Standoff Detection of Persistent Chemical Agents on Surfaces

Emily Meyer

MIT Lincoln Laboratory
Lexington, MA 02420

Defense Threat Reduction Agency
8725 John J Kingman Road
Fort Belvoir, VA  22060-6201

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Define technology roadmap for standoff surface contamination sensing based on science and technology gaps relative to operational needs and threats.  Power Point presentation.

Chemical Agent Detection, Stand off detection, Sensors, active, passive, LIDAR
Standoff Detection of Persistent Chemical Agents on Surfaces

Emily Meyer, PhD
Benjamin Ervin, PhD

Group 47
MIT Lincoln Laboratory

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Persistent Chemical Agents on Surfaces

Why are persistent agents a serious threat?

- Reduces fighting capacity and efficiency (e.g. MOPP gear)
- Slows military operational tempo (OPTEMPO)
- Reduces freedom of maneuver
- Inflicts casualties
- Persistent

Strong need for ability to detect surface contamination, ideally while avoiding contamination of equipment or personnel
Persistent and Nonpersistent Agents

Primary use of agents (Terrain and Equipment Denial vs. Anti-Personnel) and primary hazard (Inhalation vs. Contact) vary with persistence.
Study Objectives and Structure:
MIT LL, JHU/APL and ECBC Team

- Define technology roadmap for standoff surface contamination sensing based on science and technology gaps relative to operational needs and threats

Operational Aspects
- Operational Scenarios, Threat Scenarios

Missions
- Recon, Consequence Mgmt., Pre/Post Decon

Technology Solutions
- Sensor Technologies

Phenomenology
- Deposition, Agent Signatures, Agent Fate

Study Outputs
- Defined missions and threats
- Achievable mission success
- Technology Solutions Technology Gaps
- Knowledge/Science Gaps

Subset of Results on Sensor Technologies Shown Today
System Analysis Process

Mission Specifics

1. Threat \( C(x,y,t) \)
2. Environment
3. Area of Responsibility (AOR)

System (Tech/Platform)

- Power
- Filtering
- Dwell Time, \( t_d \)
- Averaging
- Assess Area, \( A_a \)
- Detector Stats
- Range
- Backgrounds \((x,y)\)
- \( C(x,y,t) \)
- Temp

Signal $/ \ (Clutter + Noise)$

P \( D \)
Sensitivity
Resolution
Area Coverage Rate (ACR)

Measures of Effectiveness

- Casualties
- Cost/Resources
- False Alarms
- Contaminated Assets

Critical Thresholds

Feedback Loop
Mission Scenarios

**Fixed Site**

**Thickened VX Scud Detonates**

**Goal:** Mapping for Consequence Management

**Maneuver**

**VX Sprayers Used Along Route**

**Goal:** Warning for Contamination Avoidance

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Operational Use Requirements

• Sensitivity: 0.1 mg/m²
  • LD<sub>50</sub> for VX is 3 – 12mg (for adult male)
  • Assume level for safety is 3 orders of magnitude lower
  • Assume area for contact hazard is the surface area of a hand (0.015 m<sup>2</sup>)

• Range:
  • Minimum: 10’s of meters to avoid contamination during detection
  • Desired: 100’s of meters to expand architecture possibilities
  • Preferred: 1000’s of meters to accommodate all mission needs

• Speed:
  • Fixed Site: Map contamination on a 3.5km x 5km APOD in 25 minutes
    • For 250m x 250m grid, will use 3.5 second interrogation time
  • Maneuver: Warn at a speed of 20kph with time to brake before entering contaminated area
    • Will assume 0.001 second interrogation time
Surface Contamination Sensing: Current Systems and Shortcomings

**M8 Colorimetric Paper**
- Standardized in 1963
- Personnel contamination
- Very slow
- False positives
- Pro: Easy to use

**M93 Fox, double wheeled sampler, Mass Spec**
- Approved for fielding in 1995
- Vehicle contamination
- Slow, 2kph
- Narrow spatial coverage

**JCSD (Emerging): Raman System**
- Developed starting in 2001
- Vehicle contamination
- Narrow spatial coverage
- Pro: Fast road coverage

Require standoff sensing methods that rapidly map wide areas while avoiding personnel/vehicle contamination

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• Areas of interest are those with concentration $> 0.1 \text{ mg/m}^2$
• Average drop diameter in lowest concentration region is $500 \mu\text{m}$
Maneuver: Drop Sizes

- Sprayers produce much smaller drop sizes than on the Fixed Site
- Average drop diameter in lowest concentration region is 50 \( \mu \text{m} \)
Drop and Film Characteristics

- Drops will spread as spherical caps until equilibrium thickness ($h_{EQ}$) is reached, at which point they begin to spread as films of thickness $h_{EQ}$.

- Contaminant distribution on substrate will depend on dissemination method and substrate-contaminant wetting properties.

\[
h_{EQ} = \sqrt{\frac{2\gamma (1 - \cos \theta_c)}{\rho g}}
\]

Peak Height of Surface Film vs. Drop Size and Contact Angle

![Graph showing peak height of surface film vs. drop size and contact angle.](image)

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Drop Spreading

- Low contact angles will result in larger contaminant surface area, larger percentage of substrate covered in contaminant
- Wetting properties will vary between contaminants and between substrates
- Values are not readily available in the open literature, so contact angle is parameterized in this analysis
Probability of Detection ($p_d$)

System $p_d$ is dependent on:

- $p_{\text{drop}}$: Probability drop is interrogated
- $p_{\text{sensor}}$: Probability sensor detects drop if interrogated

System $p_d$ could be very poor even with a "perfect" sensor ($p_{\text{sensor}} = 1$): $p_d = p_{\text{drop}} \cdot p_{\text{sensor}}$
Probability of Detection ($p_d$)

\[ p_d = p_{\text{drop}} \cdot p_{\text{sensor}} \]

**High Sensitivity**
- Low Area Coverage Rate
- Low Probability of Encountering a Drop

**Lower Sensitivity**
- Higher Area Coverage Rate
- Higher Probability of Encountering a Drop
Choice of Interrogation Area

- Interrogation area required for a $p_d$ of 95% will depend on drop size and contaminant concentration.
  - For larger drops, a higher concentration is required.
  - A typical sheet of M8 paper (area = 65 cm$^2$) will not be able to detect $C_{obj}$ for the Fixed Site with sufficiently high $p_d$.

Desired detection capability will define necessary size of interrogated area.
Outline

• **Example Mission Scenarios**
  – Current Technologies
  – Operational Requirements
  – Concentration Profiles
  – Contaminant Phenomenology

• **Potential Standoff Technologies**

• **Application to Scenarios: Fixed Site**
  – Raman Spectroscopy
  – Active and Passive LWIR Spectroscopy

• **Application to Scenarios: Maneuver**
  – Active and Passive LWIR Spectroscopy

• **Conclusions**
Potential Technologies for Standoff CWA Detection

- Consider technologies that have been demonstrated to be capable of “true” standoff CWA detection
  - No sample collection
  - No special substrates required
  - Nothing but photons interacting with contaminant

- Evaluate technologies based on:
  - Sensitivity (SNR, Range, Dwell Time)
  - Selectivity (Interferents, clutter)
  - SWAP (platform compatibility)
  - Maturity (TRL ≥ 2 required)
Potential Detection Technology: Raman

- Laser photon excites molecule into virtual state
- Raman scattering when frequency of photon emitted as molecule relaxes is shifted ($v_{\text{out}} > v_{\text{in}}$ for Stokes, $v_{\text{out}} < v_{\text{in}}$ for Anti-Stokes)
- Highly specific technique
- Signal is typically fairly weak at eye-safe laser power
Optimizing Raman Signal: Importance of Deposition Details (VX)

- For wavelengths at which VX absorbs strongly (e.g. deep UV), only the first micron of molecules is expected to contribute to Raman signal.
- Same volume can have very different surface area depending on wetting.
Potential Detection Technology: LWIR Reflectance

- CWAs have strong absorption features in the LWIR, which also coincides with atmospheric window.
- Acquire reflectance data vs. $\lambda$ either at a single point or at each pixel in a hyperspectral image to map out contamination.
- Active or Passive techniques can be used.
Potential Detection Technology: Passive and Active LWIR Reflectance

Passive
- Differential radiance determined by measuring difference in radiance between clean and contaminated areas with an FTIR spectrometer
- Primarily an outdoor technique
- Sensitive to environmental factors
- Imaging detectors provide wide area coverage

Active
- Either tunable laser or radiant heater as source
- Record reflectance in a given direction with IR Camera for laser source or imaging FTIR spectrometer for heater
- Strong angular dependence presents problems in field testing
- Active area of research
Passive LWIR Signal Equations

\[
L_{\text{clean}} = B - R_{\text{surf}}(B - L_{\text{sky}})
\]

\[
L_{\text{cont}} = B - R_{\text{cont}}(B - L_{\text{sky}})
\]

\[
B = \frac{2hc^2\nu^3}{\exp(hc\nu/kT) - 1}
\]

(Planck Radiance of surface)

Differential Radiance:

\[
\Delta L = (R_{\text{surf}} - R_{\text{cont}})(B - L_{\text{sky}})
\]

Passive Radiance at Observation Angle

\[L_{\text{cont}}\]

\[L_{\text{clean}}\]

\[\Delta L\]
Active LWIR Signal Equations

**User-Controlled Parameters:**

- Laser power ($P_{\text{laser}}$) limited by SWaP, eye-safety
- Interrogation time ($\tau$) limited by mission time constraints
- Solid angle ($\Omega$) limited by required standoff distance, size constraints on optics

**Equations:**

$$\Omega = \pi \left( \frac{d_{\text{optics}}}{D_{\text{standoff}}} \right)^2$$

$$\phi = \text{Fraction Covered in contamination}$$
Signal Equations: Reflectivity

\[ R_{\text{cont}} = (\rho_{\text{cont}})(\rho_{\text{cont}}^*) \]

where \[ \rho_{\text{cont}} = \frac{\rho_{01} + \rho_{12}\tau^2}{1 + \rho_{01}\rho_{12}\tau^2} \]

- Substrate reflectivity \((\rho_{12})\) scales double-pass transmission \((\tau^2)\)
- For a minimally reflective substrate, the air-contaminant reflectance amplitude \((\rho_{01})\) will dominate
- For a highly reflective substrate with sufficient transmission, absorption features from the double-pass transmission will dominate

Reflectance properties are a function of both substrate and contaminant properties, and determine signal quality at detector.
Transmission and Reflectance Coefficients (VX Example)

- Absorption spectral features (seen in $\tau$) become less clear as film thickness increases.
- Front face reflectance amplitude ($\rho_{01}$) is relatively small compared to other two parameters.
- Film thickness and contaminant-substrate reflectance amplitude will combine to determine relative strength of $\rho_{12} \tau^2$ term.
Detection Capabilities and Contaminant Distribution: Signal Quality

Signal can be strong, but without clear spectral features and thus low-quality.
Active LWIR Signal Equations: Scattering Properties

User-Controlled

\[ N_{\text{cont}} = P_{\text{laser}} \cdot \tau \cdot \Omega \cdot f_{\text{BRDF}} \cdot [(1 - \phi) \cdot R_{\text{clean}} + \phi \cdot R_{\text{cont}}] \]

System Properties

\[ N_{\text{clean}} = P_{\text{laser}} \cdot \tau \cdot \Omega \cdot f_{\text{BRDF}} \cdot R_{\text{clean}} \]

\[ \Omega = \pi \left( \frac{d_{\text{optics}}}{D_{\text{standoff}}} \right)^2 \]

\( \phi = \text{Fraction Covered in contamination} \)

Scattering properties are a function of substrate, and determine signal strength at collocated detector.
Outline

• **Example Mission Scenarios**
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  – Contaminant Phenomenology

• **Potential Standoff Technologies**
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  – Active and Passive LWIR Spectroscopy

• **Application to Scenarios: Fixed Site**
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• **Application to Scenarios: Maneuver**
  – Active and Passive LWIR Spectroscopy

• **Conclusions**
Fixed Site

- Baseline Technology: **M8 Paper**
- Can take advantage of fixed site by pre-placeing cooperative or carefully chosen substrates around the base
Fixed Site: Tower Platform w/ Stands

- Fixed site scenario allows unique opportunities for “remote” detection of contaminants

- Designing substrates for pre-placement around Fixed Site could enhance detection:
  - Known background to simplify analysis
  - Coatings engineered to optimize wetting
  - SERS substrates for Standoff Raman
  - Retroreflectors for Active LWIR detection

- Known, pre-interrogated substrates minimize effects of clutter
Raman Setup

Analysis will focus on Raman excitation in UV region ($\lambda = 248$ nm)

<table>
<thead>
<tr>
<th>Agent</th>
<th>$\sigma_R$ [1]</th>
<th>$T_{max}$ (µm)</th>
<th>$\sigma_R$ [2]</th>
<th>Frequency shift [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB</td>
<td>1.2</td>
<td>360</td>
<td>540</td>
<td>10$^{-30}$ cm$^2$ sr$^{-1}$ molecule$^{-1}$</td>
</tr>
<tr>
<td>HD</td>
<td>3.0</td>
<td>4,800</td>
<td>8.4</td>
<td>[1] 1.0 cross-section</td>
</tr>
</tbody>
</table>

1. High cross-section
2. Low fluorescence
3. Solar blind

120 m

Range: 0.1 - 1 km
UV Raman Analysis

Transmit:
- Illuminate entire stand w/ laser ($\lambda = 248$nm)
- 437 stands interrogated in 25 minutes ($\tau = 3.5$ s)
- Eye Safe Power ($\lambda = 248$nm, $\tau = 3.5$ s): 0.86 mW/cm$^2$

Receive:
- Aperture size: $D = 0.203$ m (8”)
- Assume entire stand is one pixel
- Majority of returning photons are at 248nm
- Filtering used to keep only shifted photons

![Optical Filter](image)
**UV Raman Analysis**

**Signal Model:**

\[
e^{-}_{255} = QE \cdot \Omega \cdot \tau \cdot P_{\text{laser}} \cdot \sigma_{R} \cdot \frac{\text{Molecules}}{A_{\text{stand}}}
\]

Where:
- QE = Detector Quantum Efficiency
- \(\Omega\) = Solid angle (sr)
- \(\tau\) = Integration time (seconds)
- \(P_{\text{laser}}\) = Laser power in photons per second
- \(\sigma_{R}\) = VX Raman cross-section = \(2.5 \times 10^{-27}\) cm\(^2\)/molecule
- \(A_{\text{stand}} = 1\) m\(^2\)

\[
\text{Molecules} = N_{\text{drop}} \cdot \text{SA}_{\text{drop}} \cdot t_{p}
\]

Where:
- \(N_{\text{drop}}\) = Number of drops on stand
- \(\text{SA}_{\text{drop}}\) = Surface Area of individual drop
- \(t_{p}\) = Penetration depth at 248nm in \(VX = 1\) µm

**Noise Sources:**
- Shot Noise
- Detector Dark Noise
- Readout Noise

**Signal + Noise Model:**

\[
\mu_{\text{signal}} = e^{-}_{255} + e^{-}_{\text{Dark Noise}} + e^{-}_{\text{Read Noise}}
\]

\[
\sigma_{\text{signal}} = \sqrt{e^{-}_{255} + e^{-}_{\text{Dark Noise}} + \left(e^{-}_{\text{Read Noise}}\right)^2}
\]

**Simple detection algorithm:**

If \(\mu_{\text{signal}} \geq\) threshold → ALARM
Active and Passive LWIR Setup

Passive

Active

Range: 0.1 - 1 km
Active LWIR Analysis

Transmit:
- Illuminate retroreflector w/ tunable laser ($\lambda = 7.0–12.5 \, \mu m$)
- 437 stands interrogated in 25 minutes ($\tau = 3.5s$)
- Signal-average 50 times during $\tau$
- Eye Safe Power ($\lambda$ in LWIR, $\tau = 3.5s$): 219 mW/cm$^2$

Receive:
- Aperture size: $D = 0.203m$ (8"
- Assume entire stand is one pixel
- Clean signal subtracted from contaminated
- Spectral signature compared to matched filter

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Passive LWIR Analysis

Transmit:
- 437 stands interrogated in 25 minutes ($T = 3.5s$)
- Assume $50^\circ$T between substrate and sky
- Treat substrate and sky as black bodies

Receive:
- Assume entire stand is one pixel
- Clean signal subtracted from contaminated
- Spectral signature compared to matched filter
**LWIR Analysis**

**Signal Model:**

Active: \[ e^- = QE \cdot \Omega \cdot \tau \cdot f_{BRDF} \cdot (P_{laser} \cdot R + L) \]

Passive: \[ e^- = QE \cdot \Omega \cdot \tau \cdot f_{BRDF} \cdot L \]

Where:
- \( QE \) = Detector Quantum Efficiency
- \( \Omega \) = Solid angle (sr)
- \( P_{laser} \) = Laser power in photons per second
- \( R \) = Reflectivity
- \( f_{BRDF} \) = Bi-directional Reflectance Distribution Function (sr \(^{-1}\))
- \( L \) = Radiance in photons per second

**Signal + Noise Model:**

\[ \mu_{signal} = e_{255}^- + e_{dark}^- \]

\[ \sigma_{signal} = \sqrt{\mu_{signal}} \]

**Noise Sources:**
- Shot Noise
- Detector Noise

\[ \alpha_{filter} = \text{VX absorption matched filter} \]

\[ d\mu = \mu_{signal} - \text{mean}(\mu_{signal}) \]

\[ mf_{signal} = \frac{\mu_{signal} \cdot \alpha_{filter}}{\sqrt{(\mu_{signal} \cdot \mu_{signal})(\alpha_{filter} \cdot \alpha_{filter})}} \]

**Matched filter algorithm:**

If \( mf_{signal} \geq \text{threshold} \) \( \rightarrow \) **ALARM**
Fixed Site: Performance Curves

- **Raman** is signal-limited and shows limited potential for detection at long range.
- **Passive LWIR** is also signal-limited at distances more than ~30 meters.
- **Active LWIR** on pre-placed retroreflective substrates shows strong potential for detection at long range.

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**Raman** is limited by physics, while **Active LWIR** shows strong potential when clutter can be minimized.
Fixed Site:

Potential Tiered Sensing Solutions

- Wide Area Coverage Detection (e.g. Central Tower or UAV)
  - Detect and potentially ID contaminant from height of 100+ meters
  - Map area of suspected contamination
- Standoff Spot Detection (e.g. UV Raman on Ground Vehicle)
  - ID with high specificity from 10s of meters in area indicated by wide area sensor
- Short-Range Spot Detection (e.g. Raman and/or LIBS on UGV)
  - Detect and ID lower levels of contamination with high sensitivity
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• Conclusions
Maneuver

- Baseline Technology: JCSD
- Will attempt larger interrogation area, standoff detection
Concentration Encountered

Assumes JCSD $p_{sensor} = 1$

- Unlikely for drops < 100 μm (even w/ wetting)
- However, shouldn’t matter unless $p_{sensor} < 0.01$
- More JCSD performance data needed

JCSD (as modeled) provides adequate warning for maneuver main force, however all scout vehicles expected to become contaminated.
Maneuver: Active and Passive LWIR

Multispectral Image Cube

Air Platform

Ground Platform

Detected agent

Illuminate scene for active LWIR

20kph

Range

Standoff Chemical-43
EEM 4/23/2010
Signal returned from any given substrate will vary from large (e.g. a retroreflector) to nonexistent (e.g. quasi-specular substrate interrogated at a glancing angle).
Substrate reflectivity will vary from pixel to pixel, introducing noise we refer to as “clutter” during background subtraction.
Maneuver: Active LWIR Performance

- In the absence of clutter, both platforms perform reasonably well.
- With clutter, performance is clutter-limited and both platforms perform poorly.
- Ability to detect only the highest concentration the vehicle is predicted to encounter, ground vehicle is likely to become contaminated.

Air vehicle equipped with Active LWIR may have potential to detect areas of highest contamination.
Maneuver: Active and Passive LWIR Performance on an Air Vehicle

- In the absence of clutter, Active LWIR performs considerably better than Passive.
- With clutter, both sensors are clutter-limited and both perform similarly.
- Active (with large laser) not expected to offer any true advantage over Passive in the clutter-limited case.

Air vehicle equipped with Active or Passive LWIR may have potential to detect areas of highest contamination.
Maneuver: A Word about Raman

• Raman was initially ruled out due to limited sensitivity at range (for eye-safe laser powers)
• Given the calculated performance of the LWIR techniques on the maneuver, Raman may be an equally viable candidate
• Will need to develop a more thorough Raman model to confirm utility in the presence of clutter
Conclusions

• Remote detection of chemical agents is challenging
  • Small drops on surfaces push sensors to very high spatial resolution
  • High spatial resolution impedes rapid, wide area coverage
  • Areal surface coverage can be low even at hazardous concentrations

• Fixed Site analysis shows potential for tiered sensing system

• “Remote” detection can be utilized on a Fixed Site to optimize detection capabilities in the fixed site scenario

• Standoff detection on the move is considerably more difficult
• Further analysis is required to assess all options
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