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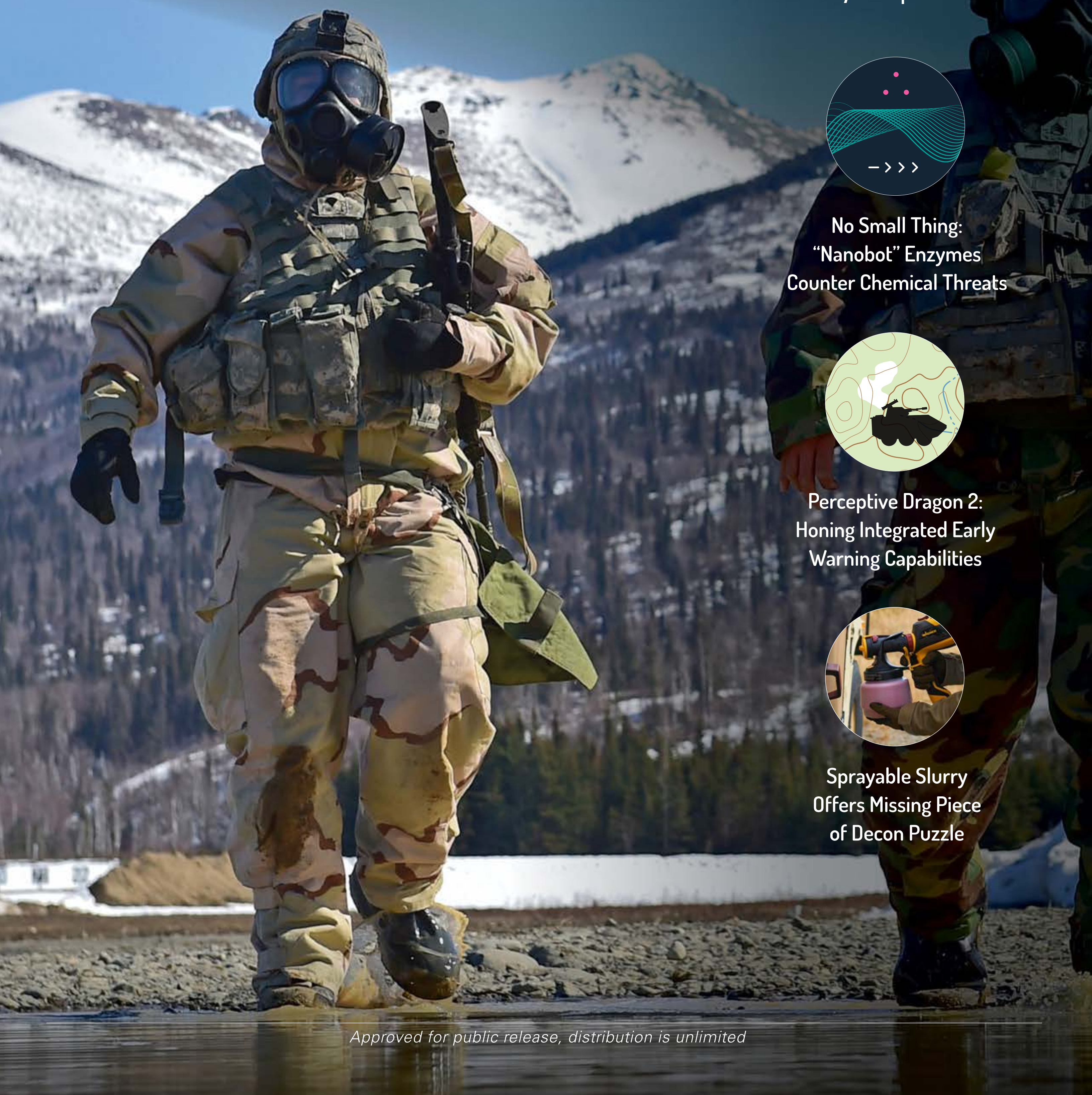

No Small Thing: "Nanobot" Enzymes Counter Chemical Threats

Perceptive Dragon 2: Honing Integrated Early Warning Capabilities

Sprayable Slurry Offers Missing Piece of Decon Puzzle

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U.S. Air Force photo by Ilka Cole

Lead DoD science and technology to anticipate, defend and safeguard against chemical and biological threats for the warfighter and the nation.

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Front cover:
A U.S. Army staff sgt. and specialist assigned to the 95th Chemical Company, "Arctic Dragons", 17th Combat Sustainment Support Battalion, U.S. Army Alaska, walk off the firing line after a Joint Service Lightweight Integrated Suit Technology stress fire. The JSLIST is the product of a four-service effort to field a common chemical protective clothing ensemble including a lightweight protective garment, multi-purpose overboots and gloves. (U.S. Air Force photo by Justin Connaher)

Back cover:
A Marine with 5th Marine Regiment, 1st Marine Division, checks the perimeter of the combat operations center during a chemical, biological, radiological, nuclear drill. (U.S. Marine Corps photo by Cpl. Will Perkins)

NO SMALL THING:

"Nanobot" Enzymes Counter Chemical Threats

Nanobots have long been dreamed of by scientists and science fiction writers alike – microscopic machines that enter the bloodstream or operate undetected. What if nature could be harnessed to provide similar capabilities? What if warfighters had the capability to both counteract and treat chemical weapon agents in real-time? The Defense Threat Reduction Agency's Chemical and Biological Technologies Department, along with Ayusman Sen, Ph.D., of Penn State University, are using enzymes that catalytically harness the chemical energy in their environment to move autonomously and do the "bot" work to neutralize the organophosphate nerve agents. While these enzymes are not nanobots by the technical definition, they function similarly.

Enzymes are naturally occurring protein catalysts of chemical reactions. Almost all metabolic processes in a cell need enzymes in order to occur at rates fast enough to sustain life. Hundreds of enzymes constantly move freely throughout our bodies and can enable the reactions of hundreds of thousands of molecules per second. Previously unknown, enzymes generate mechanical force when they facilitate a reaction.

Proteins have traditionally been regarded as drifters, catching a ride in the cell cytoplasm by passive diffusion and encountering reactants and other enzymes by chance. However, Sen and his team have demonstrated that proteins can swim along a path toward higher levels of reactant. More importantly, when enzymes catalyze a reaction, they inexplicably move, possibly due to a change in the shape of the enzyme upon catalysis. These newly discovered features make enzymes an attractive material for developing nanobots.

Additionally, according to Sen, if you attach the enzyme to a support, this force gets transmitted to the fluid, and then combined, the two will act as nanofluidic pumps. In essence, the chemical that it is pumping through the enzymes becomes the fuel, which in turn pumps in the antidote. These non-mechanical pumps provide a precise control overflow rate without the aid of an external power source and are capable of turning on in response to specific analytes in solution.

In this way, Sen's team , backed by DTRA CB funding, made enzyme-powered nanobot pumps that destroy organophosphate nerve agents while simultaneously administering an antidote to the body. Exposure to these chemicals during military combat or terrorist attacks can cause permanent neurological damage and, in some cases, death.

According to Sen, there are enzymes that decompose nerve agents, which fuels the pumping actions. By attaching the enzyme to a reservoir, like a gel that is filled with nerve agent antidote, when it comes in contact with a nerve agent, it pumps out the agent and pumps in the antidote. It's a one-two punch — it pumps out the agent and pumps in the antidote. In this case, the antidote is an enzyme called organophosphorus acid anhydrolase.

However, the enzyme-reservoir combination has to be in or on a body before exposure to a nerve agent, like a prophylaxis or a sunscreen. According to Sen, nanobot pumps could someday be incorporated into protective clothing for the military or first responders. He is also exploring applications for nanobots based on other enzymes, for example, an insulin-pumping device to treat diabetes and an enzyme-powered drug-delivery system.

In the event of an attack, the ability to both counteract and treat organophosphate nerve agents could save warfighters' lives while restoring readiness and enabling mission success.

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Perceptive Dragon 2: Honing Integrated Early Warning Capabilities

Time and space to maneuver saves lives on the modern battlefield. More information, with more time to decide, allows commanders to make quick decisions that protect warfighters and allow them to accomplish their mission. The Defense Threat Reduction Agency's Chemical and Biological Technologies Department recently held an Advanced Technology Demonstration (ATD) to test technologies that could arm warfighters with the time and information required to safely and effectively accomplish their mission, despite their operating environment.

The Integrated Early Warning (IEW) ATD addressed chem/bio challenges through a series of demonstrations and test events called Perceptive Dragon. The goal of the latest event, Perceptive Dragon 2 (PD2), was executing an "on-the-move," multi-service field demonstration of the IEW 'system of systems' prototype solution.

The demonstrations assessed the utility and feasibility of current and future chemical, biological, radiological and nuclear (CBRN) tactical voice and data communications to enable common battlefield awareness and understanding.

Better situational awareness of the CBRN threat environment helps commanders make and execute well-informed decisions on the battlefield. Building on the success of the previous Perceptive Dragon demonstration, PD2 was the culminating integration event, and was primarily technology focused for tactical combat environments. The IEW ATD is part of a larger chem/bio defense program campaign to develop advanced capabilities.

The PD2 demonstration involved two CBRN training scenarios based on a recent Marine Expeditionary Force exercise and used with Army and Marine forces operating together.

In the first scenario, warfighters moved to contact and defeat an enemy, but a chemical threat is detected, precipitating the decision to shift the main maneuver effort to a supporting effort. The second focused on an air assault to defeat enemy forces at an objective with a shift to an alternate landing zone, along with use of personnel protective equipment, following detection of radiological or chemical threats.

A simulated maneuver environment with CBRN threats was created to complete the demonstration. Real-world mobile and communication network assets were employed in the simulated scenarios to provide a realistic operational context for data/information flow into the Marine and Army situational awareness architectures. In addition, both actual

PD2 Key accomplishments included:

- Integration of multiple fixed and mobile sensors (real and emulated) using Integrated Sensor Architecture.
- Rapid sharing of tactical situational awareness within the Marine Corps C2 system with information sharing between Marine and Army C2 systems within operationally-realistic bandwidth constraints.
- Advanced tasking between LIDAR/RADAR and autonomous unmanned sensor platforms for integrated chemical cloud characterization.
- Integration of emulated warfighter physiological monitoring data into the C2 architectures.

Marines monitoring mission progress inside the representative Combat Operations Center (COC). (Jason Hudson, Global Systems Engineering)

IEW capability tools demonstrated:

- Enabled forces to obtain better definition of the location and rough extent of possible contamination with presumptive identification.
- These technologies positively impacted their ability to recommend force protection and maneuver decisions (e.g. MOPP or avoid) to the commander.
- It provided time savings from data collection to decision point compared to current processes and capabilities.
- It increased situational awareness, confidence in assessing risks, data gathering speed and decision-making ability.

Deep Purple Unmanned Aerial System (UAS) being prepared for a mission. (Jason Hudson, Global Systems Engineering)

and simulated stand-off CBRN detection systems were employed as a trigger to initiate CBRN operations.

The PD2 demonstration gathered important operator and subject matter expert feedback on the operational utility of the proposed technological solutions.

Warfighter participation was critical to the success of PD2. With minimal training time, the operators quickly incorporated the myriad of decision-based toolsets and CBRN sensing technologies into their mission planning and execution. During mission debriefs, Marine and Army participants provided invaluable feedback to the demonstration team.

In addition to CBRN scenario runs, a physiological status monitoring workshop was conducted at the end of the final demonstration day. This workshop included a demonstration and discussion with the Marine and Army participants in order to gauge their impression of wearable technologies, understand what form factors would be acceptable in a deployed environment and outline where the data should flow at the tactical level.

A display application, termed "Leaderboard" developed by the U.S. Army Natick Soldier Research, Development and Engineering Center, was used to categorize and display heat stress information for each warfighter. Such information is intended to give commanders better real-time indication of force conditions and improved overall situational awareness. This demonstration provided context for a follow-on discussion as to how wearable technologies might be used for personal, host-based chem/bio monitoring in the future. The feedback from the discussion was favorable with operators agreeing on the potential value of wearing technologies during real-world operations and training.

Areas for advancement include decision management algorithms needed for both mission planning and execution, friendly force locations should be incorporated to identify units at risk of contamination, and improvements in hazard area mapping with more robust use plans and procedures are needed in conjunction with additional operational testing.

PD2 successfully showcased a variety of new sensor data collection, processing, analysis and movement concepts in the context of a realistic combat scenario. Timely sensor data and CBRN event summaries were successfully and efficiently moved among Marine and Army Command and Control systems for commander situational awareness.

Plans are already underway for Perceptive Dragon 3, which is expected to take place in the summer of 2019 with a focus on driving CBRN-related decisions in the tactical planning process, cooperative unmanned systems and dismounted reconnaissance.

The end result of the Perceptive Dragon series of demonstrations is to give field commanders better information faster, allowing them to make sound decisions on protecting the warfighter and achieving mission success.

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Sprayable Slurry Offers the Missing Piece of Decon Puzzle

Quickly and safely decontaminating mission-critical equipment from Chemical Warfare Agents (CWAs) is a complicated puzzle. Warfighters must piece together chemistry, equipment, resources and logistics — and it must be immediate — in order to ensure combat effectiveness. One way that the Defense Threat Reduction Agency's Chemical and Biological Technologies Department is helping warfighters in this threat environment is by developing a sprayable slurry that can quickly and safely decontaminate CWAs.

Immediate decontamination is not the simple process of washing away the chemical agent. Current efforts require the application of the decontaminant for lengthy contact times of 30 minutes to several hours, and large amounts of water for rinsing to avoid material corrosion. This can be a logistical burden to deployed warfighters due to the copious amounts of water required.

It's also a chemistry puzzle. CWAs can be absorbed by equipment surfaces, so a decontaminant must first chemically coax absorbed agents in a process called partitioning. Then, the agents must be detoxified, either by binding (a process called adsorption) or by chemically destroying them. The ideal decontaminant should rapidly partition, adsorb and destroy vapor and contact hazards from multiple CWAs while being logistically feasible (i.e., no rinsing), easily deployed and effective on multiple materials and surfaces. Previously, nothing like this has ever been developed to support the warfighter.

This was the challenge undertaken by a team from the Decontamination Sciences Branch at the U.S. Army Research, Development and Engineering Command Chemical and Biological Center (RDECOM – C&B Center). Funded by DTRA CB, they combined fundamental chemical principles with previous decontamination studies to successfully develop a new and effective decontaminant: the Sprayable Slurry for detoxification of CWAs.

To do this, the team first identified a solvent, sulfolane, that effectively partitioned absorbed agents from surfaces. Partitioning is important because it dissolves the agents in a solvent that supports detoxification by chemical reaction. Sulfolane also mixes efficiently with water, which supports destruction of CWAs by chemical hydrolysis.

Then the team mixed in a second ingredient, zirconium hydroxide ($Zn(OH)4$), that adsorbs CWAs and chemically destroys them. Zirconium hydroxide was first studied as a promising new filter material precisely because it has excellent adsorption properties and wide-ranging reactivity toward numerous types of CWAs and toxic industrial chemicals.

Lastly, the team added a third ingredient, dibromo-dimethyl hydantoin (DBDMH), used industrially for drinking water purification and treatment and paper bleaching. DBDMH oxidizes and destroys CWAs, similar to the action of bleach, but without corroding critical equipment. Once the components were selected, the research team tested multiple ingredient ratios to establish important formulation variables to optimize decontamination.

Testing at RDECOM C&B Center's Toxic Chamber Facility confirmed that the Sprayable Slurry can reduce the amount of CWAs on military relevant materials and complex surfaces by up to 1,000-fold. The decontamination process consists of applying the Sprayable Slurry onto surfaces less than 15 minutes after a contamination incident. Partitioning, adsorption and chemical reaction begin immediately and continue with as much time as the mission allows to react with and detoxify the CWA. The research team also showed an immediate reduction in vapor hazards after spraying, which minimizes operational risk and allows warfighters to continue their mission.

The Sprayable Slurry can be produced in a variety of military-relevant colors.

Using Sprayable Slurry, warfighters recently demonstrated CWA vehicle decontamination (using a HUMVEE with simulated contamination) during hands-on, operationally-relevant training scenarios at Joint Base Lewis-McChord. (Photo from CBOA 2018)

Sprayable Slurry has a paint-like consistency and military-relevant pigments. Thickening agents have also been added to improve the slurry appearance and adherence of the decontaminant to multiple surfaces. Once prepared, it has a storage life of almost one month, which allows premixing for near future chemical or biological incidents.

The research team at RDECOM C&B Center's Toxic Chamber Facility completed live-agent laboratory efficacy testing on complex surfaces mock-ups containing grooves, screw threads and curved surfaces and areas such as a HUMVEE door. Warfighters also demonstrated the application for vehicle decontamination during hands-on, operationally-relevant training scenarios.

They demonstrated that application of the non-aqueous slurry can be done in a single step. Unlike current decontaminants, the slurry requires no application brush, no scrubbing or agitation, no rinsing, and does not significantly degrade test materials. Thus, it is logistically feasible and supports both immediate and operational decontamination by individuals, crews and unit teams.

Although CWA decontamination is the primary focus of the current testing, future tests at the Naval Surface Warfare Center Dahlgren Division will establish the effectiveness of Sprayable Slurry against biological agents, such as Bacillus anthracis spores. Additional programs, managed by Glenn Lawson, Ph.D., of DTRA CB, are in progress to identify and optimize the applicator used to apply the slurry.

As a result of this innovative chemistry, the Department of Defense is one step closer to providing the warfighter with a means to rapidly and effectively defend themselves against CWAs. Its use will greatly reduce the time and resources needed to restore combat power after a chemical or biological attack.

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Within the Defense Threat Reduction Agency's Research and Development Directorate resides the Chemical and Biological Technologies Department. This publication highlights the department's advancements in protecting warfighters and citizens through the innovative application of science and technology research.

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