Chromatography can easily analyze it with either a Flame Ionization Detector or Mass Spectroscopy. In addition, it is a potential surrogate for either VX, Soman, or both.

For screening experiments, dyes can be attractive since the treatment effectiveness can be clearly seen, and accurate analysis can be easily done using a spectrophotometer (Figure 5). The comparison of two dyes (methylene blue and methylene orange) with properties of VX and Soman is presented in Table 10 and indicates that the dyes may be reasonable simulants for these compounds.

Table 8. Several possible simulant materials to represent the chemical agent VX. This table shows the chemical structure of the potential simulant and lists pros and cons for use as a simulant.

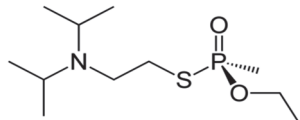
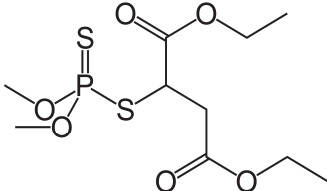
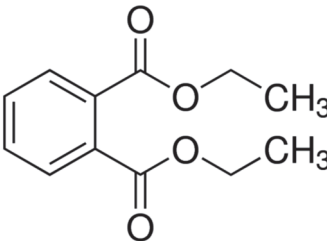
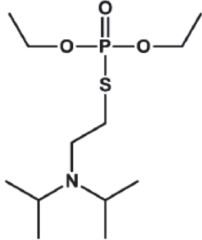
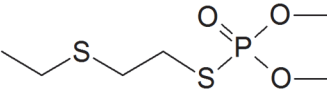
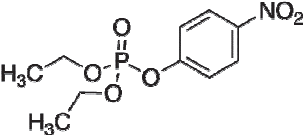
Agent	Simulant	Pros	Cons
VX -O-ethyl-S-[2-diisopropylamino)ethyl] methylphosphonothioate 	Malathion 	*Commercially available *Not as toxic as other organophosphates, still used as a pesticide and control of mosquitoes	*Somewhat expensive \$36.70 for 100 mg
	Diethyl phthalate (DEP) 	* Commercially available *Very inexpensive \$60.00 for 1 kg *Believed to have low toxic potential	*Dissimilar chemical structure
	Diethoxyphosphate-VX (DEVX) 	*Very similar chemical structure	*Not commercially available; must be synthesized *Highly toxic
	Demeton-S 	*Similar chemical structure to VX, particularly at the phosphorus *Commercially available	*Expensive, >\$100 for 100 mg
	Paraoxon 	*Commercially available	* Expensive, >\$70 for 100 mg

Table 9. Several possible simulant materials to represent the chemical agent soman. This table shows the chemical structure of the potential simulant and lists pros and cons for use as a simulant.

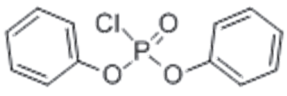
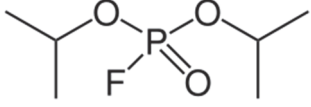
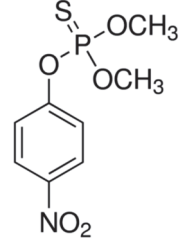
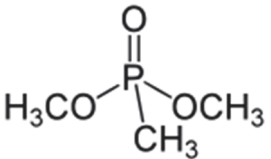
Agent	Simulant	Pros	Cons
Soman -GD -Dimethyl-2-butyl methylphosphonofluoridate -pinacolyl methylphosphonofluoridate	Diphenyl chlorophosphate (DPCP) 	*Commercially available *Inexpensive: \$72.80 for 100g	*Larger mass
	Diisopropyl fluorophosphate (DFP) 	* Commercially available *Stable for 2 years *Similar phosphate structure	*Expensive \$348.50 for 1g
	Methyl Parathion 	* Commercially available	*Extremely toxic upon acute inhalation, oral, and dermal exposure *Somewhat expensive \$50.70 for 100mg
	Dimethyl methylphosphonate (DMMP) 	*Commercially available *Inexpensive \$60.40 for 500g *Can also be used to simulate VX	

Figure 5. Use of Methylene Blue to assess effectiveness of Graphene Oxide Membranes (Study conducted by Petery and Griggs 2015).



Table 10. Comparison of Properties of Two Dyes (methylene blue and methylene orange) with VX and Soman.

Property	Methyl Blue	Methyl Orange	VX	Soman
Number of Carbons	16	14	11	7
Molar Mass, g/mol	319.85	327.33	267.37	182.18
Density, g/mL	1.77	1.28	1.008	1.022

Formulations

Determining the formulation for testing depends on the level of testing required and the type of decontamination effluent being evaluated. Initial testing formulations can consist of ultra-pure water spiked with easily traceable probe compounds (e.g., methylene blue). As testing becomes more sophisticated, the effluent formulations should include more relevant simulants and background water matrix components (e.g., natural organic matter (NOM) and total dissolved solids (TDS)). Final testing will involve a completed formulation containing the appropriate simulant agent, decontamination agents, gray-water constituents, and background water matrix components.

To limit the cost and hazard of testing with actual CBRN agents, identification of a limited number of tests is recommended to compare removal efficiency of the chosen simulants to the corresponding CBRN agent, using an identical treatment apparatus and water quality characteristics. Once the correlation of treatment efficiency between the real and simulated agents is established, more complex testing matrices can be conducted using simulants, with results extrapolated back to CBRN agents.

The range of concentrations of various effluent components can be chosen based on the discussions provided above, with modifications made as necessary for a particular treatment scenario. For example, a formulation for testing treatment of effluent from decontamination of armored vehicles after exposure to VX might include the following:

- Simulant for VX: 200 mg/L
 - This represents 1 g/m² VX contamination (Table 4); assuming 10% agent loss due to hydrolysis

- Some simulants may be limited by solubility. Malathion, for example, has a solubility of approximately 100 mg/L.
- STB: 40% or HTH: 10% W/W
 - Representative STB/HTH concentration used for chemical decontamination of vehicles
- Used motor oil: 25 mg/L
 - Used motor oil can simulate oil, grease, and trace metals (Table 5). Alternatively, each component can be added separately using previously characterized, research-grade sources.
- TSS: 40 to 120 mg/L for White Mission
 - Representative loading after vehicle decontamination (Table 5), obtained via addition of clay and/or sand. Exact concentration can be determined based on operational parameters.
 - 10 to 100 times higher for off road Green mission
- TDS from vehicle washing: 200 to 1000 mg/L for White mission
 - Representative loading after vehicle decontamination (Table 5). Exact concentration can be determined based on operational parameters.
 - 10 to 100 times higher for off road Green mission
 - Additional TDS will be contributed by bleach and surfactant additives. For example, a 10% HTH solution will add approximately 2500 mg/L of TDS.

Another alternative to this recipe-style effluent creation is to collect effluent from gray-water sources, such as commercial car washes or military gray-water discharge, to form the background matrix to which simulants and decontamination agents can be added. In this case, characterization of the initially collected effluent is important to help understand removal data.

6 Conclusions

Waste effluent from decontamination poses a significant logistical burden and liability due to potential recontamination from stored hazardous wastes and/or release into the environment. Technologies with the capacity to treat waste effluent will not only alleviate some of these issues, but will also help decrease water requirements for decontamination by enabling limited reuse of the treated water. It was necessary to develop simulated effluent water with similar water quality characteristics to evaluate approaches for CBRN effluent treatment. A preliminary characterization of treatment water has been investigated by providing an overview of the types of materials likely to be found in decontamination effluent, an estimation of the concentrations of these compounds in the effluent, and an example of simulant compounds for safe and inexpensive evaluation tests.

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
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