Livermore scientists are helping federal, state, and local agencies prepare for the so-called poor-man’s atomic bomb.
Because of their availability and relative ease of dispersal, toxic and often lethal chemicals are potentially attractive weapons for terrorists. A chemical agent attack could result in high casualties, especially if the release occurs in an office building, indoor stadium, airport, or train station. The economic losses would be significant as well because of the time involved to remediate the area following such an attack. Federal and state agencies are thus working with major transportation centers to strengthen plans for responding to the possible use of chemical warfare agents. (See the box on pp. 6–7.)

Livermore researchers—environmental scientists, analytical chemists, and emergency response experts—have extensive experience helping federal agencies such as the Department of Energy and the Department of Homeland Security (DHS) prepare for a possible incident involving weapons of mass destruction, including chemicals, biological agents, and radiological devices. Over the past two decades, the Laboratory has made important contributions to homeland security with new kinds of miniaturized detectors, advanced chemical decontamination compounds, extremely sensitive analytical techniques, and more thorough decision-making processes required for quick and effective response to an incident.

At the Laboratory’s Forensic Science Center (FSC), chemists have been working closely with chemical warfare agents since the early 1990s to support treaty verification and U.S. intelligence efforts. Founded in 1991, FSC supplies analytical expertise to counter terrorism, aid domestic law enforcement, and verify compliance with international treaties. FSC researchers analyze virtually every kind of chemical evidence, some of it no greater than a few billionths of a gram.

In addition, the center is one of two U.S. laboratories internationally certified for identifying chemical warfare agents, sometimes referred to as the poor-man’s atomic bomb.

Since 2008, Lawrence Livermore has been working closely with the Environmental Protection Agency (EPA) to prepare for incidents involving chemical weapons. FSC serves as EPA’s environmental reference laboratory for developing and validating reliable, accurate, and extremely sensitive methods to analyze chemical warfare agents and their degradation products. Laboratory researchers have also characterized many toxic industrial compounds because the molecular structure and health effects of these substances are similar to those of known chemical warfare agents.

Livermore analytical chemist Carolyn Koester is principal investigator for the partnership with EPA. “We want to help EPA labs ensure that all public areas are safe after an incident involving chemical weapons,” she says. Making sure the public can return to a facility following dispersal of a chemical warfare agent will probably require analyzing hundreds, perhaps thousands, of samples over the course of days or weeks as workers monitor the intense cleanup efforts after an attack.

Sensitive Detection Methods

The 1980 Comprehensive Environmental Response, Compensation, and Liability Act (also known as the Superfund Act) designated EPA as the primary federal agency responsible for the environmental remediation (cleanup) following acts of terrorism. In this capacity, EPA would take a lead role after an attack, providing expertise on effective decontamination approaches for indoor and outdoor areas.
If an incident involving chemical weapons were to occur on U.S. soil, a select group of EPA laboratories, part of the agency’s Environmental Response Laboratory Network, would quickly become involved. The laboratories, using Livermore-developed techniques, would first determine the nature and extent of the contamination and would later help monitor decontamination and restoration activities. According to Koester, the EPA laboratories must be prepared for any kind of sample—liquid, solid, or vaporous and ranging from plants to clothing to carpeting.

FSC Director Dennis Reutter says that, before a facility can reopen, agencies must state with confidence that no harmful residue remains following decontamination. A major challenge is thus to develop techniques that can detect and identify extremely low concentrations of chemicals. He notes that Livermore’s characteristic approach is to probe the lower limits of detection for many types of chemical and explosive compounds isolated during an investigation. For chemical weapons and their degradation products, he says, “We’re pushing detection limits as low as 1 part per billion or even trillion.”

At the same time, analysis methods must also be as fast as possible to give on-scene responders answers within hours instead of days. High-throughput methods will allow EPA laboratories to keep up with possibly thousands of samples. Reutter adds that Livermore could provide surge capacity to help EPA analyze a large number of samples.

For the past year, Livermore researchers have been training analysts from several EPA laboratories to use the new techniques.

A Chemical Weapons Primer

Chemical warfare agents are nonexplosive compounds that can kill, injure, or incapacitate. The chemicals traditionally used to make these weapons are not widely available, but recipes for producing them are found on the Internet. Some have even been deployed in terrorist incidents.

The more toxic compounds (such as sarin, soman, cyclosarin, tabun, and VX) work by attacking the nervous system. Others may induce blistering (mustards and lewisite), choking (chlorine, phosgene, and diphosgene), or vomiting. In addition, some nonlethal compounds are designed to incapacitate an attacker or help disperse a crowd. The chemicals may be in solid, liquid, or gas form, but most liquids and solids can be made volatile for quick dispersal as aerosols and vapors over a large area.

Chemical warfare compounds can enter the body through the skin, eyes, and respiratory tract. Depending on the agent, its concentration, and the length of exposure, physical effects may be immediate or delayed.

An agent’s persistence—how long it remains dangerous after dissemination—also varies widely. Gaseous agents such as chlorine, sarin, and some other nerve agents lose effectiveness after only a few minutes or hours, provided they are not trapped in porous materials. In contrast, persistent agents may linger in the environment for up to several weeks, which complicates decontamination efforts. Liquids such as blister agents and the oily VX nerve agent do not easily evaporate into a gas and therefore primarily pose a contact hazard.

A Long History in Warfare

Although chemical weapons may seem like a modern warfare technology, archeologists have discovered instances of toxic chemicals used in ancient conflicts. For example, in 256 A.D., Persian soldiers pumped lethal fumes from a brazier burning sulfur crystals and bitumen into tunnels, killing Roman soldiers hiding underground.

The horrifying capacity of these agents was evident during World War I. In 1915, the German military released 168 tons of chlorine gas in Belgium, killing an estimated 5,000 Allied troops. Sulfur mustard, the major cause of chemical casualties in that war, was used first by the Germans and later by Allied soldiers. Since then, chemical weapons have factored into other conflicts. For example, Iraq used chemical weapons, including mustard gas, against Iranian troops and Iraqi Kurds during the prolonged war in the 1980s.

Terrorists deployed chemical weapons against civilian populations for the first time in 1994, when the extremist Aum Shinrikyo cult released sarin gas in Matsumoto, Japan, leaving 7 dead and 280 injured. The following year, the cult released sarin vapor in the Tokyo subway system, killing 12 commuters and hospitalizing nearly 1,000. Because of the efficient decontamination effort, the subway was back in operation the following day.

Accidents involving toxic industrial chemicals, many of them close cousins to modern warfare agents, demonstrate the potential of chemical agents to kill and injure. For example, in 1984, an explosion at an industrial pesticide plant in Bhopal, India, released methyl isocyanate gas, killing more than 4,000 and sickening tens of thousands. Closer to home, two freight trains collided near Graniteville, South Carolina, in 2005, and a ruptured tank car released 70 tons of chlorine gas. Nine people died, at least 250 people were treated for chlorine exposure, and about 5,400 residents were forced to evacuate for nearly two weeks.

Outlawed by Chemical Weapons Convention

The United Nations classifies chemical warfare agents as weapons of mass destruction. The 1993 Chemical Weapons Convention (CWC), which has been ratified by 186 countries, including the U.S., bans the development, production, acquisition,
and learn about procedures, including additional safety practices, required for working with chemical warfare agents. Analytical chemist Heather Mulcahy says, “The EPA labs have not previously worked with these compounds, but they are familiar with toxic materials and low-concentration samples. They also have considerable experience working with pesticides, whose characteristics are similar to those of some chemical warfare agents.”

The first set of developed techniques focused on the compounds that terrorists would most likely manufacture and deploy. Extremely small quantities of these agents were used to develop analytical methods. As the EPA personnel gain expertise with these techniques, Livermore scientists will add new ones for analyzing other agents. EPA laboratory analysts have also visited Livermore to work alongside experts in the field of chemical warfare detection. Personnel from additional EPA laboratories are expected to begin training this year.

To help in evaluating a laboratory’s readiness for a terrorist incident, Livermore chemists have synthesized minute amounts of chemical warfare agents and sent them to the EPA laboratories for identification. “In the first proficiency test,” says Koester, “the participating labs did very well in quantifying trace amounts of agents.”

Preparing LAX for Attack

Livermore scientists are also helping to strengthen management plans for responding to a chemical attack. One of the most exhaustive efforts is a multi-institutional collaboration to develop emergency response plans for airports, including Los Angeles International

The chemical warfare agents sarin (left) and VX (right) attack the nervous system. In these molecular diagrams of the two compounds, black is carbon; gray, hydrogen; blue, oxygen; purple, phosphorus; orange, fluorine; yellow, sulfur; and green, nitrogen. (Rendering by Sabrina Fletcher.)
Airport (LAX), the world’s sixth busiest, and San Francisco International Airport (SFO), the world’s twenty-first busiest.

Ellen Raber, deputy program manager for chemical, biological, radiological, nuclear, and high-yield explosives countermeasures in Livermore’s Global Security Principal Directorate, emphasizes the need to quickly restore a major airport facility after an attack. “A deliberate attack on an airport could have far-reaching impacts, not only in terms of public health but also in economics,” Raber says. For example, if SFO were shut down, the lost revenue would top $85 million per day. The closure would also affect the national and international air transportation network and reduce public confidence in these facilities.

In 2006, Raber led an exercise in which Livermore researchers worked with SFO managers and state and local agencies showing how the airport could effectively respond to an attack involving biological agents such as anthrax. More recently, Laboratory scientists have applied their expertise and developed guidance documents and methods for
response and recovery to a chemical warfare attack.

Livermore scientists participated in DHS’s Chemical Restoration Operational Technology Demonstration Final Demonstration Event in October 2009. The three-day exercise, which took place at Ontario International Airport in southern California, capped three years of planning, studies, and experiments conducted by Lawrence Livermore, Sandia, Oak Ridge, and Pacific Northwest national laboratories. Funded by the DHS Chemical and Biological Science and Technology Division, the event focused on procedures, plans, and technologies to rapidly restore an airport or major transportation center to normal operations following a chemical attack. Raber says that EPA has also been a key contributor to strengthening response capabilities and has provided significant operational and technical requirements.

As part of the exercise, Laboratory scientists collaborated with personnel from LAX, DHS, and EPA as well as state emergency response groups, including the California National Guard. Livermore efforts focused on shortening the time required to decontaminate, restore, and reopen an LAX terminal under a hypothetical scenario.

The Livermore contribution also included strengthening emergency conduct-of-operations models, such as developing organizational structures with clear lines of responsibility. Much of this effort was led by the Laboratory’s Environmental Protection Department because of its expertise in responding to environmental releases of health-endangering materials. Livermore scientist Sav Mancieri, who leads this effort, says, “In addition, we have a strong understanding of the environmental regulations that are key to effectively responding to such an event, and our researchers have worked closely with EPA’s on-scene coordinators.”

Recovery from a chemical agent release will present many challenges, caused in part by likely contamination to large open spaces, confined spaces, sensitive equipment (such as computers), and many types of materials. “The restoration of an airport is an extremely complex process, but it must be done quickly and effectively,” Raber says. “Waiting for the agent to naturally dissipate will not be an option.”

The demonstration featured a scenario in which an undetermined quantity of sarin was released in a busy LAX terminal. Sarin, a nerve agent, is one of the most toxic and rapidly acting compounds. Its vapor can spread easily by airflow typical of air-conditioned indoor environments. Demonstration participants reviewed every response step, from the first 911 calls and the arrival of LAX police, firefighters, and hazardous material personnel to the protracted course of decontamination, restoration, and reopening of the facility.

The final product from the demonstration, a suite of national-level guidance documents issued jointly by DHS and EPA, should prove helpful to any large transportation facility in the nation. Livermore environmental scientist Don MacQueen has been instrumental in coordinating and resolving comments in preparation for the documents’ release and in determining the requirements for environmental sampling that would immediately follow a chemical release.

Strong Science Guides Remediation

Restoring a location to operation after a chemical attack will likely be a large and complex undertaking. The first step, identifying the chemical agent, will be performed by first responders such as the California National Guard civil support teams, who have air-sampling equipment to detect and identify a nerve agent such as sarin. Once the compound is identified, sampling would determine the extent of contamination and what areas require decontamination. According to Mancieri, on-scene managers will need to know how long agents remain on various surfaces and how best to decontaminate those surfaces.

To better understand how chemical warfare agents interact with typical indoor materials, a team led by former Livermore environmental scientist Adam Love tested a representative group of agents (sarin,
mustard, VX, and cyclosarin). All of the chemicals were applied to a number of materials, including painted wallboard, glass, stainless steel, concrete, vinyl floor tile, heating and air-conditioning ducts, escalator handrails, caulking, and other common indoor objects.

“The military has done a lot of work on the effects of chemicals on outdoor environments and military surfaces,” says Love. “But prior to our study, little research had been done on civilian materials.” He notes that tests involving actual chemical warfare agents, rather than surrogates, provide more realistic data concerning surface interactions under different environmental conditions.

The experimenters discovered that in vapor form, chemical warfare agents can penetrate both organic and inorganic porous materials, making decontamination more difficult. New data on agent persistence are helping researchers to refine operational guidelines and make cleanup operations more rapid and less expensive.

According to Love, every decontamination strategy is effective under some conditions, but no single approach is likely to be effective and efficient in restoring an entire facility. For example, with some porous materials, such as rubber handrails and vinyl tile, vaporous agent penetrates deeply, and bleach and foams are not effective. Stronger disinfectants are available, but would damage the objects, leaving removal a more efficient option. Another option is to apply a sealer over an object, in effect trapping the agent, but a Livermore study showed that some agent still manages to escape. Therefore, several strategies will probably be required, based on an understanding of agent–material interactions and the efficacy of the different decontamination approaches.

Clearly, planning is essential for efficient recovery from a chemical weapons release, to reduce the length of the remediation effort by days or weeks and to restore public confidence in a major facility. With EPA laboratories receiving the best training and major agencies adopting realistic and efficient remediation plans, Lawrence Livermore scientists are increasing the nation’s ability to respond effectively to any incident involving chemical warfare agents and protect human health and the environment.

—Arnie Heller

Key Words: chemical warfare, Chemical Weapons Convention (CWC), decontamination, Forensic Science Center (FSC), Los Angeles International Airport (LAX), mustard, Organization for the Prohibition of Chemical Weapons (OPCW), San Francisco International Airport (SFO), sarin, VX.

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